Measurements of electron impact optical excitation functions

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Optical excitation function measurements for electron-atom and electron-ion collisions are reviewed. Sources of experimental error are discussed and, for cases in which adequate documentation is provided, publications are reviewed for accuracy of experimental method. The effects of polarization of the emitted radiation and methods of normalization are considered. The reliability of specific reported data is discussed based on these considerations, on the results of consistency checks, and, where possible, on comparison with other measurements. Data sources for 50 atoms and 20 atomic ions are identified. Comparative plots are presented for cases in which enough data are available: H, He($n^{1}S$, $n^{1}P$, $n^{1}D$, $4^{3}S$, $3^{3}P$), He⁺, Ne, Ne⁺, Ar, Ar⁺, Xe, Li, Na, K, Mg, Mg⁺, Ca, Sr, Sr⁺, Cu, Zn⁺, Cd, Hg, and Mn.

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LIST OF SYMBOLS

A_{ab}	radiative transition probability
A_i	parameter in equation of Bethe-Fano
,	line
B	instrumental polarization sensitivity
C_{n}	coefficient describing cascade from
r	levels having principal quantum num-
	bers $> p$
Ε	electron energy
E_i	energy of the level j
$\vec{E_0}$	energy intercept of Bethe-Fano line
E_n	energy at which the polarization
r	passes through zero

E_R .	parameter in expression defining $F(E)$
I, I_{\parallel} , I_{\perp}	light intensity: total, polarized with
	electric vector, respectively, parallel
	and perpendicular to the electron
	beam
\boldsymbol{J}_i	cascade contribution to excitation of
	level j
Р	polarization of light corrected for ob-
	servational effects
P'	observed polarization of light
P_0	polarization parameter (threshold po-
	larization for neutral targets)
Q	level excitation cross section
Q'	line excitation cross section
R	Rydberg constant
R_T	relative signal (values from the litera-
	ture)
S_{j}	relative signal (defined in Appendix C)
a	index in expression for C_p
a_0	Bohr radius
b	index in expression defining $F(E)$
c_{j}	parameter in equation of Bethe-Fano
	line
d, e, f, i, j, k	used to identify general atomic levels
f_{j}	oscillator strength of transition from
	ground state to level j
n	principal quantum number
р	specific value of n
t	radiative lifetime
β	scale factor in equation for Bethe-
	Fano line
arphi	angle of observation with respect to
	the electron beam
θ	orientation of polarizing filter
Ψ	$90-\varphi$

INTRODUCTION

Optical excitation functions were among the first electron-atom interactions to be studied experimentally but, although measurements have continued for over 70 years, the apparent simplicity of the experiments has led to the publication of a very great deal of unreliable data. Some 20 years ago Moiseiwitsch and Smith (1968) published the first comprehensive review of the data, both experimental and theoretical, and noted that there were serious discrepancies, not merely between theory and experiment, but between different experiments. That review stimulated further, more careful, experimental studies, and in the last two decades there have been a number of excellent and well-documented measurements. The range of target species has been considerably increased, as Fig. 1 shows, and now includes many positive ions as well as atoms in metastable and other excited states.

Our objective in this paper is to review the whole range of experimental data in a manner that we hope will be seen as "constructively critical." We stress the great im-



FIG. 1. Periodic table showing only those elements for which a measurement of the excitation function of at least one spectrum line has been reported. In cases of those marked * or +, excitation of an excited atom target or of an ionized target, respectively, have been reported.

portance of proper documentation of experimental procedures, for without such documentation a fully objective critique is not possible. Many published reports are not well documented, and our analysis is perforce somewhat subjective. With one most important exception, we shall make no comparison with the predictions of theory. Our reason for this is simply that it does not appear to us that *detailed* calculations have much to offer at the present time. The exception, which we discuss in detail in Appendix C, is our use of the Bethe approximation as a guide, and indeed as an aid to calibration, in the case of vertain optically allowed excitations.

A. Excitation cross sections

We distinguish between cross sections for exciting a spectrum line and those for exciting an atomic level. The latter are true atomic parameters and their determination is the ultimate aim of the experiment; however, it is the former that one measures or, more correctly, deduces from one's measurements of target density, electron beam current, photon flux, and collision geometry. The process of data reduction must include checks for linearity in all variables to ensure that single electron-atom collisions are responsible for the observed signal. The process should also involve the measurement of the polarization of the light or the elimination of the effects of this polarization, including those due to differential sensitivity of the photometric system to light polarized in different planes. This last step is, even now, infrequently made. The remaining differences between the line and level excitation cross sections lie in the population of the level by cascade from higher excited states (a topic we discuss in Appendix B) and the branching ratio for decay of that level by paths other than the one observed. In most cases recourse to theory is necessary to take account of such alternative decay paths, but sometimes two or more paths lie in accessible spectrum regions and provide the opportunity for the measurement of a branching ratio or for

the extension of the photometric calibration to wavelengths at which primary standards are lacking.

B. Sources of inaccuracy

There are three major categories of error: those due to secondary processes, errors of interpretation, and errors of measurement. The influence of secondary processes, such as the imprisonment of resonance radiation or the transfer of excitation in atom-atom collisions, can in principle be reduced to insignificance by making measurements over a range of pressures extending to values low enough that such processes are shown to make no contribution. On the other hand, cascade population of the state under study is always present, and a proper allowance invariably requires some *estimate* of the contribution from unobserved upper states.

The most common error of interpretation is to overlook the influence of polarization both in respect of the radiation being studied and especially of the sensitivity of the radiometric system. We discuss this problem in Appendix A.

Errors of measurement occur in any experiment. In the present context, the most serious are probably in the determination of the target density, with absolute radiometry and the geometry of the excitation region close behind. The measurement of the pressure in a collision chamber has been made more accurate by the development of capacitance manometers, but thermal effects are often overlooked and a too simple conversion of pressure to target density is made. Problems with mercury manometers are nowadays less common because they are less frequently used, but we draw attention to a comprehensive study of this field by Thomas *et al.* (1985).

The general question of the imprisonment of resonance radiation is fairly well understood, at least in the context of narrow electron beams passing axially within cylindrical collision chambers filled with gas (Phelps, 1958; Heddle and Samuel, 1970), but the possible importance of this effect within atomic beam scattering geometries is not so widely appreciated. The particular problem arises in this case because the low transverse velocities of the atoms in the beam lead to large absorption cross sections for resonance radiation propagated perpendicularly to the atom beam. This phenomenon was first noted by Gould (1970) in studies of excitation and polarization in sodium. At the very lowest densities this does not matter, because the optical depth perpendicular to the beam axis remains small. However, as the density increases, the optical depth rises in all directions, but first becomes nonnegligible in this perpendicular direction. Resonance radiation can then escape readily along the beam axis, but less readily in a transverse direction. The sample of the total excitation observed perpendicular to the beam therefore decreases, and the value of the cross section is progressively underestimated as the beam density increases. Pohl (1975) shows an example of this phenomenon, though he did not consider that this angular redistribution process would be adequate to explain his observations.

Confinement of the electron beam by an axial magnetic field is sometimes employed in order to obtain sufficient current to make a measurement possible, but two types of error become more likely as a consequence. Both arise because electrons moving in directions that make comparatively large angles to the axis are constrained to travel with the beam, spiraling around the axis, rather than being blocked by an aperture in the electron gun. The first, and generally the more important error, is the increased path length in the interaction region determined by the value of the secant of this angle, while the second is the reduction in the observed polarization as a result of the poorer definition of the beam direction. This latter point is discussed in Appendix A. There are a number of possible causes of the transverse velocities that lead to spiraling. The most obvious is the isotropic emission from the cathode, but space charge and electron optical effects will also contribute. Taylor et al. (1974) discuss in detail the causes of spiraling and the effect on the interaction path length and present measurements that indicate that path length corrections may be kept to a very low level by careful design and selection of operating conditions.

C. The presentation of data

We have not attempted here to present "recommended data" for all observed transitions, but have deliberately restricted the range shown in our figures to comparisons of different work. Where two or more determinations have been made in absolute units, this comparison is of both shape and size. In other cases we have normalized the different data to a common scale, though, where the comparison is between data taken with very different energy resolutions, this might have been done in different ways. Data have sometimes been published with a poor energy scale, and it is frequently not clear whether the abscissa is "electron energy" or "applied potential." We have felt free to make limited horizontal adjustments to aid the comparisons.

D. Related reviews

A major review of electron excitation of metastable atoms has recently been published by Fabrikant *et al.* (1988). The authors, who have themselves been responsible for some very detailed experimental studies, discuss both experimental and theoretical techniques and show quite extensive graphical and tabular data. They describe in detail the occurrence of resonances in the excitation of metastable states and devote some 20% of their paper to an account of their own substantial contribution to the study of the kinematics of the excitation process. Their paper includes 352 references, some as recent as 1987.

After the present review was essentially complete, we were shown the manuscript of an important paper by van der Burgt, Westerveld, and Risley of North Carolina State University. This reviews the literature on photoemission cross sections in the extreme ultraviolet for transitions in excited atoms and atomic ions formed in electron collisions with atoms and molecules. The targets include H, N, O, the inert gases, and a number of molecules that are stable gases at room temperature. The paper includes a table of more than 500 cross-section values for wavelengths between 25.6 and 193.1 nm, and the authors draw attention to the severe inconsistencies between values reported by different laboratories. They give a detailed discussion of methods used for the normalization of cross-section measurements.

II. ATOMIC HYDROGEN

Measurement of the excitation functions of atomic hydrogen has fundamental importance. It is also technically demanding because the resonance line lies in the vacuum ultraviolet where absolute radiometry is much less accurate and conventional methods for the determination of target density are virtually impossible to apply. Despite these difficulties Williams (1976) has made an absolute measurement, free from polarization effects, of the excitation function of the Lyman alpha line (121.6 nm) at energies between the threshold and 13 eV using velocityselected electrons and paying particular attention to resonance structure. He used a phase-shift analysis of elastic scattering to determine the target density and made the radiometric calibration in terms of the quantum yield of a freshly evaporated aluminum film (Samson and Cairns, 1965). Williams (1981) measured the differential cross section for excitation of the 2p state and also the total excitation cross section at 54.4 eV. Long et al. (1968) measured the relative excitation function from threshold to 200 eV and calibrated their data, which were obtained at

90° to the electron beam in terms of the Born approximation (Bell and Moiseiwitsch, 1963; Bell, 1965) at their highest energy. Ott et al. (1970) measured the polarization for energies up to 700 eV. For any other element we would probably consider the results of these experiments to be in very good agreement, but the special situation of atomic hydrogen leads us to examine the data more critically. The oscillator strength f_i of the Lyman alpha line is 0.416, the threshold energy is 10.2 eV, the polarization parameter P_0 is 0.42, and the Bethe parameter c_{2n} is 0.408. We note first that the polarization, shown in Fig. 2(a), behaves very much as we would expect, both in the threshold region and at higher energies where the Bethe approximation should give a reasonable description. We now consider in detail the normalization of the relative excitation function of Long et al. (1968) and develop the equation of the Bethe-Fano line, to which the data should be asymptotic at high energies. The measurements are of Q_{90} ; so the slope of the line describing *direct* excitation will be (see Appendix C)

$$1.5 \times 10^{-13} (f_j / E_j) (1 - P_0 / 2) / (1 - P_0 / 3)$$

= 5.62 × 10⁻¹⁵ cm²eV

and the intercept will be at $(R/4c_{2p})\exp[P_0/$ $(2-P_0)$]=6.39 eV. Cascade population will modify this line in two ways. Transitions from directly excited S and D states will contribute a constant amount while transitions from P states via S and D states will increase the slope of the line. Table I shows values of the cascade contributions from states with n = 3-6 calculated from the Born cross-section data of Vainshtein (1965) and the transition-probability data given in Bethe and Salpeter (1957). A reasonable extrapolation suggests that the constant (at high energies) increase will be 2.8×10^{-16} cm²eV and that the slope will be increased by $4.0 \times 10^{-17} \text{ cm}^2 \text{eV}$ to 5.66×10^{-15} cm²eV. The effect of the uniform increase will be to displace the intercept on the abscissa to lower energy by an amount given by the ratio of the increase to the total slope; this places the intercept at 5.70 eV. In Fig. 2(b) we show the un-normalized experimental



100 Energy (eV)

FIG. 2. Excitation of Lyman alpha. (a) Polarization of Lyman

alpha radiation; the solid curve is the Bethe approximation

data [Table 2, column 5 of Long *et al.* (1968)]. These data have not converged to the asymptotic line, and we have fitted them to a curve of the form log(E/5.7)*F(E), where F(E) is a factor discussed in Appendix C and defined by Eq. (C6).

The slope of this line is 6.55 eV in the relative units

QE	$(10^{-18} \text{ cm}^2 \text{eV})$	QE (10	$(-18 \text{ cm}^2 \text{eV})$
~	(a) From directly excite	d S and D states, expressed a	as the product QE
3s-2p	103.6	3 <i>d</i> -2 <i>p</i>	77.5
4s-2p	22.4	4 <i>d</i> -2 <i>p</i>	27.3
5s-2p	8.6	5 <i>d</i> -2 <i>p</i>	12.9
6s-2p	4.3	6 <i>d</i> -2 <i>p</i>	6.8
	138.9	· · · · · · · · · · · · · · · · · · ·	124.5
) From dire	ectly excited P states via $d(C)$	A S and D states expressed as $DE / d(\log E) (10^{-18} \text{ cm}^2 \text{ eV})$	the slope of a Bethe-Fano lin
	From 4p	13.23	
	5p	8.47	
	60	5.15	
	-	26.85	

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TABLE I. Cascade nonulation of the 2n state of hydrogen. Data from Vainshtein (1965)

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10

(a)

٥.

0.2

0.0

15

10

О₉₀ * Е

(b)

٥ø

²olarization

0.4

0.2

0.0

10

1000

shown and implies that a calibration factor of

...

$$5.66 \times 10^{-15}/6.55 \text{ cm}^2 = 8.64 \times 10^{-16} \text{ cm}^2$$

has to be applied to the data. This is some 2% smaller than that used by Long et al. (1968), who drew their asymptote through the point at highest energy, but slightly overestimated the cascade contribution. The accuracy of this calibration factor clearly depends on the appropriateness of our choice of F(E), but it can certainly not exceed 9.02×10^{-16} cm², which corresponds to the highest energy point on the asymptote; we believe that values of $8.64\pm0.40\times10^{-16}$ cm² encompass the true value. Table II shows the absolute measurements of Williams (1976, 1981) and the calibrated values of Long et al. (1968) at 11 and 54.4 eV, corrected for polarization using the measured values of Ott et al. (1970) and, in the latter case, interpolated between the data taken at 48.6 and 68.6 eV. At both energies the results of Williams (1976, 1981) are about 13% higher.

Kauppila *et al.* (1970) measured the ratio of the cross sections for exciting the 2s and 2p states of hydrogen from threshold to 1 keV by observing the 121.6-nm radiation emitted from the collision region and from a region a few centimeters downstream where atoms in the metastable 2s state were quenched by an electrostatic field. They show an excitation function obtained by multiplying their measured ratios by the 2p excitation function of Long *et al.* (1968) up to 200 eV and that given by the Born approximation at higher energies. Williams (1976), using velocity-selected electrons, has measured the 2s excitation cross section in absolute terms up to 12.6 eV. At 11 eV he finds a value for the 2s/2p cross-section ratio of 0.68 compared to 0.63 (after corrections for polarization) found by Kaupilla *et al.* (1970) at that energy.

Walker and St. John (1974) measured the excitation functions of the first five members of the Balmer series for energies up to 450 eV in molecular and partially dissociated hydrogen. They made an absolute calibration in terms of measurements in static molecular hydrogen and estimate their absolute accuracy as 30%. Mahan *et al.* (1976) measured relative excitation functions for the 3S, 3P, and 3D components of the Balmer alpha line (656.3 nm). They separated the contributions from the three components by modulating the exciting-beam current at frequencies between 0.1 and 30 MHz and synchronously detecting the in-phase and out-of-phase signals. They calibrated their data using the Born approximation for the total n = 3 excitation cross section.

TABLE II. Cross sections for exciting the 2p state of hydrogen (units of 10^{-17} cm²).

Energy (eV)	Williams ^a	Long et al. ^b	Polarization
11.0	2.43	2.15	17%
54.4	7.81	6.94	12.5%
199.1		4.27	-1%

^aWilliams (1976, 1981).

^bLong et al. (1968).

III. THE INERT GASES

A. Helium

The simple spectrum and chemical stability of helium have made it the "ideal" subject for study, and many more measurements have been reported than for any other target. The most striking feature of the data published prior to the 1968 review by Moiseiwitsch and Smith was the substantial disagreement in the shapes of the excitation functions, even in the case of lines from the ¹S levels, which are unpolarized and might be expected to be relatively free from the effects of collisional transfer of excitation. Since then there have been a number of careful studies, and though there are still discrepancies, the overall picture is more satisfactory.

1. The ¹S states

The most fully documented experiment is the "benchmark" measurement of the excitation of the $n^{1}S$ (n=3-6) levels by Van Zyl et al. (1980). They measured the target density by a dynamic expansion technique [described in detail by Van Zyl et al. (1976)] with corrections for thermal transpiration. Their radiometric calibration was made in terms of a copper-melting-point blackbody and an NBS¹-calibrated tungsten strip lamp. In addition to these measurements, which are central to any absolute determination (though they have not been made with such accuracy in any other excitation experiment), Van Zyl et al. (1980) made careful measurements of the slit function of their monochromator and of the profile of their electron beam, and also took account of size of source effects and the fact that the finite lifetimes of the excited states led to a loss of excited atoms from the field of view of their radiometer. This attention to detail led to corrections of a few percent, which are certainly significant in the light of the overall precision of their measurements. The primary results of this experiment are the values for the emission cross sections of the spectrum lines from the n ¹S levels to the 2 ¹P level at five energies between 50 and 2000 eV, shown in Table III. The most accurate results are those at 500 eV, which have a mean uncertainty of 3.5% at a "high" confidence level of, the authors claim, approximately 98%.

Van Zyl *et al.* (1980) deduced from their line crosssection data values for the level excitation cross sections by using branching ratios derived from the transitionprobability tables of Wiese *et al.* (1966) and cross sections for the n ¹P levels measured by Moustafa Moussa *et al.* (1969). The dominant uncertainty introduced here comes from this cascade correction; the recently calculat-

¹National Bureau of Standards, now called the National Institute of Standards and Technology.

	n = 3	n = 4	n=5	n = 6
E (eV)	$\lambda = 728 \text{ nm}$	$\lambda = 505 \text{ nm}$	$\lambda = 444 \text{ nm}$	$\lambda = 417 \text{ nm}$
50	35.2±2.9	8.08±0.58	3.09±0.27	1.47±0.16
100	24.9±2.8	5.61±0.25	$2.30 {\pm} 0.12$	0.97±0.07
500	9.23±0.32	2.05 ± 0.057	0.78±0.026	0.374±0.016
1000	5.11±0.32	1.11 ± 0.036	0.425 ± 0.022	0.212±0.019
2000	2.75±0.15	$0.583 {\pm} 0.024$	$0.233 {\pm} 0.010$	$0.108 {\pm} 0.006$

TABLE III. Cross sections in units of 10^{-20} cm² for exciting the n ¹S-2 ¹P lines of helium. Data from Van Zyl *et al.* (1980): Table I.

ed values of the transition probabilities by Theodosiou (1987), while much more extensive and systematic, are in very good agreement with those used.

There have been six other measurements of the excitation cross section of the n ¹S levels (or the lines from these), and in Table IV we show the mean ratios of these cross sections to those of Van Zyl et al. (1980) for all the energies they have in common. The data of Moustafa Moussa et al. (1969) show the best overall agreement with the results of Van Zyl et al. (1980); indeed, only one data point (for $3^{1}S$ at 100 eV) lies outside the range of 1.00 ± 0.09 . On the basis of this agreement we suggest that the results of Moustafa Moussa et al. (1969), which extend to 6 keV, offer the best interpolation and highenergy extrapolation of the data of Van Zyl et al. (1980). Accordingly we show in Fig. 3 their results expressed as a weighted mean of the 3, 4, 5, and $6^{1}S$ data: the weights are the ratios of the $n^{1}S$ to the $4^{1}S$ cross sections as determined by Van Zyl et al. (1980), which, as shown in Table V, are essentially independent of energy. For energies below 50 eV we use other data to indicate the shape of the excitation function. Aarts et al. (1968) quote a maximum value at 35 eV, which is 2.07 times their value at 100 eV and, though their absolute values are suspect, the relative values agree quite well with the benchmark and with Moustafa Moussa et al. (1969) for energies greater than 100 eV. However, their value at 35 eV, even when normalized to the benchmark value at 100 eV, does appear a little high. Zapesochnyi and Feltsan (1965) report only line cross sections, but cascade corrections will be small below 50 eV, and as their data show by far the best energy resolution over a substantial range of ener-

TABLE IV. Ratios of n ¹S cross sections to those of Van Zyl *et al.* (1980).

Line cross sections	
St. John et al. (1964)	1.36±0.16
Zapesochnyi and Feltsan (1965)	1.53±0.10
Showalter and Kay (1975)	1.14±0.09
Level cross sections	
Miller (1964)	$1.32{\pm}0.18$
Aarts et al. (1968)	1.15±0.12
Moustafa Moussa et al. (1969)	1.00±0.09
van Raan et al. (1971)	1.18±0.06

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gies, we show it in Fig. 3 normalized at 50 eV to the benchmark. The threshold structure in these excitation functions is shown most clearly in a paper by Heddle (1977). The line drawn through the data at high energy has the slope of -1, corresponding to the Bethe approximation for an optically forbidden excitation, but has no further significance.

While the level excitation cross section is important for comparison with theory, the cross section for the excitation of a particular spectrum line is the quantity that is directly measured and is the more useful for the intercomparison of different experiments. It is also the quantity required for the estimation of cascade corrections to the population of the upper state of the observed transition and, via branching ratios and the extrapolation procedures discussed in Appendix B, to other states. We therefore show in Fig. 4 the cross section for excitation of the $4^{1}S-2^{1}P$ transition at 505 nm as measured by Van Zyl et al. (1980) together with the results of Zapesochnyi and Feltsan (1965) normalized to the former at 50 eV. We have chosen to present these data as Bethe plots of cross section times electron energy, because this generally simplifies interpolation and even extrapolation of the data.



FIG. 3. Excitation function of the $4^{1}S$ level of helium: (\bigcirc) Van Zyl *et al.* (1980), absolute measurement; (+) Moustafa Moussa *et al.* (1967), absolute measurement; (\diamondsuit) Aarts *et al.* (1968), normalized at 100 eV; (\cdots) Zapesochnyi and Feltsan (1965), normalized at 50 eV.

Electron energy (eV)	50	100	500	1000	2000
$3^{1}S/4^{1}S$	2.53	2.57	2.59	2.63	2.70
$5^{1}S/4^{1}S$	0.483	0.523	0.485	0.490	0.493
$6^{1}S/4^{1}S$	0.256	0.246	0.260	0.272	0.266

TABLE V. Ratios of n ¹S to 4 ¹S cross sections. Data from Van Zyl *et al.* (1980): Table III.

2. The ¹D states

Observation of light from these states is complicated by the fact that the light is polarized and measurements require correction unless they are made in a fashion that eliminates all polarization effects. There have been a number of measurements of the polarization, and we show in Fig. 5 the values obtained for the $4^{1}D-2^{1}P$ transition at 492 nm in three quite different experiments. McFarland (1967) isolated the line by a filter and had therefore essentially zero instrumental polarization. Clout et al. (1971) eliminated polarization effects by making their entire photometric system sensitive to only one plane of polarization in the way described in Appendix A. Van Raan et al. (1971) measured a polarization sensitivity B of 0.110 and corrected their measurements for it. These three measurements are in very good agreement for energies less than 250 eV, though at higher energies, where the cross sections are smaller and the measurements consequently less precise, they diverge somewhat. Close to threshold we show the data of Heddle et al. (1974) joined, but not normalized, to the Clout et al. (1971) data.

While there are data for several of the lines from the ${}^{1}D$ states, the $4 {}^{1}D - 2 {}^{1}P$ line at 492 nm has been studied most extensively. The cross-section measurements of



FIG. 4. Bethe plot for the 505-nm line of helium. Absolute data points are from Van Zyl *et al.* (1980). The line below 50 eV, from Zapesochnyi and Feltsan (1965), has been normalized at 50 eV.



FIG. 5. Polarization of the 492-nm line of helium: (+) McFarland (1967); (\odot) Clout *et al.* (1971); (\triangle) van Raan *et al.* (1971); (----) Heddle *et al.* (1974); (\clubsuit) theoretical threshold value (0.60).

Showalter and Kay (1975) are well documented and were made free of polarization effects by placing a polarizing filter aligned at 54°44' to the electron beam in the optical path. Their absolute radiometry was made in terms of a tungsten ribbon filament lamp. Of the other measurements that require consideration, Zapesochnyi and Feltsan (1965) made no polarization corrections despite the strong instrumental polarization that would be present because their optical monochromator required the light to pass through three prisms, with light polarized in the dispersion plane being preferentially transmitted at each of the six faces. Their data are of value despite this because they show very good energy resolution from the threshold to 50 eV, and the differential effect of the uncorrected polarization will not be large over this range of energies.

The results of Aarts et al. (1968) and of Moustafa Moussa et al. (1969) are again internally consistent, but with a ratio of 1.25:1. While the results of these workers were considered to be in the best accord with the ${}^{1}S$ benchmark, their positive polarization values are much smaller than those shown in Fig. 5, and this must cast some doubt on their accuracy. The cross-section data of van Raan et al. (1971) are larger than those of Moustafa Moussa et al. (1969) except at the highest energies where they decrease more rapidly than E^{-1} and are therefore suspect. Figure 6 shows these data normalized to the value of Moustafa Moussa et al. (1969) at 200 eV together with the absolute data of Showalter and Kay (1975) and that of Zapesochnyi and Feltsan (1965) normalized to their value at 50 eV. At energies above 80 eV all the data are satisfactorily consistent, but there is significant divergence at lower energies. We place the greatest reliance on the absolute, polarization-free measurements of Showalter and Kay (1975) extended toward the threshold by the relative, good resolution data of Zapesochnyi and



FIG. 6. Excitation function of the 492-nm line of helium: (+) Moustafa Moussa *et al.* (1969), absolute measurement; (\triangle) van Raan *et al.* (1971), normalized at 200 eV; (\Box) Showalter and Kay (1975), absolute measurement; $(\cdot \cdot \cdot \cdot)$ Zapesochnyi and Feltsan (1965), normalized at 50 eV.

Feltsan (1965). The data available for other lines of this series are less complete, but we show in Fig. 7 our interpretation, which is principally based on the absolute data of Moustafa Moussa *et al.* (1969) above 100 eV and on the relative data of Zapesochnyi and Feltsan (1965) between threshold and 50 eV.



FIG. 7. Excitation functions of the $n {}^{1}D - 2 {}^{1}P$ lines of helium: (+) Moustafa Moussa *et al.* (1969); (\triangle) van Raan *et al.* (1971); (\Box) Showalter and Kay (1975); (\cdots) Zapesochnyi and Feltsan (1965).

3. The ¹P states

Excitation to the ${}^{1}P$ states may be studied by observing the radiative transitions to the ground state or to the metastable $2^{1}S$ state. The relative intensities of the corresponding lines depend strongly on the target density and on the dimensions of the scattering chamber, because resonance radiation absorbed within the chamber reexcites the upper state, which has a "second chance" to emit the longer wavelength line. This process, known as the trapping or imprisonment of resonance radiation, is well known, though the very low densities required to reduce the effect are perhaps not so well appreciated. Absolute radiometry is difficult for either line. The resonance lines lie in the vacuum ultraviolet where this is never easy, and the intensity of the longer wavelength line reflects the small branching ratio and is much more sensitive to imprisonment effects. It is of no advantage to use a target density high enough to give essentially complete conversion of resonance radiation to the longer wavelength because deexcitation of the ^{1}P -state atoms by collision with other atoms could not then be neglected. van Raan and van Eck (1974), Showalter and Kay (1975), and Westerveld and van Eck (1977) discuss the scale of this and related effects. The polarization of the light is also affected (Heddle and Lucas, 1963), because the reference direction provided by the electron beam is lost.

Table VI lists the seven measurements made since 1969 and identifies the transitions observed. In every case the authors have either made an absolute determination or have normalized their data in some way to the Bethe approximation, but the details of the normalization and the allowance for cascade has shown certain variations. We have used the approach described in Appendix C to carry out a consistent normalization of all the data. The cascade population is important, and we have used the ${}^{1}S$ data of Van Zyl et al. (1980) and the ^{1}D data of Moustafa Moussa et al. (1969) to estimate this. Table III gives the cascade contribution from ${}^{1}S$ states to the $2 {}^{1}P$ state directly, and we can immediately construct the analogous table for other ${}^{1}P$ states using the transition probabilities of Theodosiou (1987). We then sum the contributions to each of the ${}^{1}P$ states, extrapolate as described in Appendix B, and express each total as a multiple of the $4^{1}S$ cross section. For example, at 100 eV the ${}^{1}S$ cascade to the $3^{1}P$ state is

$$(3.89+1.48+0.59+0.60)\times 10^{-20} \text{ cm}^2$$

where the last figure is extrapolated, and this we can write as $0.69 \times Q_{4S}$. At other energies the factor is slightly different, but the mean value is 0.70 ± 0.01 . Similar calculations allow us to write for the total cascade population

$$J_{2P} = 3.75Q_{4S} + 3.79Q_{4D} ,$$

$$J_{3P} = 0.70Q_{4S} + 0.60Q_{4D} ,$$

$$J_{4P} = 0.20Q_{4S} + 0.16Q_{4D} ,$$

$$J_{5P} = 0.08Q_{4S} + 0.06Q_{4D} ,$$

	n =	2		3		<u>A</u>	5
Author	λ/nm	58.4	53.7	501.6	52.2	396.5	361.4
а		19.5		22.1		28.1	22.0
		1.13		1.06		1.20	1.23
		983		276		107	56
b				16.5			
				0.91			
				273			
с		23.6	23.1		20.4		
		1.01	1.01		1.05		
		1197	287		108		
d		19.5	23.5		21.5		
	*	1.06	0.96		1.02		
		1105	285		109		
e				21.0			
				1.06			
				266			
f		21.3	20.7				
		1.03	1.00				
		1059	245				
g		28.8	30.7		22.8		
		1.11	1.16		1.05		
		1081	262		110		

TABLE VI. Observations of lines from the n¹P states of helium. Each entry shows the energy E_0 of the intercept (eV); the scale factor β ; and the cross section at 100 eV (10⁻²⁰ cm²).

^aMoustafa Moussa *et al.* (1969). The data reported by these authors had been corrected for an unspecified amount of cascade population.

^bvan Raan *et al.* (1971). The data reported by these authors had been corrected for an unspecified amount of cascade population.

^cde Jongh (1971). These authors made measurements free from polarization effects; the others applied corrections for polarization.

^dDonaldson *et al.* (1972). The data published by these authors had already been fitted to a smooth curve. These authors made measurements free from polarization effects; the others applied corrections for polarization.

^eShowalter and Kay (1975).

^fWesterveld, Heideman, and van Eck (1975). These authors made measurements free from polarization effects; the others applied corrections for polarization.

^gShemansky et al. (1985). The data published by these authors had already been fitted to a smooth curve.

with the coefficients in the last equation being extrapolated.

The published data have been obtained bv polarization-free methods or have been corrected by their authors. A cascade correction has been made in a number of cases, and where the information is given we have added the values used and so obtained "cascade included" data for our analysis. In two cases (Donaldson et al., 1972; Shemansky et al., 1985) the published data are the result of the fitting of the observations to a normalizing curve, and we do not expect to obtain good fits. The first result of the normalization procedure is E_0 , the intercept of the Bethe-Fano line, and we note the minimum value in each case. The data of Shemansky et al. (1985) gave very high values; the number of data points at high energies was too small to allow us to examine the effect of ignoring those at the highest energy, as our procedure requires and which we found to be necessary in the case of the first three measurements. In Table VII we show the values of E_0 found by the original authors and the values found by our analysis. We also show the values calculat-

given by the	iven by the present analysis.								
Author	2 ¹ P	3 ¹ P	4 ¹ <i>P</i>	5 ¹ P					
а		20.0	25.4						
	19.5	22.1	28.1	22.0					
b		21.3							
		16.5							
С	22.7	22.7	21.3						
	23.6	23.1	20.4						
d	27.4	18.4	21.4						
	19.5	23.5	21.5						
e	L ·								
		21.0							
f	24.6	22.1							
	21.3	20.7							
g	32.9	35.8	25.7						
	28.8	30.7	22.8						
h	22.1	21.2	21.0	20.8					

TABLE VII. Intercepts (in eV) of Bethe-Fano lines. The upper

value is that given by the original analysis and the lower is that

^{a-g}As Table VI.

^hKim and Inokuti (1968).

ed by Kim and Inokuti (1968). In the light of these results we have used the theoretical values to define, with the known oscillator strengths and cascade contributions, the scale factors β , which we show in Table VI together with values of the excitation cross sections at 100 eV. In Figs. 8(a) and 8(b) we show the normalized excitation functions for the 2 and $3^{1}P$ states. Ligtenberg et al. (1988) have measured the cross sections for exciting the 58.4- and 53.7-nm lines using synchrotron radiation as their radiometric standard and reported values for an energy of 300 eV at the 1987 International Conference on the Physics of Electronic and Atomic Collisions. We have modeled the approach to the Bethe-Fano line using the expression of Eq. (C6) and show the result for the $2^{1}P$ in Fig. 8(a). The polarization of ultraviolet light from the ¹P states has been determined by Mumma et al. (1974) from observations at various angles, and, using a reflection polarizer, by McConkey et al. (1988), whose



FIG. 8. Excitation of resonance lines of helium. (a) Excitation function of the 2¹P level of helium: (\bigcirc) Donaldson *et al.* (1972); (\times) Westerveld, Heideman, and van Eck (1979); (\diamondsuit) Shemansky *et al.* (1985). The solid line is the result of a fit of the data of Westerveld, Heideman, and van Eck (1979) to Eq. (C6) with $E_R = 100$ eV and b = 0.32. (b) Excitation function of the 3¹P level of helium using data for the 53.7-nm (left) and 502-nm (right) lines: (\bigcirc) Donaldson *et al.* (1972); (\square) de Jongh (1971); (\times) Westerveld, Heideman, and van Eck (1979); (\diamondsuit) Shemansky *et al.* (1985); (+) Moustafa Moussa *et al.* (1969); (\triangle) van Raan *et al.* (1971); (∇) Showalter and Kay (1975).

measurements extend to 450 eV and show that the polarization passes through zero at 375 eV, a value reasonably consistent with the intercepts of the Bethe-Fano lines discussed above. Steph and Golden (1982) have deduced values for the polarization of the directly excited 58.4-nm line (i.e., free from cascade) from measurements of differential scattering cross sections and of electronphoton correlation parameters. Heddle and Lucas (1963) have measured the polarization of the 501.6-nm line up to 200 eV, and Heddle *et al.* (1977) have shown that the polarization of this line falls very rapidly from its expected threshold value.

4. The triplet states

The excitation of the triplet states is strongly dependent on pressure, especially at high energies, but only two experiments have explored this dependence adequately. van Raan et al. (1974; see also van Raan and van Eck, 1976) showed that measurements at pressures well below 1 mTorr were necessary for the proper correction of data on the $3^{3}P$ and $4^{3}D$ states, though their measurements do not extend below 100 eV and are only relative measurements, normalized to van Raan et al. (1971). Showalter and Kay (1975) did not use such low pressures, though their paper is also well documented, particularly in respect of their absolute radiometry, and their data include points at 50 and 60 eV. Figure 9 shows our interpretation of the excitation function of the $4^{3}S$ level corrected for cascade. Van Raan et al. (1974) give both raw and cascade-corrected data, from which it appears that the cascade correction they have used is equivalent to $0.05 \times Q'_{3P}$. Our own assessment of the cascade con-



FIG. 9. Excitation function of the $4^{3}S$ level of helium: (\triangle) van Raan *et al.* (1971), absolute measurement; (∇) van Raan *et al.* (1974), normalized at 100 eV; (\times) Anderson *et al.* (1973), normalized at 100 eV; (\square) Showalter and Kay (1975), absolute measurement; (\cdots .) Zapesochnyi and Feltsan (1965), normalized at 35 eV.

tribution agrees with this, and we have used it to correct the data of Showalter and Kay (1975). van Raan et al. (1971) worked at somewhat higher pressures and their data above 100 eV are progressively too high. At 100 eV their value is in excellent agreement with that of Showalter and Kay (1975), but it is some 15% higher than that of van Raan et al. (1974). We do not understand this discrepancy, as the latter paper states explicitly that the data were normalized to their earlier absolute measurements. We have normalized their data to the 100-eV value, and at 300 eV (the only other energy at which a proper comparison can be made) the agreement with Showalter and Kay (1975) is very good. Below 35 eV we have used the results of Zapesochnyi and Feltsan (1965) to indicate the shape of the excitation function, but the substantial discrepancy at 50 and 60 eV gives us little confidence in the absolute cross sections in the region where they should be most easily measurable. We also show the relative data of Anderson et al. (1973) normalized at 100 eV, but these do not help to resolve the problem. The situation is worse for the $3^{3}P$ and $4^{3}D$ states for which the pressure dependence is even greater. We have made no attempt to resolve the discrepancies in the data of van Raan et al. (1971, 1974) because the latter paper gives somewhat inconsistent values in its Table I and Figs. 3(b) and 4(c); however, we show in Fig. 10 apparent excitation cross sections for the 388.8-nm line on their authors' own scales. Below 50 eV we show the relative measurements of Zapesochnyi and Feltsan (1965) and of Whitteker and Dalby (1968) normalized to those of van Raan et al. (1971) at 40 eV. These two relative measurements agree extremely well in shape and clearly continue the form of the van Raan et al. (1971) data. In Fig. 11 we show measurements of the polarization of this line from close to threshold up to 50 eV by Whitteker and Dalby (1968) and by Humphrey et al. (1987). The



FIG. 10. Excitation function of the $3 {}^{3}P-2 {}^{3}S$ line of helium at 388.9 (nm): (\triangle) van Raan *et al.* (1971), absolute measurement; (∇) van Raan *et al.* (1974), absolute measurement; (\Diamond) Whitteker and Dalby (1968), normalized at 40 eV; (\Box) Showalter and Kay (1975), absolute measurement; ($\cdot \cdot \cdot \cdot$) Zapesochnyi and Feltsan (1965), normalized at 40 eV.



agreement between these polarization measurements is excellent. We also show the high-resolution data of Defrance (1980) near 58 eV as an inset. Whitteker and Dalby (1968) also measured the excitation and polarization functions of the 1083-nm line $(2^{3}P-2^{3}S)$ of helium to 50 eV. Both van Raan et al. (1974) and Showalter and Kay (1975) show the extremely strong pressure dependence of ${}^{3}D$ excitation where the analysis is further complicated by the unobserved cascade population from Fstates. An indication of the extent of the problem is given by Anderson et al. (1969, 1973) using time-resolved measurements, and recently Kay and Simpson (1988) have determined cross sections for the 3,43D, 4,5,6 ^{3}F , and 5 ${}^{3}G$ states at 100 eV from a study of the decay of the 588- and 447-nm lines. Bogdanova and Yurgenson (1986b) have studied the excitation of the n=3 states of helium for energies up to 200 eV using 14-nS pulsed electron beams. By this means they were able to reduce significantly the effects of collisional transfer and cascade, but at the expense of energy resolution near the thresholds. They used a target gas pressure of 8 mTorr and calibrated their intensity using the 728-nm line cross section of Van Zyl et al. (1980). Excitation of the 4F states has been studied directly by Jobe and St. John (1967), but at pressures high enough that secondary processes would be important. The excitation function of the 32-nm line from the doubly excited $2p^{23}P$ state has been measured by Westerveld, Kets, et al. (1979) from threshold (59.7 eV) to 150 eV, and van den Heuvell, van Linden, et al. (1980) have shown that the polarization of this line changes little, if at all, with energy and suggest that this might provide a polarization standard of 0.10 at this wavelength.

5. The metastable states and resonances

Mason and Newell (1987) have measured the excitation function of the combined singlet and triplet metastable states using a crossed-beam time-of-flight method. Their data extend to 150 eV and are normalized to measurements over a smaller range of energies by Borst (1974). Bogdanova and Marusin (1970, 1975) measured absolute excitation functions for the singlet and triplet metastable states by observing sensitized fluorescence of neon and cadmium, respectively. Shpenik et al. (1984) have studied the dynamics of the excitation process close to the threshold, and Brunt et al. (1977b) and Buckman, Hammond, Read, and King (1983) have studied the threshold region with very high energy resolution. Bolduc and Marmet (1975) have observed resonance structure near 60 eV in the metastable excitation function. Resonances close to the thresholds for excitation of optically allowed transitions have been studied by Kisker (1972a), Brunt et al. (1977c), and Heddle (1977, and references therein). van der Burgt et al. (1986) studied the excitation of 16 states between 57 and 66 eV. They noted that cascade population only affected the ${}^{3}P$ states and that postcollision interaction was of major importance. Defrance (1980) observed and analyzed the structure near 60 eV in the polarization functions as well as the excitation functions of a dozen states.

6. Excitation to ionic states

The 468.6-nm line, which corresponds to the transition from n = 4 to n = 3 in the helium ion, has been studied often. Figure 12 shows the agreement, both in shape and in absolute value, of measurements by Zapesochnyi and Feltsan (1965), St. John and Lin (1964, 1967), and Weaver and Hughes (1967). Haidt and Kleinpoppen (1966) measured the polarization of the light, finding a value near threshold of 0.13, but their excitation function was only a relative measurement. Moustafa Moussa and de Heer (1967) made measurements up to 3 keV, which agree quite well with the other data in Fig. 12 as regards the shape, but are a factor of 2 smaller. We have noted earlier that the absolute values found by this group for the ${}^{1}S$ cross sections are in excellent agreement with the benchmark data of Van Zyl et al. (1980), and the present discrepancy is strange. Shemansky et al. (1985), who seem to be unaware of the data shown in Fig. 12, suggest on other grounds that a cross section 1.5-3.3 times the latter value might be expected. Anderson et al. (1967b) measured the excitation functions of four of the lines ending on the n=3 state and normalized their data to the St. John and Lin (1967) value for the 468.6-nm line. Moustafa Moussa and de Heer (1967) and Shemansky et al. (1985) have measured the excitation functions of the lines at 164.0 and 121.5 nm, which terminate on the n=2 state, the former to much higher energy. The radiometry of the latter group is probably more accurate, though the disagreement between the two data sets is no



FIG. 12. Excitation function of the 468.6-nm line of He⁺, all data are absolute: (\bigcirc) Zapesochnyi and Feltsan (1965); (\square) Weaver and Hughes (1967); (\diamondsuit) St. John and Lin (1967); (+) Moustafa Moussa and de Heer (1967).

worse than for the 468.6-nm line. The most reliable absolute measurement of the excitation function of the first resonance line at 30.4 nm is probably that of Forand *et al.* (1985), whose results agree very well with a measurement at a single energy (200 eV) by Bloemen *et al.* (1981). Semenyuk *et al.* (1983) have measured the excitation functions of the first three resonance lines in relative terms: their normalization did not allow for the wavelength dependence of the sensitivity of their monochromator and is not correct.

Table VIII summarizes the reported observations of transitions in He^+ . With the exception of the resonance lines, all the lines of He^+ are unresolved multiplets and the excitation functions are not amenable to simple analysis. Sutton and Kay (1974) used fast pulse excita-

TABLE VIII. Wavelengths (nm) of observed transitions in He^+ .

	a fair anna a saona			
Lower Upper n n	1	2	3	4
2	30.4 ^{a-d}	-		
3	25.6 ^{a,d}	164.0 ^{a, e}		
4	23.7 ^d	121.5 ^{a,e,f}	468.6 ^{a,g-k}	
5			320.3 ⁱ	
6			272.3 ⁱ	
7			251.1 ⁱ	541.2 ^k

^aMoustafa Moussa and de Heer (1967).

^bBloemen et al. (1981).

^cForand et al. (1985).

^dSemenyuk et al. (1983).

^eShemansky et al. (1985).

^fMcConkey et al. (1988).

^gWeaver and Hughes (1967).

^hSt. John and Lin (1967).

ⁱAnderson et al. (1967).

^jHaidt and Kleinpoppen (1966).

^kZapesochnyi and Feltsan (1965).

tion and deduced the relative strengths of the components from the time-delay spectrum at the single energy of 200 eV. McConkey *et al.* (1988) measured the polarization of the 121.5-nm line from threshold to 480 eV and discussed their results in terms of the relative importance of the $4s \rightarrow 2p$, $4p \rightarrow 2s$, and $4d \rightarrow 2p$ components. They concluded that, because the threshold polarizations corresponding to these components would be 0, 0.43, and 0.49, respectively, the $4s \rightarrow 2p$ component dominates the excitation near threshold.

B. Neon

There are two major studies of excitation of lines in the visible and near uv and ir regions, neither of which made any measurement of nor correction for polarization. Feltsan et al. (1966) made absolute measurements of 28 lines having the $2p^{5}3p$ or 4p upper state and 22 lines from states with excited s or d electrons, many of the latter being unresolved blends. They were able to make corrections for the cascade population of the $2p^{5}3p$ states. They quote an absolute accuracy of 40%. Sharpton (1968) and Sharpton et al. (1970) used a somewhat different approach to determine absolute excitation functions for a rather greater range of transitions. They measured the excitation function for the strongest line from each upper state from threshold to 200 eV and measured the absolute excitation cross sections for these and many more lines at an electron energy of 100 eV. They make corrections for cascade population and also discuss the general form of the excitation functions of states of different angular momentum. They quote relative uncertainties of 15-20 % but do not make any estimate of the accuracy of their absolute radiometry. Both note a sharp peak at threshold in the excitation function of the $2p_{10}$ state.

Bogdanova and Marusin (1972) measured the excita-



FIG. 13. Excitation function of the $2p_7$ -1s₄ line of neon at 638.2 nm: (\bigcirc) Feltsan *et al.* (1966); (\times) Sharpton (1968).



FIG. 14. Excitation function of the $4d'_4 - 2p_9$ line of neon at 576.4 nm: (\bigcirc) Feltsan *et al.* (1966); (\times) Sharpton (1968); (\triangle) Bogdanova and Marusin (1972).

tion functions of seven lines having the $2p^{5}5s$ upper state configuration and one line from the $2p^{5}4d$. Smirnov and Sharonov (1973) measured the excitation cross sections for 35 lines in the near uv with $2p^5np$ (n = 4, ..., 9)upper states. Both of these experiments used the data of Feltsan et al. (1966) for calibration. Shaw et al. (1984) measured the excitation functions of the $np'[1/2]_0$ (n =3,4,5) levels using a pulsed excitation technique to discriminate against cascade population, which is reasonably small for these states. Their intensity calibration was made in terms of a calculated value for the 444-nm line of helium, which is fortunately in excellent agreement with the benchmark measurement of Van Zyl et al. (1980). The only polarization measurement seems to be that of Eckhardt et al. (1979), who give the polarization function of the $2p_5$ -1s₃ line at 626.6 nm from 100 to 1000 eV, a region in which the excitation is due almost entirely to cascade. Figures 13-16 compare some of these mea-



FIG. 15. Excitation function of the $3p_1$ - $1s_2$ line of neon at 352.0 nm: (\bigcirc) Feltsan *et al.* (1966); (\times) Sharpton (1968); (\triangle) Shaw *et al.* (1984); (\Box) Smirov and Sharonov (1973).



FIG. 16. Excitation function of the $2p_{10}$ -1s₅ line of neon at 703.2 nm, showing the threshold peak: (---) Feltsan *et al.* (1966); (----) Sharpton (1968).

surements. As Fig. 13 shows, the excitation functions of Feltsan et al. (1966) and Sharpton (1968) generally agree quite well in shape, though this is not a truly representative example because the ratio of the sizes of the cross sections is more commonly around 1.5 or even more. Figure 14 illustrates the general tendency of the excitation functions measured by Bogdanova and Marusin (1972) to rise more gradually from threshold. Figure 15 shows one of the measurements of Shaw et al. (1984) and of Smirnov and Sharonov (1973). Walker (1971) has examined the near-threshold regions of the $2p^{5}3p$ states and finds that most of them show evidence of a sharp onset or even a peak. Figure 16 shows the near-threshold region of the $2p_{10}$ excitation function showing the sharp threshold peak. Kisker (1972a), using velocity-selected electrons, has shown that there is much resonance structure close to threshold in some of the $2p^{5}4p$ states.

1. Excitation to states of the 2p⁵3s configuration

There are four states of this configuration; two, the $1s_2$ and $1s_4$ in Paschen's notation, are the upper levels of the resonance lines at 73.6 and 74.4 nm and have predominantly singlet and triplet character, respectively. The $1s_3$ and $1s_5$ are triplet levels with J = 0 and 2, respectively. The fullest investigation is that of Phillips et al. (1985), who studied all four levels using laser fluorescence to determine the rate of excitation of each state. In the case of the radiating levels the effective lifetime is substantially increased by imprisonment of resonance radiation. For these levels they normalized their relative measurements to the sum of calculated (Born approximation) direct excitation cross sections and measured (Sharpton et al., 1970) cascade. In the case of the metastable levels they took the population for electron energies greater than 90 eV to be due entirely to cascade and again used measured cross sections for this contribution. They estimate their absolute accuracy to be 28%. They show Bethe-Fano plots for the radiative levels, but do not comment on the intercepts. The intercept of the $1s_4$ line is at 18 eV, close to what we would expect, but for the other line it is about 13 eV, which suggests to us that either insufficient allowance has been made for cascade or that too much allowance has been made differentially at high energies. We believe the latter to be the case, as the ratio of the slopes of the Bethe-Fano lines is, at a value of 10, smaller than the ratio of the oscillator strengths. Despite this caveat we believe that they have made a much fuller and more correct allowance for cascade than is commonly found. There are three other measurements of the excitation of the metastable levels. Mityureva and Penkin (1983) made absolute measurements using the absorption of light from a hollow cathode lamp to determine the excited atom concentration. They only show excitation functions corrected for cascade. At 30 eV their crosssection values are about 80% of those of Phillips et al. (1985). Teubner et al. (1985) and Mason and Newell (1987) used a time-of-flight technique to separate the metastable and radiating atoms and determined the sum of the cross sections for exciting the two metastable states. There is a very good agreement in the shape of their excitation functions, which both fall rather faster with increasing energy above the maximum than that of Phillips et al. (1985). Teubner et al. (1985) normalized their data using a measured value (Dillon and Lassettre, 1975) for excitation of the singlet metastable state of helium; their value is 90% of that of Phillips et al. (1985) at the maximum, falling to 70% at 90 eV. For energies close to the threshold, resonance structure has been observed by Brunt et al. (1977a) in unresolved vuv (vacuum ultraviolet) lines of neon, and in the production of metastable atoms by Buckman, Hammond, King, and Read (1983) and Shpenik et al. (1984). These last authors discuss the collision dynamics in some detail.

2. Excitation to ionic states

Walker and St. John (1972) measured the excitation functions of some 50 states of Ne II having an excited s, p, or d electron outside a $2p^4$ core from threshold to 300 eV or, in some cases, to 1 keV. They examined the polarization of the light and found it to be zero or quite small. It would appear that Fig. 9 of their paper is printed upside down. Smirnov and Sharonov (1973) measured excitation cross sections for 38 lines of Ne II. They show four typical excitation functions. There are only 12 lines common to these two experiments, and in Fig. 17 we compare the data for two of them. The cross-section values of Smirnov and Sharonov (1973) are, on average, three times those of Walker and St. John (1972) and the spread is very large.

3. Inner-shell ionization

Hertz (1969) measured the excitation functions for the doublet of Ne II at 46.1 and 46.2 nm, which results from



FIG. 17. Excitation function of lines of Ne II: (a) 295.6 nm $(3p \, {}^{4}S-3s \, {}^{4}P)$; (b) 333.4 nm $(3p \, {}^{4}D-3s \, {}^{4}S)$. (×) is Walker and St. John (1972) and (\diamondsuit) is Smirov and Sharonov (1973).

the removal of a 2s electron and the subsequent decay to the ion ground state from threshold to 500 eV. Dijkkamp and de Heer (1981) have normalized the measurements of Luyken *et al.* (1972) for this doublet made at energies up to 4 keV. Hertz (1969) has also measured the excitation functions of the lines at 41 and 45 nm excited by the simultaneous removal of one 2p electron and the excitation of a second. He also observed the 49-nm triplet multiplet emitted following double ionization of a 2s and a 2p electron. This has also been observed, with better resolution, by Papp *et al.* (1977), who give the excitation function of the corresponding singlet transition as well. Smirnov and Sharonov (1972) have measured the excitation functions of seven lines of Ne III corresponding to transitions between terms of the $2p^{3}3l$ configurations from threshold to 500 eV. A later paper from the same group (Samoilov *et al.*, 1977) expresses doubts about the cross sections quoted in this first paperand presents further data for some 25 lines. Samoilov *et al.* (1976) have measured cross sections for exciting 33 lines of Ne IV and 17 lines of Ne V and show representative excitation functions. Their intensity calibration was made in terms of the Ne I data of Feltsan *et al.* (1966).

C. Argon

There have been two extensive absolute investigations of the excitation of visible and near-infrared transitions of Ar I. Feltsan and Zapesochnyi (1967) measured excitation cross sections for some 75 lines and show excitation functions for 49 of these, including a number having common upper states. Ballou *et al.* (1973) made a systematic study of the $3p^5ns$, np, and nd states. Their approach was to measure the excitation function of a strong line from each state and to determine the branching ratios for the various decay paths from measurements of relative intensities in a radio frequency discharge. Figure



FIG. 18. Excitation functions of four lines of argon: (a) $4d_4-2p_8$, 735.3 nm; (b) $2p_1-1s_2$, 750.3 nm; (c) $2p_5-1s_4$, 751.4 nm; (d) $2p_2-1s_2$, 826.5 nm. (\odot) is Feltsan and Zapesochnyi (1967) and (\times) is Ballou *et al.* (1973).

18 shows the general state of consistency of the two experiments. With two exceptions the agreement in shape is reasonable, and the mean ratio of the absolute values is 1.2 ± 0.4 (Feltsan/Ballou) with a trend to higher values with increasing wavelength. This is within the quoted uncertainties. Significant shape differences occur for the p_1 and p_5 states, which have double maxima. Feltsan and Zapesochnyi (1967) do not observe this feature at all in lines from the $2p_1$ and $3p_1$ states and find it to be rather small for the $2p_5$ and $3p_5$ states. We have resolved the conflict in the case of the p_1 states in the light of unpublished measurements by Haque (1971), who found the feature to be well developed in both states. Bogdanova and Yurgenson (1987b) studied excitation to the $2p_i$ (i =1-9) states with a target gas pressure of 12 mTorr using pulsed excitation (10-15 nS) to reduce the effects of collisional transfer and cascade population and found values considerably smaller than those of the previous measurements. Their intensity calibration used the helium 728-nm line cross section measured by Van Zyl et al. (1980).

1. Excitation to states of the $3p^{5}4s$ configuration

As in neon, two of the four states of this configuration are metastable and two are the upper states of the first resonance doublet at 104.8 and 106.9 nm. The excitation functions of both lines have been measured by Zhukov et al. (1972) to 150 eV and by McConkey and Donaldson (1973) to 2 keV. de Jongh (1971) and Mentall and Morgan (1976) have measured the 104.8-nm line only. This last measurement was calibrated in terms of the N I line at 120 nm formed by dissociation (Mumma and Zipf, 1971), whereas the other measurements were normalized using the Bethe approximation, but with an uncertain allowance for cascade. Mentall and Morgan (1976) claim that their measurement is free from all polarization effects, but, though they made their observations at 55° to the electron beam, they assumed that their grating was insensitive to polarization as though it were a mirror. Their excitation function peaks at a significantly higher energy than any of the others. The measurements of de Jongh (1971) and of McConkey and Donaldson (1973) were truly polarization free. Dassen et al. (1977) have measured the polarization of the resonance doublet combined in unknown proportions. Zhukov et al. (1972) made no measurement of nor allowance for polarization; the main significance of their data is in the sharpness of the rise from threshold of both lines. Forand et al. (1988) have measured the excitation cross sections for each of these lines at the single energy of 200 eV using Born approximation (Vainshtein, 1965) cross sections for the first five members of the hydrogen Lyman series as calibration standards. Their values are 15-20 % less than those of McConkey and Donaldson (1973).

The excitation function of the combined metastable states has been measured by Borst (1974) to 50 eV and by Mason and Newell (1987) to 142 eV. Both these measurements were made by a time-of-flight technique and the shapes of the excitation functions agree well. Borst (1974) established an absolute scale by two independent methods, and Mason and Newell (1987) normalized their data to this. Mityureva and Smirnov (1985) measured the excitation functions for the two metastable states separately, measuring the concentration of atoms in the two states by absorption of light from a hollow cathode lamp. They assumed a Doppler profile for the emission line. Any self-absorption would lead to an overestimate of the excitation cross section. Their data extend only to 30 eV for the J = 0 state and to 70 eV for the J = 2; both functions have maxima at slightly lower energy than in the other measurements. The sum of their cross sections are some 20% greater than the combined value of Borst (1974), but the shape agrees reasonably well. A later paper (Mityureva and Smirnov, 1986) extends measurements on the J=2 state down to the threshold region and makes a comparison with other data.

For energies close to the threshold, resonance structure has been observed by Brunt *et al.* (1977a) in unresolved vuv lines of argon and, in the production of metastable atoms, by Buckman, Hammond, King, and Read (1983) and Shpenik *et al.* (1984). These last authors discuss the collision dynamics in some detail.

2. Excitation to ionic states

Forty-seven transitions from states of the $3p^4nl$ configurations to the ground state of Ar^+ have been studied, free from all effects of polarization, by Tan and McConkey (1974). They show excitation functions from threshold to 2 keV for six groups of lines; that for a further group is given by Tan *et al.* (1974). They calibrated in terms of resonance lines of helium and neon, which were in turn based on Bethe-Fano plots. They claim a relative accuracy of 10% with 15-25% additional absolute uncertainty. Excitation functions for one of these lines and for two further ones are given by Shevera *et al.* (1978) from threshold to 400 eV in relative terms.

There are four measurements of the excitation functions of lines corresponding to transitions between excited states of Ar^+ . The most extensive is by Feltsan and Povch (1970), who report peak cross sections for 25 lines and show excitation functions of 17 from threshold to 200 eV. They did not measure polarization, but noted that an axial magnetic field had little effect on the shape of the excitation functions. Their measurements were absolute and they claim an uncertainty of 35%. Latimer and St. John (1970) studied eight lines from the $3p^44p$ configuration and the 5s-4p doublet at 421.8 and 422.3 nm. Six of these are laser lines. They did not measure polarization. Their measurements were absolute, but we believe were subject to a systematic error for which we are able to suggest some correction. In the same apparatus and on the same occasion they measured the excitation cross section of the $4^{1}S$ level of helium. The value they quote is appreciably larger than that found by Van Zyl et al. (1980); in the light of this observation, we believe their published values should be renormalized by multiplication by 0.63. Clout and Heddle (1971) measured the excitation and polarization functions for seven lines. They calibrated their cross-section scale in terms of the 492.2-nm line of helium using a value that is higher than we adopt in Sec. III.A.2; we believe that their published values should be multiplied by a factor of 0.84. Bogdanova and Yurgenson (1987a) studied the pressure dependence of the excitation functions for nine lines. Their intensity calibration was made in terms of the helium 505-nm line cross section measured by Van Zyl et al. (1980). We show the results of these four measurements for the 465.8-nm line (renormalized appropriately) in Fig. 19. The data of Feltsan and Povch (1970) rise more slowly than the others, but the agreement in shape is generally quite good, though the magnitudes differ significantly. Figure 20 shows the ratios of the peak cross-section values for eight lines studied in two or more of the four experiments. We have some doubts concerning the data of Feltsan and Povch (1970). The values in their table do not all agree with their graphs. Specifically, the table value for the line at 454.5 nm is half the graph value; for the line at 488.0 nm, it is double. We would not normally draw attention to a discrepancy of this nature as it could easily be a drafting oversight in omitting a scale factor (many of the other graphs are marked " $\times 0.5$ "), but in these cases another line from the same upper state has been measured and the crosssection ratios are in much better accord with the radiative transition probabilities of Wiese et al. (1969) if the values are taken from the graphs. On the other hand, they find that the cross sections for the 440.0-, 480.6-, and 500.9-nm lines, which all originate from the $4p \, {}^{4}P_{5/2}$ state, are almost equal, while the radiative transition probabilities are in the ratios of 2:5:1. For three lines not shown in Fig. 20, Bogdanova and Yurgenson (1987a) find cross-section values substantially larger than those of



FIG. 19. Excitation function of the 465.8-nm line of Ar II: (\Box) Bogdanova and Yurgenson (1987a); (\odot) Clout and Heddle (1971); (\times) Feltsan and Povch (1970); (\triangle) Latimer and St. John (1970).



FIG. 20. Ratios of peak cross sections for lines of Ar II to the values found by Latimer and St. John (1970): (\times) Bogdanova and Yurgenson (1987a); (\bigcirc) Clout and Heddle (1970); (+) Feltsan and Povch (1970).

Feltsan and Povch (1970); this, taken with the general trend shown in Fig. 20, indicates to us that the results of Feltsan and Povch (1970) become progressively too small at shorter wavelengths.

Rostovikova *et al.* (1973a) have studied excitation of lines corresponding to transitions between terms of the $3p^{3}nl$ configuration of Ar III. They report peak cross-section values for 33 lines and show two "typical" excitation functions extending to 400 eV. They normalized their data to lines of Ar I and II.

3. Inner-shell ionization

Ionization of one of the 3s electrons is followed by a radiative transition to the doublet ground state emitting the lines at 92.0 and 93.2 nm. The excitation functions of both components have been measured, free from all polarization effects, from threshold to 2 keV by Tan et al. (1974), who normalized their data to an unpublished result of van Eck (1971). A Bethe-Fano plot of their data for the 92.0-nm line has a reasonable intercept, but rather strange behavior above 1 keV. Forand et al. (1988) have measured the excitation cross sections for each of these lines at the single energy of 200 eV and find good agreement with these values. The intensity calibration of this measurement was made in terms of Born approximation cross sections for the Lyman series of hydrogen. The value they adopt for the line emission cross section of the Lyman alpha line $(4.3 \times 10^{-17} \text{ cm}^2)$ is in excellent agreement with our calibration shown in Fig. 2. Both components were also observed by Zapesochnyi et al. (1974) up to 150 eV. These authors normalized to a Born calculation (Omidvar et al., 1972). They used velocityselected electrons to show considerable detailed structure in the excitation function of the 92.0-nm line at energies up to 60 eV and indicate the energies of the $3s^23p^4nl$ states of Ar II and of the $3s^23p^5nl, n'l'$ doubly excited states of Ar I, which may decay to the $3s3p^6$ state by an Auger process. Papp et al. (1977) have measured the excitation functions of the lines at 76.9 and 88.7 nm, which result from the double ionization of a 3s and 3p electron leaving the Ar^{++} ion in a singlet or triplet P state. Their data extend to 400 eV and they claim an absolute accuracy of 30%. The cross-section scale was calibrated using the results of van Raan (1973).

D. Krypton

Feltsan (1967) has measured the excitation functions of 32 lines in the visible and near-infrared spectrum of Kr I, up to 100 eV in most cases. The data are absolute with a quoted uncertainty of 40% and include at least one line from each state of the $4p^{5}5p$ and 6p configurations. Polarization was not considered. Bogdanova and Yurgenson (1987c) studied excitation of the $2p_i$ (i=1-9) levels using pulsed excitation at a target gas pressure of 9.5 mTorr. They found cross-section values of about 30% of those of Feltsan (1967). Their intensity calibration was made in terms of the helium 728-nm line cross section measured by Van Zyl *et al.* (1980). Kisker (1972a) has observed resonance structure close to threshold in the excitation functions of four $3p_i$ states.

1. Excitation to states of the 4p⁵5s configuration

de Jongh (1971) has measured the excitation function of the 116.5-nm line from threshold to 1 keV normalized by the Bethe approximation, but with an uncertain allowance for cascade. Yakhontova (1970) measured the excitation functions of both resonance lines in relative terms up to 300 eV. Her data falls rather more slowly than that of de Jongh (1971). Zhukov et al. (1973) have made similar measurements up to 150 eV with rather better energy resolution. Pavlov and Yakhontova (1975) measured the cross sections at 150 eV for exciting each line in terms of the value, 7.73×10^{-20} cm², for the He⁺ 164-nm line measured by Moustafa Moussa and de Heer (1967). Their value for the 116.5-nm line is some 15% greater than that of de Jongh (1971). Close to threshold the combined doublet has been observed by Brunt et al. (1977a) and by Al-Shamma and Kleinpoppen (1977), who also measured the polarization. Mityureva et al. (1986) have measured the excitation functions of the two metastable states from threshold to 40 eV. They determined the concentration of metastable atoms by the absorption of light from a hollow cathode lamp. Mason and Newell (1987) measured the excitation function of the combined metastable states by a time-of-flight method and normalized their data to an electron scattering measurement by Trajmar et al. (1981). Their data, which extend to 150 eV, show a sharper onset and a more rapid fall after the maximum than that of Mityureva et al. (1986) and are smaller by a factor of 1.75 in the region of the maximum.

For energies close to the threshold, resonance structure has been observed in the production of metastable atoms by Buckman, Hammond, King, and Read (1983) and Shpenik *et al.* (1984). These last authors discuss the collision dynamics in some detail.

2. Excitation to ionic states

Two measurements of the excitation functions of lines between states of the $4p^4nl$ configuration of Kr II differ significantly in magnitude. Rozgachev and Yaroslavtseva (1970) report cross-section values for 23 lines between 40 and 140 eV. Some of their identifications are clearly wrong, and in other cases lines from the same upper state show different behavior. Rostovikova et al. (1973b) report maximum values of cross sections for 126 lines of Kr II and 57 of Kr III. They do not identify the transitions and show only specimen excitation functions that are certainly in error and should be disregarded. They show onset energies of 60-80 eV for lines whose upper states must lie below the double ionization potential of krypton, which is at 38.6 eV. Samoilov et al. (1975a) tabulate cross-section values for a number of lines of Kr II and also indicate cascade corrections that in some cases exceed the direct excitation cross section.

3. Inner-shell ionization

Shevera et al. (1978) have observed the excitation functions of the 96.4-nm line of Kr II and the 78.8- and 83.8-nm lines of Kr III, which result from the removal of a 4s electron and of a 4s and 4p electron, respectively. van Raan (1973) gives values for the cross section at 300 eV for exciting the first of these lines (and also the Kr II line at 91.7 nm), and Papp et al. (1977) give values at the maxima for the Kr III lines. These cross sections are not of high accuracy. Akagi et al. (1983) measured the excitation function of a line of Kr III at 90.6 nm that results from ionization of a 3d electron followed by an Auger process in which one of the 4s electrons fills this vacancy and the other 4s electron is ejected. The subsequent radiative transition populates the upper state of the 78.6-nm line and appears to be the principal source of excitation to this state.

E. Xenon

Feltsan and Zapesochnyi (1968) measured the excitation cross sections for 34 lines of Xe I and show excitation functions for 32 of these from threshold to 100 eV. Their measurements were absolute and they quote an uncertainty of 40%. Rostovikova et al. (1973c) measured cross sections for 36 lines using data from the former experiment for calibration. Despite this, the ratio (Feltsan/Rostovikova) of peak cross sections for the 10 lines common to the two experiments ranges from 0.3 to 1.3. They show typical excitation functions from which it is clear that their energy resolution is quite poor. They used an electron gun having a cathode 13×190 mm with a beam current of 50 mA and viewed the excitation along the length of the cathode. We note that a very slow onset of excitation in neon was observed by Bennett (1961), who also used a very long cathode. Borozdin and Smirnov (1979) measured the excitation functions in relative



FIG. 21. Excitation functions for lines of xenon from the (a) $3p_7$ and (b) $3p_8$ levels: (\bigcirc) Feltsan and Zapesochnyi (1968), $3p_7$ -1 s_3 , 864.8 nm, $3p_8$ -1 s_5 , 467.1 nm; (\triangle) Rostovikova *et al.* (1973c); (\times) Borozdin and Smirnov (1979); $3p_7$ -2 s_5 , 2858 nm, $3p_8$ -2 s_5 , 3047 nm.

terms for 11 lines in the infrared using a lead sulphide detector. There are just two cases in which transitions from the same upper states $(3p_7 \text{ and } 3p_8)$ have been observed at different wavelengths and the agreement in shape, while not good, is not unreasonable. Figure 21 shows excitation functions for lines from the two levels for which there are two or more measurements. We have normalized the data of Borozdin and Smirnov (1979) to those of Feltsan and Zapesochnyi (1968) at the maxima of emphasize the extent of the agreement. Kisker (1972b) has observed resonance structure near the thresholds for excitation of lines from the $3p_6$, $3p_8$, $4p_5$, and $5p_8$ states.

1. Excitation to states of the $5p^{5}6s$ configuration

Mukhitdinova and Yakhontova (1968) show the excitation function of the 147-nm line to 100 eV in relative terms. Pavlov and Yakhontova (1975) measured the excitation cross sections for this line and for the 129.6-nm line at an energy of 150 eV. Brunt *et al.* (1977a) have observed the excitation of the combined resonance lines with high energy resolution close to threshold, as have Al-Shamma and Kleinpoppen (1978), who also measured the polarization in this region. Excitation of the combined metastable states has been observed by Mason and Newell (1987) from threshold to 150 eV. They normalized their data using values close to threshold given by Blagoev *et al.* (1984). Penkin and Smirnov (1986) measured the excitation cross section of the J=2 metastable state using absorption of the 881.9-nm line to determine the metastable atom density; they show the excitation function to 32 eV.

For energies close to the threshold, resonance structure has been observed in the production of metastable atoms by Buckman, Hammond, King, and Read (1983) and Shpenik *et al.* (1984). These last authors discuss the collision dynamics in some detail.

2. Excitation to ionic states

Rostovikova *et al.* (1973c, 1973d) and Samoilov *et al.* (1975b) have measured the excitation functions of many lines of ionized xenon. The first paper presents data for Xe II and III, the second for Xe IV, V, and VI, while the third paper extends the data on Xe II. They show only representative excitation functions; their absolute values, though calibrated in terms of the Xe I data of Feltsan and Zapesochnyi (1968), are of more doubtful accuracy.

3. Inner-shell ionization

Shevera et al. (1978) have observed the excitation functions of the 110-nm line of Xe II and the 90.2- and 101.8-nm lines of Xe III, which result from the removal of a 5s electron and of a 5s and 5p electron, respectively. van Raan (1973) gives a value for the cross section at 300 eV for exciting the second of these lines, and Papp et al. (1977) give values at the maxima for both of the Xe III lines. Akagi et al. (1983) measured the excitation function of a line of Xe III at 108.9 nm, which results from ionization of a 4d electron followed by an Auger process in which one of the 5s electrons fills this vacancy and the other 5s electron is ejected; they also measured the excitation function of the 90.2-nm line, which is very largely excited by the cascade represented by the former line. The absolute scale is plainly not correct because the cascade exceeds the total 90.2-nm emission by some 20%; however, there is a not unreasonable agreement with the result of Papp et al. (1977), though this is probably fortuitous.

IV. THE ALKALI METALS

While target densities of the inert gases can be determined from direct measurements of pressure and temperature, the problem is much more difficult in the case of metal vapors. Many workers have attempted to deduce target densities from measurements of condensation rates or the absorption of resonance radiation; however, the accuracy is not high and internal calibration using the Bethe approximation offers the best solution and provides a test of the accuracy of absolute measurements because the relevant oscillator strengths are known rather accurately.

The principal measurements on the alkali elements have been on the resonance lines that dominate the spectrum, and the work of Gallagher and his colleagues at the Joint Institute for Laboratory Astrophysics represents a systematic study of the excitation and polarization functions of the resonance lines of the five elements. Many of the series lines of the neutral atoms have been studied with somewhat less absolute accuracy, and there have been many measurements of individual lines of the alkali ions that give little more than shape information.

Measurements of excitation from the 3P state of sodium are discussed in Sec. X and from lithium, potassium, rubidium, and cesium ions in Sec. XI.

A. Lithium

1. Excitation of the valence electron

The most significant measurements on the resonance lines of lithium are those of Leep and Gallagher (1974), who discuss earlier work, and those of Zapesochnyi, Postoi, and Aleksakhin (1976). The latter used a crossedbeam system and operated with a target density between 10^{10} and 10^{12} atoms/cm². They used a 127° electron monochromator. They did not study the polarization of the light. A Bethe plot of *QE* against log*E* for their data does not tend to a straight line and indicates considerable overestimation at high energies. We therefore believe the data of Leep and Gallagher (1974) to be the best available, though the published results require some correction in the light of more recent measurements on cascading transitions.

Leep and Gallagher (1974) also used a crossed-beam system, but with target densities no greater than 5×10^9 atoms/cm³. They measured the polarization of the unresolved doublet and made corrections for finite solid angle effects and for the isotopic composition of their sample. They did not measure the target density accurately nor do absolute radiometry, but calibrated the experiment using the Bethe approximation and the known oscillator strength of the transition. They needed to make



FIG. 22. Bethe plot for excitation of the 2P doublet level of lithium: (\bigcirc) Leep and Gallagher (1974); (\times) Zapesochnyi, Postoi, and Aleksakhin (1976).

a correction for cascade population and used cross sections measured by Aleksakhin and Zapesochnyi (1966, 1967). More recently, Zajonc and Gallagher (1979) have measured the excitation functions of the 3S, 4S, 3D, and 4D states, which dominate the cascade to the 2P state. Their values are significantly greater and we have recalculated the cascade correction and the normalization constant using the methods outlined in Appendix C. By extrapolating from these measured values we find that, at high energies, the product of energy and cascade contribution is 1.14×10^{-14} cm²eV. The oscillator strength is 0.750 and the threshold energy 1.847 eV, which give a value of 6.09×10^{-14} cm² for the parameter A_i of Eq. (C5). We take as the signal values the Q_T of Table I of Leep and Gallagher (1974) to construct our Table IX. A least-squares fit to the data in this table gives a scale factor β of 8.39×10⁻¹⁷ cm², which is some 7% less than the value used for the original calibration. The analysis also gives a value for the intercept of the Bethe plot of 1.09 eV. This is higher than the theoretical result (0.69 eV) of Vainshtein et al. (1965), but is more in accord with the energy at which the polarization of the light passes through zero, as discussed by Heddle (1979), who showed that a ratio of these two energies of e^3 might be expected. The present value for E_0 gives a ratio of 18.9. Figure 22 shows the modified Bethe plot. We have fitted the data point at 2.7 eV and all those above 23 eV to an expression

TABLE IX. Bethe normalization of the data of Leep and Gallagher (1974) for the resonance doublet of lithium. Values in columns 4-6 are all $\times 10^{-14}$ cm²eV. Least-squares fit gives slope of 8.39×10^{-17} cm² and an intercept at 2.20×10^{-15} cm²eV, which corresponds to an energy intercept at 0.0361 for $\log E_0$; $E_0 = 1.09$ eV.

E	S	SE	A logE	CE	$A \log E + CE$
1404	1.706	2395	19.17	1.14	20.31
1103	2.104	2321	18.53	1.14	19.67
802	2.765	2218	17.69	1.14	18.83
601	3.543	2129	16.93	1.14	18.07

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of the form given in Eq. (C6) and find values for E_R and b of 44.4 eV and 0.32, respectively. Above 23 eV the data are described to better than 1.5% by these values, which correspond to the dashed curve shown in this figure. We also show in this figure the data of Zapesochnyi, Postoi, and Aleksakhin (1976), which we have corrected for cascade population. The polarization measurements of Leep and Gallagher (1974) have been discussed by Heddle (1983), who shows that they are in excellent accord with the threshold value expected on grounds of conservation of angular momentum (Percival and Seaton, 1958) and with the high-energy behavior predicted by the Bethe approximation.

The excitation functions of the S and D states have been measured by Zajonc and Gallagher (1979) in terms of the resonance line cross sections and should therefore also be scaled by a factor of 0.93. They did not measure the polarization of the lines from the D states, and their theoretical correction for polarization could be improved by using the values measured by Hafner and Kleinpoppen (1967) for the 3D-2P line at 610 nm. This measurement is slightly suspect because their excitation function does not tend to a 1/E dependence at high energies, but the energy at which the polarization passes through zero (49 eV) is, at 12.6 times the excitation energy, in excellent agreement with the pattern noted by Heddle (1983) for optically forbidden excitations.

2. Inner-shell excitation and ionization

Excitation functions for seven states for which the inner electrons have been excited or removed have been reported, but only in relative terms. Feldman and Novick (1967) and Slavik et al. (1976) measured the excitation function of the 1s2s2p ⁴P metastable state from threshold at 57 eV to 90 and 80 eV, respectively, using different detection methods and found similar behavior. Zhmenyak (1982) measured the excitation function of the 20.75-nm line from the $1s2p^{22}P$ state from its threshold at 64 eV to 1 keV. Adler et al. (1973) measured the excitation function of the 1s2p ³P state from the ground state of the neutral atom from threshold at 64 eV to 350 eV and the polarization function up to 100 eV. They estimate a value for the excitation cross section at 100 eV of $3 \times 10^{-22 \pm 1}$ cm² and determined the radiative lifetime of the state to be 45±5 nS. Zhmenyak et al. (1982a) observed the first four members of the n ¹P-1 ¹S series of Li II and show the excitation functions of the first two on a relative, but internally consistent, scale. They also observed the first and second members of the n^2P-1^2S series of Li III on the same scale of intensities. Their data extend from threshold to 1 keV. Aleksakhin et al. (1984) have identified six lines that have as their upper and lower states autoionizing levels of neutral lithium. They show the excitation function from threshold to 300 eV of one of these lines (293.4 nm) and note that, at 70 eV, it is comparable in intensity with the 8P-2S resonance doublet. They also show the excitation function of the $3^{3}S-2^{3}P$ line of Li II, which, at 300 eV, is still increasing.

B. Sodium

There are two major and complementary papers that between them establish the absolute scale of the excitation cross sections. Enemark and Gallagher (1972), using a crossed-beam system, measured the excitation and polarization of the unresolved D lines from threshold to 1003 eV. They applied a correction for cascade population using S and D excitation function data of Zapesochnyi and Shimon (1965) and normalized their measurements using the Bethe approximation. Phelps and Lin (1981) measured the excitation and polarization functions of six members of the sharp and principal series and seven of the diffuse series, as well as three of the nP-4Slines and spot measurements of four fundamental lines at 15 eV. Their measurements were absolute. Radiometry was based on a quartz-iodine irradiance standard, and target density was determined from the transmission of light from a sodium resonance lamp excited by a xenon arc continuum. We believe that these authors are unique in using such a light source for this purpose. Usually a discharge lamp is used as the source, and distortion of the profile, even if not self-absorption, leads to underestimation of the target density and consequent overestimation of the excitation cross sections. The importance of this shows in the extremely good agreement between these two determinations of the D line cross section; Phelps and Lin (1981) find values that are some 6-10%greater than those of Enemark and Gallagher (1972). The cascade correction applied by Enemark and Gallagher (1972) tended at high energies to a QE value of 1.2×10^{-14} cm²eV. The Phelps and Lin (1981) data give 1.65×10^{-14} cm²eV, and we have applied this value to modify the correction and to recalibrate the Enemark and Gallagher (1972) result. This also leads to a scaling of the Phelps and Lin (1981) values. We show in Fig. 23



FIG. 23. Excitation function of the D lines of sodium: (\times) Enemark and Gallagher (1972); (\circ) Phelps and Lin (1981).

the result of this recalibration. The published values of Enemark and Gallagher (1972) have been multiplied by 1.006 and those of Phelps and Lin (1981) by 0.942 and are in excellent agreement above 20 eV. Both of these experiments were very fully documented, and this heightens our confidence that these excitation functions are reliable. Close to threshold Hafner (1973) and Cherlenyak et al. (1985) made relative measurements, while Stumpf and Gallagher (1985) normalized their data using the Bethe approximation. All three measurements are shown in Fig. 24 and agree very well in the shape of the excitation function. Stumpf and Gallagher (1985) also measured the excitation function of the 3D-3P line at 818 nm and found values somewhat smaller than those reported by Phelps and Lin (1981). Application of the scale factor 0.942 to the latter results yields very close agreement.

1. Inner-shell excitation

Feldman and Novick (1967) report the excitation function, in relative terms only, of a long-lived state that they tentatively identify as $2p^{5}3s^{3}p^{4}D$. Zhmenyak *et al.* (1982b) show excitation functions for lines at 39.6 and 40.5 nm, which they identify as due to transitions from the $2p^{5}3p({}^{3}P)3s^{2}D$ and $2p^{5}3p^{3}s^{4}S$ states to the ground state of the atom. They quote absolute values obtained by comparison with the resonance line of the sodium ion for which a calculated cross section was used. They find a fairly sharp peak at a few eV above threshold in both cases. DuBois *et al.* (1981) have measured the anisotropy coefficient for excitation of a 2p electron and find a minimum in a similar position.

2. Excitation to ionic states

This occurs by ionization of one or more of the 2p electrons in conjunction with possible excitation of the 3s



FIG. 24. Excitation function of the sodium D lines close to threshold: $(\cdot \cdot \cdot \cdot)$ Cherlenyak *et al.* (1985); (---) Hafner (1973); (---) Stumpf and Gallagher (1985).

electron. Apart from some preliminary work there are two nonoverlapping reports. Zhmenyak et al. (1983) observed lines from states of the $2p^5nl$ configuration of Na II (n=3,4,5,6,7; l=0,2) to the ground state of the ion and from states of the $2p^4nl$ configuration of Na III (n=3,4; l=0,2) to that ground state. They show excitation functions from threshold to 1 keV for four of the Na II lines and seven of the Na III. They used a crossedbeam system and calibrated in terms of a theoretical value for the $3s'[1/2]_1$ level, which is the upper state of the 37.2-nm resonance line. Smirnov and Shapochkin (1981a) and Shapochkin and Smirnov (1981) report measurements on ionic (Na II) lines that do not involve the ground state of the ion. The first paper lists peak cross sections for 44 classified lines and for 13 that are unidentified. They show excitation functions for three of the upper states, $3p[1/2]_1$, $4s'[1/2]_0$, and $3d[1/2]_1$. The second paper lists peak cross sections for 15 of the upper states studied in the first paper, but four of these are inconsistent with the sum of the line cross sections from that paper. Using published data on radiative lifetimes they deduce radiative transition probabilities for 50 lines from these upper states. However, the values they present are not consistent with their cross-section values. It is difficult to have much confidence in this work.

C. Potassium

As in the case of sodium there are two extremely welldocumented experiments whose results can be combined to improve the accuracy of both. Chen and Gallagher (1978) measured the excitation and polarization functions of the 4P-4S resonance doublet and normalized their relative data to the Bethe approximation using a calculated cascade contribution (Vainshtein et al., 1965). Phelps et al. (1979) measured excitation and polarization functions for 24 lines absolutely. They used a tungsten strip lamp as a radiance standard and measured their target density by the absorption of light from a potassium resonance lamp excited by the continuum of a xenon arc. Their results for the resonance lines are in excellent shape agreement with those of Chen and Gallagher (1978), but are some 10% higher. We have used their measured values for the cross sections of the cascading transitions to recalibrate the Chen and Gallagher (1978) experiment and find that the values given in their Table I should be multiplied by 1.061. Excellent agreement then results if the data of Phelps et al. (1979) are multiplied by 0.934. Figure 25 shows the effect of this recalibration. There is one anomalous result in the work of Phelps et al. (1979). Their values for the polarization of the resonance line are significantly higher than those of Chen and Gallagher (1978) and are not wholly consistent with the predictions of theory (Heddle, 1983). All their other polarization data, for sodium as well as potassium, seem to show a much greater consistency. Close to threshold Papp et al. (1983) have studied the excitation function using a trochoidal electron monochromator; their result



FIG. 25. Excitation function of the resonance doublet of potassium: (×) Chen and Gallagher (1978); (○) Phelps *et al.* (1979); (——) Papp *et al.* (1983).

is also shown in Fig. 25. Postoi *et al.* (1974) have reported signs of resonance structure both near threshold and at about 20 eV, the latter of which they suggest is due to resonances based on inner-shell excited states.

1. Inner-shell excitation

Feldman and Novick (1967) and Slavik *et al.* (1976) have observed excitation to the long-lived $3p^{5}4s 3d^{4}F$ state using different detection mechanisms. The two measurements gave similar excitation functions, but neither was really an absolute determination. Aleksakhin *et al.* (1981a) observed radiation from the $3p^{5}4s 3d^{4}P_{5/2}$ states and show the excitation function of one line, from the latter state, at 72.3 nm. They used a crossed-beam system and used synchrotron radiation for relative sensitivity calibration. Their absolute cross sections are derived from theoretical values for the ion resonance lines.

2. Excitation to ionic states

Aleksakhin, Vukstich, and Zapesochnyi (1974) show excitation functions for three resonance lines of K II at 60.1, 60.8, and 61.3 nm from threshold to 200 eV. Vukstich et al (1974) show, in addition, the second resonance doublet at 46.5 and 46.9 nm. Postoi et al. (1975) have measured in absolute terms the excitation functions of 36 lines of K II in the visible and near uv. They give a table showing the cross-section values at 100 eV and at the maxima, but the few excitation functions they publish are not identified with the spectrum lines. Aleksakhin, Bogachev, and Zapesochnyi (1975) show the excitation function of the 76.6-nm line of K III corresponding to the transition $3s3p^{62}S-3s^{2}3p^{52}P$. Smirnov and Shapochkin (1981b) report cross sections for 16 lines of K III calibrated in terms of the K II data of Postoi et al. (1975); however, they show only one excitation function, and it is labeled with an incorrect wavelength.

D. Rubidium

Chen and Gallagher (1978) have measured the excitation and polarization functions of the resolved resonance doublet from threshold to 1500 eV using crossed electron and atom beams and have normalized their measurements to the Bethe approximation using an experimental value for the radiative oscillator strength and theoretical values for the cascade contribution and the Bethe intercept (Vainshtein et al., 1965). The value of energy at which their measured polarization passes through zero is in quite good accord with this value of the Bethe intercept. The only experimental data on the cascading transitions are in papers by Shimon (1964) and Zapesochnyi and Shimon (1966a): the former has clearer diagrams, but the latter covers more transitions and gives crosssection data. They show excitation functions for five members of the sharp series, six members of the principal series, and seven members of the diffuse series from threshold to 30 eV. They claim an absolute accuracy of 30-35%, but we believe this is rather optimistic.

1. Inner-shell excitation

Feldman and Novick (1967) measured the excitation function of the $4p^{5}5s4d^{4}F$ long-lived state from threshold to 50 eV and quote a maximum cross section of order 10^{-18} cm². Aleksakhin *et al.* (1981a) measured the excitation function of the $4p^{5}5s5p^{4}S-4p^{6}5p^{2}P$ line at 82.4 nm from threshold to 35 eV and quote a peak cross section of 2.8×10^{-18} cm².

2. Excitation to ionic states

Aleksakhin, Vukstich, and Zapesochnyi (1974) have measured the excitation functions of the three resonance lines of Rb II at 69.7, 71.2, and 74.2 nm from threshold to 200 eV normalized to calculated values. Shimon (1964) shows the excitation function of a line of Rb II at 478 nm, and Zapesochnyi and Shimon (1966a) report cross sections at 70 eV for this and 14 other lines of the ion. Smirnov and Shapochkin (1979a) present tables of cross sections, cascade corrections, and transition probabilities for many states of Rb II. It is not possible to make any tests for consistency of these data as they are plainly incomplete. We attach no importance to this paper and cite it only as a warning. Smirnov and Shapochkin (1979b) have measured excitation cross sections for 35 lines of Rb III between 260-360 nm. They quote peak cross sections for 28 of these (and values at 70 eV for the remainder) and show three excitation functions representative of all the lines. They used a crossed-beam system, though their atomic beam had a divergence of 33°, and calibrated in terms of the Rb II data of Zapesochnyi and Shimon (1966a).

E. Cesium

Chen and Gallagher (1978) measured the excitation and polarization function of the $6^2 P_{3/2}$ - $6^2 S_{1/2}$ resonance line at 852 nm from threshold to 1500 eV and normalized their data to the Bethe approximation using calculated (Vainshtein et al., 1965) values for the cascade population and for the intercept of the Bethe line, but an experimental value for the radiative oscillator strength. The only other determination made with crossed beams and extending over a wide range of energies is that of Zapesochnyi, Postoi, and Aleksakhin (1976). Their data are considerably larger and show a slower rise from threshold, features which are common to their results for all the alkalis. The only extensive study of excitation to other states is by Zapesochnyi and Shimon (1964, 1966b): the first paper shows clearer excitation functions, and the second gives further detail and tabulates cross-section values for seven members of the sharp series, five of the principal series, eight of the diffuse series, and five of the fundamental series. The excitation functions of all but the fundamental series show a slight enhancement around 12-15 eV. Postoi et al. (1973), using a 127° electron monochromator, have demonstrated the existence of resonance structure both at this energy and closer to the ionization threshold. Gehenn and Reichert (1977), also using a 127° monochromator, have shown very clearly that there is a sharp resonance peak immediately above threshold in both components of the resonance doublet, a feature also seen in the results of Zapesochnyi, Postoi, and Aleksakhin (1976).

1. Inner-shell excitation

Feldman and Novick (1967) have measured the excitation function of a long-lived state of cesium from threshold to 30 eV. Aleksakhin *et al.* (1981a) have observed light from a number of autoionizing levels and show the excitation function of a line at 108.5 nm, which has the $6p^{5}6s5d {}^{4}P_{5/2}$ state as its upper level, alongside an ejected electron function (Pejcev and Ross, 1977) to demonstrate the common origin.

2. Excitation to ionic states

Postoi *et al.* (1975) studied excitation of 40 lines of Cs II and give a table of cross sections determined in absolute terms. They also show some excitation functions, but these are not identified with particular transitions. Aleksakhin, Vukstich, and Zapesochnyi (1974) show the excitation functions of the three resonance lines of Cs II at 81.4, 90.1, and 92.7 nm from threshold to 200 eV and quote cross sections based on normalization to theory. Smirnov and Shapochkin (1979c) show the excitation function of a line of Cs III at 276 nm and quote cross sections for this line and eight others based on normalization to the Postoi *et al.* (1975) Cs II data.

V. THE ALKALINE EARTHS

Excitation from the metastable states of strontium and barium is discussed in Sec. X; excitation from ions of all the alkaline earths is discussed in Sec. XI.

A. Beryllium

The only measurements reported on neutral beryllium are those of Aleksakhin and Zayats (1974). They show excitation functions for the 2*P*-2*S* resonance line, the 4*D*-2*P* and $2^{3}P$ - $2^{3}S$ lines, and the $2^{2}P$ - $2^{2}S$ resonance line of Be II. Their data are relative but internally consistent. They also quote cross sections, on the same consistent scale, for three other lines, including the $2p^{2}{}^{3}P$ displaced term, at an electron energy of 30 eV. All the excitation functions show significant enhancement above 50 eV. The ordinate scale is incorrectly labeled, and though we have attempted to normalize these data using the Bethe approximation, we do not believe that any sensible figure can be quoted.

B. Magnesium

The excitation function of the resonance line at 285 nm has been measured from threshold to 1400 eV by Leep and Gallagher (1976) and over smaller, but still substantial, energy ranges by Karstensen and Koster (1971) and by Aleksakhin et al. (1973). Shpenik et al. (1979) have studied the threshold region using a trochoidal electron monochromator. Leep and Gallagher (1976) also measured the polarization function, and their results are in accord with the expected high-energy behavior (Heddle 1979, 1983). They normalized their cross-section measurements to the Born values of Robb (1974) using also his values for the cascade contribution. The measurements of Aleksakhin et al. (1973) are absolute, but their values lie some 40% below those of Leep and Gallagher (1976). They also show a significant enhancement above 50 eV and do not give a sensible Bethe plot. The rise from threshold is rather slower than in the other data. Karstensen and Koster (1971) made only relative measurements. Figure 26 is a composite that we believe gives the best overall picture of the excitation function.

Aleksakhin *et al.* (1973) also quote cross sections for a further 37 lines of Mg I and show excitation functions for 9 of these, including the intercombination line at 457 nm. The values quoted are much smaller than the Born approximation would suggest. Shpenik *et al.* (1979) show excitation functions for eight lines (some blended), and we show in Fig. 27 composite excitation functions for the 518-nm $(4^{3}S-3^{3}P_{2})$ and 553-nm $(4^{1}D-3^{1}P)$ lines with their data normalized to that of Aleksakhin *et al.* (1973). However, their greatly improved resolution would suggest that the peak cross-section values are even larger than those shown in this figure.



FIG. 26. Excitation function of the magnesium resonance line at 285.2 nm: (\bigtriangledown) Kartstensen and Koster (1971); (\times) Leep and Gallagher (1976); (\Box) Shpenik *et al.* (1979).



FIG. 27. Excitation function of lines of Mg I: (a) 518.4 nm $(4^{3}S-3^{3}P)$; (b) 552.8 nm $(4^{1}D-3^{1}P)$. (\odot) is Aleksakhin *et al.* (1973) and (_____) is Shpenik *et al.* (1979).

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1. Inner-shell ionization

Vukstich *et al.* (1980) show excitation functions for the $2p^{5}3s^{2}P-2p^{6}3s^{2}S$ line of Mg II at 24.9 nm, the $2p^{5}3d$ and $2p^{5}3s^{1,3}P-2p^{6}S$ lines of Mg III at 18 and 23 nm, and the $2s2p^{6}S-2s^{2}2p^{5}P$ line of Mg IV at 32 nm, the last of these showing considerable structure. The data are relative and extend to 1 keV. DuBois *et al.* (1981) have measured the anisotropy coefficient for ionization of a *p* electron and find that it has a minimum at 75 eV and passes through zero at 2.5 keV.

2. Excitation to ionic states

Leep and Gallagher (1976) measured the excitation and polarization functions of the unresolved resonance doublet and normalized their data to their value for the Mg I resonance line. The ratio of their cross sections at the respective maxima is 0.071. Karstensen and Koster (1971) measured the excitation function only for the unpolarized $3^{2}P_{1/2}$ - $3^{2}S$ line at 280 nm, but made spot measurements for five other lines. The ratio of the maximum cross sections of the ion and neutral resonance lines is 0.28, and the form of the excitation function is more sharply peaked. Aleksakhin et al. (1973) measured the excitation functions for the resolved doublet and show data that are virtually identical in form for the two components. This is rather surprising, because they neither measured nor corrected for polarization and we would expect the excitation functions to be different. Perhaps their spectrometer had high polarization sensitivity. Their value for the peak cross section for the combined doublet is only 1% of their value for that of the neutral resonance line. Taken with their apparently very low values for other lines, this leads us to wonder whether there has been a transcription error in their table of cross sections. They measured cross sections for three other lines of Mg II and show excitation functions for two of these. We show in Fig. 28 the excitation functions of the



FIG. 28. Excitation function of the resonance doublet of Mg II at 280 nm: (\times) Leep and Gallagher (1976); absolute measurement; (\odot) Aleksakhin *et al.* (1973), normalized at the maximum.

combined resonance doublet with the data of Aleksakhin et al. (1973) normalized to that of Leep and Gallagher (1976). As a consequence of our earlier observation we have not applied any polarization correction to the former data; such a correction would have improved the agreement around the peak.

C. Calcium

Garga et al. (1974) have made extensive measurements of excitation functions in absolute terms. They used a crossed-beam system and measured their target densities using published (Okudaira, 1970) ionization cross sections. They quote an absolute uncertainty of 40%. They give cross-section values for 43 lines of Ca I and show excitation functions (mainly to 30 eV, but some of 300 eV) for 26 of these, including eight from displaced terms of the 3d4p, $3d^2$, and $4p^2$ configurations. Ehlers and Gallagher (1973) have measured excitation and polarization functions of the 4P-4S resonance line of Ca I at 423 nm from threshold to 1400 eV. They normalized their data using the Bethe approximation to define an asymptotic slope and made allowance only for cascade population originating in higher P states. In doing this they treated the intercept of the Bethe-Fano line as a completely free parameter. This can, however, be estimated in two ways. It has been calculated by Kim and Bagus (1973), who find 1.90 eV. It can also be deduced (Heddle, 1979) from the energy at which the polarization passes through zero; Ehlers and Gallagher (1973) find 37.0 eV for this energy, giving 1.84 eV for the Bethe-Fano line intercept, in excellent agreement with the calculated value. We have renormalized these data. In the notation of Eq. (C3) we set $E_0 = 1.87 \text{ eV}, f = 1.75, \text{ and } E_i = 2.933 \text{ eV}$ to find

$$QE = 8.95 \times 10^{-14} \log E - 2.43 \times 10^{-14} \text{ cm}^2 \text{eV}$$

for the high-energy asymptote of the excitation cross section of the 4P state. We add to this the cascade contribution, which we take as increasing the slope by 0.5% (following Ehlers and Gallagher, 1973) and as 1.2×10^{-17} cm² at 1400 eV from an extrapolation of the data of Garga *et al.* (1974) for the S and D contribution. This gives us for the level excitation cross section the asymptotic behavior

$$QE = 9.00 \times 10^{-14} \log E - 7.75 \times 10^{-15} \text{ cm}^2 \text{eV}$$

Of this excitation, 1.1% will appear in the transition to the 4s 3d ¹D metastable state, and the line excitation cross section is therefore

$$Q'E = 8.90 \times 10^{-14} \log E - 7.66 \times 10^{15} \text{ cm}^2 \text{eV}$$
.

The intercept of this line is at 1.22 eV, and we show in Fig. 29 the data of Ehlers and Gallagher (1973) (the R_T of their Table I) fitted to a line with this intercept. The asymptotic slope of this line is 63, which gives a scale factor $(8.9 \times 10^{-14}/63) = 1.41 \times 10^{-15}$ cm² to be applied to the R_T values and gives the scale shown on the right-



FIG. 29. Bethe plot for the resonance line of Ca I at 422.7 nm. Data are from Ehlers and Gallagher (1973). The Bethe-Fano line and the dashed curve are discussed in the text.

hand ordinate. This renormalization represents an increase of 10.4%. The absolute uncertainty in these normalized cross sections is predominantly that of the radiative oscillator strength for which three experimental determinations agree to better than 5%. We have fitted the data for energies above 10 eV to the form given in Eq. (C6) and find values for E_R and b of 92.5 eV and 0.366, respectively. The fit is less satisfactory than in the case of lithium (Fig. 22) with discrepancies of up to 3%. The resonance line cross-section data of Garga et al. (1974) is a factor of 2 smaller, extends only to 30 eV [though an extension to 300 eV is shown by Aleksakhin et al. (1971b)] and is more sharply peaked, as shown in Fig. 30. The different shape may be to some extent a consequence of ignoring polarization, but their measurements were made at a target density high enough $(2-5 \times 10^{11} \text{ cm}^{-3})$ to cause some depolarization. Garga et al. (1974) also observed the intercombination line at 657 nm and quote a peak cross section of 3.8×10^{-17} cm² at 3.4 eV. Dobryshin et al. (1982) measured the excitation func-



FIG. 30. Excitation function of the resonance line of Ca I at 422.7 nm: (\times) Ehlers and Gallagher (1973) as renormalized in Fig. 29; (\odot) Garga *et al.* (1974), normalized at the maximum.

tions of all three of the $4 {}^{3}P_{0,1,2}$ levels by observing laser fluorescence from each level and found that they all had the same form. They determined the target density from measurements of the transmission of light from a resonance lamp whose profile they measured. They took the oscillator strength of the resonance line to be 1.49 and consequently underestimated the cross sections. Their published values should be multiplied by 175/149=1.17. These corrected values are in reasonable accord with the statistical weights of the three levels, and the value for the $4 {}^{3}P_{1}$ level is 10 times that of Garga *et al.* (1974). This smaller value probably reflects significant loss of excited atoms by diffusion out of the observed collision region before radiating.

1. Inner-shell ionization

Ugrin (1978) has measured the excitation functions of the $3p^{5}3d^{3}P_{1}$, $3p^{5}3d^{3}D_{1}$, and $3p^{5}4s^{1,3}P_{1}$ states of Ca III from observations of their transitions at 49.1, 44.0, and 41.0/40.4 nm to the ion ground state. He has also observed the 51.1- and 53.4-nm lines of Ca II from the autoionizing quartet states of the $3p^{5}3d4s$ configuration and shows the excitation function of the latter. These data extend to 300 eV and are relative only.

2. Excitation to ionic states

The only quantitative measurements are those of Garga et al. (1974), who give cross-section values at the maxima and at 30 eV for the $4^{2}P$ - $4^{2}S$ and $5^{2}S$ - $4^{2}P$ doublets, but a preliminary report by Aleksakhin et al. (1971a) shows the excitation function of the $4^{2}P_{3/2}$ - $4^{2}S_{1/2}$ line at 383 nm.

D. Strontium

Starodub et al. (1973) and Aleksakhin, Garga, et al. (1974) have made extensive absolute measurements of excitation cross sections of (respectively) singlet and triplet states of Sr I, and they show excitation functions for many of these from threshold to 30 eV or, in some cases, to 300 eV. Their data include several displaced terms and they note the influence of series perturbations. They used crossed electron and atom beams, though their target densities $(10^{11}-10^{12} \text{ cm}^{-3})$ are probably high enough to depolarize the resonance lines significantly. They claim an absolute accuracy of 30-40%. The excitation function of the intercombination line at 689 nm is shown by Aleksakhin et al. (1971a) from threshold to 30 eV. Chen et al. (1976) measured the excitation and polarization functions of the 5P-5S resonance line at 461 nm from threshold to 1497 eV. They also used crossed beams, but with densities less than 5×10^8 cm⁻³, and calibrated their measurements using the Bethe approximation (Kim and Bagus, 1973) with an experimental value of the radiative oscillator strength and cascade estimated from the measurements of Starodub *et al.* (1973). Their values for the cross section are some 1.75 times those of Starodub *et al.* (1973), but there is a very reasonable agreement in shape as we show in Fig. 31. The difference in magnitude is probably a further consequence of the high target density in the latter experiment. Kazakov *et al.* (1985) show that the structure observed by Chen *et al.* (1976) in both excitation and polarization functions is more complex and suggest that it is due to resonances rather than cascade.

1. Inner-shell excitation and ionization

Aleksakhin *et al.* (1978) observed the lines of Sr I at 58.4 and 62.4 nm and identify the upper states as $4p^{5}5s^{2}nl$. They show the excitation function of the first line from threshold to 300 eV. Aleksakhin *et al.* (1978a) show the excitation functions of four lines of Sr III and one of Sr IV and suggest that the excitation mechanism is ionization of a *p* electron followed by single or double autoionization.

2. Excitation to ionic states

Starodub *et al.* (1973) measured the cross sections for ionization into the $5{}^{2}P_{1/2,3/2}$ and $6{}^{2}S_{1/2}$ states and show excitation functions for one member of each doublet. Chen *et al.* (1976) measured the excitation and polarization functions of each component of the ionic resonance doublet. The cross-section ratios within the doublets agree well, but the absolute values differ by a factor of 1.5. The form of the excitation functions agree very well up to the maximum near 30 eV but diverge at higher enrgies, as shown in Fig. 32.



FIG. 31. Excitation function of the resonance line of Sr I at 460.7 nm: (\times) Chen *et al.* (1976), absolute measurement; (\bigcirc) Starodub *et al.* (1973), normalized at the maximum.



FIG. 32. Excitation function of the resonance line of Sr II at 407.8 nm: (\times) Chen *et al.* (1976), absolute measurement; (\bigcirc) Starodub *et al.* (1973), normalized at the "shoulder" near 21 eV.

E. Barium

Aleksakhin, Zapesochnyi, et al. (1975) measured the excitation cross sections of 49 states of Ba I, including several displaced terms of configurations 5d6p, 5d7p, and $6p^2$, and show excitation functions for 22 lines from threshold to 30 eV with some to 300 eV. They used crossed beams and claim an absolute uncertainty of $\pm 40\%$. Chen and Gallagher (1976) measured the excitation and polarization functions of the resonance line at 553 nm. They used crossed beams, but with a much lower target density, and normalized their data to the Bethe approximation using data from Kim and Bagus (1973). They used the experimental values of Aleksakhin, Zapesochnyi, et al. (1975) to estimate the cascade contribution. The two determinations of the resonance line excitation function differ in three ways: the values of Aleksakhin, Zapesochnyi, et al. (1975) are about 70% of those of Chen and Gallagher (1976); the onset of their excitation function is noticeably more gradual; and there appears to be some enhancement above 30 eV.

1. Inner-shell ionization

Aleksakhin *et al.* (1978) have measured the excitation function of a line of Ba II at 71.2 nm, which has an unidentified autoionizing term as its upper state. Aleksakhin, Bogachev, and Ugrin (1977) show the excitation functions of five lines of Ba III between 55 and 75 nm having upper state configurations $5p^{5}5d$ or 6s. Aleksakhin, Bogachev, *et al.* (1977) also show two of these, but in addition they show the excitation of a line of Ba III at 69.5 nm, which results from the ionization of one of the 4*d* electrons of Ba I and a subsequent Auger process. Aleksakhin *et al.* (1981b) give relative values for the peak cross section of the five Ba III p^{5} lines. Wendt and Karstensen (1984) measured the cross sections of three of these lines in absolute terms using an argon photoionization chamber to calibrate their spectrometer and the Ba I resonance line data of Chen and Gallagher (1976) to establish the cross-section scale. They report data at single energies and make a comparison with the abovementioned relative data. The agreement is surprisingly poor: they find the ratio of the cross sections for exciting the lines at 58.7 and 55.5 nm to be 1.1, while Aleksakhin *et al.* (1981b) find 3.2.

2. Excitation to ionic states

Aleksakhin, Zapesochnyi, et al. (1975) measured the excitation cross sections for the line transitions from the 6^2P , 6^2D , and 7^2S states of Ba II and show excitation functions for three of the lines from threshold to 300 eV. Chen and Gallagher (1976) measured the excitation function of the resonance doublet and the polarization function of the $P_{3/2}$ component. The two experiments agree excellently in the size of the cross sections, but the more gradual onset and high-energy enhancement of the data of Aleksakhin, Zapesochnyi, et al. (1975) are again apparent.

VI. ELEMENTS WITH d¹⁰sⁿ OUTER SHELLS

The closed d shells of these elements lead to fairly simple spectra, but there are a significant number of coreexcited states with energies much the same as those of the simple terms. The most important elements in this group are zinc, cadmium, and mercury, where the principal aims of excitation function studies have been to understand the mechanisms responsible for laser action and to describe the very prominent resonance structure close to the thresholds for excitation.

Excitation from excited states of copper and mercury is discussed in Sec. X and from zinc, cadmium, and mercury ions in Sec. XI.

A. Copper

Borozdin et al. (1977) and Krasavin et al. (1982b) studied the excitation of many lines of Cu I and show excitation functions up to 200 eV for 8 and 14 lines, respectively. The first paper does not identify the eight lines. They used an electron gun with a very large cathode and an extended target beam. Their radiometric standard was the 391-nm bandhead of nitrogen. Aleksakhin et al. (1979b) used a conventional crossed-beam system to study excitation of 18 lines and show excitation functions for nine of these to 30 eV with extension to 300 eV in three cases. Their radiometry was done in terms of tungsten and deuterium lamps. They compare their cross-section values for five lines with those of Borozdin et al. (1977). The latter data are substantially larger and the maxima lie at higher energies. A similar trend is apparent in the data of Krasavin et al. (1982b), who do not



FIG. 33. Excitation function of lines of Cu I: (a) 296.1 nm $(4p'^2F_{7/2}-4s^2^2D_{5/2})$; (b) 333.8 nm $(4p'^4F_{7/2}-4s^2^2D_{5/2})$. (\bigcirc) Krasavin *et al.* (1982b) (published data $\times 0.1$); (\times) Aleksakhin *et al.* (1979b).

cite the work of Aleksakhin *et al.* (1979b). We compare their data for the only two lines for which they both show excitation functions in Fig. 33. Smirnov (1985b) studied 42 lines of Cu II and gives cross-section values at 50 eV and eight representative excitation functions, though his table of observed lines refer to a further ten that are not shown.

B. Silver

Krasavin *et al.* (1982c, 1983) report cross-section measurements of, respectively, 14 lines of Ag I and 42 lines of Ag II. They quote cross-section values at 50 eV for all lines and show excitation functions to 250 eV for ten and six lines, respectively.

C. Gold

Shafranyosh *et al.* (1981) measured excitation cross sections for eight lines of Au I using a crossed-beam method in which the target density was determined by self-absorption of resonance radiation. They quote cross-section values at 30 and 50 eV for five weak lines and additionally at the maximum for three lines from the 6p ²P states. They show the excitation function of the resonance line at 267.6 nm from threshold to 300 eV.

D. Zinc

1. Excitation of the valence electrons

There has been no extensive study of excitation of the lines of Zn I. Table X summarizes the observations. Zapesochnyi and Shevera (1963) made relative measurements to 20-25 eV with an emphasis on structure close to threshold. Zapesochnyi and Palinchak (1966) used a crossed-beam system and made the only measurements for the resonance line. Their energy resolution was not as good and, for the resonance line only, their data extend to 100 eV. Shpenik et al. (1974) used velocityselected electrons and observed the structure in some triplet states with better resolution for energies up to 10-12 eV. Bogdanova et al. (1981) were particularly concerned with pressure effects and show excitation functions up to 150 eV and cross-section values at 100 eV based on normalization to the Zn II data of Penkin et al. (1972).

2. Excitation to ionic states

Inaba et al. (1986a) studied the excitation of 36 lines of Zn II, including seven involving displaced terms. They used a crossed-beam system and determined the target density from measurements of the absorption of the intercombination line of Zn I at 307.6 nm from a discharge lamp. For the transition probability of this line they used a value of 5.0×10^4 s⁻¹, appreciably greater than the $3.29 \times 10^4 \pm 10\%$ given by Reader et al. (1980), and their cross-section values should therefore be multiplied by 0.66. Their data extend to 200 eV and are in guite good shape agreement with earlier work (Anderson and Lee, 1970; Penkin et al., 1972); however, even when corrected, the data are larger by a factor of 2 or more. We show an example in Fig. 34. Because any ignored distortion of the profile of the line emitted by the discharge lamp would lead to an overestimation of the excitation cross

TABLE X. Lines of Zn I for which excitation functions are available.

availaule.					
Transition	λ/nm	а	b	C	d
$4^{1}P-4^{1}S$	213.9		+	,	
$6^{1}S-4^{1}P$	518.2	+			+
$7 {}^{1}S-4 {}^{1}P$	429.8	+			
$4^{1}D-4^{1}P$	636.2	+			+
$5^{1}D-4^{1}P$	463.0	+			
$5^{3}S-4^{3}P_{2}$	481.1	+	+	+	+
$4^{3}P-4^{1}S$	307.6	+	+	+	
$4^{3}D-4^{3}P_{2}$	334.5	+		+	
$5^{3}D-4^{3}P_{2}$	280.0	+	+		

^aZapesochnyi and Shevera (1963).

^bZapesochnyi and Palinchak (1966).

^cShpenik *et al.* (1974). ^dBogdanova *et al.* (1981).



FIG. 34. Excitation function of the $5^{2}S_{1/2}$ - $4^{2}P_{3/2}$ line of Zn II at 255.8 nm: (\diamond) Anderson and Lee (1970); (+) Penkin *et al.* (1972); (\circ) Inaba *et al.* (1986a), published data *0.66 as discussed in the text.

sections, we cannot be confident that they are more accurate than this factor suggests.

E. Cadmium

1. Excitation of the valence electrons

The excitation function of the resonance line of Cd I at 228.8 nm was measured by Zapesochnyi and Palinchak (1966) from threshold to 100 eV. Shpenik et al. (1974), using a 127° electron monochromator, observed this and seven other lines up to 10-12 eV. The most extensive measurements are those of Sovter et al. (1974), who show excitation functions up to 15 eV for 26 lines. They used a differentially pumped system and, for wavelengths greater than 370 nm, a depolarizing filter. Absolute cross-section values for these lines and 10 others are given based on absolute measurements by Zapesochnyi and Shevera (1964) of the lines at 430.7 and 515.5 nm. Note that the other reference cited for this data, Zapesochnyi and Shevera (1962), does not mention these lines at all and gives no absolute values. Sovter et al. (1974) claim an absolute accuracy no better than 55%. Bogdanova et al. (1978) show excitation functions for a number of lines for energies up to 150 eV. The energy resolution is very poor, and though they have used the crosssection values of Sovter et al. (1974) for calibration, the values are rather discordant, as Fig. 35 shows. The data of Shpenik et al. (1974) show considerable structure and, as they are only relative, we have scaled them so that this structure can be seen most clearly.

Mazing et al. (1974) have studied excitation of the $5 {}^{3}P_{0}$ metastable state of cadmium. They measured the concentration of metastable atoms by observing the transmission of the 467.8-nm line using a scanning Fabry-Perot interferometer to select a narrow band of



FIG. 35. Excitation functions of lines of Cd I: (a) 466 nm $(6^{1}D-5^{1}P)$; (b) 515 nm $(7^{1}S-5^{1}P)$. (\triangle) is Bogdanova *et al.* (1978), (\bigcirc) is Sovter *et al.* (1974), and (---) is Shpenik *et al.* (1974), relative scale.

frequencies within the profile of the line. Attenuations of 0.2% or less were observed. They give values for the cross section at four energies between 17 and 48 eV. At 17 eV their value of 1.8×10^{-16} cm² is 36 times that for the 5³P₁ state at 14 eV and rather larger than the 5¹P cross section; their value does not appear to be reasonable.

2. Excitation to ionic states

An extensive study of ionization to both simple and displaced terms of Cd II has been made by Goto *et al.* (1983, 1984). Their data are absolute and extend to 200 eV. They found little variation of polarization with energy, but the values that they present suggest that their corrections for instrumental effects are inadequate. The clearest evidence is the value of 8% that they find for the 274.9-nm line from the $6s^{2}S$ state, which we would expect to be unpolarized. They determined the target density in their cadmium beam from the transmission of the intercombination line of Cd I (326.1 nm) from a He-Cd discharge tube, and any self-absorption, which they

discount but we do not, will lead to an underestimate of the target density and a consequent overestimate of the cross sections. A light-emitting diode calibrated against tungsten and deuterium lamps was used for absolute radiometry. The two papers present absolute excitation functions for 10 and 39 lines, respectively, and the latter also gives cross sections at 50 eV for a further 21 lines. There are three other measurements on a more limited number of lines over a similar range of energies. They all find a more gradual decline of the cross section for energies above 100 eV; we are inclined to attribute this to the higher cadmium densities used and therefore prefer the more recent work using crossed beams. The absolute values of the cross sections found in these three experiments are less, however, by mean factors of 2.4 (Anderson and Lee, 1970: 8 lines), 1.9 (Varshavskii et al., 1970a: 10 lines), and 1.9 (Bogdanova et al., 1978: 5 lines), a consistency that casts doubt in our minds about the absolute accuracy.

Bogdanova and Yurgenson (1986a) studied the excitation of the resonance line at 226.5 nm using a pulsed electron beam. Their measurements were made with pulse widths of 400, 200, 100, and 50 ns. They show that an extrapolation to zero pulse width gives an excitation function essentially identical in shape to that of the $5^{2}P_{1/2}$ level determined by Goto *et al.* (1983) from measurements of the excitation functions of that line and of lines corresponding to cascade transitions.

Inaba *et al.* (1986b) have measured the excitation cross sections for ten lines of Cd III from states of the $4d^{8}5s^{2}$ configuration at 160 eV and show excitation functions of the six states involved. They calibrated in terms of the 274.9-nm line of Cd II and their values may therefore be rather high.

F. Mercury

1. Excitation of valence and core electrons

The simple spectrum and convenient roomtemperature vapor pressure of mercury have led to its being the most frequently studied species after helium, and it is perhaps surprising that the absolute values of the excitation cross sections are so poorly established. Jongerius (1962) measured the excitation functions of 31 lines from threshold to about 20 eV and tabulates values for the differential cross section at 15.4 eV. These numbers should be multiplied by 4π to give the quantity usually quoted. In the cases of the 184.9- and 253.7-nm resonance and intercombination lines, the calibration was not direct but relied on as assessment of the relative contribution of the (known) cascade population of the $6^{1}P$ and $6^{3}P_{1}$ states. And erson et al. (1967a) measured the excitation functions of 44 lines up to 90 eV, but only 11 of these were common to the Jongerius (1962) data; in these cases their cross sections were larger by a mean factor of 1.4 for $\lambda > 400$ nm, but slightly smaller at shorter wavelengths. Apart from the somewhat higher energy resolution of Jongerius (1962), the shapes of the excitation functions agree quite well. A much earlier study by Thieme (1932) measured absolute excitation functions for 12 of the lines studied by Anderson *et al.* (1967a) to 300 eV, but with quite poor energy resolution. Indeed, the only structures observed were the very prominent peaks in the ¹S excitation functions. His absolute values are some three times larger than those of Anderson *et al.* (1967a), and his excitation functions generally decrease rather more rapidly at high energies, as shown in Fig. 36 in which the data of Thieme (1932) and Jongerius (1962) have been normalized to those of Anderson *et al.* (1967a).

Anderson (1966) shows, in his thesis, excitation functions for some lines for which only cross-section data are given by Anderson et al. (1967a). There is considerable divergence in shape between transitions from the higher $n^{1}P$ states to the 7¹S and 7³S states, which illustrates the problems of overlapping weak lines. The lines at 607.2 and 671.6 nm, which are identified as having the $8^{1}P$ state as the upper level, are, in fact, from the coreexcited $5d^{9}6s^{2}6p$ J = 1 state at 78813.4 cm⁻¹, which Martin et al. (1972) describe as 58% ³P. Their excitation functions are, however, much more as ${}^{1}P$ functions, and there is a strong transition at 126.8 nm to the ground state. The cross-section values found by Anderson et al. (1967a) will be seriously affected by the imprisonment of this resonance line and therefore are not reliable. It is hardly surprising that Thieme (1932) also misidentified the 607.2-nm line. However, he shows, in addition, the excitation function for a line at 612.3 nm that also appears in an even earlier paper by Schaffernicht (1930). No later paper refers to this line, but it corresponds to a transition from the core-excited $5d^96s^26p^1D_2$ state at 78 676.7 cm⁻¹ to the normal $6s7s^{3}S_{1}$. Thieme's data indicate that the cross section is about 10% of that of the 435.8-nm line at 60 eV.

Kaul (1979) made a measurement of the cross section for excitation of the $6^{3}P_{1}$ state at 50 eV by a method that was first used by Cristofori et al. (1963) to calibrate a detector for Lyman alpha. He observed both the 253.7nm light from the decay of the state and the 407.8- or 435.8-nm light emitted in the cascade transition from the $7^{1}S$ or $7^{3}S$ state and measured the rates of the individual signals and of the time-delayed coincidence signal. From a knowledge of the angular correlation function for the successive transitions and the solid angles and other dimensions involved, the number of excited atoms can be found and thence the excitation cross section. In effect the radiometric calibration is being done without a standard lamp, the excitation tube being "self-calibrating." The value found by Kaul (1979) is 4.34×10^{-17} cm². Anderson et al. (1967a) did not observe the 253.7-nm line, and Jongerius (1962) determined the cross section only out to 18 eV. There is an indication (Arnot and Baines, 1935; Ornstein et al., 1935) that the cross sections at 15 and 50 eV are about the same. If we assume this to be the case, it appears that the value found by Jongerius



FIG. 36. Excitation functions of four lines of Hg I: (a) $6p' {}^{3}P_{1} - 7 {}^{3}S_{1}$ at 607.2 nm; (b) $9 {}^{1}P - 7 {}^{1}S$ at 623.4 nm; (c) $8 {}^{1}S - 6 {}^{3}P$ at 491.6 nm; (d) $6 {}^{3}D_{2} - 6 {}^{1}P$ at 577.0 nm. (______) Anderson *et al.* (1967a); (+) Thieme (1932); (______) Jongerius (1962).

(1962) is, at 2.64×10^{-17} cm², only 61% of that of Kaul (1979). If, however, we replace, where possible, the values used by Jongerius (1962) for the cascade transitions (by means of which he determined the 253.7-nm cross section) by the values found by Anderson *et al.* (1967a), the cross section is increased and brought into good agreement with that of Kaul (1979). We regard this as *some* evidence that the data of Anderson *et al.* (1967a) are the more accurate.

Zapesochnyi *et al.* (1964) reported a tentative measurement of the relative excitation function of the 184.9nm resonance line up to 100 eV. Ottley *et al.* (1974) measured the excitation and polarization functions up to 15 eV for natural mercury. McLucas *et al.* (1982) made similar measurements, using laser excitation and subsequent fluorescence to probe the excited atoms, and extended the measurements to specific isotopes. From measurements of excitation rates in a low-pressure discharge, Post (1984) has fitted an absolute cross-section scale to the relative excitation function of Ottley *et al.* (1974) and finds a value of $(2.1\pm0.6) \times 10^{-16}$ cm² at 15 eV, which is far greater than that determined by Jongerius (1962). He shows that cascade makes a much smaller contribution to the excitation than Jongerius (1962) had assumed.

A number of experiments have concentrated on the details of the structure observed close to the thresholds for excitation and have made no attempt to measure cross

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sections. Table XI lists the most important of these. Federov and Mezentsev (1965), Heideman et al. (1969), and Ottley and Kleinpoppen (1975) were particularly concerned with the polarization functions, and only the last of these used velocity-selected electrons. A later paper by Zaidi et al. (1978) compared the polarization of the 253.7-nm line from the I = 0 isotopes and the natural isotopic mix. Shpenik et al. (1976) and Shpenik (1977) used a trochoidal monochromator giving a resolution of 30-100 meV. Smit and Fijnaut (1965) used the retarding potential difference method of Fox et al. (1955). Although the structure is much sharper in their excitation function, careful study shows that it cannot all be a correct rendering of the variation of cross section with energy, but contains a contribution from the derivative of the cross section with respect to energy as a consequence of the energy modulation of the electron beam (Heddle, 1968). This is most apparent in the reduction of the height of the first maximum at 8 eV and in the depth of the minimum at 10 eV. Although Zapesochnyi and Shevera (1963) did not use velocity-selected electrons, their energy resolution is a little better than that of Jongerius (1962). Figures 37 and 38 show the excitation functions of the 253.7- and 546.1-nm lines and demonstrate the effect of improved resolution.

Excitation functions of the metastable states of mercury have been measured by Newman et al. (1985) and Zu-

λ (nm)	Transition	а	b	с	d	е	f	g
407.8	$7^{1}S-6^{3}P$							E
491.6	8 ¹ S-6 ¹ P	E	E					Ε
410.8	9 ¹ S-6 ¹ P	E						E
546.1 ^h	$7^{3}S-6^{3}P$	E	E, P	E				E
334.1	8 ³ S-6 ³ P		,				\boldsymbol{E}	E
671.6	$6p'^{3}P-7^{1}S$	E						
623.4	$9^{1}P-7^{1}S$	Ε						
253.7	$6^{3}P-6^{1}S$	Ε				E, P	\boldsymbol{E}	E
690.7	8 ³ P-7 ³ S	\boldsymbol{E}						
579.1	$6^{1}D-6^{1}P$	Ε			E, P			
434.7	$7 {}^{1}D-6 {}^{1}P$	E	Р		P			
577.0	$6^{3}D-6^{1}P$		Р		P			
296.7	$6^{3}D-6^{3}P$							E
313	$6^{3}D-6^{3}P$				•			E
365/6	$6^{3}D-6^{3}P$	E					E	E
302	$7^{3}D-6^{3}P$						E	

 TABLE XI. Measurements of the threshold region in Hg I: E, excitation function; P, polarization function.

^aZapesochnyi and Shevera (1963) to 25 eV. ^bFederov and Mezentsev (1965) to 14 eV. ^cSmit and Fijnaut (1965) to 18 eV. ^dHeideman *et al.* (1969) to 20 eV. ^cOttley and Kleinpoppen (1975) to 9 eV.

^fShpenik *et al.* (1976) to 12 eV. ^gShpenik (1977) to 13 eV.

^h435.8 and 404.7 nm also.







FIG. 37. Excitation function of the 253.7-nm intercombination line of Hg I: (____) Jongerius (1962); (. . .) Ottley and Kleinpoppen (1975); (- -) Shpenik *et al.* (1976). All data were normalized to 4.34×10^{-17} cm² at 15.4 eV (via Jongerius) following Kaul (1979) and displaced vertically for clarity.

FIG. 38. Excitation function of the $7{}^{3}S_{1}$ - $6{}^{3}P_{2}$ line of Hg I at 546.1 nm: (_____) Anderson *et al.* (1967a); (_____) Shpenik (1977); (. . .) Smith and Fijnaut (1965). All data were normalized to Anderson *et al.* (1967a) at 14 eV and displaced vertically for clarity.

bek and King (1987) from threshold to 17.2 eV with an energy resolution of 20 meV. Some discrimination between the four states involved was made by a careful choice of the material used as the detector of metastable atoms and by the use of a simple, but effective, velocity filter for the electrons ejected by them. These measurements were only relative. Their identification of a newly discovered metastable state just above the ionization potential has been questioned by Cowan et al. (1988), who suggest an alternative interpretation. Borst (1969, 1977) measured the excitation functions of the $6^{3}P$ and $^{3}D_{3}$ metastable states and normalized them using a simultaneous trapped-electron measurement. A number of very different methods have been used to measure the excitation functions of the $6^{3}P_{0}$ and $6^{3}P_{2}$ states separately. Krause et al. (1977) observed the "forbidden" radiation at 265.6 and 227.0 nm, respectively, emitted from the odd isotopes of mercury and also the sensitized fluorescence of nitrogen by the latter state and show excitation functions up to 8.5 eV. Hanne et al. (1985) studied the excitation of these states with a resolution of 50 meV using laser-induced fluorescence. Their excitation functions extend to 8 eV; they also measured the ratios of the cross sections for exciting the $M_1 = 0, 1, 2$ sublevels of the $6^{3}P_2$ state.

We mention a paper by Semenova and Smirnov (1977) if only to note that it is one of the least useful papers we have examined. These authors claim to have measured the excitation functions of 78 lines from threshold to 400 eV. They show no excitation functions and quote cross sections at the maxima for only 31 lines. These values are between 1.5 and 70 times those of Jongerius (1962) or Anderson et al. (1967a). For the 253.7-nm line they quote a maximum value of 1.68×10^{-16} cm², which is not at all unreasonable if their energy resolution were of the same order as these authors, but they then substract from that value a cascade contribution of 52% based on their own data. They used an electron gun with a very large cathode $(13 \times 190 \text{ mm})$, and we would not expect highenergy resolution; nevertheless, the maximum of the 253.7-nm excitation function does lie below the threshold for any cascade process.

2. Excitation to ionic states

Anderson and Lee (1970) measured the excitation functions for three lines of Hg II from threshold to 260 eV. Varshavskii *et al.* (1970b) made absolute measurements of excitation of 11 lines, but show excitation functions only for the resonance line at 194.2 nm and a typical Beutler line. They claim an accuracy of $\pm 80\%$. Their value for the peak cross section for exciting the line at 284.8 nm is only 40% of that of Anderson and Lee (1970). This is the only line common to these experiments. Semenova and Smirnov (1978) present peak cross-section data for 38 lines of Hg II and show four typical excitation functions. Their value for the 284.8-nm line is 70% of that of Anderson and Lee (1970). However, their values are ten times the latter's for the lines at 615.0 and 734.6 nm. This has to be an error because these three lines form a cascade sequence, $7^2 D_{3/2}$ - $7^{2}P_{3/2}$ - $7^{2}S_{1/2}$, and the apparent cross sections must be larger for the lower steps. For five other lines common to the work of Varshavskii et al. (1970b) and Semenova and Smirnov (1978), the data show a similar large discrepancy that suggests to us that there has been some error, perhaps in printing. They both observe the 398.3nm line corresponding to the $6p^2 P_{3/2}$ -5 $d^9 6s^{22} D_{5/2}$ transition, finding peak cross sections of 1.0 and 6.2×10^{-19} cm^2 , respectively. Crandall *et al.* (1975) have measured the branching ratio for this line and the 165.0-nm resonance line to be $\frac{1}{350}$. Using this result we can estimate the cross section for exciting the latter line to be 3.5 or 22×10^{-17} cm². Both of these estimates appear large in the light of the value found by Varshavskii et al. (1970) for the cross section for exciting the $6^2 P_{1/2} - 6^2 S_{1/2}$ line at 194.2 nm of 0.7×10^{-17} cm².

Blagoev and Dimitrov (1986) have measured excitation cross sections for nine lines of Hg II and ten of Hg III arising from displaced terms. They show excitation functions for three lines of each from threshold to 300 eV.

VII. ELEMENTS WITH p^n OUTER SHELLS

In this section we consider the elements of groups III-VI of the periodic table. The inert gases have been considered in Sec. III, and there have been no measurements reported on the halogen atoms.

A. Boron

The only reported measurement is by Kuchenov and Smirnov (1981), who used a crossed-beam arrangement with target densities of about 10^{10} cm⁻³. They observed the resonance doublet at 250 nm, the doublet at 209 nm from the $2s2p^{2}D$ displaced state, and an ion line at 345 nm, which has the $2p^{2}D$ state as its upper level. They show excitation functions up to 200 eV and quote peak cross-section values that are surprisingly large: 5.16×10^{-16} cm² for the 209-nm doublet, for example.

B. Aluminum

Shimon, Nepiipov, and Zapesochnyi (1975) measured the excitation functions of the five resonance lines (4S, 3D to 3P) from threshold to 300 eV and show the excitation functions up to 30 eV. They were not able to resolve the weak $D_{3/2}$ component at 309.28 nm from the much stronger $D_{5/2}$ 309.27-nm line and used the transitionprobability data of Wiese *et al.* (1969) to separate them. The S-state excitation functions show a slight indication of some structure close to threshold.

C. Gallium

Shimon, Nepiipov, et al. (1975) measured the excitation functions of 15 lines ending on the ground state, including 5 from core-excited $4s4p^{2}4P$ states. They quote cross sections at a number of energies up to 300 eV, but show the excitation functions over a much smaller range of energy. They also show excitation functions (over the full 300-eV range) for four lines of Ga⁺. Nepiipov (1975) published peak cross-section values for the five coreexcited lines, which are identical to those in the other paper, but shows an excitation function for the strongest line, which falls more rapidly beyond its maximum. He quotes an uncertainty of 40% for these measurements.

D. Indium

Shimon and Nepiipov (1974) measured the excitation functions of 17 lines ending on the doublet ground state, including 5 from core-excited states. The separation of the $J = \frac{1}{2}$ and $\frac{3}{2}$ terms of the ground state is large enough that resolution of the doublet structure presents no difficulties, and the published data show an inconsistency in the ratio of the cross sections, indicating a probable stray-light problem. Their numerical data extend to 300 eV, except for the core-excited lines, but their excitation functions are only shown to 25 or 50 eV. They also measured the excitation functions of five lines of In⁺ and show these over the full 300 eV.

E. Thallium

1. Excitation of the outer electrons

An extensive study of the excitation functions of thallium lines has been made by Shimon, Nepiipov, and Zapesochnyi (1972) and by Zapesochnyi, Shimon, and Nepiipov (1973). They used a vapor cell target and noted strong pressure effects, especially the enhancement of the 352.9-nm line consequent on the absorption of the 276.8nm resonance line. Shimon et al. (1973) discuss this in more detail. The first paper shows excitation functions for 19 lines to 30 eV and for 4 lines to 150 eV, the latter group emphasizing the different behavior of the ${}^{2}D_{3/2}$ and ${}^{2}D_{5/2}$ functions. The second paper gives values of the absolute excitation cross sections at their maxima for these lines and also for the two lines at 221.2 and 267.2 nm from the $6s6p^{24}P$ state to the doublet ground state. Excitation functions for these two lines are given by Shimon, Nepiipov, et al. (1972). The uncertainty in these absolute data is quoted as 50%. Chen and Gallagher (1977) measured the relative excitation functions of the 377.6- and 276.8-nm lines and the unresolved 351.9- and 352.9-nm lines from threshold to 1500 eV. They normalized their measurements for the first two lines using the Bethe approximation with calculated cascade contributions and intercepts, but experimental values of the oscillator strengths. Because the 352.9- and 276.8-nm line cross sections are related by a known branching ratio, Chen and Gallagher were able to separate the contributions to the unresolved 352-nm doublet and determine the excitation function of the 351.9-nm line. Their result for this line agrees quite well with that of Zapesochnyi, Shimon, and Nepiipov (1973), but both seem to be too large at high energies, judging by a Bethe plot. The agreement is poor for the 276.8-nm line, probably as a consequence of imprisonment of resonance radiation in the latter experiment. Chen and Gallagher (1977) also measured the polarization function of the 276.8-nm line and find good agreement with a Born calculation above some 10 eV with a minimum at lower energies.

2. Excitation to ionic states

Nepiipov and Shimon (1973) studied the excitation of 16 lines of Tl^+ (including four from $5d^96s^26p$ states) and two lines of Tl^{++} . They show excitation functions of 15 of these to 300 eV and quote peak cross-section values. Shimon *et al.* (1976) extended these measurements, in relative terms only, to eight lines in the vacuum ultraviolet, most of them involving the ground state. Shimon (1983) has analyzed these data and presents values for the level excitation cross sections and the cascade contributions. He quotes uncertainties of 30-40%.

F. Carbon

There have been no measurements reported for neutral carbon. Experiments on the excitation of carbon ions are described in Sec. XI.

G. Silicon

Kolosov *et al.* (1981) have studied excitation of lines of neutral silicon. They list 14 lines between 198 and 288 nm with their excitation cross sections at 50 eV. They show three excitation functions, but do not identify the lines involved. They determined their target density by condensing silicon vapor from their beam source, and their radiometry was done in terms of the 391.4-nm band of N_2^+ "whose excitation cross section is well known." It is difficult to have much confidence in these data. Peterkop (1985) has calculated the cross sections for some of these lines and finds values that are considerably smaller.

H. Germanium

Kolosov and Smirnov (1982a) have measured the excitation functions of 17 lines of germanium and show seven excitation functions representative of these. They have also measured the excitation cross sections at 25 eV for a further 28 lines. Their methods were similar to those for their measurements on silicon, and similar comments apply. Peterkop (1985) again finds considerably smaller values.

I. Tin

Kolosov and Smirnov (1986) measured excitation cross sections of 60 lines of tin and give values at 50 eV. They show excitation functions of 41 lines to 250 eV. Kolosov and Smirnov (1985) studied the ionization of tin into excited states by observing 12 lines. Two of these result from the removal of one of the *s* electrons to produce a $5s5p^{24}P$ state that decays to the ground ${}^{2}P$ doublet with the emission of lines at 215 and 237 nm. These are the strongest lines they observed. They show excitation functions of five of the lines and quote cross-section values for all 12. The radiometric standard for both papers was the 417-nm line of helium (Van Zyl *et al.*, 1980), and they quote an uncertainty of $\pm 25\%$.

J. Lead

Aleksakhin *et al.* (1979a) have measured excitation cross sections for 24 lines of lead and show excitation functions for eight of these. They used a crossed-beam system and conventional radiometry and quote an absolute uncertainty of 30-40%. They also observed four lines of Pb II and two of Pb III but do not show excitation functions for these. Aleksakhin *et al.* (1978b) observed a number of lines between 54 and 126 nm and identified most of them as due to Pb II, III, and IV. Their measurements are only relative, but they show excitation functions for three lines each of Pb II and III and one line of Pb IV from threshold to 300 eV. They note that some of the strongest lines result from the removal of a 6s electron to give Pb II or of a 5d and a 6p electron to give Pb III.

K. Nitrogen

Stone and Zipf (1973) have measured the excitation functions of four lines of atomic nitrogen. For the strongest lines, at 113.4 and 120.0 nm, they show the excitation functions from threshold to 400 eV. They determined their target density by resonance absorption using a discharge in helium with "a trace of nitrogen added." Their radiometry was done in terms of the cross section for the production of Lyman alpha radiation by electron impact on molecular hydrogen, and recent measurements of this cross section by Woolsey *et al.* (1986) indicate that all their cross-section values should be multiplied by 0.6. Spence and Burrow (1980), in a trapped-electron experiment, have found that there is a threshold peak in the excitation of the $2s^23p$ ⁴P state of nitrogen that is the upper state of the line at 120 nm.

L. Bismuth

The excitation of 20 lines of Bi I, 7 lines of Bi II, and 2 lines of Bi III has been studied by Shafranyosh, Starodub, et al. (1981) using a crossed-beam method. They determined the target density from measurements of the selfabsorption of the resonance line and used conventional radiometry. They quote uncertainties of 30-40%. They quote cross sections at 30 and 50 eV for all lines and peak values for the stronger lines of the neutral atom. They show excitation functions of eight lines to 45 eV. Smirnov (1985a) has measured the excitation functions of eight lines of neutral bismuth and two of Bi⁺ forbidden by the Laporte rule. The radiative lifetimes of 5-16 ms required that substantial corrections be made to the observed cross sections to compensate for the drift of excited atoms out of the observing region. Correction factors of several hundred were necessary. He shows excitation functions for eight lines and quotes cross-section values for all ten. His radiometric calibration was made in terms of the helium ¹S data of Van Zyl *et al.* (1980), and he quotes an uncertainty of 26% for the basic crosssection measurements; however, he makes no statement about the overall accuracy, which depends strongly on the values used for the radiative lifetimes. Smirnov (1986b) extended the measurements on Bi II to a total of 42 lines and gives cross-section values at 50 eV for all of these and excitation functions for 35, though he shows only 18 separate curves.

M. Oxygen

Zipf and Erdman (1985) present excitation functions for three lines of neutral oxygen at 98.9, 102.7, and 130.4 nm from threshold to 300 eV. These data represent a reconsideration of earlier measurements (Stone and Zipf, 1974) in the light of improved primary data (Zipf, 1986) and of some further, unpublished studies by Kao and Zipf (1985). The measurement of the target density used a resonance absorption technique, and the revised radiometry was based on recent determinations of the cross section for excitation of Lyman alpha by dissociation of molecular hydrogen. Stone and Zipf (1974) had previously studied the excitation of the 130.4- and 135.6-nm lines, and the more recent measurement suggests that these data were too large by a factor of 2.8. Zipf and Kao (1986) have studied the excitation of the autoionizing states $3s''^{3}P$ and $2s2p^{5}{}^{3}P$, which can also decay with the emission of lines at 87.8 and 79.2 nm, respectively. They show the excitation function of the first of these lines from threshold to 300 eV and give a value at 100 eV for the other. Zipf et al. (1985) have measured the excitation function of the O⁺ line at 83.4 nm, which results from the removal of a 2s electron from the neutral atom. They show an excitation function and give cross-section values from threshold to 325 eV. Haasz (1976) has studied excitation of some oxygen lines at longer wavelengths and quotes effective cross sections, but his data were obtained at rather high pressures and in the presence of very high pressures of nitrogen and may not be characteristic of the free atom.

VIII. ELEMENTS WITH dⁿ OUTER SHELLS

We have made a somewhat arbitrary decision to consider in this section those elements with unfilled d shells and no f electrons, though we would have included palladium and excluded lanthanum had there been any measurements to report on these elements.

With the exception of one paper on manganese, all measurements reported on elements in this section have been made by Yu. M. Smirnov of the Moscow Power Institute and his colleagues, and it is convenient to outline the common features of their work. These experiments are of great technical difficulty as a consequence of the refractory nature of the materials and their complex and closely spaced spectra. Vapor beams were generated by electron beam melting of a metal target held in a watercooled crucible. Powers of several kW were necessary, and temperatures at the liquid surface from which the atomic beam was evaporated could be as high as 3100 K, depending on the specific material. Beam densities were measured by weighing material condensed onto thin titanium foils; depositions of order 1 mg/cm² were typical and were determined to about 1%. The density in the interaction region, some 28 cm from the crucible, was generally about 10^{10} cm⁻³. The atomic beam passed through an electron gun having a cathode 190×13 mm and a tetrode structure. Currents of 25 mA were used and the electron beam was square-wave modulated at 830 Hz. They claim that 90% of the electrons have energies within 1 eV, but the slow onsets reported for all excitation functions suggest that the inhomogeneity is much worse than this. Electron energies of up to 250 eV were used. Light was collected in a direction parallel to the long axis of the gun, analyzed by a grating monochromator (1200 lines/mm), and synchronously detected. The spectrum resolution was 1-2 Å. The radiometric calibration was made in terms of the 391- and 428-nm bandheads of molecular nitrogen, and they usually claim a relative consistency of about 10% with an absolute uncertainty of 35% reflecting that of the nitrogen data. Their excitation functions are generally rather featureless and have slow, concave-upward onsets extending over several volts. We believe that these are probably instrumental artifacts, that the true excitation functions might have sharper onsets in many cases, and that their maxima may well lie lower in energy than shown. They usually show excitation functions for a limited number of lines, and these seem often to be grouped just by their shape. None of their papers gives a full account of their system or their procedures, but refer to others that are not always very helpful. In the one case in this section where a comparison can be made with measurements with a more usual geometry, their cross-section values are substantially larger.

A. Yttrium

Kuchenev and Smirnov (1984) studied excitation of 87 doublet and 32 quartet lines of neutral yttrium. They show excitation functions to 200 eV and quote crosssection values for 39 lines of which 11 were not classified. Using the same system Kuchenev and Smirnov (1982a) had studied the excitation of 12 lines of Y^{++} and show excitation functions to 200 eV for six of these.

B. Titanium

Kolesov *et al.* (1979) report measurements of the excitation cross section of an *unspecified* line at energies of 20, 30, and 70 eV. This paper shows a diagram of the apparatus used for this and many other measurements; though parts of the diagram are numbered, they are not identified or discussed in the text. Kuchenev and Smirnov (1983a) measured the excitation cross sections at 50 eV for 17 lines of Ti^+ and show excitation functions to 200 eV for 6 of these lines.

C. Zirconium

The only measurements reported on zirconium are those of Kuchenev and Smirnov (1983b), who give crosssection values for 18 lines and show 9 representative excitation functions.

D. Vanadium

Melnikov and Smirnov (1982a) measured the excitation cross sections for 32 quartet and 19 sextet lines of V I and show 12 excitation functions typical of different states. Krasavin *et al.* (1982a) show excitation functions for seven of the sextet states, and these do not agree with those shown in the earlier (at date of submission) paper. Their cross-section values are also substantially different.

E. Niobium

Kuchenev and Smirnov (1982b) measured the excitation functions of 21 lines and the cross sections at 50 eV for a further 45.

F. Chromium

Melnikov and Smirnov (1982b) measured excitation functions for 16 septet and 7 quintet lines of Cr I and show excitation functions for seven families. Melnikov and Smirnov (1981) measured the excitation functions for 17 lines of Cr II and show 3 representative examples.

G. Molybdenum

Bogdanov *et al.* (1982) studied excitation of 13 lines of Mo I and 30 of Mo II. They quote cross sections at 50 eV

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(a)

and show nine excitation functions for specific neutral lines and two of the ion.

H. Manganese

Melnikov et al. (1981a, 1981b, 1982) measured the excitation cross sections of 24 of the sextet lines, 13 of the octet lines, and 14 lines of Mn II. In the case of the lines at 539 and 543 nm, which connect the lowest octet states to the ground state, a substantial allowance had to be made for the loss of excited atoms from the observation region because of their long (0.1 ms) lifetimes. Shafranyosh, Shishova, et al. (1981) observed seven lines of Mn I and five of Mn II using a conventional crossedbeam system. They determined the target density from measurements of the self-absorption of the resonance lines and made their radiometric calibration using tungsten and deuterium lamps. Their values differ substantially from those of Melnikov et al. (1981a, 1982). Table XII compares the maximum values of the cross sections for the three lines of Mn I common to the two experiments and also the energies at which the maxima occur. Figure 39 compares the shapes of the excitation functions for the resonance lines, but really gives no useful information beyond that of Table XII. A very crude estimate, based on the transition-probability data of Reader et al. (1980), indicates that at high energy the cross sections lie somewhere between the two measurements. The measured cross sections will be affected by the imprisonment of resonance radiation. Shafranyosh, Shishova, et al. (1981) do not mention this process, but Melnikov et al. (1981a) made a correction that appears to have been excessive. Both measurements give values at 20 eV larger than the electron scattering experiment of Williams et al. (1978).

I. Iron

Kolosov and Smirnov (1983a) measured the excitation cross sections at 50 eV for 74 lines of Fe I and show excitation functions of 36 of these. Kolosov and Smirnov (1982b) measured excitation cross sections for 21 lines of Fe II at 50 eV and show excitation functions for three of these.

J. Cobalt

Kolosov and Smirnov (1983b) measured the excitation cross sections at 50 eV for 45 lines of Co I and show 12

TABLE XII. Cross sections for excitation of lines of Mn I.

	$E_{\rm max}$ (eV)		Q _{max} (10^{-18} cm^2)
λ (nm)	a	b	а	b
280	12	24	200	1800
358	12	30	2.4	38.5
403	5	14	77	500

^aShafranyosh, Shishova, et al. (1981). ^bMelnikov et al. (1981).



××××

×

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FIG. 39. Excitation functions of resonance multiplets of Mn I at 280 nm (a) and 403 nm (b): (×) Melnikov et al. (1981a); (0) Shafranyosh, Shishova, et al. (1981).

excitation functions representing 27 of these. Kolosov and Smirnov (1984) measured excitation cross sections for 17 lines of Co II at 50 eV and show excitation functions of two of these.

IX. THE LANTHANIDES

The spectra of the lanthanides are especially complex and, though the temperatures necessary to produce adequate beam densities are for the most part less than for the metals considered in Sec. VIII, measurements of excitation functions still present considerable technical difficulties. With the exceptions of holmium and lutetium, all the absolute cross-section data have been obtained by L. L. Shimon and his colleagues at Uzhgorod State University, and there are many features common to all their measurements. They used crossed-beam systems of a conventional type with target densities of 10^{10} cm⁻³ and their radiometry was based on tungsten and deuterium lamps. They quote absolute uncertainties of 30-40%. Except for the measurements in the vacuum ultraviolet, they used a grating monochromator of 2 Å/mm dispersion with slit widths of 0.2 mm. The data on holmium and lutetium is by Smirnov's group at the

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Moscow Power Institute, whose experimental methods we discussed in the introduction to Sec. VIII.

A. Samarium

Shimon, Golovchak, and Garga (1981) measured excitation cross sections for 52 lines (or blends) that terminate on the ground, ${}^{7}F$, multiplet. They quote values at 30 and 100 eV for all these lines and show the excitation function of the 443-nm line from threshold to 300 eV. Mityureva (1980) made relative measurements on 18 lines and shows excitation functions for 4 of these up to 100 eV.

B. Europium

Golovchak et al. (1978) studied excitation of lines of Eu I in which a single 6s electron is excited (13 lines and 11 excitation functions), both 6s electrons are excited (4 and 3), and a 4f electron is excited (5 and 1). Values of cross sections are given at the maximum and at 100, 200, and 300 eV, and the excitation functions are shown from threshold to 60 eV. Shimon et al. (1977) measured the excitation cross section of 10 lines from the $6^{7}P$ and $6^{9}P$ states of Eu II. They quote cross-section values at the maxima and show excitation functions from threshold to 300 eV for six of the lines. Shimon, Golovchak, et al. (1983) recalibrated the scale of these last two papers and note that all the cross-section values should be multiplied by a factor of 4.84. They extended the study of excitation of the 4f electron and show excitation functions for the five such lines of Eu I observed previously and also for two lines of Eu II. Goldovskii and Shimon (1976) measured the excitation functions, in relative terms, of eight lines resulting from the ionization of a p electron. These lie in the vacuum ultraviolet between 54 and 107 nm and they show the excitation functions up to 250 eV. In seven cases a threshold energy of about 30 eV was found, but for one line at 68.3 nm, the threshold was at 75 eV. Goldovskii et al. (1979) showed that this line arose from double ionization of two p electrons.

C. Gadolinium

Shimon *et al.* (1984) measured excitation cross sections for 29 lines of Gd I and list the values at the maximum and at energies of 30, 100, 200, and 300 eV for 19 of them, the remaining 10 being given at 30 eV only. They show excitation functions of six specific lines from threshold to 60 eV and note that all are very similar apart from the threshold region. They could detect no lines of Gd II and conclude that the cross sections for ionization into excited states are very small.

D. Holmium

Bodylev *et al.* (1984) measured the excitation functions of 39 lines of Ho I and give cross-section values and show excitation functions up to 250 eV for all of them.

E. Thulium

Shimon, Garga, et al. (1983) measured excitation cross sections of 26 lines at Tm I. They show excitation functions to 30, 60, or, in some cases, 300 eV. The data include lines from the $6s 6p^{1,3}P$ states and from a number of states in which one of the 4f electrons is excited to 5d, and they draw attention to the different forms of excitation function associated with the possible terms of the remaining $4f^{12}$ core.

F. Ytterbium

Shimon, Golovchak, et al. (1981) measured excitation cross sections for 36 lines of Yb including 26 resulting from simple excitation of a 6s electron, 2 from excitation of a 4f electron, 2 from excitation of both 6s electrons, 4 unidentified lines, and 2 lines of Yb II. They give crosssection values at the maxima and at 100, 200, and 300 eV and show excitation functions from threshold to 60 eV for 15, 1, 2, 4, and 1 lines from each of these groups, respectively. Goldovskii et al. (1977) measured relative excitation functions for six groups of lines between 66 and 102 nm that result from the ionization of a 5p electron.

G. Lutetium

Krasavin and Smirnov (1984) measured excitation functions for 45 lines of Lu I and show these up to 250 eV. Smirnov (1986a) measured excitation cross sections at 50 eV for 50 lines of Lu II and shows 7 excitation functions to 250 eV representative of 40 of these. The radiometry of both experiments was based on the data of Van Zyl *et al.* (1980) for helium.

X. EXCITATION FROM EXCITED TARGETS

Studies of excitation by electron impact on excited targets pose many extra problems. The concentration of target species will certainly be very low, and there may well be more than one excited state present. It will be particularly difficult to determine target densities, and, even though the cross sections will be larger than those from the ground state, the net signal is going to be quite small.

A. Helium

Gostev *et al.* (1980) measured excitation functions of the $3^{3}P$, 3 and $4^{3}D$, and $3^{1}P$ states by electron impact on atoms in the $2^{3}S$ metastable state. The metastable atoms

were produced by the selective neutralization of a 400-eV ion beam in a multichannel graphite collimator. They determined their target density by absorption of the 1083-nm line and found values of $6\pm 2\times 10^9$ cm⁻³ corresponding to a conversion efficiency of 25%. Their data extend from threshold to 10 eV, and the cross-section values are, at their maxima, 3 or more orders of magnitude greater than those from the ground state.

Mityureva and Penkin (1975) used a discharge source to produce metastable atoms that were allowed to diffuse into a collision chamber 5 cm away in which they were subjected to controlled electron impact. They measured target densities by line absorption and found values of 10^{11} cm⁻³, but they do not distinguish between singlet and triplet metastable atoms. They show the excitation function for only the 388.8-nm line, but on such a compressed energy scale that no comparison with the data of Gostev *et al.* (1980) is possible.

B. Neon

Mityureva and Penkin (1975) also measured the excitation functions of the 640.2-nm line of Ne I and the 332.4-nm line of Ne II. Their data are not absolute, but they estimate peak cross sections several orders of magnitude greater than those for excitation from the ground state.

C. Argon

Mityureva (1985) studied the excitation of the $2p_9$ state $({}^{3}D_3)$ by electron impact on metastable argon atoms. The metastable atoms were produced by controlled electron impact in two vacuum-tube-type guns and allowed to diffuse to the excitation region. She measured the target density by line absorption, noting that the absorption profile would be narrowed because of the essentially transverse motion of the metastable atoms, and found values of several 10^8 cm⁻³ with a 4:1 ratio of J=2 to J=0 metastables. She shows the excitation function of the 811.5-nm line up to 10 eV and argues that the data represent excitation from the J=2 level. The peak value of 9×10^{-15} cm² is some 400 times that for excitation from the ground state.

D. Sodium

Stumpf and Gallagher (1985) measured excitation from sodium atoms that had been aligned by optical pumping into a pure spin and angular momentum $(M_L = 1, M_S = \frac{1}{2})$ 3P state to the 3D state. They observed the 819-nm line at 90° to the electron beam and normalized their data using Born and Born-Ochkur values of cross sections and polarization fractions to define the behavior at high energies. Their results are shown in Fig. 40. The maximum value of the cross section is, at 3.8×10^{-15} cm², eight times that for excitation of the 3D state from



FIG. 40. Excitation functions of the 3D-3P line of Na I at 819 nm following excitation from the aligned 3P state, and of the 3P-3S line following excitation from the ground state: (\bigcirc) Stumpf and Gallagher (1985), 819 nm; (\times) Enemark and Gallagher (1972), 3P.

the ground state. The onset is very steep, but the excitation function is otherwise very similar indeed, both in shape and magnitude, to that for the 3P state excited from the 3S ground state.

E. Strontium

Aleksakhin and Shafranyosh (1977) measured excitation functions for five lines of Sr I from metastable states. They produced a modulated beam of target atoms by passing a beam of strontium through a pulsed gas discharge and monitored the concentration by line absorption, finding values of 5×10^8 and $2-4 \times 10^9$ cm⁻³, respectively, for the ${}^{1}D_{2}$ and ${}^{3}P_{0,2}$ states. They show excitation functions up to 30 eV and quote values for cross sections and their ratios to those from the ground state. They conclude from the form of the excitation functions that the initial state is ${}^{3}P$ rather than ${}^{1}D$, though we are not wholly convinced by their argument.

F. Barium

Aleksakhin and Shafranyosh (1975) used the same technique as for strontium to produce a modulated beam of metastable barium atoms and show the excitation function of the 606.3-nm line to 30 eV. They quote cross sections for six triplet lines with the assumption that the excitation is from the ³D metastable state. Aleksakhin *et al.* (1982) used a significantly modified method to isolate excitation from the ¹D metastable state. Using a gas discharge, they produced an unmodulated beam containing both singlet and triplet metastable atoms and illuminated this with modulated light of 582.6-nm wavelength, which corresponds to the 6s 5d ¹D-5d 6p ¹P transition. The upper level decays readily to the ground state (branching ratio ≈ 30), and the populations of the singlet metastable and the ground state are modulated in antiphase. They show excitation functions for three lines to 300 eV and give cross-section values for five lines, including three from core-excited levels.

G. Copper

Aleksakhin *et al.* (1985) measured the excitation function of two lines of Cu I excited by electron impact on metastable copper atoms and compare that for the $4p'^2F_{7/2}-4s^{2\,2}D_{5/2}$ at 296.1 nm with the excitation function of the same line from the ground state, which we show in Fig. 33(a). Their data are relative only, but the function for excitation from the metastable state is very much sharper.

H. Mercury

Korotkov and Kazakov (1977) studied excitation of the 7 ${}^{3}S$ state by electron impact on metastable atoms. They used a system of two perpendicular electron guns. The first used a pulsed electron beam to excite mercury atoms to the 6 ${}^{3}P$ states, and the second, pulsed after a time delay to allow the ${}^{3}P_{1}$ state to decay, excited the metastable atoms that remained to higher states. They show a combined function for excitation from both metastable states and refer to a paper "in press" in which excitation from the J=0 state is given, which allows them to deduce and show the excitation function from the J=2 state. This latter paper does not appear to have been published.

Korotkov (1977) has studied excitation by electron impact on $6{}^{3}P_{1}$ atoms leading to atoms in the $6{}^{3}P_{2}$ metastable state. The target atoms were produced by absorption of the intercombination resonance line at 254 nm, and the metastable atoms were detected by secondary electron emission from a platinum surface. He shows the excitation function in absolute terms to 8 eV. With the light source turned off the experiment measures the cross section for excitation from the ground state, and agreement with the results of Borst (1969) is claimed.

XI. EXCITATION FROM IONIC TARGETS

Itikawa *et al.* (1984) have published a useful annotated bibliography on electron collisions with positive ions that contains many references to excitation collisions. The conventional crossed-beam study of ion excitation has so far been limited to low degrees of ionization (four-timesionized nitrogen is the most highly ionized target studied so far), and we draw attention in Sec. XI.J to a new technique, using an electron beam ion trap, that has been used to study much more highly ionized targets even though, at present, the range of impact energies appears to be limited to below the relevant ionization potential.

A. Helium

Excitation of the 2S state of He^+ was studied by Dolder and Peart (1973) using electron and ion beams crossed

at 90°. The ions were produced in a low-voltage hotcathode source, accelerated to 5 keV, and selected by 60° deflection in a magnetic field. After leaving the excitation region the ions traveled for 15 cm before entering a magnetic field of 0.15 T, which quenched any ions in the 2S state to the 2P state from which they decayed (t=0.13 ns) with the emission of the 30.4-nm line. This light was detected by fluorescence of sodium salicylate and piped to a photomultiplier tube. They placed their data on an absolute scale by normalizing to the Born approximation, including cascade at 1 keV. Their data show significant structure between threshold and the energy of the n=3 level. This paper contains a full account of the problems of the method and of the analysis procedure.

Dashchenko *et al.* (1975) studied the excitation of the 2P state using electron and ion beams crossed at 90°. The ions were produced in a magnetically confined discharge source and selected by a 180° mass spectrometer. The collision region was observed directly, the entrance slit of a grazing incidence monochromator being mounted on the electron gun. Light was detected using an open multiplier. They normalized their data to theory (Coulomb-Born II) at 217 eV. The energy resolution of this measurement was rather low, and the cross section rose slow-ly from threshold. Semenyuk (1984) repeated the measurements of 2P excitation with improved energy resolution and found a sharper onset and some low-energy structure.

In Fig. 41 we show the results of all three experiments. One should not place much confidence in the relative positions of the low-energy features, as the energy scale is not well defined.

B. Argon

Zapesochnyi, Imre, *et al.* (1973) describe apparatus for studying excitation in collisions between ions and electrons. Ions produced in a magnetically confined discharge source are analyzed in a 50-cm radius 180°



mass spectrometer and are then excited by a perpendicular electron beam. Light emitted in the third perpendicular direction is dispersed and detected. The ion and electron beams are square-wave modulated to enable the electron-ion signal to be distinguished from coherent backgrounds that result from interactions of the ions and electrons separately with the background gas. They discuss the problems of electrical interaction between the modulated beams and the effect of finite lifetimes on the observed excitation signals. They used this system to measure the functions for excitation of lines of Ar II from an Ar⁺ target. Their intensity calibration was made in terms of the cross sections for excitation from the neutral atom measured by Feltsan and Povch (1970). They show excitation functions in absolute terms for five lines up to 35 eV, the threshold energy for excitation for the neutral atom, but only for the line at 488 nm do their data extend to 100 eV.

C. Krypton

Zapesochnyi, Imre, *et al.* (1973) used the same system as for argon to measure the excitation functions of five lines of Kr II from the ion ground state. Their data extend only to 32 eV, the threshold for excitation of these lines from the neutral atom. Imre *et al.* (1974) measured the excitation functions of two lines of Kr III by electron impact on the Kr⁺⁺ ion.

D. Lithium

Rogers *et al.* (1978) have studied the excitation of Li⁺ from the ground state to the $2^{3}P$ state by electron impact for energies up to 162 eV. They discuss the theory of the measurement in great detail and include an analysis of the effects of space charge in both the ion and electron beams and of the effect of the lifetime of the excited atoms. They produced their ion beam by thermionic emission and obtained currents of 6 μ A at 1 keV. They give a full analysis of the experimental uncertainties.

E. Potassium, rubidium, and cesium

Zapesochnyi, Imre, Aleksakhin, et al. (1986) describe an electron-ion excitation system that they have used to study electron collisions with K^+ , Rb^+ , and Cs^+ . The ion beams are produced by a surface ionization source followed by a 90° electrostatic analyzer. Light from the collision region was dispersed by a Seya-Namioka monochromator and detected by an open multiplier. The radiometric calibration was made in terms of a calculated value for the excitation cross section at 400 eV of the $4p^{5(^2P_{3/2})5s[3/2]_1$ state of Rb^+ , the upper level of the 74.1-nm resonance line, and extended to other wavelengths using published data on N₂ and argon. They claim an overall accuracy of a factor of 2 for this calibration. They show excitation functions for a number of lines of each element to some 300 eV and interpret these in terms of capture of the impacting electron and the subsequent decay by autoionization or radiation of the states so formed. The excitation functions of the resonance lines of the singly charged ions show three maxima (two narrow and one rather broader) close to threshold, which they interpret as due to resonances, and a broad maximum at a few times the threshold energy that represents the usual form of an optically allowed excitation. The lines of the doubly charged ions arise from states in which one of the outermost s electrons has been removed. The singly charged ion has an s^2p^6 configuration, and they interpret this excitation process as proceeding via excitation of one each of the s and p electrons and subsequent autoionization. The observed lines correspond to transitions to the $P_{1/2}$ level of the ground state of the doubly charged ion. Imre et al. (1986) show the excitation functions for the other component of these doublets. For each element they observe a line of the neutral atom having a very sharp excitation function. These lines are among those identified by Aleksakhin et al. (1981a) as being from autoionizing upper states (though the specific transitions are described differently here) and are here excited as a result of dielectronic recombination.

F. Beryllium

Taylor et al. (1980) have measured the excitation and polarization functions of the unresolved 2P-2S doublet of Be⁺ at 313 nm for energies up to 740 eV. Their paper describes in considerable detail the analysis of the measurements and the sources of uncertainty. This analysis is perhaps fuller than usual because the authors were well aware that the measurements did not agree with quite sophisticated theory in respect of either the excitation cross sections or the polarization of the light. The ion source was a hot-cathode discharge and the mass-analyzed beam was cross fired by an electron gun. Light from the collision region was observed at 90° and, after passing through a polarizing filter, was detected by a red-blind photomultiplier tube. Absolute radiometry was done in terms of a tungsten strip lamp calibrated against a blackbody standard. It has been shown (Heddle, 1979) that the observed excitation cross sections and the polarization of the light are quite consistent with each other in the context of the Bethe approximation. The most recent calculations (Mitroy and Norcross, 1988) have been able to reproduce the measured polarization, but the discrepancy in the cross-section values is still not resolved.

G. Magnesium

Zapesochnyi, Kelman, et al. (1976) have measured the excitation functions of the resonance doublet of Mg II at 280 nm and of the 4S-3P 292.9./293.6-nm doublet, which is a major source of cascade population, from threshold to 100 eV. They show both a line excitation function and

a level excitation function, corrected for cascade using their own data. Zapesochnyi et al. (1984) extended these measurements using velocity-selected electrons and observed structure in the excitation function of the resonance doublet below the ionization potential. The onset of their excitation function is much more gradual than we would expect in the light of their claimed energy resolution of 0.3 eV, because the cross section should have a finite value at the threshold. In a paper concerned with measurements of dielectronic recombination in magnesium, Belic et al. (1983) show a near-threshold excitation function for the resonance doublet that is much more abrupt, and they refer to unpublished measurements made by their colleagues who had reported measurements on Al⁺⁺ (Belic et al., 1981). They have told us privately (Belic et al., 1988) that these measurements also included the polarization of the light and that this passed through zero at an energy of about 60 eV. We have used this information to produce Fig. 42, which is a Bethe plot of the data of Zapesochnyi, Kelman, et al. (1976) for the 3P level. These data are not corrected for polarization; so the intercept of the Bethe-Fano line is not at 3 eV but is displaced to lower energy, as discussed by Heddle (1979). We can estimate the slope of the asymptote from the known oscillator strength, 0.94, of the transition and the polarization parameter P_0 , which we expect to be 0.42, and find a value of 2.92×10^{-14} cm²eV. The experimental value is 2.35×10^{-14} cm²eV, indicating that the absolute calibration of the experiment is some 20% low.

H. Calcium

Taylor and Dunn (1973) measured the excitation and polarization functions of the resonance doublet (the H and K lines) of Ca⁺. They formed their ion beam by surface ionization followed by mass analysis and obtained



FIG. 42. Bethe plot for the 3P doublet level of Mg II. Data of Zapesochnyi, Kelman, et al. (1976).

currents of 0.1 μ A at 750 eV. Their electron beam was magnetically confined, and they discuss the necessary path length corrections in some detail. Light from the collision region passed through one of two interference filters and a polarizing filter and was counted by a cooled photomultiplier tube. The paper contains very detailed accounts of the data handling and analysis procedures, including the profiling of the beams and the absolute radiometry, which was done in terms of a blackbody standard. Their data extend to 700 eV for the K line and to 335 eV for the unpolarized H line.

Zapesochnyi, Kelman, et al. (1976) measured the excitation functions of the resonance lines and of the 5S-4P and 4D-4P cascading doublets and the polarization function of the K line to 100 eV. They used a surface ionization source to give a current of $0.1-1.0 \ \mu$ A and a highcurrent electron gun. Light from the collision region was analyzed by a grating monochromator and counted by a cooled photomultiplier tube.

Frontov (1985) has repeated the excitation measurements of the latter group for the resonance doublet using velocity-selected electrons and finds substantial structure below the ionization potential.

We show in Fig. 43 the excitation and polarization



FIG. 43. (a) Polarization function of the K resonance line of Ca I at 393.4 nm: (\odot) Taylor and Dunn (1973); (\times) Zapesochnyi, Kelman *et al.* (1976). (b) Excitation function (expressed as a Bethe plot) of the K line of Ca I at 393.4 nm: (\odot) Taylor and Dunn (1973); (\times) Zapesochnyi, Kelman *et al.* (1976).

functions for the K line at 393.4 nm. The two measurements of the polarization function are in excellent agreement, and the absolute cross-section determinations agree to an extent that would be worthy of comment in an inert gas.

I. Strontium

The only measurements of excitation of Sr^+ are described by Zapesochnyi, Kelman, *et al.* (1976). They used the same method as for calcium and show the excitation functions of the 407.8-nm resonance line and the 430.5-nm 5S-5P and 346.7- and 347.5-nm 5D-5P cascade transitions to 100 eV. They also show the polarization function of the resonance line.

J. Barium

Crandall et al. (1974) measured the excitation function of four lines of Ba II, the resonance doublet, 455.4 and 493.4 nm, and cascading transitions from the 7S and 6Dstates for energies up to 747 eV. They produced their ion beam by surface ionization at a temperature of 2200 K; they estimate that at this temperature some 13.5% of the ions in the beam would be in the metastable 5^2D state. Their account of the analysis of their data is particularly full and detailed. They isolated the lines using four interference filters, three of which transmitted a significant amount of another line. They were able to deduce the true signals at each wavelength from measurements of the transmissions and calculated branching ratios. Because the excitation functions of positive ions are finite at threshold, it is possible to assess the contribution made by excitation from metastable ions to the signal in the threshold region from measurements made immediately below and above threshold; this they also did. They assumed that the shape of the excitation functions from the ground $6^2 S$ state and from the metastable $5^2 D$ state are the same. We agree that there will probably be substantial similarity at high energy, but we have doubts about the validity of this assumption at low energies. They also measured the polarization functions of the resonance doublet and of the 6D-6P cascade transition.

Zapesochnyi, Kelman, et al. (1976) measured the excitation functions of one of the resonance lines, 455.4 nm, cascade transitions from the 7S and 6D states, and the 4F-5D line at 233.5 nm. They claim to have measured the polarization also, but do not show any such data. They produced their ion beam both by surface ionization, which gave a metastable content of 13-14% and in a discharge, which allowed this to be varied, making it possible to correct the observations for excitation from the metastable state. They isolated the various lines using a grating monochromator. The agreement between their results and those of Crandall et al. (1974) is extremely good, except close to threshold where their broader elec-

TABLE XIII. Measurements of excitation cross sections and polarization of lines of Ba II excited by electron-ion impact.

λ (nm)	Transition	Measurement		
455.4	$6^2 P_{3/2} - 6^2 S_{1/2}$	Q ^{a,b,c}	P ^{a,b?}	
493.4	$6^2 P_{1/2} - 6^2 S_{1/2}$	$\tilde{Q}^{a,c}$	P^{a}	
490.0	$7^{2}S_{1/2}-6^{2}P_{3/2}$	$\tilde{O}^{a,b,c}$		
413.1	$6^2 D_{5/2} - 6^2 P_{3/2}$	$\tilde{O}^{a,b,c}$	Pa	
416.2	$6^2 D_{3/2} - 6^2 P_{3/2}$	đ		
233.5	$4^{2}F-5^{2}D_{5/2}$	Q ^b		

^aCrandall et al. (1974).

^bZapesochnyi, Kelman, et al. (1976).

^cFrontov *et al.* (1985).

^dNot resolved from 413.1 nm by a.

tron energy distribution shows up as a more gradual onset of excitation.

Frontov *et al.* (1985) extended these measurements using velocity-selected electrons and observed considerable structure below the ionization potential though the onset of excitation still does not appear very abrupt. Table XIII summarizes the observations.

Marrs *et al.* (1988) have reported the first excitation measurements made with a highly ionized target. They used an electron beam ion trap to generate and store a significant concentration (about 2×10^4 ions/cm length of the beam) of Ba⁴⁶⁺ ions and observed radiation from this neonlike system. Operation of the trap limited the range of impact energy to less than the ionization potential of the target ion, but they were able to measure the excitation cross sections for three lines at two energies, calibrating their intensity scale in terms of calculated radiative recombination rates.

K. Zinc

Rogers et al. (1982) have made the only measurements of excitation of Zn^+ by electron impact. They produced their ion beam in a hot-cathode discharge source run with an overall potential of no more than 12 eV to reduce the production of ions in the long-lived $3d^94s^2D$ state. Their radiometric calibration was made in terms of a vacuum photodiode calibrated at the National Bureau of Standards (NBS) and they isolated the lines under study using interference filters. They measured the excitation and polarization functions of the resonance doublet at 202.5 and 206.2 nm to 790 eV, but could not separate this from the 4D-4P cascade at 206.5 and 210.1 nm. They also measured the excitation function of the 5S-4P cascade doublet at 250.2 and 255.8 nm to 388 eV.

L. Cadmium

Hane *et al.* (1983a) measured the excitation functions of the 441.6- and 214.4-nm lines of Cd II using a crossedbeam system. They produced their ion beam in an electron bombardment source and, after electrostatic deflection, had a current of $1-2 \mu A$ at 500 eV, though this included more highly ionized species than the Cd⁺ under study. They show excitation functions up to 18 eV. The 441.6-nm line originates from the $4d^{9}5s^{2}{}^{2}D_{5/2}$ state and populates the $4d^{10}5p^{2}P_{3/2}$ state, which is the upper level of the 214.4-nm resonance line. Their absolute radiometry was made in terms of tungsten and deuterium lamps using an LED (light-emitting diode) as a transfer standard. The ${}^{2}D$ state has a lifetime of 800 ns, and only 8.3% of the ions excited to this state radiate within the field of view of the detector.

Hane *et al.* (1983b) extended these measurements to include the 6S-5P and 5D-5P doublets at 257.3/271.9 and 219.5/231.3 nm, the other resonance line at 226.5 nm, and a second line from a displaced term, $4d^{9}5s^{22}D_{3/2}^{2}P_{1/2}$, at 325.0 nm. They made some measurements of the polarization of the light, but made no corrections to their cross-section measurements.

M. Mercury

Crandall et al. (1975) studied the excitation of the 165.0- and 398.4-nm lines of Hg II following electron impact on a beam of Hg⁺. These lines correspond to transitions from the $6p {}^{2}P_{3/2}$ state to the ground $6s {}^{2}S_{1/2}$ and the metastable $5d {}^{9}6s {}^{2}D_{5/2}$ states, respectively. The ion beam was produced in a source that was normally operated as an electron bombardment source, but could be operated in a discharge mode. Beam currents of 0.1 μ A at 750 eV were obtained with a metastable component of about 10%. Light at 165.0 nm from the collision region was detected by a solar-blind photomultiplier tube placed inside the vacuum system, the absolute sensitivity being determined in terms of a photodiode calibrated at NBS. An interference filter was used to select the line at 398.4 nm and the absolute calibration was made in terms ultimately of a blackbody source. The measurements at 165.0 nm required correction for the presence of light at 194.2 nm from the $6p {}^{2}P_{1/2}$ state and for the fact that excitation can occur from the metastable ions in the beam; they give a very full account of this in an Appendix. Their data for the 165.0-nm line extend to 274 eV, but for the much weaker 398.4-nm line they give cross-section values at only three energies.

Phaneuf *et al.* (1976) studied the excitation of the 284.7-nm line of Hg II $(7s \, {}^{2}S_{1/2} - 6p \, {}^{2}P_{3/2})$ by electron impact on a predominantly ground-state ion beam. They used an arc discharge source to produce their ion beam, but their experiment was otherwise very similar to that of Crandall *et al.* (1975). Their results extend to some 300 eV. They also measured cross sections for the excitation of the 479.7-nm line of Hg III from the ground states of Hg⁺ and Hg⁺⁺. This line corresponds to a two-electron transition from the $5d^86s^2 J=4$ state and is a laser line. They present data for each excitation process at only three energies.

N. Carbon

Lafyatis and Kohl (1987) measured the cross section for exciting the $2s2p^{2}D-2s^{2}2p^{2}P$ line of C II at 134 nm in an experiment in which beams of C^+ ions and electrons crossed at 45°. The ion beam was produced in a hot-cathode Penning discharge source and was 1 μ A at 4.2 keV. It contained about 10% of ions in the $2s2p^{24}P$ metastable state, a proportion estimated from measurement of the 233-nm light emitted on decay to the ground state. The authors estimate that excitation from the metastable state contributes no more than 5% to their observed signal. They made their absolute radiometry by measuring the transmissions of their optics, the solid angle from which light was collected, and the quantum efficiency of their solar-blind photomultiplier tube. This last was determined in terms of a photodiode calibrated at NBS. Their analysis is quite fully described and they show excitation cross sections from threshold to 16 eV.

Taylor *et al.* (1977) measured the excitation cross section for the resonance doublet of C IV at 155 nm at an electron energy of 10.2 eV. They used a Penning discharge source to produce a 0.1-0.2- μ A beam of 29 keV C³⁺ ions and observed light emitted at right angles to the ion and electron beams with a solar-blind photomultiplier tube calibrated in terms of a standard photodiode. They extended their measurements to other collision energies using a light pipe to double the photon collection efficiency, though at the expense of absolute calibration. They show the excitation function from threshold to 530 eV. Gregory *et al.* (1979) also show this excitation function and tabulate the cross-section values above 10.5 eV.

Lafyatis and Kohl (1987) measured the excitation cross section of this resonance line at two energies. They used a hot-cathode Penning discharge source to give a beam of about 0.5 μ A at 14 keV that intersected their electron beam at 45°. Light was detected by a solar-blind photomultiplier tube with a CsI cathode that was calibrated in terms of a standard photodiode. They extended their measurements to six further energies, but in relative terms only. They show the excitation function from threshold to 20 eV. Their absolute values are less precise than that of Taylor *et al.* (1977), but their data in the threshold region show a much sharper rise due in part to the improved energy resolution given by the 45° intersection of the ion and electron beams.

O. Nitrogen

Gregory *et al.* (1979) measured the excitation cross section of the resonance doublet of N v at 124 nm by electron impact on N⁴⁺ at an energy of 15.5 eV. Their ions were produced in a Penning discharge source and gave a beam of about 1 μ A at 39 keV. Light from the collision region was detected by a solar-blind photomultiplier tube inside the vacuum chamber that viewed the interaction region directly. The photomultiplier was calibrated against a standard photodiode. They extended their measurements to other energies using a light pipe to enhance the collection efficiency, though at the expense of the absolute calibration. They allowed for anisotropy of emission using calculated values for the polarization of the emitted light. The paper includes an assessment of experimental uncertainties and of current-dependent secondary effects. They show the excitation function for the resonance doublet up to 52 eV.

Bradbury *et al.* (1973) measured the excitation cross section of this doublet at four energies between 130 and 405 eV, but their results are larger than we would expect on the basis both of the measurement by Gregory *et al.* (1979) and of theory.

P. Aluminum

Belic *et al.* (1981) have reported on absolute measurement of the excitation function of the $3^{2}P-3^{2}S$ doublet of Al III at 186 nm from the threshold to 400 eV by electron impact on the doubly charged Al⁺⁺ ion. They claim an absolute calibration uncertainty of 11% with typical relative uncertainties of 6% and note that there is evidence of resonance structure close to the threshold.

Q. Gallium

Stefani et al. (1982) measured the cross section for exciting the resonance line of Ga II at 141.4 nm by impact of 46.9 eV electrons on Ga⁺. Ions were produced in a discharge source and beams of 0.04–0.2 μ A at 1 keV were used. The beam contained a small fraction of ions in the 4s4p ³P metastable state, and the amount was estimated by observing electron impact excitation of the ions and noting the proportion that occurred below the threshold for ionization from the ground state. They extended their measurements in relative terms to other energies by removing a limiting aperture from the light detection path to increase the solid angle from which light was collected. No excitation from the metastable to the radiating ${}^{1}P$ state was detected. They show the excitation function and tabulate cross-section values to 398 eV.

R. Thallium

Zapesochnyi, Imre, Kontrosh, *et al.* (1986) have measured the excitation function of the intercombination resonance line of Tl II at 190.8 nm from threshold to 300 eV. They used a discharge source to produce a $0.6-\mu A$ beam of Tl⁺ at 1 keV with minimal contamination by metastable ions. They isolated the 190.8-nm line using a grating monochromator. They show the excitation function and comment on the wealth of structure below the ionization potential. Gomanai (1987) studied the excitation of the resonance doublet of Tl III at 126.7 and 155.9 nm between threshold and 250 eV in collisions of elec-

trons and ground-state Tl^+ ions. He discusses the relative contributions of simultaneous ionization of one of the 6s electrons and excitation of the other and of ionization of a d electron and subsequent rearrangement.

APPENDIX A: POLARIZATION MEASUREMENT AND CORRECTION

Light emitted following impact excitation has a cylindrical rather than a spherical symmetry because the electron beam imposes a symmetry axis on the system. This light will be distributed nonisotropically and will be polarized; measurements should be made in such a way that the extent of the anisotropy does not affect the results. This may be done either by measuring the polarization or by observing a truly representative sample of the light, and we first consider the latter approach. It is convenient to describe the angular distribution in terms of dipoles, oriented parallel and perpendicular to the axis, which emit fluxes I_{\parallel} and I_{\perp} per unit solid angle perpendicular to the axis, and to define the polarization P by

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

The total flux emitted into the unit solid angle in a direction making an angle φ with the axis is given by

$$I_{\parallel}(\varphi) = I_{\parallel} \sin^2 \varphi + I_{\perp} \cos^2 \varphi , \qquad (A1)$$

$$I_{\perp}(\varphi) = I_{\perp} , \qquad (A2)$$

$$I(\varphi) = I_{\parallel} \sin^2 \varphi + I_{\perp} (1 + \cos^2 \varphi)$$

$$= (I_{\parallel} + I_{\perp})(1 - P\cos^2\varphi) .$$
 (A3)

The total emitted flux, I, found by integrating this over all directions, is

$$I = (8\pi/3)[I_{\parallel} + 2I_{\perp}];$$

so we can write Eq. (A3) as

$$I(\varphi) = I \frac{1 - P \cos^2 \varphi}{1 - P/3}$$

Measurements made at 90° to the exciting beam will only give a result proportional to the total flux if the photometric system has a sensitivity to light polarized in the plane containing the beam axis that is half of that to light polarized in a perpendicular plane. In general, the relative sensitivities of monochromators have a dependence on wavelength and this can be quite substantial, as Fig. 44 illustrates. This shows the response of a grating monochromator with the abrupt changes due to Wood's anomalies; prism instruments often exhibit a stronger polarization sensitivity, but less wavelength dependence because of differential reflection at the prism surfaces. At visible and near-ultraviolet wavelengths it is very simple to establish the correct relative sensitivities by placing a polarizing filter in front of the photometer with its transmission axis at an angle θ to the plane containing the exciting beam, such that $\sin^2\theta = 2\cos^2\theta$, or $\theta = 54.7^\circ$.



FIG. 44. Response of a grating monochromator (and an S-20 photocathode) to light from a quartz-halogen lamp polarized parallel (\parallel) and perpendicular (\perp) to the dispersion plane.

The light transmitted by this filter is plane polarized at this angle, whatever the state of the incident light, and the polarization sensitivity of the monochromator is not important.

It is well known that if $\varphi = 54.7^\circ$, commonly called the "magic angle," then $I(\varphi)$ is directly proportional to I, whatever the relative values of I_{\parallel} and I_{\perp} , and measurements have frequently been made at this angle in the belief that this gives the truly representative sample. This will only be the case if the photometric system has equal sensitivities to light polarized in the two principal directions. Clout and Heddle (1969) note that this could be achieved by placing a polarizing filter with its transmission axis at 45° to the plane containing the exciting beam, but suggest that the loss of light that this entails would be overcome if, instead, the exciting beam were rotated about the optic axis by 45°. It would then make equal angles of 54.7° to the optic axis and to the principal axes (parallel and perpendicular to the grating rulings or the prism vertices) of the monochromator. This orientation, which some have referred to as the "double magic angle," has proved to be of particular value in the vacuum ultraviolet (de Jongh, 1971; Donaldson et al., 1972). At longer wavelengths the same result can be obtained by placing a half-wave plate in the optical path with its axis at 22.5° to the plane containing the exciting beam; this has the effect of rotating the planes of polarization by twice this angle, or 45°. Wave plates are dispersive and the effect of retardations other than 180° is discussed by Clout et al. (1971).

The measurement of the polarization of the light requires knowledge of the polarization sensitivity of the photometric system at each wavelength. If the ratio of the sensitivities to light polarized parallel and perpendicular to the exciting beam is B, then a polarization, measured at 90° to the beam to be P', corresponds to a true polarization P given by

$$P = \frac{1 - B + (B + 1)P'}{1 + B + (B - 1)P'} .$$

Measurement of the polarization sensitivity requires a source of known polarization. It is unwise to rely on a discharge source of a tungsten lamp, but radiation corresponding to certain transitions (from S or $P_{1/2}$ states, for example) is known to be unpolarized and can give information at specific wavelengths. Figure 44 shows that caution is required if interpolation has to be done. If substantial signal is available, then a polarizing filter set at 45° to the exciting beam will establish B = 1, but a much more effective use of such a filter is to set it with its transmission axis parallel to the more sensitive direction and to treat the system of polarizer and monochromator as the polarization analyzer. This can then be rotated about the optic axis to measure, in turn, I_{\parallel} and I_{\perp} . This rotation needs only to be done optically and a half-wave plate placed in the optical path can be used to do this. If the plate is first set with its fast axis parallel to the exciting beam and then rotated by 45°, the analyzer will measure the two fluxes. Clout et al. (1971) show that this approach will allow the polarization to be determined even if the polarizing filter is somewhat imperfect and if the retardation of the wave plate is not 180°.

The polarization can be deduced from direct measurements of the angular distribution of the light, though there is still a need for a calibration of instrumental polarization sensitivity. There is a further complication in that the region from which light is collected will normally vary with φ (approximately as $\csc\varphi$), but the two factors may be assessed together by measuring the angular distribution of a known isotropic line. Measurements of this type have been made by McFarland and Soltysik (1963) and by Mumma *et al.* (1974).

The finite solid angle subtended at the excitation region by the optical system has an effect on the measured values both of the polarization and the total intensity, which we shall consider just for the case of observation at 90° to the exciting beam with a photometer having no sensitivity to polarization, such as an end window photomultiplier tube. The measured signals will be proportional to Eqs. (A1) and (A2) averaged over the collection solid angle, and we write for the total signal and the polarization

$$\langle I \rangle = I \frac{1 - P \langle \cos^2 \varphi \rangle}{1 - P / 3} ,$$

$$\langle P \rangle = P \frac{1 - \langle \cos^2 \varphi \rangle}{1 - P \langle \cos^2 \varphi \rangle} ,$$

using $\langle \rangle$ to denote the average values. We have extended some results quoted by Taylor (1972) and calculated $\langle \cos^2 \varphi \rangle$ as a function of the collection semiangle, $\Psi = 90 - \varphi_{max}$ for the cases of a circular and a square aperture. If we express the angle in radians, the results for the circular and square apertures are represented very well by $\Psi^2/4$ and $\Psi^2/3$, respectively. Only for semiangles > 10° is the effect likely to be at all significant. Similar effects will result from any lack of parallelism in the exciting beam, but the angles involved are likely to be too small to cause significant errors unless the beam is constrained by a magnetic field, in which case the effects of Larmor precession, as discussed by Moiseiwitsch and Smith (1968), may also be significant.

APPENDIX B: ESTIMATES OF CASCADE POPULATION

There are some atoms for which the cascade population of a state can be measured directly because the appropriate spectrum lines lie in an accessible region of the spectrum. However, this is not so in the majority of cases and a knowledge of branching ratios is required. Figure 45 shows a schematic energy level diagram in which states d, e, and f are of different parity from states i, j, and k. We consider excitation of state j and observe the $j \rightarrow f$ transition. Direct cascade population will occur from states such as e and d, and indirect cascade population from states such as i. If we can measure the cross section for exciting the $e \rightarrow k$ transition, we can deduce the cascade contribution from state e to be $Q_{ek}(A_{ej}/A_{ek})$, where the A_{ab} are radiative transition probabilities. It is not necessary to consider indirect cascade because the measurement of the cross section for the excitation of the $e \rightarrow k$ transition includes this. If, on the other hand, we have to rely on calculated values for the excitation cross sections, we need to include the indirect cascade explicitly.

Close to the threshold for excitation or, indeed, at any energy where the cross sections are affected by resonance structure, it is very difficult to determine how much of the structure is genuinely a part of the excitation process and how much is a consequence of cascade.

At energies of a few times the threshold energy the excitation functions of states of the same character (all ${}^{1}D$ states, for example) are very similar in shape, and knowledge of the cascade contribution from one or more



FIG. 45. Schematic energy-level diagram to illustrate the population of level j by cascade.

of these allows an estimate to be made of the total contribution. It has been claimed from time to time that the cross sections for exciting similar states should depend on the principal quantum number n, as n^{-3} , for no better reason, it seems, than that hydrogenic p-state transition probabilities vary asymptotically in this manner. Variants of this claimed behavior include other powers (especially integer powers) and the use of an effective principal quantum number n^* , for which there may be a little more justification. While there is no sound basis of choice for an *a priori* value of an index, we have found a dependence of this type fairly useful in the analysis of real data. For those (rather few) cases for which three or more members of a series have been studied, a power law does seem to give a not unreasonable basis for extrapolation, so that one may estimate the cascade contribution from yet higher members of the series. Note that the quantity we extrapolate is not the excitation cross section itself, but the product of the cross section and the appropriate branching ratio, which is the actual cascade component. Such extrapolations appear to be justified to the same extent as those of cross sections. We write J_n to represent the cascade from the nth level, and with $J_n \sim n^{-a}$ we can express the total cascade contribution from levels n > p as $C_p J_p$ where $C_p = p^a \sum_{p=1}^{\infty} n^{-a}$. We have calculated values of C_p for a range of p and a and show these in Fig. 46.

Table XIV details our analysis of the cascade from n ¹S to n ¹P states of helium at an energy of 500 eV. The cascade to the 2 ¹P state is just the line cross section measured by Van Zyl *et al.* (1980), and that to the 3 and 4 ¹P states is found by multiplying those measured values by branching ratios obtained from the radiative transition probabilities of Theodosiou (1987). Figure 47 shows these values plotted on logarithmic scales from which we



FIG. 46. Cascade parameter C_p , discussed in the text, expressed in terms of the extrapolation index a and the principal quantum number p of the last observed member of the cascading series.

	3 ¹ S	4 ¹ S	5 ¹ S	6 ¹ S	а	C_p	$7 + {}^{1}S$	J
$2^{1}P$	9.23	2.05	0.78	0.374	4.65	1.20	0.45	$12.9 = 3.72Q_{4S}$
3 ¹ <i>P</i>		1.41	0.50	0.231	4.47	1.29	0.30	$2.44 = 0.71 Q_{4S}$
$4^{1}P$			0.36	0.157	4.57	1.25	0.20	$0.72 = 0.21 Q_{4S}$

TABLE XIV. Cascade to helium $n^{-1}P$ from $n^{-1}S$ at 500 eV in units of 10^{-20} cm².

obtain values of the index a. Figure 46 then gives the corresponding values of C_p for each case, and we can then sum the total cascade, which we show both as a cross section and, in the final column of Table XIV, as a multiple of the $4^{1}S$ cross section.

APPENDIX C: THE APPLICATION OF THE BETHE APPROXIMATION TO ABSOLUTE CALIBRATION

The cross section for electron impact excitation of a state j connected optically to the ground state can be represented asymptotically by

$$Q_{j} = \frac{4\pi a_{0}^{2}}{E/R} \frac{f_{j}}{E_{j}/R} \ln(4c_{j}E/R) , \qquad (C1)$$

where E is the kinetic energy of the electron, E_j the excitation energy, R the Rydberg constant, a_0 the radius of the first Bohr orbit, and f_j and c_j the parameters that describe the magnitude of the cross section and the angular distribution of the scattered electrons. Parameter f_j is known as the optical oscillator strength and is dimensionless. The units of Q are those of a_0^2 . Fano (1954) pointed out that Eq. (C1) could be cast in the form

$$Q_i E = A_i \ln(4c_i E / R) \tag{C2}$$

and suggested that a plot of $Q_j E$ against $\ln(E)$ should tend at high energies to a straight line with a slope proportional to f_j/E_j and an intercept on the abscissa at $E = E_0 = R/4c_j$. If we substitute numerical values and change to common logarithms we can write Eq. (C2) as

$$Q_j E = 1.50 \times 10^{-13} (f_j / E_j) (\log E - \log E_0) \text{ cm}^2 \text{ eV}$$
, (C3)

where the energies are now in electron volts.



FIG. 47. Cascade population of the n ¹P states in helium from the ¹S states.

This equation has frequently been used as the basis for the calibration of cross-section measurements because there are many cases for which a value for the optical oscillator strength is known more accurately than the cross section could be measured. There are two complicating factors. The first is that the measurements must take account of the polarization of the light as Eq. (C3) refers to the total excitation cross section. Heddle (1979) has discussed the transformation of the equation if the measurements are not corrected for polarization. The second complication arises from cascade population that does not all have the same energy dependence as Q_i . This has in the past been taken into account either by an iterative procedure or by adding the cascade component to the line described by Eq. (C3). We have used a variant of the latter method in our analysis of the data discussed earlier and give here an account of our procedure.

We take the measured signal, including cascade, to be S_i and define a scale factor β by

$$\beta S_j = Q_j + J_j , \qquad (C4)$$

where J_j is the total cascade population that we assume to be known in absolute terms. Substitution in Eq. (C3) gives

$$S_i E = (A_i \log E + J_i E) / \beta - A_i \log E_0 / \beta , \qquad (C5)$$

with $A_j = 1.5 \times 10^{-13} f_j / E_j$ cm²eV. From a plot of $S_j E$ against $(A_j \log E + J_j E)$ we find the scale factor $[\beta = 1/(\text{slope})]$ and the value of E_0 or c_j $[\log E_0 = (\text{intercept on abscissa}) / A_j = 0.531 - \log c_j]$.

If the signal is large, this is a straightforward procedure; however, with small signals there is a danger that a systematic bias may occur at high energies where the cross section becomes small. We illustrate our analysis using measurements of the excitation of the 52.2-nm line of helium made by de Jongh (1971). The data are shown in Fig. 48, and we have to decide on the straight line that best describes the high-energy asymptotic behavior. We do not know the value of the intercept on the energy axis, but we expect that it will be close to the threshold energy E_i , which is 23.74 eV. If we examine the behavior of a line drawn as a "best fit" through a number of contiguous points at progressively higher energies, we see that its slope falls at first, then becomes almost constant (for energies of 200-1000 eV) and then rises. The corresponding intercept moves to lower and then to higher energies. Our interpretation of this behavior is that the $Q_i E$ product approaches the asymptote from below and the data show the true excitation cross section (including cascade) up to about 1000 eV, but at higher energies the data are



FIG. 48. Bethe plot of the helium 4P data of de Jongh (1971). The line represents a visual estimate of the "best" Bethe-Fano line in the sense discussed in the text.

progressively and significantly augmented as a consequence of secondary processes, of which the most important is probably the presence of slow electrons in the beam. We conclude that the solid line shown on Fig. 48, which has the minimum slope, is the best guide. Because we are seeking to calibrate the cross-section values we cannot simply subtract the cascade contribution, but using the form of Eq. (C5) we calculate lines of best fit for groups of points and adopt that giving a minimum value for the intercept on the abscissa. The number of points needs to be selected with care. Too few will lead to rather erratic behavior and too many will conceal significant curvature; the choice can be aided by the correlation coefficient, but there remains a subjective element. We have used two systematic approaches: a moving sample of 5, 6, or 7 contiguous points and a group of from 3 to npoints running downward from the nth point. In this example there are 22 data points, the first at 30 eV and the 22nd at 2000 eV; in Table XV we show the energy axis

TABLE XV. Energy axis intercepts of lines fitted to 5, 6, 7 contiguous data points for excitation of the 52.2-nm line of helium (de Jongh, 1971). The minimum values are underlined.

n _{max}	5 points	6 points	7 points
10	42.3	41.2	39.8
11	37.6	38.5	38.7
12	33.8	35.9	37.0
13	27.0	30.9	33.3
14	<u>19.4</u>	24.4	28.2
15	20.9	20.9	24.4
16	24.7	24.3	23.2
17	27.9	23.8	23.7
18	34.2	30.9	26.5
19	38.3	38.7	34.1
20	42.3	40.4	40.0
21	60.9	45.7	43.2
22	33.6	43.2	39.1



FIG. 49. Intercept of the Bethe-Fano line using data from a range of points as discussed in the text. The highest point used in the fit is n_{max} .

intercepts of lines fitted to groups of 5, 6, and 7 contiguous points (defined by that at the highest energy of the group). We see that minima occur in each case if the *lowest* energy point in each group is the tenth point, at 150 eV. In Fig. 49 we show the energy axis intercepts for lines fitted to all points from the tenth to a variable upper limit of 12-22. This shows a monotonic decrease as the highest point included is reduced from 22 to 17 with a broad minimum below that. We conclude that we should reject the topmost five or six points and take as the best estimate of the minimum intercept the mean of the three lowest values, 20.4 eV. The analysis also gives a value of 1.05 for the scale factor.

The fact that the energy intercept of the Bethe-Fano line is not equal to the threshold energy has not always been appreciated and, perhaps as a consequence of this, the line has sometimes been considered as describing the behavior at all energies and not just as a high-energy asymptote. A more realistic approach has been to multiply the Bethe cross section by an energy-dependent factor F(E) that vanishes at the threshold and tends to unity at high energy. Chen and Gallagher (1976, 1978) found that a factor $[1-(E_i/E)^{0.5}]$ gave a good representation of their data for the alkaline earths and alkalis, respectively. Shemansky et al. (1985) used $(1-E_i/E)$ as part of their analysis of their helium resonance line data. These are two examples of a more general factor that we write as $[1-(E_i/E)^a]^b$. The two indices allow greater flexibility in adjusting the rate at which the cross section approaches the high-energy Bethe asymptote. We have examined a range of data using this form of factor, and while it is an improvement over the single parameter form, it is not good at energies where the convergence is nearly complete. We have therefore tried a form of factor that must show good convergence and we write

$$F(E) = \{1 - \exp[(E_j - E)/E_R]\}^b.$$
 (C6)

In this equation the parameter E_R determines the energy

at which the convergence approaches completion, and the index b controls the general shape of the curve at lower energies. We show in Figs. 8(a), 22, and 29 the results of this parametrization for three cases in which the data extend to energies high enough that convergence is essentially complete and in Fig. 2(b) for an extremely important case in which this is not so. In all four cases index b has a value close to 0.36.

Following McFarlane (1974), Heddle (1979) has shown how a determination of the energy E_p at which the polarization of a line passes through zero can be used to estimate a value for the energy intercept E_0 , for within the Bethe approximation these energies are related by $E_p = e^3 E_0$. Heddle (1983) extended that analysis and developed relationships, which apply to optically forbidden excitations as well as to the optically allowed ones, between the slope of the polarization versus log(energy) curves and a polarization parameter which, for neutral atoms, is equal to the threshold polarization, a quantity often difficult to measure directly.

For optically forbidden excitations the Bethe approximation predicts that the product $Q_j E$ will become asymptotically independent of energy to good approximation. This result is valuable in extending to high energies data on lines that contribute to the cascade population of states accessible by optically allowed paths. Inokuti (1971) and Matsuzawa *et al.* (1979) have discussed the departures from constancy.

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