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Measurements of relative subshell photoionization cross sections in the noble gases by ultraviolet photoelectron spectroscopy

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A method is described for the measurement of relative subshell photoionization cross sections (SPCS) in the noble gases by the technique of ultraviolet photoelectron spectroscopy. Values are reported for the photoionization cross sections of the neon $2p$, krypton $4p$, xenon $5p$, and xenon $5s$ levels relative to that of the argon $3p$ level. The photon energies used for these measurements were 21.22, 40.81, and 48.37 eV. Approximate absolute subshell photoionization cross sections deduced from these relative cross sections are compared to other absolute SPCS obtained from total photoabsorption measurements and also from theory. Results of some relative photoionization cross-section measurements for the outer p bands associated with the halide ions in solid alkali halides and the outer d bands of metallic gold and silver are also presented. Close similarities in variation with photon energy and atomic number are found between the relative photoionization cross sections of the outer p bands of the alkali halides and the outer p levels of the noble gases, but the photoionization cross sections of the d bands of both gold and silver exhibit quite different properties from those found for the outer p bands and levels of both alkali halides and noble gases. A general conclusion is drawn concerning cross sections for photoionization from electron energy bands in solids.

I. INTRODUCTION

A full understanding of the photoionization process is of importance in several areas of current interest in physics.[1,2] Consequently, subshell photoionization cross sections (SPCS) have been the subject of theoretical and experimental work over a number of years. (See, for example, Refs. 1 and 2 and other references contained therein.)

The noble gases are ideal materials for the study of SPCS due to (i) the relative simplicity of quantum-mechanical calculations for free atoms and (ii) the ease with which these substances may be handled in the laboratory.

Some recent experimental investigations of SPCS and related quantities in the noble gases over a wide range of photon energies have been performed by Krause,[3,4] Wuilleumier,[4,5] Siegbahn and co-workers,[6] Henke and Elgin,[7] Samson,[8,9] Cairns,[9] and Ederer and Tomboulian,[10] while recent calculations of SPCS have been undertaken by Henry, Bates, and Viegle,[11] Kennedy and Manson,[1] and others. The theoretical basis for these calculations is due largely to Bethe and Salpeter (see, for example, Ref. 12).

To date, most comparisons between measured and calculated SPCS for atoms have been made indirectly by summing the individual, calculated SPCS values at a particular photon energy to form a "total photoabsorption cross section" and comparing this value with that obtained from total photoabsorption measurements made at the given energy.[1,5,8,11] There are some problems with this approach due largely to the multiplicity of different ionization and excitation events that may occur when a photon interacts with an atom.[4,6,13,14] Despite these difficulties, most calculations show at least a gross agreement with experiment, the work of Kennedy and Manson[1] being somewhat superior in this regard to that of Henry, Bates, and Viegle.[11] For this reason the results of relative SPCS measurements presented here will be compared with the theoretical work of the former authors.

Since the photoelectron kinetic energy associated with a particular photoionization process in a gas is restricted to a narrow range, determined to a large extent by the degree of monochromaticity of the photon source, different photoionization processes can generally be studied independently of each other by the use of an electron energy analyzer, as employed in modern photoelectron spectroscopy techniques. Many problems associated with total photoabsorption measurements are thus avoided.

A technique is described here whereby accurate relative SPCS measurements may be performed. A photoelectron spectrometer, whose aperture subtends a large solid angle in the target region, is used so that good signal intensity is maintained. Uncertainty in the measured SPCS values owing to variation of photoelectron intensity with angle over the spectrometer entrance is shown to be ca. 2%. Correction of measured photoelectron line intensities for the variation in transmission efficiency of an electron energy analyzer as a function of photoelectron kinetic energy[15,2] is also discussed briefly.

Values, accurate to 10% or better are reported for the SPCS of neon $2p$, krypton $4p$, and xenon $5p$ and $5s$ subshells, relative to the argon $3p$-level SPCS, at several photon energies in the 20–50-eV range. The choice of the argon $3p$ level as a reference is arbitrary. These relative SPCS values are then expressed in absolute units (megabarns) by the use of approximate absolute argon $3p$-level SPCS obtained from total photoabsorption measurements.[8] Absolute SPCS values thus obtained are compared to the results of other total photoabsorption measurements[8,10] and to the theoretical calculations of Kennedy and Manson.[1]

A comparison of the present outer p-level SPCS values for the noble gases with the results of photoionization cross-section measurements for the p bands associated with the halide ions in the alkali halides and the d bands of gold and silver leads to conclusions concerning cross sections for photoionization from electron energy bands in solids.

II. APPARATUS AND EXPERIMENTAL PROCEDURES

The photoelectron spectrometer and helium-resonance-lamp photon source used in these measurements, both constructed within this department, have been described in detail elsewhere.[16,17] Basically the spectrometer consists of a 90° sector spherical, electrostatic electron energy analyzer of 2.54-cm mean radius. The resolving power R usually quoted as the figure of merit for this type of analyzer is defined by

$$R = E_0/\Delta E\,, \tag{1}$$

where E_0 is the pass energy of the analyzer and the resolution ΔE is the full width at half-maximum (FWHM) of the analyzer lineshape. For the present instrument $R = 50$.

Because the accuracy and feasibility of SPCS measurements of the type described here depend to a large part on strong signal intensity rather than good resolution, a high analyzer pass energy of 15 eV was found desirable for reasons that will be further elucidated when the analyzer transmission efficiency is discussed below.

Electrons from the energy analyzer are detected by a channeltron solid-state electron multiplier. The subsequent pulses are then processed by a standard set of modular pulse-detection units, and counted by a multichannel analyzer operating in multiscalar mode. Spectra are acquired by varying the accelerating/retarding voltage on the spectrometer entrance-slit system, as described elsewhere,[15] in synchronization with the channel-advance clock of the multiscalar.

The helium resonance lamp[17] used in this work produces useful photon intensities at 21.22, 40.81, and 48.37 eV.[18] Satellite lines of the 21.22-eV radiation (having ca. 10% of the intensity of the main line), at 23.09 and 23.74 eV[18] need also to be considered when measured spectrometer line intensities are interpreted in terms of SPCS, as will be described later in this section.

In order to measure SPCS for the various levels of neon, krypton, and xenon relative to the argon $3p$ level, each of the former gases was mixed in turn, in known proportions, with argon, in a previously evacuated flask of ~1-liter volume. The relative proportions of the two gases, were determined by partially filling the evacuated flask first with argon, and then with the other gas, noting the intermediate and final pressures using a mercury manometer. The partial pressure of argon in the mixture was simply the intermediate pressure, and the partial pressure of the other gas, neon, krypton, or xenon, was the difference between this pressure and the final pressure in the flask. Pressure variations due to temperature changes in the gases as they expanded into the mixing vessel were found to be insignificant. The possibility of the loss of argon from the partially filled flask during the addition of the second gas was investigated by the use of a high-sensitivity mass spectrometer which analyzed the residual gases in the manifold through which the flask was filled, after mixing was completed. No loss of argon was found to occur. Typical partial pressures for the gas mixtures used during the measurements were from $\frac{1}{8}$ to $\frac{1}{6}$ atm.

The gas inlet system to the spectrometer is shown in Fig. 1. Because a difference in the rate of flow through the needle-valve and capillary inlet system was anticipated for the individual components of a gas mixture owing to the different atomic weight and viscosities of the component gases,[19] an auxiliary chamber of ~50-ml volume was placed between the 1-liter gas reservoir and the needle valve. Thus 50 ml of sample gas could be drawn at a time from the larger flask into this smaller volume without disturbing the proportions of the gas mixture in the larger reservoir.

Because of the low base pressure of the spectrometer chamber (~5×10^{-7} Torr), the high initial pressure in the 50-ml auxiliary volume and the small gas flow rate into the spectrometer (~10^{-2} Torr liter sec^{-1}), the flow rate could be kept constant by adjustment of the precision needle valve until more than 99% of the gas originally in the volume had been expended. Since the rate of gas flow was maintained in this manner until a particular 50-ml sample was virtually exhausted, the time-averaged composition of the gas flowing into the spectrometer while a spectrum was recorded could be assumed to be the same as the composition of the gas originally mixed.

The validity of the procedure described above was checked (i) by comparing relative line intensities from consecutively recorded photoelectron spectra of gases drawn from a particular 1-liter gas reservoir, (ii) by recording spectra from gas reservoirs of various compositions, and (iii) by taking a spectrum from the entire contents of a 1-liter flask. Not only was the validity of the gas-mixing procedure verified by the excellent consistency of photoelectron intensity (variations $\leqslant 5\%$ from the mean) produced by the above procedures, but also it was possible to deduce simultaneously that variation of the photon flux from the resonance lamp over the recording time of a spectrum (~1 h) was small. To reduce to a minimum the effect of lamp-intensity variations, spectra were obtained by accumulating many (~10^3) rapid scans (~1 sec) of the electron spectrometer over the electron kinetic-energy range of interest (0–40 eV).

III. PHOTOELECTRON ANGULAR DISTRIBUTIONS AND ANALYZER TRANSMISSION EFFICIENCY

It has been shown both theoretically[1,12,20] and experimentally[3,4,21] that for an unpolarized incident photon beam the differential subshell photoionization cross section, $d\sigma(nl)/d\Omega$, for photoelectrons from the lth subshell of the nth shell of an atom can be written as

$$\frac{d\sigma(nl)}{d\Omega}=\frac{\sigma(nl)}{4\pi}\left[\left(1-\tfrac{1}{2}\beta\right)+\tfrac{3}{4}\beta\sin^2\psi\right], \qquad (2)$$

where $\sigma(nl)$ is the total SPCS, ψ is the angle between the incoming photon beam and the direction in which the resultant photoelectron is emitted, and β, which can in general be a function of n, l, and the kinetic energy E of the ejected photoelectron, is the asymmetry parameter. The possible range of the function $\beta(E)$ for any n and l is such that [1,5,20,21]

$$-1\leqslant\beta(E)\leqslant 2\,. \qquad (3)$$

From expression (2) the number of photoelectrons emitted from the n, l subshell of atoms of number density N (in a diffuse gaseous target) into the solid angle $d\Omega$ at an angle ψ to a highly collimated photon beam of intensity Φ_0 is proportional to dI, where,

$$\begin{aligned} dI&=\Phi_0 N\frac{d\sigma(nl)}{d\Omega}d\Omega\\ &=\frac{\Phi_0 N}{4\pi}\sigma(nl)\left[\left(1-\tfrac{1}{2}\beta\right)+\tfrac{3}{4}\beta\sin^2\psi\right]d\Omega\,. \end{aligned} \qquad (4)$$

In order to measure a total SPCS, $\sigma(nl)$, while avoiding complications due to the angular-distribution effects expressed in Eqs. (3) and (4), ψ is often chosen to be 54.73° (see, for example, Refs. 5 and 21) since at this angle

$$\left[\left(1-\tfrac{1}{2}\beta\right)+\tfrac{3}{4}\beta\sin^2\psi\right]=1$$

for all β. Thus the measured intensity of photoelectrons will be proportional simply to the total SPCS, $\sigma(nl)$, of the energy level from which they originate.

For accurate SPCS measurements to be made in this way the solid angle subtended by the aperture through which photoelectrons are accepted must necessarily be limited. The consequence of this limitation is a reduced signal intensity compared to that obtainable, without significant reduction in accuracy, by other methods, such as the one illustrated in Fig. 2 and now described.

Photoelectrons originating from a point source at the intersection of the photon beam with the y axis enter the spherical electron energy analyzer through the circular slit of angular width $\delta\kappa$. Electrons are prevented by a metal stop from passing through this slit into the energy analyzer for 20° on either side of the x axis.

Equation (4) can readily be transformed into the coordinates of Fig. 2 and integrated over all θ to obtain an expression proportional to the total intensity of those photoelectrons from the n, l sub-

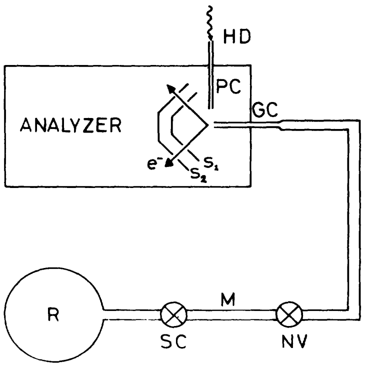

FIG. 1. Schematic of the gas-inlet system to the photoelectron spectrometer showing the gas reservoir (R), stop cock (SC), manifold (M), needle-valve (NV), gas inlet capillary (GC), helium discharge region (HD), photon collimator (PC), and the entrance slits to the analyzer (see also Fig. 2) (S_1 and S_2). Note that the region between S_1 and GC is field free.

shell of the atoms in question which pass through the slip; thus

$$I = \frac{\Phi_0 N}{4\sqrt{2\pi}} \delta\kappa\sigma(nl) \int_0^{2\pi} H(\theta)[(1+\tfrac{1}{4}\beta) - \tfrac{3}{8}\beta \sin^2\theta]d\theta , \tag{5}$$

where $H(\theta)=1$ for all θ where the slit is open and 0 for all θ where the slit is closed. From symmetry considerations it is easily seen that integral (5) need only be evaluated over the first quadrant. Furthermore, it need only be evaluated where the integrand is nonzero. Hence

$$I = \frac{\Phi_0 N}{\sqrt{2\pi}} \delta\kappa\sigma(nl) \int_{\pi/9}^{\pi/2} [(1+\tfrac{1}{4}\beta) - \tfrac{3}{8}\beta \sin^2\theta]d\theta . \tag{6}$$

Integration yields

$$I = \frac{\Phi_0 N}{\sqrt{2\pi}} \delta\kappa\sigma(nl)(1.22 + 0.013\beta) . \tag{7}$$

The residual term, 0.013β, which is dependent upon the particular photoelectron angular distribution of the subshell under investigation, is seen to constitute no more than 2.1% of expression (7) since $|\beta| \leq 2$ [from the inequality (3)].

Two assumptions made in the development of Eq. (7) for the intensity of photoelectrons entering the electron energy analyzer have been checked experimentally and found to be valid. First, it was assumed that the gas in the source area was diffuse, i.e., that the probability of inelastic electron-atom scattering was small. Inspection of the spectra obtained in the present work revealed no scattered background or structure which could be associated with photoelectrons inelastically scattered from gas atoms. The pressure in the source area, though difficult to estimate, was quite low since no attempt was made to enclose the source region. Chamber pressure during the course of the measurements was $\sim 1 \times 10^{-4}$ Torr.

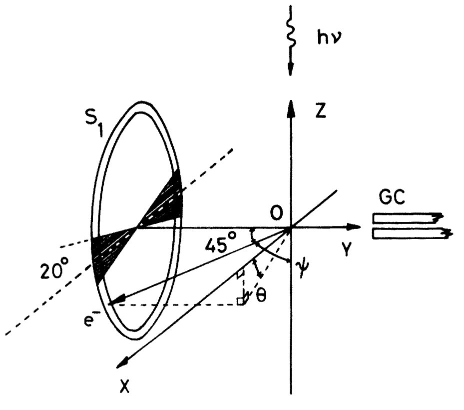

FIG. 2. Diagram of the gas-inlet/photon beam/slit system relevant to the consideration of photoelectron angular-distribution effects in the present work. The open end of the gas-inlet capillary GC is only ca. 0.5 mm from 0 in the actual instrument.

The second assumption which was confirmed was the degree to which the source of the photoelectrons approximated a point source. This was checked by observing the effect of small movements of the gas inlet capillary on the spectra. Movements of the capillary as little as 1 mm in either direction (see Fig. 2) from the optimum position produced a dramatic drop in the measured intensity of photoelectrons from the sample gas, and in one direction a sharp increase in photoelectrons identified as originating from the capillary material. These observations are consistent with the high degree of collimation of the photon beam (achieved by the use of approximately 5 cm of a 1-mm Pyrex capillary as a collimator) and the use of a 1-mm gas inlet capillary, resulting in an effective source volume of about 1 mm^3.

Another consideration of importance for the interpretation of photoelectron line intensities in terms of SPCS is the effect of the electron-energy-analyzer transmission efficiency as a function of the kinetic energy of the photoemitted electrons. This has been described in detail elsewhere.[2,15] Equation (19) of Ref. 2 provides a useful description of this effect and is directly applicable to the present situation:

$$A_m = CAE_0^2/E , \tag{8}$$

where A_m is the measured photoelectron line intensity found by integrating under the photoelectron peak of interest, A is the true line intensity, and C is a geometrical constant of the instrument. Thus to compare line intensities measured at a fixed analyzer pass energy E_0, as in the present case, it is necessary to multiply the area under each photoelectron peak by the corresponding photoelectron kinetic energy E. The advantages, in terms of increased signal intensity, derived from operation of the electron analyzer at a high pass energy are clearly seen from Eq. (8).

IV. RESULTS AND DISCUSSION

Some typical spectra from neon-argon, krypton-argon, and xenon-argon gas mixtures are shown in Figs. 3–5. The structure in the very-low-electron kinetic-energy region of these energy distribution curves was found to be independent of the flow of sample gas into the spectrometer and was presumably due to scattered electrons produced by the photon beam striking solid objects in the lower part of the analyzer chamber. In comparison with the remaining peaks of the spectra the number of very low-energy electrons can be seen from Eq.

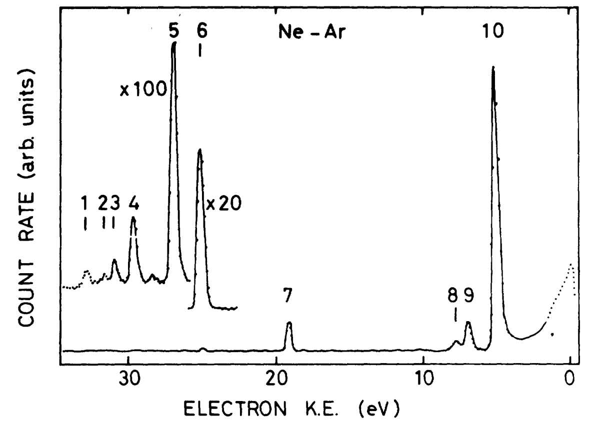

FIG. 3. Photoelectron spectrum from a neon-argon gas mixture (1.11:1.00 by volume) using a helium-resonance-lamp photon source. The numbered photoelectron peaks are as follows: 1, argon $3p_{1/2,3/2}$, $h\nu=48.37$ eV; 2, neon $2p_{1/2,3/2}$, $h\nu=52.90$ eV; 3, neon $2p_{1/2,3/2}$, $h\nu=52.24$ eV; 4, neon $2p_{1/2,3/2}$, $h\nu=51.02$ eV; 5, neon $2p_{1/2,3/2}$, $h\nu=48.37$ eV; 6, argon $3p_{1/2,3/2}$, $h\nu=40.81$ eV; 7, neon $2p_{1/2,3/2}$, $h\nu=41.81$ eV; 8, argon $3p_{1/2,3/2}$, $h\nu=23.74$ eV; 9, argon $3p_{1/2,3/2}$, $h\nu=23.09$ eV; 10, argon $3p_{1/2,3/2}$, $h\nu=21.22$ eV.

(8) to be grossly exaggerated by instrumental effects.

Photoelectron peaks from the mixtures owing to 21.22-eV helium resonance radiation are all to be found below an electron kinetic energy of 10 eV. Adjacent to and overlapping these peaks are some photoelectron lines of lower intensity produced by the 23.09- and 23.74-eV satellites[18] of the main 21.22-eV radiation. The remainder of the peaks are due to 40.81-eV radiation and associated satellites at 48.37, 51.02, 52.24, and 52.90 eV.

Measured intensities of the dominant photoelectron lines were corrected for the contribution from overlapping satellites by determining the ratio of the main-to-satellite radiation intensity for each individual spectrum, using a convenient line.

Finally, in order to obtain relative SPCS values, consideration has to be given not only to the relative numbers of constituent atoms in each gas mixture but also to the average length of time that atoms, having different masses, spend in the target region of the spectrometer, since the probability of emission of a photoelectron from a given atom is directly proportional to the length of time it spends within the photon beam. From the kinetic theory of gases it may be seen that at a given temperature the average kinetic energy per atom for each of the isotopic species present in a mixture is the same. Therefore, if the gas is allowed to expand freely away from a point, such as the end of the inlet capillary tube, the average velocity with which atoms of isotopic mass m leave this point is proportional to $1/\sqrt{m}$. Hence the average time, $\langle t_l\rangle$, that such an atom spends in the target region is

$$\langle t_l\rangle = c\sqrt{m}\,, \tag{9}$$

where c is a function of temperature and experimental geometry only. As each of the noble gases

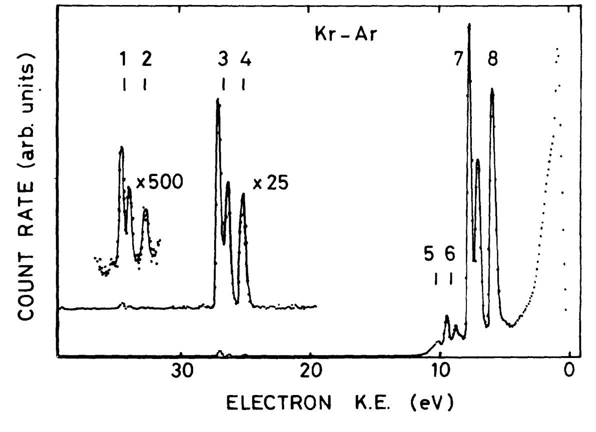

FIG. 4. Photoelectron spectrum from a krypton-argon gas mixture (1.19:1.00 by volume) using a helium-resonance-lamp photon source. The numbered photoelectron peaks are as follows: 1, krypton $4p_{1/2,3/2}$, $h\nu=48.37$ eV; 2, argon $3p_{1/2,3/2}$, $h\nu=48.37$ eV; 3, krypton $4p_{1/2,3/2}$, $h\nu=40.81$ eV; 4, argon $3p_{1/2,3/2}$, $h\nu=40.81$ eV; 5, krypton $4p_{1/2,3/2}$, $h\nu=23.74$ eV; 6, krypton $4p_{1/2,3/2}$, $h\nu=23.09$ eV; 7, krypton $4p_{1/2,3/2}$, $h\nu=21.22$ eV; 8, argon $3p_{1/2,3/2}$, $h\nu=21.22$ eV.

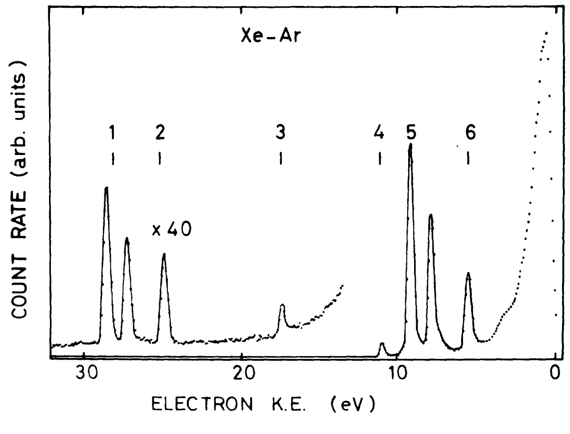

FIG. 5. Photoelectron spectrum from a xenon-argon gas mixture (3.02:1.00 by volume) using a helium-resonance-lamp photon source. The numbered photoelectron peaks are as follows: 1, xenon $5p_{1/2,3/2}$, $h\nu=40.81$ eV; 2, argon $3p_{1/2,3/2}$, $h\nu=40.81$ eV; 3, xenon $5s_{1/2}$, $h\nu=40.81$ eV; 4, xenon $5p_{3/2}$, $h\nu=23.09$ eV; 5, xenon $5p_{1/2,3/2}$, $h\nu=21.22$ eV; 6, argon $3p_{1/2,3/2}$, $h\nu=21.22$ eV.

TABLE I. Table of SPCS for the noble gases measured relative to that for argon.

	$h\nu = 21.22$ eV		$h\nu = 40.81$ eV		$h\nu = 48.37$ eV	
Atomic level	Photoelectron kinetic energy (eV)	Relative SPCS (±10%)	Photoelectron kinetic energy (eV)	Relative SPCS (±10%)	Photoelectron kinetic energy (eV)	Relative SPCS (±10%)
Ar 3*p*	5.37	1	24.96	1	32.52	1
Ne 2*p*	...	...	19.20	4.11	26.76	9.43
Kr 4*p*	6.89	1.17	26.48	1.61	34.04	2.43
Xe 5*p*	8.43	0.92	28.03	0.47	...	...
Xe 5*s*	...	...	17.51	0.025	...	...

consists of known proportions of different stable isotopes, it is necessary to consider the average time, $\langle t_2 \rangle$, that atoms of a particular atomic number Z spend in the target region of the spectrometer. Thus from Eq. (9),

$$\langle t_2 \rangle = c \langle \sqrt{m} \rangle , \qquad (10)$$

where $\langle \sqrt{m} \rangle$ is the weighted mean of the square roots of the isotopic masses for atoms having a particular Z.

From Eq. (10) it is seen that each measured photoelectron peak intensity can be corrected for the velocity distribution effect just discussed by dividing by the appropriate $\langle \sqrt{m} \rangle$ for the gas in question.

A summary of the SPCS values measured relative to the argon 3*p* level and corrected for sample-gas composition, analyzer transmission efficiency, helium resonance satellite radiation, and velocity distribution effects is presented in Table I. The photoelectron kinetic energies listed in Table I and used here for the analyzer-transmission-efficiency correction, as per Eq. (8), have been deduced from (i) the measured electron binding energies for the inert gases owing to Lloyd[22] and Siegbahn *et al.*,[6] and (ii) the photon energies of the helium resonance lines listed in Ref. 18.

The measured relative SPCS of Table I may be converted approximately to absolute units, as in Table II, for the purpose of comparison with theory and with other experimental results, provided that the argon 3*p*-level SPCS is estimated for the particular photon energies of interest here. Reasonable estimates can be made from total photoabsorption measurements in argon such as those of Samson[8] provided that (i) the photon energies used are well removed from the "discrete adsorption windows"[8] as is the present case, and (ii) the 3*s* level does not make too large a contribution to the total photoionization cross section in this energy range. This follows from an examination of the *s*/*p* ratios for the noble gases reported in the literature,[6,9] from the (5*s*/5*p*) ratio for xenon (0.05) found here using 40.81-eV photons (see Table I), from theoretical calculations

TABLE II. Table of SPCS for the noble gases. The present values are deduced from the data of Table I and the argon photoabsorption cross section of Ref. 8. Comparison is made with values deduced from the total photoabsorption measurements of Samson (Ref. 8) (S), and Ederer and Tomboulian (Ref. 10) (ET), and also with the calculated subshell photoionization cross sections of Kennedy and Manson (Ref. 1) (KM) and Amusia *et al* . (Ref. 23) (A).

	$h\nu = 21.22$ eV Absolute SPCS (Mb)			$h\nu = 40.81$ eV Absolute SPCS (Mb)			$h\nu = 48.37$ eV Absolute SPCS (Mb)		
Atomic level	Present (±10%)	Other expt. (S)	Theory (KM)	Present (±10%)	Other expt.	Theory	Present (±10%)	Other expt. (S)	Theory (KM)
Ne 2*p*	...	...	...	9.9	8.2S 9.0(ET)	8.1-*L* 6.9-*V*	7.3	8.7	7.5-*L* 6.3-*V*
Ar 3*p*	36.4	36.4	25.1-*L* 19.1-*V*	2.4	2.4(S)	5.1-*L* 12.0-*V*	0.78	0.78	4.1-*L* 1.4-*V*
Kr 4*p*	42.6	36.5	33.0-*L* 21.3-*V*	3.9	3.9(S)	10.0-*L* 5.7-*V*	1.9	1.6	7.1-*L* 2.8-*V*
Xe 5*p*	33.3	29.5	51.0-*L* 30.9-*V*	1.1	1.8(S)	9.7-*L* 3.4-*V*	...	1.4	5.6-*L* 1.7-*V*
Xe 5*s*	...	...	...	0.06	...	0.13-*L* 0.09-*V* 0.04(A)	...	...	0.16-*L* 0.12-*V* 0.08(A)

on the noble gases by Amusia *et al.*,[23] and from a related experiment by Lynch *et al.*[24] on argon. Other reported s/p ratios are 0.04 (Ref. 9) and 0.05 (Ref. 6) for argon at a photon energy of 29.7 eV ($3s/3p$) and for neon at a photon energy of 40.81 eV ($2s/2p$), respectively. It appears that a good estimate of the outer p-level SPCS for any noble gas can be made, for photon energies of up to 20 eV above the outer s-level ionization threshold, from the total photoabsorption cross section, by reducing these values by ~5%; that is, by the estimated contribution of the outer s subshell to the total photoabsorption cross section (A more accurate estimate for this correction. might be obtained from a consideration of the variation with photon energy of the s/p ratios given, for example, by Amusia *et al.*[23] or by experiments such as that by Lynch *et al.*[24].) Thus the argon $3p$-level SPCS in Table II for the 40.81- and 48.37-eV photon lines have been taken to be 95% of the total photoabsorption cross section as measured by Samson.[8] For the 21.22-eV photon line, the argon $3p$-level SPCS was taken to be equal to the total cross section, since this photon energy is below the argon $3s$-level ionization threshold.[6] The approximate absolute SPCS listed in Table II for the other noble gases have been obtained from these estimated argon $3p$-level SPCS and the measured relative SPCS of Table I.

Also contained in Table II is a comparison of the measured p-level SPCS of the present work with some other total photoabsorption cross sections measured by Samson[8] and by Ederer and Tomboulian.[10] Values due to Samson are denoted by S, those due to Ederer and Tomboulian by ET. Where appropriate, the measured total photoabsorption values of these workers have been reduced by 5% for reasons identical to those considered for the case of argon above.

The accuracy with which the argon total photoabsorption cross section is known is a factor of major importance in assessing the accuracy of the absolute SPCS values found from the present relative SPCS measurements. Differences of up to 15% or more appear to exist between the measured total photoabsorption cross-section values for the noble gases reported by various workers[1,8,10,25] over the photon energy range of present interest. Uncertainty in the argon photoabsorption cross section near the first nondiscrete absorption minimum (at 40–50-eV photon energy) appears to be ca. 15%.[11] Nevertheless, it can be seen from Table II that good agreement exists between the SPCS values measured here and those found from total photoabsorption measurements, particularly when the uncertainties, including those of the present measurements (ca. 10%) are considered. The one exception is the xenon $5p$-level SPCS for the photon energy 40.81 eV; this is discussed further below. The agreement between the value of the neon $2p$-level SPCS at a photon energy of 50 eV reported by Wuilleumier,[4] 7.8 Mb, and the value found here at 48.37 eV, 7.3 Mb, is also very satisfactory.

As already noted, the difference, for the xenon $5p$-level, between the cross-section value obtained here at a photon energy of 40.81 eV and that obtained from the total photoabsorption measurement of Samson[8] at a similar photon energy, exceeds expectation. As this cross-section value falls amongst the smallest measured for outer p levels of the noble gases in the present photon energy range, a possible explanation for the difference may be that the photoelectron spectroscopy technique described herein is a more suitable one for the measurement of small photoelectron cross sections; as can be seen from Fig. 5, the xenon $5p$ photoelectron line intensity is easily measured at a photon energy of 40.81 eV by the present technique. This may not be so for the techniques which have been used in total photoabsorption measurements.[8,10]

Also included in Table II, for the purpose of comparison, are calculated SPCS due to Kennedy and Manson[1] (these values are denoted by KM). Calculations were performed by these authors using both the dipole-length (denoted in the table by the postscript-L) and the dipole-velocity (denoted by postscript-V) approximations. Differences between the calculated values obtained by these two different methods serve to indicate the confidence limits for the calculations.[1] Graphical interpolation was used to find the theoretical SPCS values for the particular photon energies of interest here from the tabulated values of Ref. 1. It can be seen from Table II, and elsewhere,[1,8] that the agreement between theory and the results of photoelectron cross-section measurements for neon is good, while for the heavier noble gases this is less true. This disagreement is particularly evident in the apparent displacement of the calculated first minimum[1] in the total photoabsorption cross section by 10–20 eV upwards in photon energy from the measured position for each of the heavier noble gases, as is readily seen from the comparison between calculated and measured total photoabsorption cross sections to be found in Figs. 2–4 or Ref. 1. Kennedy and Manson,[1] in their discussion of the possible reasons for these displacements suggest that either the calculated SPCS for the outer s levels are underestimated in the regions of the first minima, or the calculated positions of the first Cooper minima in the outer p-level subshell photoionization cross sections are displaced. In view of the small s/p ratios found for the noble gases over the range of photon energies of interest here, as discussed earlier in this section, the second of these alternative explanations offered by the above authors appears to be correct. In fact, the xenon $5s$-level SPCS as measured here (see Table II) is smaller than either of the calculated values of Kennedy and Manson.

V. EXTENSION TO SOME SOLIDS

From the information summarized in Tables I and II and also from other photoelectron measurements made in this laboratory on the p bands of the alkali halides[26,27] and the d bands of gold and silver,[28] (using the same photoelectron spectrometer and helium resonance lamp as for the present work) we now draw some interesting semiquantitative comparisons between the photoionization cross sections in these materials.

Because the alkali halides are highly ionic compounds,[29] it seems reasonable to expect similarities between the behavior of the photoelectron cross sections of the outer p bands of these materials and the photoelectron cross sections of the p subshells of the noble gases owing to similarities between the electronic structure of a noble-gas atom of atomic number Z, a halide ion of atomic number $Z-1$, and an alkali-metal ion of atomic number $Z+1$. In Fig. 6 the outer p-level SPCS of neon, argon, krypton, and xenon, measured at a photon energy of 40.81 eV are compared to the corresponding halide-ion outer p-band photoelectron line intensities for the same photon energy. The line intensity for each halide ion was found by averaging the measured intensity from a number of alkali-halide compounds containing the particular halide and normalizing the results arbitrarily to the bromide-ion line intensity. For consistency, the relevant noble-gas SPCS of Table I have been normalized to the krypton $4p$-level SPCS for the purpose of comparison in Fig. 6. Although the measured halide-ion photoelectron line intensities have not been corrected for a number of factors important for SPCS measurements from solids,[2] the similarity in trend between the cross sections of the p bands associated with the halide ions and the outer p levels of the noble gases is quite apparent.

Variations with photon energy in the photoionization cross sections of the halide p bands and silver and gold d bands can be estimated from the measured photoelectron line intensities if the relative photon fluxes of the lines emitted by the helium resonance lamp are known. Approximate relative photon fluxes for the three helium lines used here are readily deduced from the argon $3p$-level SPCS of Table II and the measured argon $3p$-level line intensities such as those shown in Figs. 3 and 4, after correction has been made for analyzer transmission efficiency. Expressed as a percentage of the 21.22-eV-line photon flux, a typical operational figure for the flux of the 40.81 eV line is 170% while for the 48.37-eV line the figure is 3%.

From these figures, and from measurements on various alkali chlorides, bromides, and iodides performed in this laboratory the photoionization cross sections of the halide p bands at a photon energy of 40.81 eV have been estimated to be 10 to 50 times smaller than at a photon energy of 21.22 eV. This result is consistent with the behavior of the outer p-level cross sections in the noble gases.

In a similar way the changes in the cross sections of the outer d bands of silver and gold with photon energy have been estimated. Since the electron mean free paths in these materials are known with reasonable accuracy for the photoelectron kinetic energies of interest here,[29] the appropriate corrections for mean-free-path effects[2] have been included in the estimates. It is found that, after corrections for electron mean free path and analyzer transmission efficiency, the photoionization cross section for the d band of both gold and silver is the same for both 21.22- and 40.81-eV radiation to within the accuracy with which such changes in cross section have at present been determined (ca. 50%, including uncertainties in relative photon flux and other possible

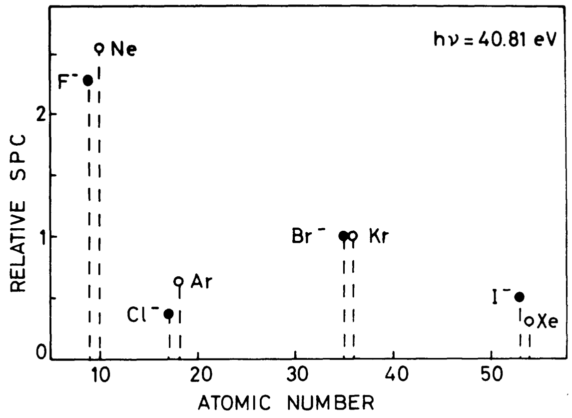

FIG. 6. A comparison of the variation with atomic number of the SPCS of the outer p levels of (i) the noble gases ○, and (ii) the halide ions in the alkali halides ● (determined approximately in the present work). The data has been normalized so that the relative SPCS of the bromide ion $4p_{1/2,3/2}$ level is unity; and similarly the inert-gas relative SPCS of Table I have been renormalized to the krypton $4p_{1/2,3/2}$ level.

effects[2]). This degree of accuracy is seen to be more than sufficient to establish the general differences in behavior between the photoionization cross sections of the p bands associated with the halide ions in the alkali halides, on the one hand, and the d bands of gold and silver on the other hand, for the range of photon energies considered here.

VI. CONCLUSIONS

The technique of photoelectron spectroscopy has been applied successfully to the measurement of subshell photoionization cross sections of the noble gases neon through xenon, relative to the argon $3p$ level, for photons in the energy range 20–50 eV.

From total photoabsorption measurements in argon[8] an approximate absolute SPCS calibration in megabarns has been obtained. The absolute SPCS for the other gases and levels obtained in this way are seen to be in good agreement with those found from other total photoabsorption measurements.[8,10] Contributions of the outer p-level SPCS to the total photoabsorption cross sections of the noble gases have been found to be 95% or more over most of the photon energy range of interest here (20–50 eV). It may thus be seen that there is significant disagreement between measured[8,25] and calculated[1] total photoabsorption cross sections in the gases argon, krypton, and xenon. Recent calculations by Amusia *et al.*[23] of the outer s-level SPCS of the noble gases carried out in the random-phase approximations and which include exchange effects indicate that the single-particle-approximation calculations of Kennedy and Manson[1] considerably overestimate the s-level SPCS over most of the photon energy region of interest here. However since the s-level SPCS represents only ~5% of the total cross section it is apparent that the discrepancy is due largely to inaccuracies in the calculated[1] outer p-level SPCS.

Finally, the similarity is noted between the behavior of the photoionization cross sections of the outer p bands associated with the halide ions in the alkali halides and the SPCS of the outer p levels in the noble gases, when considered both as a function of atomic number and as a function of photon energy. Comparison of the behavior of these p-band and p-level photoionization cross sections with that found for the outer d bands of gold and silver suggests strongly that the dependence of the photoionization cross section of the electrons in a given band of a solid upon photon energy is determined largely by the atomic levels from which the band originated.

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