Angular Distributions of Photoelectrons and Partial Photoionization Cross-Sections

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Phil. Trans. R. Soc. Lond. A 1970 **268**, 141-146
doi: 10.1098/rsta.1970.0067

Phil. Trans. Roy. Soc. Lond. A. **268,** 141–146 (1970) [141]
Printed in Great Britain

Angular distributions of photoelectrons and partial photoionization cross-sections

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An experimental arrangement is given for measuring the angular distribution of photoelectrons. The asymmetry coefficient β is found to be 0.3 for Ar, and 0.3 and 0.12 for N_2 at 584 Å when the residual ion core is left in its $X^2\Sigma$ and $A^2\Pi$ states, respectively. The partial photoionization cross-sections are given for O_2 at 186, 209, 247, 330, and 460 Å. New ionization potentials for O_2 are found at 23.5, 24.6 and 27.3 eV ± 0.3 eV. The effects of autoionizing transitions on the population of vibrational states of N_2^+ are illustrated.

INTRODUCTION

It has become apparent in the last few years that the technique of photoelectron spectroscopy is a powerful tool in probing atomic and molecular structure. It provides a direct method for determining ionization energies and it is practically the only method available for measuring partial cross-sections in the photoionization process. By partial photoionization cross-section is meant the probability that an incident photon will eject an electron from a particular orbital and hence leave the ion in a known state. The measured value for this probability is likely to differ from theoretical predictions unless theory includes the effects of autoionization. Data emphasizing this point are discussed later. On the experimental side difficulties exist in measuring the true transition probabilities, because the electrons are ejected in preferred directions with respect to the plane of polarization of the ionizing flux. In most electron energy analysers the electrons are sampled at one specific angle and will not, in general, measure true transition probabilities. Because of this directional effect, the problem is further complicated when a monochromator is used to produce the ionizing flux, since radiation emerging from a monochromator is partially polarized with the degree of polarization varying with wavelength. Thus, for accurate measurements of partial cross sections either we have to analyse all the photoelectrons in a 4π geometry or else we have to know their angular distribution. Normally, it is not practical to collect all of the photoelectrons and so it is necessary to know how they are distributed.

ANGULAR DISTRIBUTION OF PHOTOELECTRONS

Theoretically, it has been shown (Cooper & Zare 1968, 1969; Tully, Berry & Dalton 1968; Cooper & Manson 1969) that for dipole transitions the number of electrons $n_p\mathrm{d}\Omega$ ejected into the elemental solid angle $\mathrm{d}\Omega$ by plane polarized radiation is given by

$$n_p\mathrm{d}\Omega = C[(1-\tfrac{1}{2}\beta)+\tfrac{3}{2}\beta\cos^2\gamma]\,\mathrm{d}\Omega, \tag{1}$$

where C is a constant which depends on the intensity of the incident radiation, the total photoionization cross-section, the gas pressure, and the ionized volume emitting into the solid angle $\mathrm{d}\Omega$. β is an asymmetry parameter which is zero for an isotropic distribution and is equal to 2 for a pure cosine squared distribution. γ is the angle between the direction of the electron and the direction of the electric vector of the photon beam. Equation (1) has been generalized (Samson 1969*a*) for partially polarized radiation, namely

$$n\mathrm{d}\Omega = C\left[(1-\tfrac{1}{2}\beta)+\frac{3\beta}{2(g+1)}(g\cos^2\alpha+\cos^2\gamma)\right]\mathrm{d}\Omega, \tag{2}$$

where the degree of polarization is defined by $g = I_x/I_z$. I_x is the intensity of the radiation vibrating along the x axis and I_z is the intensity vibrating along the z axis (see figure 1). The angles α and γ are the direction cosines with respect to the x and z axis.

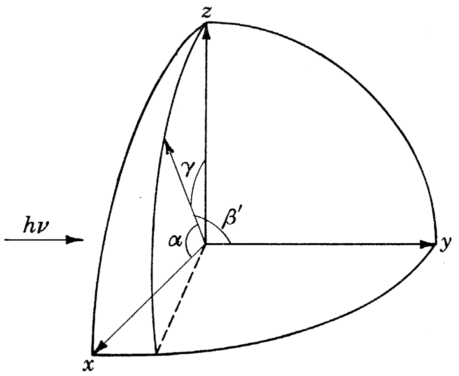

Figure 1. Photon beam travelling in the y direction and interacting with a molecule at the origin of the xyz axes. Photoelectron is ejected with direction cosines α, β' and γ.

When $\alpha = \gamma = 54^\circ\,44'$, then $\cos^2\gamma = \frac{1}{3}$ and we see that the distribution of the electrons is completely independent of the degree of polarization of the ionizing radiation and of β. Integrating equation (2) over a finite solid angle Ω_{54} centred about $\alpha = \gamma = 54^\circ\,44'$ we obtain

$$N_{54} = \Omega_{54}C_{54}, \tag{3}$$

where N_{54} is the total number of electrons ejected into the solid angle Ω_{54}. That is no matter how large the solid angle observed by a detector centered on the angle $\alpha = \gamma = 54^\circ\,44'$, the signal is simply proportional to the solid angle. This then should be the angle of observation to obtain quantitative data on transition probabilities and Franck–Condon factors.

To obtain the asymmetry factor β which uniquely describes the angular distribution of the photoelectrons for a given degree of polarization it is necessary to measure the number of electrons ejected at two specific angles. From equation (2) it can be seen that provided $\alpha = \gamma$ the results are independent of the degree of polarization of the incident radiation. Thus, if we take $54^\circ\,44'$ as one angle of observation, then $N_{54} = \Omega_{54}C_{54}$. As a second angle, take $\alpha = \gamma = 45^\circ$. To obtain N_{45}, the total number of electrons ejected into the solid angle Ω_{45} centred on 45°, we again integrate equation (2) with respect to this direction and obtain

$$N_{45} = \Omega_{45}C_{45}(1+\tfrac{1}{4}\beta)+\tfrac{1}{4}\pi\beta C_{45}(3\cos\theta-\cos^3\theta-2), \tag{4}$$

where θ defines the solid angle about the direction $\alpha = \gamma = 45^\circ$, that is, $\Omega_{45} = 2\pi\,(1-\cos\theta)$. From the ratio of equations (4) and (3)

$$\frac{N_{45}}{N_{54}} = (1+\tfrac{1}{4}\beta)\,\frac{\Omega_{45}C_{45}}{\Omega_{54}C_{54}}+\tfrac{1}{4}\pi\beta\,(3\cos\cos\theta-\cos^3\theta-2)\,\frac{C_{45}}{\Omega_{54}C_{54}}. \tag{5}$$

For angles of θ up to about 10° the second term on the right side of equation (5) is less than 1% of the first term. Thus

$$N_{45}/N_{54} \simeq f(1+\tfrac{1}{4}\beta), \tag{6}$$

where f is the fraction $\Omega_{45}C_{45}/\Omega_{54}C_{54}$. The constants C contain the ionized volumes which may be different at the two angles. If two detectors are used then the values of C will contain their relative efficiencies. The fraction f can be determined by measuring the ratio N_{45}/N_{54} for helium, since $\beta = 2$ for the ejection of an s shell electron. Once f is known, equation (6) can be used to determine β for any other gas and for any wavelength.

Results

The value of β was determined for Ar, $N_2(X^2\Sigma_g)$, and N_2 $(A^2\Pi_u)$ using the technique described above. The analyser was a spherical grid retarding potential type described previously (Samson & Cairns 1968) with the addition of two Bendix channel electron multipliers (Channeltrons). Figure 2 shows a diagram of the analyser with the orientation of the Bendix Channeltrons. The value of f in equation (6) was determined by ionizing helium with 304 Å and assuming $\beta = 2$. Independently, however, β was found to be approximately 2 by measuring the solid angles involved, the ionizing volumes, and the relative detector sensitivities. However, the calibration against He was assumed to be more accurate.

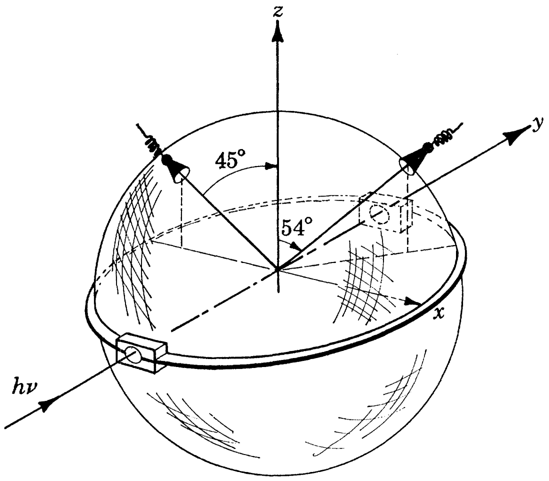

FIGURE 2. Spherical retarding potential electron energy analyser with two Bendix channel electron multipliers oriented at angles of 45° with respect to the $-x$ and $+z$ directions and 54° 44′ with respect to the $+xyz$ directions, respectively.

Introducing Ar into the analyser and ionizing with the 584 Å line β was found to be equal to 0.3. N_2, also ionized by 584 Å gave $\beta = 0.3$ for the $X^2\Sigma_g$ transition and $\beta = 0.12$ for the $A^2\Pi_u$ transition. That is, the distributions were very nearly isotropic. Figure 3 illustrates the angular distribution of electrons ejected by unpolarized radiation when $\beta = 0$, 0.3, and 2. These findings are in good agreement with the results of Berkowitz, Ehrhardt & Tekaat (1967) and Berkowitz & Ehrhardt (1966).

PARTIAL PHOTOIONIZATION CROSS-SECTIONS

The partial photoionization cross-sections for producing ions in various electronic states varies with wavelength. Moreover, if an autoionizing transition is involved the cross-sections are likely to vary drastically from that of the direct ionization process. Autoionization is very common near the ionization threshold of most molecules. To illustrate examples of the variation in cross-section with wavelength and for autoionizing transitions, O_2 was ionized with high energy photons while N_2 was ionized near threshold.

In the last section it was shown that true partial cross-sections are obtained by analysing the electron energies at an angle of 54° 44′ with respect to the direction of the incident radiation and the major direction of polarization. Future measurements will be made at this angle. However, the present results were taken at right angles to the photon beam, but with an apparatus capable of gathering electrons over a large solid angle (Samson & Cairns 1968).

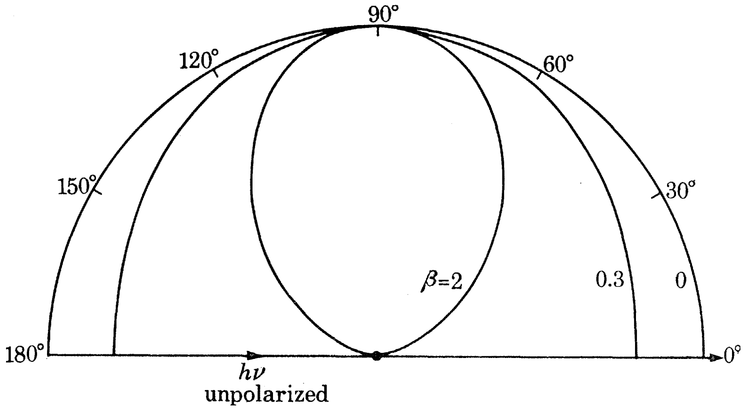

Figure 3. Cross-section of the angular distribution of photoelectrons in polar coordinates in the direction of the ionizing radiation. The asymmetry parameter, $\beta = 0$, 0.3, and 2.

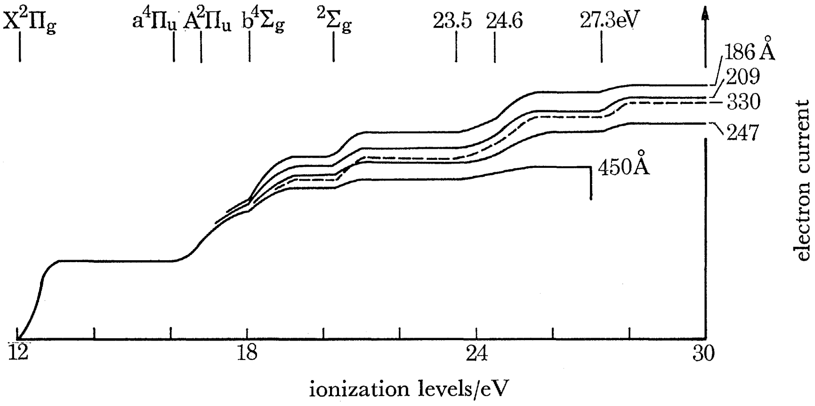

Figure 4. Retarding potential curve for O_2 ionized by 186, 209, 247, 330 and 460 Å. The step heights of each curve were normalized to the $X^2\Pi_g$ state.

Oxygen

The probability of producing O_2^+ in its higher states of ionization was measured at 460, 330, 247, 209 and 186 Å relative to the production of O_2^+ in its ground $X^2\Pi_g$ state. The results are shown in figure 4. The resolution in these curves is not sufficient to observe vibrational structure. The steps are all caused by electronic transitions as indicated by the vertical arrows. There is a general trend for the partial cross-sections of the higher ionized states to increase relative to the ground state as the ionizing energy is increased. The 330 Å line is an exception for energy states lying above 20 eV. This may be caused by a high lying autoionizing state at 330 Å.

New ionization levels have been found at 23.5, 24.6, and 27.3 eV with an estimated accuracy of about ±0.3 eV. The level at 24.6 eV is close to the Rydberg limit observed by Codling &

Madden (1965). They observed limits at 24.564 and 24.754 eV and suggested these were the $v = 0$ and $v = 1$ states, respectively, of the $c^4\Sigma$ state. Leblanc (1963), in his rotational analysis of O_2, predicted this state to lie at 24.56 eV. In this energy range it is entirely possible that some of these new levels are caused by double electron excitations where one electron is ejected and the other remains in an excited bound state. Although simultaneous excitation and ionization transitions have not yet been identified in molecules the process has recently been observed in helium (Samson 1969*b*). However, since the binding energy of a 2s electron in atomic oxygen is 28.475 eV and in the molecular form this binding energy should not be changed by much, it is possible that the states observed at 23.5 and 24.6 eV refer to the ejection of a $\sigma_u 2s$ electron while the state at 27.3 eV refers to the ejection of a $\sigma_g 2s$ electron.

No major transitions were observed between 27.3 eV and the limit of our photon energy range, namely 66.6 eV. However, weak transitions undoubtedly occur, e.g. double excitations. With the present signal to noise ratio no positive identification of higher energy states could be made.

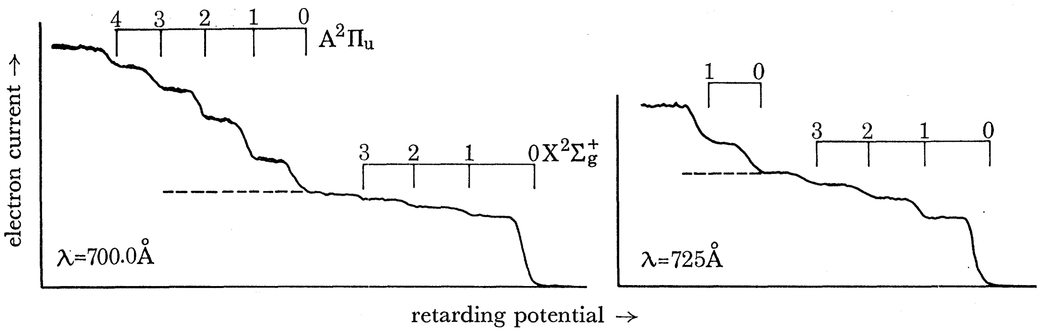

FIGURE 5. Retarding potential curves for N_2 ionized by 700 and 725 Å illustrating the different population of vibrational steps in the $X^2\Sigma$ state for the two wavelengths caused by autoionization effects.

Nitrogen

The population of vibrational levels in molecular ions is generally expected to be governed by the Franck–Condon principle. That is, a transition from the ground state of the neutral molecule to the ion populates vibrational levels in accordance with the overlap integrals of the wavefunctions of the two states involved. However, if the primary absorption process involves a highly excited state which subsequently autoionizes into the particular ionic state of interest the vibrational distribution is quite different. In this case the population is controlled by the overlap integrals of the highly excited state and the state of the ion. An example of this is illustrated in figure 5 where the vibrational structure of N_2^+ is shown in its first two electronic states. The population of vibrational levels in the ground electronic state does not agree with the Franck–Condon factors when ionized by 725 Å. At 700 Å there is close agreement. When the absorption spectrum of N_2 is studied, it is observed that an autoionizing Rydberg state exists at 725 Å and interference with the expected Franck–Condon factors can be anticipated. This effect occurs at many wavelengths and for most gases, especially near the first ionization thresholds. Data taken at 584 Å and shorter wavelengths are generally free from autoionizing effects (figure 6) and the heights of the vibrational steps give reasonable Franck–Condon factors.

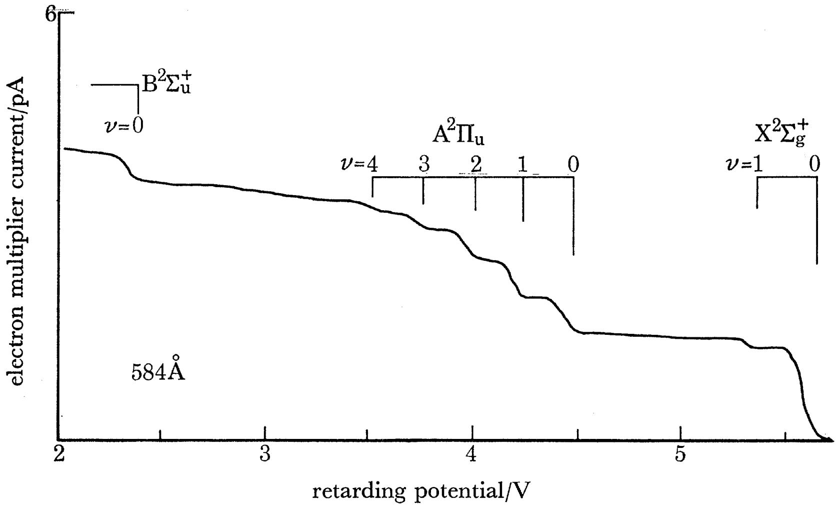

FIGURE 6. Retarding potential curve for N_2 ionized by 584 Å illustrating the true Franck–Condon distributions of vibrational levels.

The author is grateful to M. Johnson of the Bendix Corporation for the two Channeltrons so necessary for the angular distribution measurements.

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