

The effects of autoionisation on vibrational branching ratios and photoelectron angular distributions in molecular photoionisation: the formation of the ground state of O_2^+ between 574 and 600 Å

K Codling[†], A C Parr[‡], D L Ederer[‡], R Stockbauer[§], J B West^{||},
B E Cole[‡] and J L Dehmer[¶]

[†] J J Thomson Physical Laboratory, University of Reading, Reading RG6 2AF, England
[‡] Synchrotron Ultraviolet Radiation Facility, National Bureau of Standards, Washington
DC 20234, USA

[§] Surface Science Division, National Bureau of Standards, Washington, DC 20234, USA

^{||} Science Research Council, Daresbury Laboratory, Warrington WA4 4AD, England

[¶] Argonne National Laboratory, Argonne, Illinois 60439, USA

Received 14 July 1980, in final form 13 October 1980

Abstract. The partial cross sections (branching ratios) for leaving the O_2^+ ion in the ground $X^2\Pi_g$ state have been determined in the region of the $v=0$ and $v=1$ components of the neutral excited Rydberg state $(2\sigma_u)^{-1}3s\sigma$ at 594.3 and 589.0 Å by photoelectron spectroscopy. These cross sections have been further subdivided into partial cross sections for leaving the ion in a particular vibrational state. Moreover the asymmetry parameter, β , has been determined for each vibrational component in this limited spectral range. Considerable variations in both cross section and β are observed.

1. Introduction

Various circumstances govern the relative strength and photoelectron angular distributions of alternative vibrational channels in molecular photoionisation. At incident wavelengths removed from ionic thresholds and resonances (shape or autoionisation), the simplest and most widespread circumstances obtains: to a good approximation electronic and nuclear motions are independent. Thus for a particular electronic state of the residual ion, the vibrational levels will exhibit relative intensities given by their Franck–Condon Factors (FCF) and will all have the same photoelectron angular distribution.

If, however, the incident photon is of such an energy that a quasi-stable state, or resonance, can be excited the situation is inherently more complex, the Born–Oppenheimer approximation may become invalid and FC factors may differ significantly from those obtained off resonance. An early example of this non-FC behaviour was reflected in the enormous difference in the vibrational intensities of the $X^2\Pi_g O_2^+$ ground state when excited by the Ne I line at 736 Å and the He I line at 584 Å (Price 1968). A major departure from this picture was recently predicted (Dehmer *et al* 1979) to occur in the vicinity of a shape resonance. The resonant trapping of the photoelectron in a quasi-discrete state by the centrifugal barrier was shown to enhance its interaction with

the molecular core. More precisely, the energy and width of the shape resonances were found to be sensitive functions of internuclear separation, resulting in a breakdown of the Franck–Condon principle. In $3\sigma_g$ photoionisation of N_2 , this was shown (Dehmer *et al* 1979) to cause both enhanced vibrational excitation of the residual $N_2^+ X^2\Sigma_g^+$ ion and a strong v dependence of the corresponding photoelectron asymmetry parameter, β . Subsequent experimental work has verified the non-FC vibrational intensities in the vicinity of shape resonances in CO (Stockbauer *et al* 1979), N_2 (West *et al* 1980) and O_2 (Nenner *et al* 1980), and the related strong v dependence of β in the case of CO (Cole *et al* 1980). Although fragmentary information existed for each of these cases, establishment of the spectral pattern of these shape resonance effects was only possible with photoelectron studies which were vibrationally and angularly resolved and which utilised a broad band, tunable light source such as synchrotron radiation (Parr *et al* 1980).

In this paper we present the first comprehensive measurements of non-FC vibrational intensities and v dependent angular distributions arising from another widely occurring circumstance—molecular photoionisation taking place within the Fano–Beutler profiles (Fano 1961) of autoionising states. Again, strong non-FC effects are predicted (see, e.g. Raoult *et al* 1981, Raoult and Jungen 1981) to arise as a consequence of resonant trapping of the excited electron in a quasi-discrete state, in this case an autoionising state. This trapping mechanism provides the opportunity for close collisions (required by the eventual decay) between the excited electron and the molecular-ion core, resulting in exchanges of energy and angular momentum. There we are concerned with the vibrational effects of this interaction. Specifically, prototype calculations on H_2 by Raoult *et al* and Raoult and Jungen have shown that autoionisation leads to non-FC vibrational intensities and v dependent β , both of which exhibit pronounced variations throughout the vicinity of the autoionisation profile. It is also clear that these variations can differ drastically from one vibrational channel to another. Hence the detailed characterisation of the photoionisation process requires mapping the *profiles* of branching ratios and β for the final ionisation channels through the spectral range affected by the quasi-discrete state, and not merely recording on-resonance and off-resonance results. Some work along these lines has been done by Bahr *et al* (1971) but without angular resolution, and by Eland (1980). We have begun a programme of measuring the vibrational effects of autoionisation using angle-resolved photoelectron spectroscopy in order to establish the experimental evidence and encourage further theoretical work. Here we show vibrational branching ratios and β associated with formation of $O_2^+ X^2\Pi_g$ via the broad autoionising $(2\sigma_u)^{-1} 3s\sigma$ state of O_2 , whose $v'' = 0$ and 1 components are centred at 594.3 and 580.0 Å (see e.g. Codling and Madden 1965, Watson *et al* 1973, Lee *et al* 1973, Dehmer and Chupka 1975). We have made measurements at several wavelengths within these two resonances in order to emphasise the differences in profiles both among the vibrational channels and relative to the net autoionisation profile.

2. Experimental

The light source used in the present investigations was the Synchrotron Ultraviolet Radiation Facility (SURF-II) at the National Bureau of Standards, Washington, DC. The monochromator employed was a high-throughput, normal-incidence, vertically dispersing instrument (Ederer *et al* 1980), incorporating an osmium-coated 1200 lines

per mm grating blazed for 1100 Å. With the electron beam of the storage ring (0.1 mm in height) acting as the monochromator entrance slit, a resolution of 0.8 Å (27 meV at 20 eV) was achieved.

Photons from the exit slit of the monochromator intersected an effusive beam of O₂ molecules and the photoemitted electrons were energy analysed using a 2" mean radius hemispherical analyser set to give a resolution of about 100 meV (Parr *et al* 1980). The analyser rotated around the *E* vector of the monochromatic synchrotron radiation, that is in a plane at right angles to the incident beam. The analyser pass energy was fixed at 5 V and the electrons preretarded. With the monochromator set at a fixed wavelength, the electrons were energy analysed over a range which encompassed all of the possible vibrational components of the ground electronic state. A multiple-scan technique was used to avoid errors due to gas pressure or channeltron gain fluctuations. The electron energy spectrum was determined at three angles: 0, 45 and 90°. Sample spectra at 0 and 90° are shown in figure 1 for an incident wavelength of 593 Å. As may be seen from the figure, counts of typically 5 × 10³ were accumulated in the strongest (*v* = 1) peak.

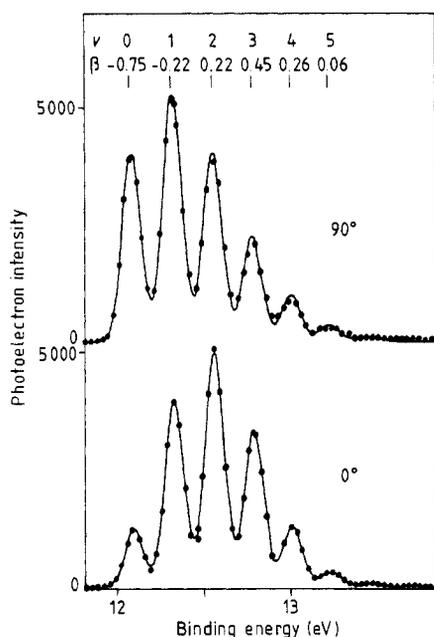


Figure 1. The photoelectron spectrum of the O₂⁺ X ²Π_g state at an incident photon energy of 593 Å, for two angles $\theta = 0$ and 90° (see equation (2.1)). The full curve is a computer fit to the data, taking the vibrational parameters of the X state as known.

To convert the raw data counts into meaningful numbers, two further pieces of information were required. Firstly one needed to know the state of polarisation (*p*) of the monochromatic radiation; *p* was determined to be 0.75 using a three-mirror polarisation analyser described in a previous publication (Parr *et al* 1980). Once the state of polarisation was known, the formula for the differential cross section of a particular photoionisation channel:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \{1 + \frac{1}{4}\beta[3p \cos(2\theta) + 1]\} \quad (2.1)$$

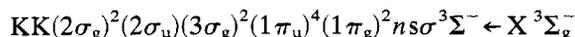
could be used to determine a second unknown, the geometrical correction factor. (In the above formula β is the so-called asymmetry parameter which characterises a particular electron angular distribution, σ is the partial cross section for the channel and θ is the direction of ejection of the electron with respect to the E vector.) The inert gases, in particular Ar and Xe, whose values of β and σ are well known in this photon (photoelectron) energy range, were used. Any departures of β from the expected values were assumed to be due to the non-cylindrical nature of the interaction region. The correction thus achieved was probably good to 2 or 3%.

It was then possible to determine a value of β for each of the six vibrational components of the $X^2\Pi_g$ electronic state using the known state of polarisation and applying formula (2.1) for the three values of θ . The β values at 593 Å, shown above the spectra of figure 1, are seen to vary quite substantially with vibrational quantum number. It should perhaps be mentioned that the spectra were taken over a range of molecular beam pressures to check on pressure-dependent effects, but none was found. At this point, knowing the β values for the various vibrational components, the three sets of data at 0, 45 and 90° could in principle be re-used to determine the integrated electron counts in each vibrational band *independent* of both the state of polarisation of the radiation or the β value, as if the measurement had been made at a 'pseudo-magic' angle. Then one could determine the vibrational branching ratio for each vibrational peak. To do this, however, one needed to know the efficiency of the preretarding lens system as a function of retarding voltage. This was determined using Ar and Xe and comparing count rates based on accurately known cross sections (Marr and West 1976, West and Morton 1978) as a function of photon (and therefore photoelectron) energy with those actually observed.

This procedure of first determining β and then the integrated counts in each of the vibrational components was followed for a number of wavelengths throughout the resonance region. It was possible to determine these parameters for the various peaks independent of any assumption of constancy of the molecular-beam density. However, it is also interesting to determine the variation of the total counts integrated over the whole vibrational sequence (proportional to the partial cross section for leaving the ion in the $X^2\Pi_g$ state) through the resonance. To obtain the information one had to assume that a constant ambient pressure in the experimental chamber, as monitored by the ionisation gauge, implied a constant molecular beam density. Relative partial cross sections could then be obtained and placed on an absolute basis by reference to earlier work using emission line sources. β values for the vibrationally summed, or unresolved, channel were also obtained.

3. Results and discussion

The potential energy curves of O_2 and O_2^+ relevant to the present experiment are shown in figure 2 (Gilmore 1965, Samson *et al* 1977). When photons of 20.86 or 21.05 eV energy are incident on ground-state O_2 molecules, the first ($n=3$) member of the Rydberg series approaching the $c^4\Sigma_g^-$ state of O_2^+ and associated with the transition



is excited. The two vibrational components ($v''=0$ and $v''=1$) of the excited state are drawn on the figure and denoted by O_2^* . Autoionisation from this excited state will lead

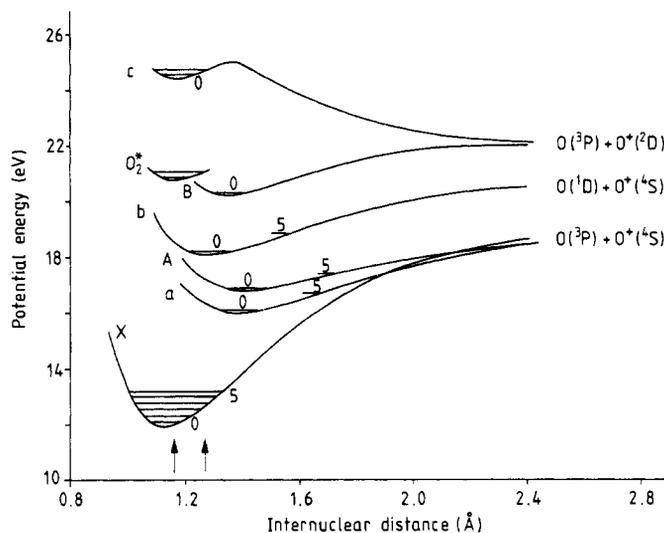


Figure 2. The relevant potential energy curves for the O_2^+ molecule: $X^2\Pi_g^-$; $a^4\Pi_u$; $A^2\Pi_u$; $b^4\Sigma_g^-$; $B^2\Sigma_g^-$; $c^4\Sigma_g^-$. The Rydberg state is denoted by O_2^* . The arrows indicate the classical limits of the ground $X^3\Sigma_g^-(v=0)$ state of O_2 .

to one of a number of final ion states (X, a, A, b, B) with branching ratios which are likely to differ quite significantly from the off-resonance value. The net effect of the interaction, however, is to produce two windows in the photoabsorption cross section. There is also expected to be a significant change in the angular distribution of the photoemitted electrons on passing through the window region since the presence of the autoionising states must affect the interference between different angular momentum components of the ejected electron's wavefunction and hence the β values.

3.1. Partial cross sections

Figure 3 shows the variation in the partial photoionisation cross section for leaving the O_2^+ ion in the ground state. The curve has been put on an absolute basis by using the data point of $7.0 (\pm 0.2)$ Mb at 594 \AA determined by Samson *et al* (1977). Two other cross sections which fall in the region of the window resonances have been determined by these workers. At 597.7 \AA there is excellent agreement with the present data but at 573.4 \AA their value of $9.7 (\pm 0.4)$ Mb seems somewhat high in the context of figure 3, for reasons not apparent to us at this time.

A comparison of this partial cross section with the total photoabsorption cross section (which according to Samson *et al* (1977) is the same as the photoionisation cross section below 600 \AA) shows an interesting difference. Whereas the total cross section shows a double minimum ($q \sim 0$), the $X^2\Pi_g^-$ state partial cross section shows a double peak ($q \gg 1$). Since the total cross section shows a 6 or 7 Mb fall and the X state cross section a 3 Mb rise, clearly one or more of the remaining partial cross sections (a, A, b, B) must show quite a dramatic drop in the resonance region. Combining the results of Samson *et al* (1977) and Edqvist *et al* (1970), one obtains the following partial cross sections at 584 \AA : X, 7.0 Mb; a, 7.1 Mb; A, 1.1 Mb; b, 5.2 Mb; B, 3.0 Mb; giving a total cross section of 23.4 Mb (see figure 4 (top)).

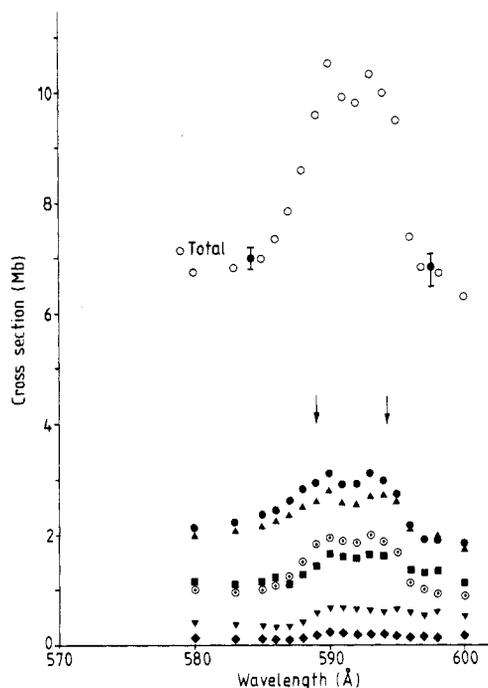
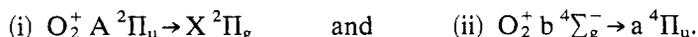


Figure 3. The partial cross sections for the $X^2\Pi_g$ state of O_2^+ (open circles) normalised to the data point of Samson *et al* (1977) at 584.3 Å. In the lower half of the figure are given the partial cross sections for the individual vibrational components: \circ , $v=0$; \bullet , $v=1$; \blacktriangle , $v=2$; \blacksquare , $v=3$; \blacktriangledown , $v=4$; \bullet , $v=5$.

One is not limited entirely to the PES techniques, however, to study the behaviour of the various partial cross sections. Fluorescence spectroscopy will allow the A and b partial cross section to be probed via the transitions



Wu *et al* (1979) have measured the cross section for production of such fluorescence in the wavelength range 750–180 Å using the Wisconsin storage ring. More recent work by Tabché-Fouhaile *et al* (1980) using the ACO (Orsay) storage ring confirms their results. It appears that the A state partial cross section rises about 10% whereas the b state shows a much larger effect, with a drop in cross section from 5.2 to about 2.8 Mb in the higher energy ($v''=1$) resonance. It would seem that the partial cross sections to the a and/or B states must fall substantially in the resonance region if the sums are to work out.

We have not discussed the possibilities of dissociation or dissociative ionisation from this excited neutral state or of ion pair formation, although such processes undoubtedly occur. Lee *et al* (1974) studied the atomic-oxygen fluorescence using synchrotron radiation and there was a small but definite enhancement of fluorescence in this region. More recently Oertel *et al* (1980) have found large changes in O^- production. However, one assumes these effects contribute rather minimally to the total cross section.

Having considered how the total cross section for leaving the O_2^+ ion in the ground state varies, one can now examine the partial cross sections for leaving the ion in a particular vibrational state. This information is presented in the lower half of figure 3. It can be seen that each component is enhanced to some extent (typically 50%) in the resonance region but that the $v=0$ component is particularly enhanced relative to the others. The earlier results of Gardner and Samson (1978) using lines at 573.4, 584.3 and 597.7 Å are in quite good agreement although they do not quote an intensity for the

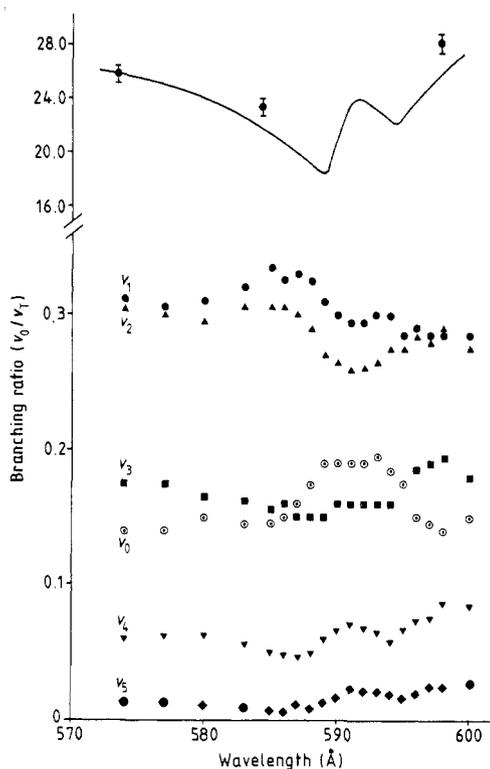


Figure 4. The total photoabsorption cross section of Watson *et al* (1972) (full curve), along with the individual points of Samson *et al* (1977). The lower data points are as follows: \circ , $(v=0)/v_T$; \bullet , $(v=1)/v_T$; \blacktriangle , $(v=2)/v_T$; \blacksquare , $(v=3)/v_T$; \blacktriangledown , $(v=4)/v_T$; \blacklozenge , $(v=5)/v_T$. v_T is the total partial cross section for the $X^2\Pi_g$ state of O_2^+ .

$v=5$ component at two of the three wavelengths. Figure 4 shows the same data in a more informative way. Here is plotted the fraction of the total cross section that goes into each vibrational component. In the absence of resonance effects these would be constant. We note again the particular enhancement of the $v=0$ component at the expense of the $v=2$ and $v=3$ components. In table 1 are listed for comparison the relative intensities at 584 \AA on the fringe of the $v''=1$ window, along with those of Gardner and Samson and recent theoretical FC factors. The agreement between the

Table 1. Vibrational intensity distributions and Franck-Condon factors, at 584 \AA .

	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$	$v=5$
a	0.145	0.330	0.305	0.155	0.053	0.010
b	0.154	0.332	0.313	0.150	0.046	0.005
c	0.176	0.357	0.298	0.131	0.033	0.005

a, Present data (average value of 583 and 585 \AA).

b, Gardner and Samson (1978).

c, Theory due to D L Albritton (1980, private communication).

two sets of experimental data is excellent, and the deviations from the FCF are believed to reflect mainly the effect of autoionisation at this single wavelength.

In figure 2, the arrows at the bottom of the figure show the classical limits of the neutral O_2 ground-state ($v = 0$) vibration. It is evident from this that the FC factors will peak in the $v = 1$ region of the X state of O_2^+ . However, when the two vibrational states of the O_2^* curve are excited at around 21 eV (the position and shape of this excited state has been drawn to mirror exactly the $c^4\Sigma_g^-$ state), the situation becomes more complex and one expects a redistribution of vibrational intensities as a function of position in the resonance region. In particular each vibrational level is observed to exhibit a different spectral pattern in figure 4. The $v = 0$ level is significantly enhanced, whereas the $v = 4, 5$ levels exhibit minima at the minima in the total cross section. The $v = 3$ curve is relatively flat and the $v = 1$ and 2 curves show what appear to be points of inflection at the resonance positions. These branching ratios reflect the decomposition of the total wavefunction of the quasi-bound complex, at each energy, onto the final vibrational channels. This is precisely the type of analysis carried out for H_2 photoionisation by Raoult and Jungen (1981) and Raoult *et al* (1981) using multichannel quantum defect theory. We hope to stimulate analogous work on the heavier diatomics with this and other ongoing measurements.

3.2. Angular distributions

A dramatic qualitative statement on the effects of autoionisation on photoelectron angular distributions for different vibrational channels is contained in figure 2. There we see that different vibrational levels have significantly different β values for a given wavelength in the resonance region. The spectral variation of this effect of autoionisation is shown in figure 5, where considerably different β values and spectral profiles are

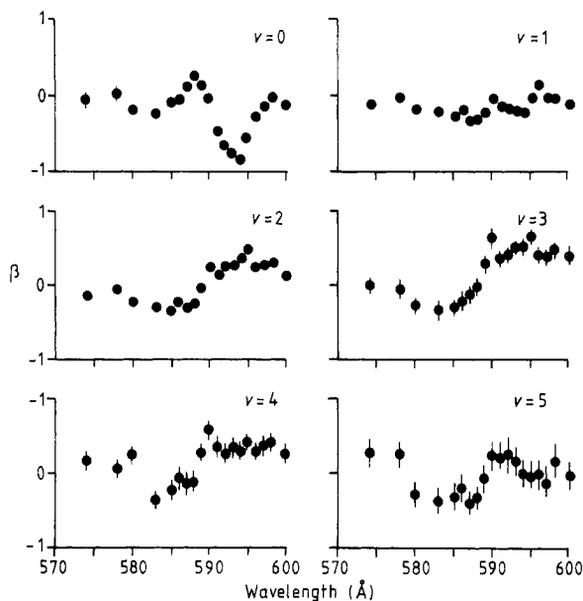


Figure 5. The variation of the asymmetry parameter β for the various vibrational components of the $X^2\Pi_g$ state of O_2^+ in the region of the window resonances.

seen within the manifold of vibrational levels of the $O^+ X^2\Pi_g$ state. Previous work with emission line sources by Carlson (1971) and Kibel *et al* (1979) indicate that β tends to zero with the onset of autoionisation. Our data, in contrast, show that the $v=0$ component behaves very differently from the others; the only component that seems little affected is the $v=1$ component and this shows the least percentage change in relative intensity (figure 4) on passing through the resonance. As in the case of the vibrational branching ratios, the v dependent β values reflect in detail the coupling of the quasi-discrete total wavefunction in the vicinity of the autoionising state into the final vibrational ionisation channels.

The only previous results with which to compare the present data are those at 584 Å. Table 2 shows this comparison. The 'unresolved' β value of $-0.27 (\pm 0.05)$ in the present experiment is obtained by weighting the various β values with the appropriate partial cross sections. There is moderate agreement with previous experimental values.

Table 2. β values at 584 Å.

Unresolved	$v=0$	$v=1$	$v=2$	$v=3, 4, 5$	Workers
$-0.26 (\pm 0.05)^a$	$-0.18 (\pm 0.05)$	$-0.28 (\pm 0.05)$	$-0.30 (\pm 0.1)$	$-0.30 (\pm 0.1)$	Present
$-0.30 (\pm 0.02)$	$-0.23 (\pm 0.03)$	$-0.28 (\pm 0.02)$	$-0.33 (\pm 0.03)$		Kreile and Schweig (1980) ^c
-0.6					Berkowitz <i>et al</i> (1967)
-0.3					McGowan <i>et al</i> (1969)
		$0.04 (\pm 0.05)$			Morgenstern <i>et al</i> (1971)
$-0.3 (\pm 0.1)$					Carlson <i>et al</i> (1972)
$+0.2$					Nakamura and Iida (1974)
			$-0.27 (\pm 0.05)^b$		Hancock and Samson (1976)
$-0.24 (\pm 0.04)$					McCoy <i>et al</i> (1978)
		$-0.27 (\pm 0.09)$			Katsumata <i>et al</i> (1979)

^a Various β values weighted by the partial cross section.

^b Presumably, an average of the values for $v=1$ and $v=2$.

^c Added in proof.

Acknowledgments

We thank R P Madden for his support and encouragement and the staff of NBS-SURF II for their valuable assistance. During most of this work, J B West was an NBS/University of Maryland SURF Fellow, and A C Parr was an NBS/Intergovernmental Personnel Act Appointee. This research programme was supported in part by the US Department of Energy and the US Office of Naval Research. We also acknowledge support from Nato, grant No 1939.

References

- Bahr J L, Blake A J, Carver J H, Gardner J L and Kumar V 1971 *J. Quant. Spectrosc. Radiat. Transfer* **11** 1853–61
- Berkowitz J, Ehrhardt H and Tekaas T 1967 *Z. Phys.* **200** 69
- Carlson T A 1971 *Chem. Phys. Lett.* **9** 23–6
- Carlson T A, McGuire G E, Jones A E, Cheng K L, Anderson C P, Lu C C and Pullen B P 1972 *Electron Spectroscopy* ed D A Shirely (Amsterdam: North Holland)
- Codling K and Madden R P 1965 *J. Chem. Phys.* **42** 3935
- Cole B E, Ederer D L, Stockbauer R, Codling K, Parr A C, West J B, Poliakoff E D and Dehmer J L 1980 *J. Chem. Phys.* **72** 11
- Dehmer P M and Chupka W A 1975 *J. Chem. Phys.* **62** 4524–34
- Dehmer J L, Dill D and Wallace S 1979 *Phys. Rev. Lett.* **43** 1005
- Ederer D L, Cole B E and West J B 1980 *Nucl. Instrum. Meth.* **172** 185
- Edqvist O, Lindholm E, Selin L E and Asbrink L 1970 *Phys. Scr.* **1** 25
- Eland J H D 1980 *J. Chem. Phys.* **72** 6015
- Fano U 1961 *Phys. Rev.* **124** 1866
- Gardner J L and Samson J A R 1978 *J. Electron Spectrosc. Relat. Phenom.* **13** 7
- Gilmore F R 1965 *J. Quant. Spectrosc. Radiat. Transfer* **5** 369
- Hancock W H and Samson J A R 1976 *J. Electron Spectrosc. Relat. Phenom.* **9** 211
- Katsumata S, Achiba Y and Kimura K 1979 *J. Electron Spectrosc. Relat. Phenom.* **17** 229
- Kibel M H, Leng F J and Nyberg G L 1979 *J. Electron Spectrosc. Relat. Phenom.* **15** 281
- Kreile J and Schweig A 1980 *J. Electron Spectrosc. Relat. Phenom.* **20** 191
- Lee L C, Carlson R W, Judge D L and Ogawa M 1973 *J. Quant. Spectrosc. Radiat. Transfer* **13** 1023
— 1974 *J. Chem. Phys.* **61** 3261
- McCoy D G, Morton J M and Marr G V 1978 *J. Phys. B: At. Mol. Phys.* **11** L547
- McGowan J W, Vroom D A and Comeaux 1969 *J. Chem. Phys.* **51** 5626
- Marr G V and West J B 1976 *At. Data Nucl. Data Tables* **18** 497–508
- Morgenstern R, Niehaus A and Ruf M W 1971 *Electronic and Atomic Collisions* ed L Branscomb et al (Amsterdam: North-Holland) p 167
- Nakamura M and Iida Y 1974 *Vacuum Ultraviolet Radiation Physics* ed E E Koch (Vieweg: Pergamon) p 170
- Nenner I, Morin P, Ferreira L F, Guyon P M, Ho K, Kollman K and Dutuit O 1980 to be published
- Oertel H, Schenk H and Baumgartel H 1979 *DESY Preprint* SR-79/28
- Parr A C, Stockbauer R, Cole B E, Ederer D L, Dehmer J L and West J B 1980 *Nucl. Instrum. Meth.* **172** 357
- Price W C 1968 *Molecular Spectroscopy* ed P Hepple (London: Institute of Petroleum) p 221
- Raoult M and Jungen Ch 1981 *J. Chem. Phys.* in press
- Raoult M, Jungen Ch and Dill D 1981 *J. Chem. Phys.* in press
- Samson J A R, Gardner J L and Haddad G N 1977 *J. Electron Spectrosc. Relat. Phenom.* **12** 281
- Stockbauer R L, Cole B E, Ederer D L, West J B, Parr A C and Dehmer J L 1980 *Phys. Rev. Lett.* **43** 757
- Tabché-Fouhaille A, Guyon P M, Nenner I and Delwiche J 1980 to be published
- Watson W S, Lang J and Stewart D T 1973 *Phys. Lett.* **44A** 293
- West J B and Morton J 1978 *At. Data Nucl. Data Tables* **22** 103–7
- West J B, Parr A C, Cole B E, Ederer D L, Stockbauer R and Dehmer J L 1980 *J. Phys. B: At. Mol. Phys.* **13** L105–8
- Wu C Y R, Phillips E, Lee L C and Judge D L 1979 *J. Chem. Phys.* **71** 769