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Energy dependence of the photoelectron branching ratio in the 5p shell of xenon†

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The technique of photoelectron spectrometry has been used to measure the $^2P_{3/2}$:$^2P_{1/2}$ branching ratio in the photoionization of the 5p shell of xenon, using discrete UV lines and synchrotron radiation, in the entire energy range between 21 and 107 eV. A strong energy dependence is observed, with a minimum around 30 eV and a maximum, slightly higher than the statistical ratio, between 60 and 70 eV. Between 21 and 40 eV, the present data confirm the earlier calculations of Walker and Waber, using the Dirac-Slater model, which predicted a minimum in the branching ratio around 30 eV, in contrast to the conclusions of a previous experimental analysis which were that this branching ratio be constant in this energy range. The discrepancy between our data and these previous measurements might be attributed to pressure effects that are found to play a major role below 40-eV photon energy. New Dirac-Slater calculations by Desclaux reproduce the experimental behavior qualitatively between 40 and 100 eV.

I. INTRODUCTION

Photoionization of the p and d shells of atoms leads to the competitive production of two final states of the ion in the spectral range above the second photoionization threshold, as a consequence of the spin orbit coupling. These are the $^2P_{3/2}$ ground state and the $^2P_{1/2}$ excited state of the ion in the case of a p-shell, and the $^2D_{5/2}$ and $^2D_{3/2}$ state for a d shell. The relative probabilities with which these two states are formed, called branching ratio, can be measured by counting, with an electron spectrometer, the number of electrons ejected with energies corresponding to the two final states of the ion.

Several measurements of this branching ratio R have been reported at a few individual wavelengths in the d shells of Zn, Cd, and Hg,[1-4] in the p shells of Pb[5] and in the outer p shell of the rare gases.[6-9] Three measurements of R have been reported, as a function of wavelength, in the spectral range extending from the first ionization threshold up to 40 eV, using discrete uv lines[10,11] or synchrotron radiation.[12] Most of these measurements show that R deviates from the statistical value $(l+1)/l$ that account for the number of possible final ionic states. Furthermore, for the 5d subshell of Hg, Dehmer and Berkowitz[10] have observed a wavelength dependence of R, in agreement with theoretical calculations using the Dirac-Slater model[1]; their results supported the qualitative prediction that R should be larger than statistical when the partial-photoionization cross sections are rising and below statistical when they are falling. In contrast to this energy dependence, Samson and co-workers[11] have reported R to be constant for the outer p shell of the rare gases up to 40 eV. In particular, in the case of the 5p shell of Xe, they quote a constant value of 1.54(8), while the calculations of Walker and Waber,[13] using the Dirac-Slater model, predicted a minimum in R around 30 eV. In addition, this value of 1.54 was in some discrepancy with other individual measurements.[6-9]

We have already reported the results of preliminary measurements[14] showing that, for the 5p shell of Xe, R was equal to the statistical ratio 2 :1 between 75 and 95 eV and suggesting a rapid variation of R between 40 and 75 eV. We present here the results of the first analysis of this branching ratio in the full energy range extending up to 100 eV above the first ionization threshold.

II. EXPERIMENTAL

In this experiment the branching ratio was measured, as a function of photon energy, by the technique of photoelectron spectrometry. Undispersed radiation from a discharge lamp or monochromatized synchrotron radiation from the ACO storage ring[15] was crossed with a xenon beam in the source region of a cylindrical mirror electron analyzer.

In the 20–40-eV region, the use of undispersed discrete lines (He I, He II, Ne II) from a Damany discharge lamp[16] was preferred since they provided a flux of photons higher by at least one order of magnitude and since continuously variable photon energy was not required.[17] The lamp was typically operated with cathode voltages of about 500 V, discharge currents between 30 and 350 mA and gas pressures of 10^{-3}–10^{-2} Torr.

In the energy range from 40 to 100 eV, synchro-

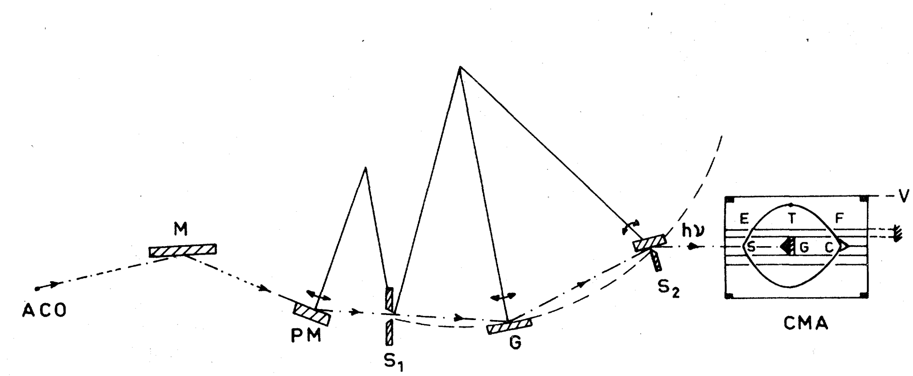

FIG. 1. Lay out of the experimental set up. M, mirror used to deflect, to the monochromator, the radiation emitted by ACO; PM, prefocusing mirror; S_1 and S_2, respective entrance and exit slits of the monochromator; G, grating; CMA, cylindrical mirror analyzer; S, source volume; E and F, respective entrance and exit slits of the electron analyzer; C, channeltron; G, gold foil monitoring the photon flux.

tron radiation was used. The continuum radiation emitted by ACO was monochromatized by means of a 1-m grazing incidence monochromator.[18] A schematic diagram of the experimental set up is given in Fig. 1. The light coming from the storage ring is reflected on the mirror (M) (grazing incidence angle of 4°) to the monochromator. A prefocusing mirror (PM) focuses this light on the entrance slit (S_1). After diffraction, on the grating (G), the monochromatic light passes the exit slit (S_2). Since our experiment required the monochromatized radiation to remain fixed in position and direction as the photon energy was varied, the S_2 is a mirror-knife-edge combination of the Codling type.[19] The energy scan is accomplished by driving G along the Rowland circle together with an automatic motion of the PM and a simultaneous rotation of the exit slit. A detailed description of the apparatus and of the operating procedure is given elsewhere.[20]

The cylindrical mirror analyzer (CMA) designed for this experiment was used with the axis of the cylinders parallel to the incident radiation, since the synchrotron radiation is elliptically polarized: photoionization differential cross sections depend thus on the orientation of the major and minor axes of the ellipse of polarization and of the electric vector magnitudes along these axes.[21,22] In the soft x-ray range, an accurate knowledge of the polarization characteristics of the synchrotron radiation is sometimes difficult to obtain, which can introduce additional errors in the determination of relative intensities in a photoelectron spectrum.[23] Thus the acceptance of a 2π azimuthal angle around the incoming photon beam is the only experimental set up giving independence from the state of polarization of the incident radiation.[21] The CMA has been designed to work in the first order focusing mode with intermediate focus point.[24,25] In the experiments presented here, the analyzer accepted electrons about the magic angle of 54°44′, which makes the results independent of any angular distribution effect. The resolution FWHM, which can be varied continuously from about 0.2% up to 1.5%, was set at 0.9%. The residual magnetic field in the whole apparatus is less than 2 mG. The transmitted electrons were detected with a channeltron Bendix CM4039, and the detector pulses were registered using a multiscaling procedure and stored in the memory of a multichannel analyzer. A detailed description of this spectrometer and the operating procedure will be given elsewhere.[26]

The electron spectrometer was connected to the S_2 of the monochromator with a flexible bellow. The photon beam leaving the S_2 was limited to a diameter of about 4 mm, fed to the source region of the CMA and monitored by measuring the current of photoelectrons emitted from a gold foil (G). Diaphragms with large openings and properly adjusted potentials prevented photoelectrons emitted from solid surfaces from entering the source volume region *S*.

The storage ring was operated at 536 MeV and a maximum current of 150 mA. The monochromator was used with a 576 lines/mm – 1° blaze angle grating. Two series of experiments were performed. In the first series, the S_2 was adjusted to cover the 60–110-eV region with a band pass varying between 0.6 and 1 eV. At that time, the mirror M used to deflect the radiation coming from the ring (see Fig. 1) was a plane mirror. The maximum flux of photons was measured to be about 10^9 photons/Å/sec around 120 Å. An example of the capability of the experimental set up in these conditions is given Fig. 2. It shows the electron spectrum following photoionziation of Xe with 93.2 eV photon energy and a monochromator band pass of 1 eV. All main features of the photoelectron and Auger spectra can be distinctly seen. In parti-

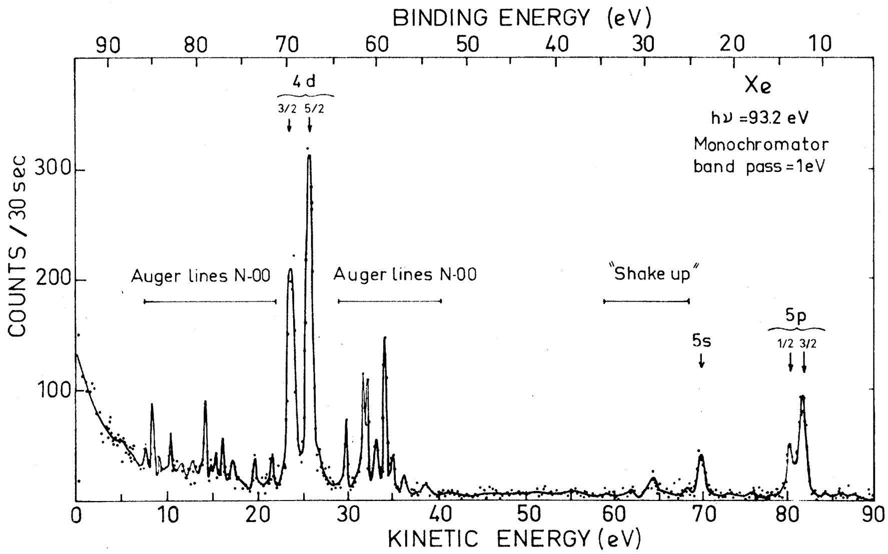

FIG. 2. Electron spectrum of Xe after photoionization by 93.2-eV photons, Electron spectrometer resolution was set at 0.9%. "Shake up" indicates the region where correlation satellites appear. Photon flux was about 10^9 photons/sec.

cular the spin-orbit components are resolved and the Auger lines clearly identified. In the second series of experiments, the 40–90-eV region was explored and the plane mirror M was replaced by a cylindrical mirror, focusing the synchrotron radiation in the vertical plane at the S_2. The flux of photons then delivered by the monochromator in the source volume of the electron spectrometer was in the 10^{10} photons/Å/sec range at 150 Å. In these conditions the band pass of the monochromator was varied between 0.2 and 0.7 eV, which allowed in all cases to clearly resolve the spin-orbit components.

III. RESULTS

Figure 3 shows typical spectra of the $^2P_{1/2}$ and $^2P_{3/2}$ peaks formed by 21.2 and 40.8-eV line radiation and by 70- and 82-eV monochromatized synchrotron radiation. The branching ratio R was taken as the ratio of the peak areas in the photoelectron spectra corrected for the energy dispersion of the analyzer. A careful analysis of the variation of R as a function of the pressure of the gas was performed, since the scattering of low-energy photoelectrons inside the source volume and along the path through the electron analyzer is known to perturb relative intensities in a photoelectron spectrum.[10,27] Measurements were taken for five different values of the pressure measured in the vacuum chamber of the spectrometer, which was proprotional to the pressure in the source volume. Table I summarizes our results for the photon energies 21.2, 30.5, and 40.8 eV at the two limits of the pressure range (8×10^{-6} and 8×10^{-5} Torr). The values previously reported by other investigators, sometimes without quantitative indication of their working pressure, are included for comparison. The influence of the pressure on the measured branching ratio is different at 21.2 and 30.5 eV. This difference can be explained by the variation, as a function of electron energy, of the total scattering cross section in Xe.[28] This cross section has a strong maximum of about 4×10^{-15}

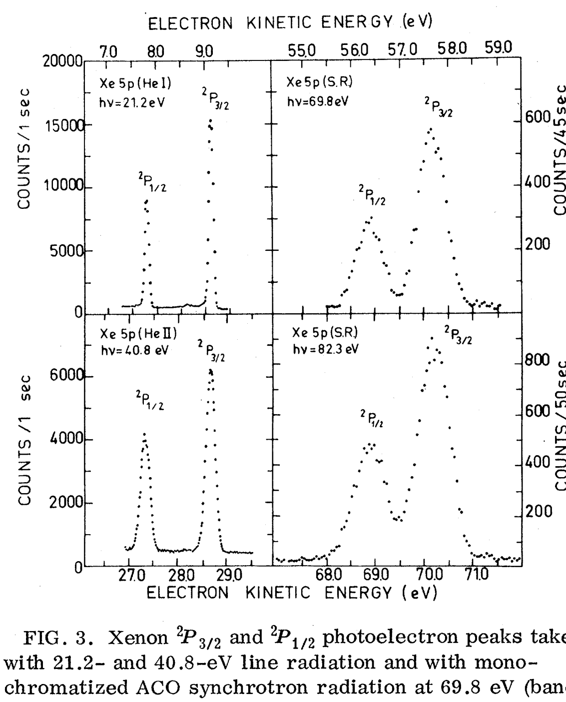

FIG. 3. Xenon $^2P_{3/2}$ and $^2P_{1/2}$ photoelectron peaks taken with 21.2- and 40.8-eV line radiation and with monochromatized ACO synchrotron radiation at 69.8 eV (band pass of the monochromator = 0.65 eV) and 82.3 eV (band pass = 0.50 eV). For these spectra, the value of the pressure was the highest limit of our pressure range (8×10^{-5} Torr in the vacuum chamber of the spectrometer). Photon flux was about 10^{10} photons/sec with synchrotron radiation.

TABLE I. Experimental $^2P_{3/2}$: $^2P_{1/2}$ branching ratio in Xe measured in low photon energies with He I, Ne II, and He II lines. The second and third columns give our results for the two limits of the pressure range we studied. Quoted errors are the statistical standard deviations. The next columns give the results obtained by other investigators.

Photon energy (eV)	Our values[a] 8×10^{-5} Torr	8×10^{-6} Torr	Samson[c] *et al.*	Rabalais and Debyes[d]	Others[e]
21.22	1.57(7)[b]	1.69(5)	1.54(8)	1.58	1.66
					1.69
					1.68(2)
30.55	1.52(5)	1.37(7)	1.56(6)		
40.81	1.56(4)	1.55(3)	1.63(7)	1.54	

[a] Pressures indicated are the background pressure in the vacuum chamber of the spectrometer. The pressure in the source volume is about twice higher.

[b] This value is the average of six independent measurements. However, the error is larger, because of the scattering tail, as discussed in the text.

[c] Private communication; see also Ref. 11.

[d] See Ref. 9.

[e] See Refs. 6–8.

cm^2 around 6 eV and decreases rapidly with increasing and decreasing electron energy. As the photoelectrons leave the source volume S, they traverse first a field-free region where their kinetic energy remains constant. Then they enter the space between the inner and outer cylinder (entrance slit E, Fig. 1) and change their energy, because of the retardation due to the negative voltage. At the top of their trajectory (point T, Fig. 1), their velocity normal to the axis is zero and their energy is down to $E_0 \cos^2(54°44') = \frac{1}{3}E_0$. Thus the kinetic energy of $^2P_{3/2}$ and $^2P_{1/2}$ electrons ejected by 21.2-eV radiation decrease, respectively, from 9.09 and 7.88 eV in the source volume to minimum values of 3.03 and 2.63 eV at T. In the second part of the trajectory they regain energy and, at the exit slit of the field region (point F) they have again their initial kinetic energy. Thus, along the largest part of their path in the analyzer, the total scattering cross section is *higher* for the $^2P_{3/2}$ electrons, although they are faster than the $^2P_{1/2}$. Consequently, the $^2P_{3/2}$ electrons suffer more losses in the analyzer than the $^2P_{1/2}$ electrons, leading to a lower value of the measured branching ratio at higher pressure. This particular behavior may explain the differences in the values quoted in the previous experiments. At 30.5-eV photon energy, the kinetic energy of the $^2P_{1/2}$ and $^2P_{3/2}$ electrons is almost everywhere higher than the energy of the maximum in the scattering cross section, which explains that the measured branching ratio is higher at higher pressure. For photon energies of 40.8 eV and up, no pressure effect was detected because of smaller magnitudes and differences in magnitude of total scatttering cross sections for the different photoelectrons. Finally our results show that pressures as low as 10^{-4} Torr may be still too high, at least with a CMA, to obtain the true branching ratio at low photon energy, since at this pressure the measured branching ratio is constant, while below 10^{-5} Torr it varies actually with energy.

The variation of the branching ratio, as obtained

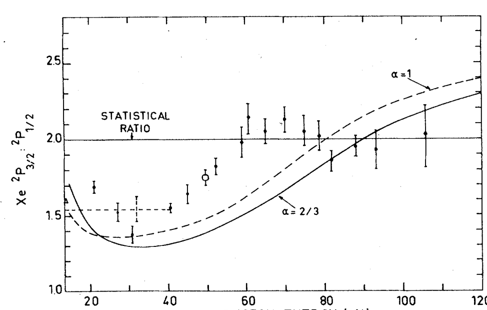

FIG. 4. Variation, as a function of the wavelength, of the $^2P_{3/2}$: $^2P_{1/2}$ branching ratio for xenon. Quoted errors are standard deviations. The experimental points are our values, except the point at 48.5 eV (Φ) that has been measured by Dehmer (Ref. 29). The horizontal dashed line up to 40.8 eV marked the constant value quoted by Samson as 1.54 (Ref. 11) with the vertical dashed line indicating his uncertainty of ±0.08. Δ = threshold value calculated by Lu (Ref. 31). Full and dashed curves are the results obtained by Desclaux (Ref. 32) with two different values for the exchange parameter α. $\alpha = \frac{2}{3}$ is expected to give the best agreement with experiments (Ref. 32).

in our experiments is shown in Fig. 4. A strong energy dependence is observed: R decreases from a value of around 1.7 at 21.2 eV, goes to a minimum around 30 eV, rises to a value a little higher than the statistical ratio 2 : 1 around 60 eV and then decreases slowly, staying around the statistical ratio, with possibly a small minimum around 85 eV. The point measured by Dehmer[29] at 48.5 eV is in excellent agreement with our results. The dashed horizontal line below 40 eV is the constant value quoted by Samson as 1.54 ± 0.08,[11] in contradiction with the present results. It should be noted, however, that the numerical values in his second set of measurements[30] could have been considered as indicating already a small energy dependence in this energy range. The point at threshold is the value (1.6) calculated by Lu[31] using the quantum defect theory.

The full and dashed curves in Fig. 4 are the results of a recent calculation by Desclaux[32] who extended up to 1000 eV the earlier calculations of Walker and Waber[13] with basically the same Dirac-Slater model in the *j-j* coupling and two different values of the exchange parameter α. They exhibit the same behavior as previously obtained below 40 eV,[13] with a minimum more or less pronounced, according to the value chosen for α. Then the theoretical ratio increases with increasing photon energy, reaches a maximum value higher than the statistical ratio at 150 eV and then decreases down to the statistical ratio. The energy at which the maximum occurs is higher than our experimental value. At 1000 eV, the calculated branching ratio is equal to the statistical ratio, in agreement with the high-energy value measured by Gelius using the Al$K\alpha$ emission line.[33]

We can conclude from this comparison, that while the Dirac-Slater model reproduces qualitatively well the general behavior of the branching ratio determined experimentally (minimum around 30 eV, followed by an increasing up to values higher than the statistical ratio), there is some discrepancy between theory and experiment on a more quantitative basis. This fact is not too surprising when one considers the crudeness of the model used in the calculations. It is effectively known that the introduction of ground-state correlations in the theoretical calculations through a multiconfiguration Hartree-Fock procedure[34] improves the agreement between theory and experiment greatly for the total $5p$ photoionization cross section at very low photon energy. The influence of electron correlations on the branching ratio below 30 eV can thus be reasonably expected to be sizable. On the other hand, above 40 eV, the $5p_{1/2}$ and $5p_{3/2}$ photoionization cross sections, as calculated in the Dirac-Slater model, do not show any Cooper minimum and decrease continuously from threshold, while recent measurements[35] have definitely shown that the total $5p$ cross section increases from about 60 up to 85 eV and then decreases again. This behavior of the $5p$ cross section is also obtained in calculations including intershell correlations in a theoretical model using the random phase approximation with exchange.[36] However, the influence of electron correlations on the branching ratio in this photon energy range is not expected to be *a priori* important; the introduction of the intermediate coupling in the theoretical model could better improve the agreement between theory and experiment.[32]

The fact that our experimental values are higher than the statistical ratio exactly in this energy range where the experimental $5p$ cross section is rising supports the qualitative statement established by Walker *et al.*[1] that the branching ratio should be higher than statistical when the partial cross sections are rising and below statistical when they are falling. The possible existence of a minimum around 85 eV could also be correlated with the existence of a maximum in the total $5p$ cross section, maximum which should not occur at the same energy for the $5p_{1/2}$ and $5p_{3/2}$ cross sections, taking into account the different binding energies. On the other hand the rising of the theoretical ratio up to a value higher than the statistical ratio from 30 to 150 eV in the Dirac-Slater calculations, cannot be attributed to the kinetic-energy effect, since there is no minimum in the calculated $5p$ cross section, and comes only from the differences in wave functions of the two bound orbitals, resulting in a different energy dependence of the matrix elements corresponding to either $5p_{1/2}$ or $5p_{3/2}$ electrons. Finally, it should also be noted that at very high energies the calculations of Desclaux yield a ratio equal to the statistical ratio in agreement with experiment,[33] while Walker *et al.* have obtained a branching ratio systematically lower than the statistical ratio for the $5d$ subshells of Zn, Cd, and Hg,[1] on the basis of a different behavior of the matrix elements near the nucleus.

Further calculations taking into account correlation effects should be developed to put the comparison between theory and experiment on a more quantitative basis. In addition, measurements of the branching ratio for the $4d$ subshell of xenon, currently in progress,[37] should bring more information on the influence of spin-orbit coupling on the photoionization processes.

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[1]T. E. H. Walker, J. Berkowitz, J. L. Dehmer, and J. T. Waber, Phys. Rev. Lett. 32, 678 (1973).

[2]D. C. Frost, C. A. McDowell, and D. A. Vroom, Chem. Phys. Lett. 1, 93 (1967).

[3]S. Süzer and D. A. Shirley, J. Chem. Phys. 61, 2481 (1974).

[4]S. Süzer, S. T. Lee, and D. A. Shirley, Phys. Rev. A 13, 1842 (1976).

[5]S. Süzer, M. S. Banna, and D. A. Shirley, J. Chem. Phys. 63, 3473 (1975).

[6]F. J. Comes and H. G. Sälzer, Z. Naturforsch. A 19, 1230 (1964).

[7]D. W. Turner and D. P. May, J. Chem. Phys. 45, 471 (1966).

[8]D. C. Frost, C. A. McDowell, and D. A. Vroom, Proc. R. Soc. Lond. 296, 566 (1967).

[9]J. W. Rabalais and T. P. Debies, J. Electron. Spectrosc. 5, 847 (1974).

[10]J. L. Dehmer and J. Berkowitz, Phys. Rev. A 10, 484 (1974).

[11]J. A. R. Samson and R. B. Cairns, Phys. Rev. 173, 80 (1968); J. A. R. Samson, J. L. Gardner, and A. F. Starace, Phys. Rev. A 12, 1459 (1975).

[12]J. E. Rowe and G. Margaritondo, Phys. Lett. 57A, 314 (1976). In this experiment, the branching ratio in the $5p$ shell of Cs was measured between 22 and 32 eV, but only in the solid phase.

[13]T. E. H. Walker and J. T. Waber, J. Phys. B 7, 674 (1974).

[14]F. Wuilleumier, M. Y. Adam, V. Schmidt, N. Sandner, and W. Mehlhorn, International Conference on the Physics of X-ray Spectra, Natl. Bur. Stand., Gaithesburg, Md., 1976 (unpublished).

[15]P. Dagneaux, C. Depautex, P. Dhez, J. Durup, Y. Farge, R. Fourme, P. M. Guyon, P. Jaeglé, S. Leach, R. Lopez-Delgado, P. Morel, R. Pinchaux, P. Thiry, C. Vermeil, and F. Wuilleumier, Ann. Phys. (Paris) 9, 9 (1975).

[16]H. Damany, licence ANVAR n° 72.968.00 (1972).

[17]When a resonance is to be scanned, continuous radiation must, of course, be used like in a recent experiment by P. C. Kemeny, J. A. R. Samson, and A. F. Starace (private communication).

[18]P. Jaeglé, P. Dhez, and F. Wuilleumier, *Vacuum Ultraviolet Radiation Physics*, edited by E. E. Koch, R. Haensel, and C. Kunz (Pergamon Vieweg, Hamburg, 1974), p. 788.

[19]K. Codling and P. Mitchell, J. Phys. E 3, 685 (1970).

[20]P. Jaeglé, P. Dhez, and F. Wuilleumier (to be published).

[21]V. Schmidt, Phys. Lett. 45A, 63 (1973).

[22]J. A. R. Samson and A. F. Starace, J. Phys. B 8, 1806 (1975).

[23]K. Codling, R. G. Houlgate, J. B. West, and P. R. Woodruff, J. Phys. B 9, L83 (1976).

[24]V. V. Zashkvara and V. S. Red'kin, Sov. Phys.-Tech. Phys. 14, 1089 (1970).

[25]J. S. Risley, Rev. Sci. Instrum. 43, 95 (1972).

[26]M. Y. Adam, F. Wuilleumier, N. Sandner, V. Schmidt, and W. Mehlhorn (to be published).

[27]J. L. Gardner and J. A. R. Samson, J. Electron. Spectrosc. 2, 153 (1973).

[28]L. J. Kieffer, At. Data 2, 293 (1971).

[29]After our first series of experiments between 75 and 95 eV, suggesting a rapid variation of R above 40 eV, J. Dehmer kindly agreed to measure this point at our request, thus confirming this suggestion (August, 1976).

[30]J. A. R. Samson (private communication).

[31]K. T. Lu, Phys. Rev. A 4, 579 (1971).

[32]J. P. Desclaux (private communication and to be published).

[33]U. Gelius, J. Electron. Spectrosc. 5, 985 (1974).

[34]J. R. Swanson and L. Armstrong, Jr. Phys. Rev. A 15, 661 (1977).

[35]J. B. West, P. R. Woodruff, K. Codling, and R. G. Houlgate, J. Phys. B 9, 407 (1976).

[36]M. Ya. Amusia, *Vacuum Ultraviolet Radiation Physics*, edited by E. E. Koch, R. Haensel, and C. Kunz (Pergamon Vieweg, Hamburg, 1975), p. 788.

[37]See also P. Shannon, J. B. West, and K. Codling (to be published).