

Vibrational-state dependence of partial cross sections and photoelectron angular distributions through autoionizing resonances: the $n=3$ Rydberg state converging to the $B^2\Sigma^+$ state of CO^+

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The branching ratios for leaving the CO^+ ion in a particular vibrational level of the ground $X^2\Sigma^+$ state have been determined as functions of photon energy through the $n=3$ autoionizing Rydberg state converging to the $B^2\Sigma^+$ state of CO^+ ; there are substantial differences between theoretical and experimental Franck-Condon factors when 'on' resonance. The branching ratios have been converted into absolute partial cross sections by normalizing to existing data obtained by using line sources. The asymmetry parameter β has also been determined for each vibrational level in this spectral range. Considerable variations in both have been observed in the region of this resonance.

1. INTRODUCTION

When a diatomic molecule such as CO is photoionized, the resulting molecular ion may be left in one of several vibrational states. At incident photon energies removed from ionic thresholds and resonances the Born-Oppenheimer approximation is assumed to be valid (the electronic and nuclear motions are assumed independent) and the intensity distribution within the various vibrational channels is given by the appropriate Franck-Condon (F.C.) factors. In addition, the photoemitted electrons associated with each vibrational state of a particular ion will have the

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same angular distribution. If, however, the incident photon is of such an energy as to excite a quasi-stable state (or resonance), the situation is inherently more complex and the F.C. factors may differ substantially from those obtained off resonance. There is also likely to be a strong vibrational-dependence (v -dependence) of the photo-electron angular distribution asymmetry parameter, β .

The variation in F.C. factors can be studied experimentally by using the technique of photoelectron spectroscopy (p.e.s.), and dramatic deviations have been noted in the region of autoionizing resonances (Doolittle & Schoen 1965; Price 1968; Collin & Natalis 1969; Carlson & Jonas 1971; Bahr *et al.* 1971, 1972; Gardner & Samson 1978; Baer *et al.* 1979; Eland 1980). Early attempts by Smith (1970) to explain this behaviour were based on the resonance profile parametrization of Fano (1961) and Mies (1968) and assumed that the dipole transition moment varies slowly with energy and internuclear distance (see also Bardsley 1968). In the recent, more detailed work by Raoult *et al.* (1981) on H_2 , this information is extracted from existing spectroscopic data and incorporated fully into theory, thus enabling prediction of how the intensities in alternative vibrational channels will vary with position within the autoionizing resonance. Recent work (Dehmer *et al.* 1979, Stockbauer *et al.* 1979) has shown an analogous breakdown of the F.C. separation in the vicinity of shape resonances, owing to the rapid variation of the dipole transition amplitude with internuclear separation. We hope the detailed measurements being reported here on CO, and related experimental studies of auto-ionization effects in O_2 (Codling *et al.* 1981) and N_2 (Parr *et al.* 1981; West *et al.* 1981), will stimulate corresponding theoretical work so that direct comparisons can be made.

Similar statements can be made about photoelectron angular distributions in the various vibrational channels. Theory (Dehmer *et al.* 1979) and experiment (Cole *et al.* 1980) have begun to address the issue of the effects of shape resonances on v -dependent β -parameters. Furthermore, the recent work by Raoult *et al.* shows in detail the variations of β for alternative rotational-vibrational levels of H_2 within autoionization resonances. However, no analogous theoretical results are available with which to compare our recent angle-resolved measurements in O_2 , N_2 and now CO. Again we hope to stimulate such theoretical work, as the behaviour of the β -parameter depends both on eigenphases and dipole amplitudes of the photoionization channels and thus gives related but complementary information about the detailed dynamics of the photoionization process.

For the measurements reported here we chose to study a relatively broad and slightly asymmetric absorption-type resonance (high q) in CO located at 72.550 nm, identified by Ogawa & Ogawa (1972) as the $n = 3$ member of the series converging to the $v = 0$ vibrational level of the $B^2\Sigma^+$ state of CO^+ . The high resolution ionization spectra of Dehmer & Chupka (1978) show this resonance as a very prominent feature and, although there are weaker structures in this spectral region, they do not appear to perturb this resonance unduly. The measurements are triply differential in that the photoelectron intensity is monitored as a function of incident wavelength, photoelectron energy and photoelectron ejection angle.

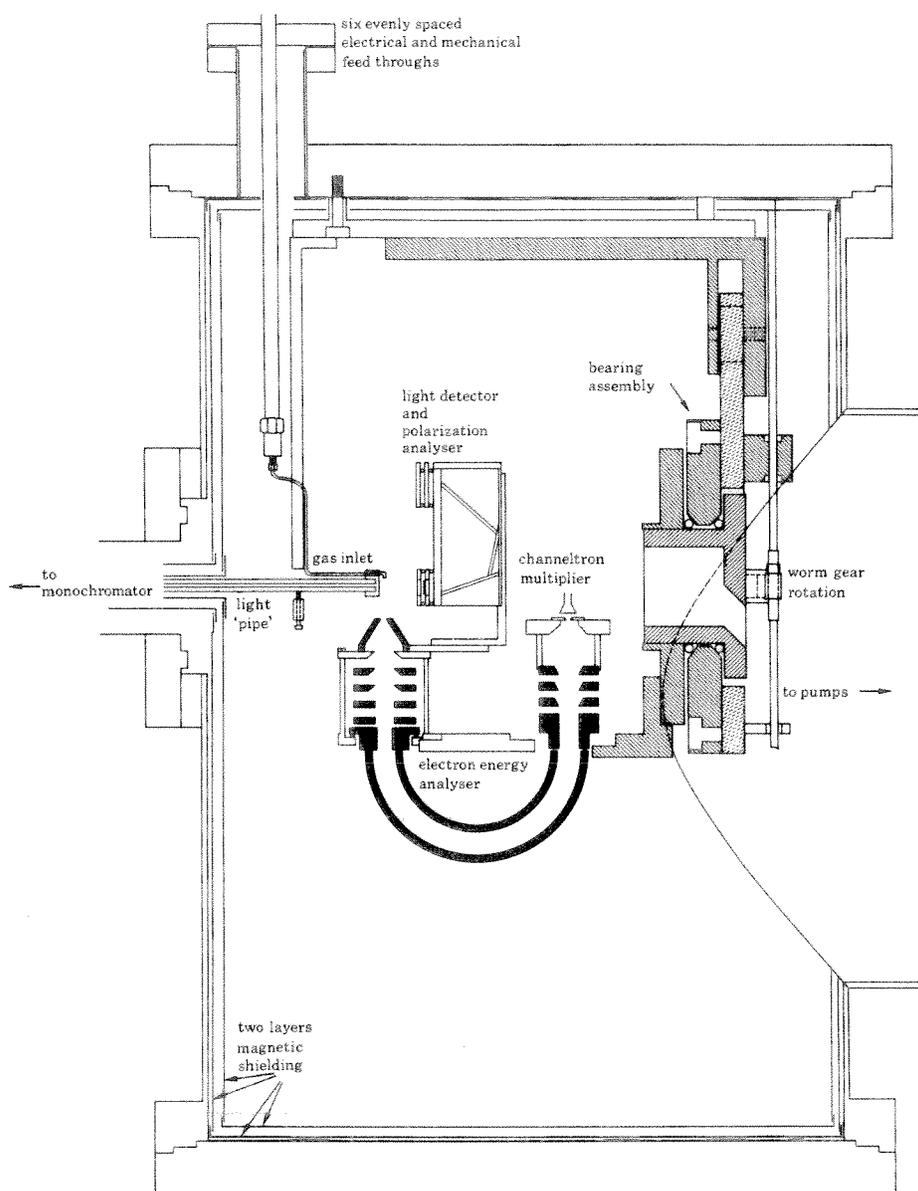


FIGURE 1. Cross section of the hemispherical electron energy analyser and associated mechanical components situated in the vacuum chamber.

2. EXPERIMENTAL

The experimental apparatus consists basically of a light source, a monochromator and a photoelectron spectrometer. The light source used was the Synchrotron Ultraviolet Radiation Facility (SURF-II) at the National Bureau of Standards,

Washington D.C. This is a 250 MeV electron storage ring, where the electrons are confined to a horizontal circular orbit 0.83 m in diameter, and thus emit a continuous spectrum of radiation. Because of the relativistic velocity of the electrons, the spectrum is shifted towards the extreme ultraviolet, and peaks at *ca.* 25 nm. It is also highly polarized (100% plane polarized in the orbit plane of the storage ring) and this is an essential feature for the experiment described here. Further details about SURF II are given by Madden (1980).

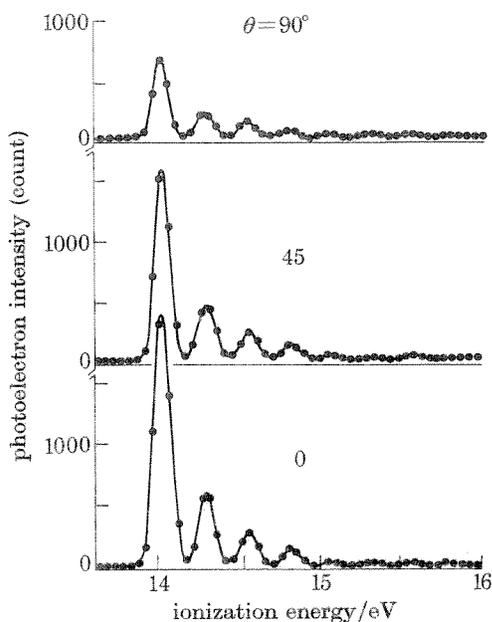


FIGURE 2. The photoelectron spectrum of the $X^2\Sigma^+$ state of CO^+ at an incident wavelength of 72.5 nm for three values of θ (see equation (2.1)). The full curves are computer fits to the data, the vibrational parameters of the X-state being taken as known.

The monochromator was a vertically dispersing Rowland-circle-type instrument, with an osmium-coated diffraction grating in normal incidence. The monochromator could scan over the range 40–200 nm, by using a grating of 1200 lines/mm blazed at 110 nm; since neither the source nor the experiment was easily movable, the instrument was designed to have constant deviation. Because the size of the electron orbit is very small (*ca.* 0.1 mm in height) it was possible to use this as the entrance slit of the monochromator, maximum use being made thereby of the source of flux; the resolution thus obtained was 0.08 nm. This feature of SURF II is unique, making it ideal for spectroscopy of this kind. The monochromator and its performance are fully described by Ederer *et al.* (1980).

A flux of about 10^{11} photons s^{-1} from the exit slit of the monochromator was channelled through a 200 mm long 'light pipe' capillary, where it intersected an effusive beam of CO molecules as shown in figure 1. The photoemitted electrons

were energy-analysed with a 2 in (≈ 5 cm) 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 monochromator synchrotron radiation, that is in a plane at right angles to the incident beam, and had an angular acceptance of $\pm 2^\circ$. The analyser pass energy was fixed at 5 V and the electrons either accelerated or retarded as required on their way through the entrance lens assembly. With the monochromator set at a fixed wavelength, the electrons were energy-analysed over a range encompassing 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° , 45° and 90° are shown in figure 2 for an incident wavelength of 72.5 nm. As may be seen from the figure, counts typically of 2×10^3 were accumulated in the strongest ($v = 0$) peak.

To convert the raw data counts into meaningful numbers, two further pieces of information were required. First one needed to know the state of polarization $p = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$ of the monochromatic radiation: p was determined to be about 0.75 by using the three-mirror polarization analyser indicated in figure 1. Once the state of polarization was known, the formula for the differential cross section for a particular photoionization channel,

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

could be used to determine a second unknown, the geometrical correction factor. (In the above formula β is the so-called asymmetry parameter that characterizes a particular electron angular distribution, σ_i is the partial cross section for the channel i , and θ is the direction of ejection of the electron with respect to the E -vector. This formula is an alternative representation of the well known Cooper & Zare (1969) form for plane-polarized light, modified to take account of the elliptically polarized nature of the radiation.) The inert gases, in particular Ar and Xe, whose values of β 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%.

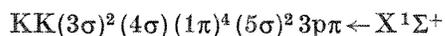
It was then possible to determine a value of β for each of the first five vibrational components of the $X^2\Sigma^+$ electronic state of CO^+ by using the known state of polarization and applying formula (2.1) for the three values of θ . At this point, the β -values being known for the various vibrational components, the three sets of data at 0° , 45° and 90° could be reused to determine the integrated electron counts in each vibrational band *independent* of both the state of polarization of the radiation and 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 pre-accelerating lens system as a function of accelerating voltage. This was determined by using

Ar and comparing count rates as a function of photon (and therefore photoelectron) energy based on accurately known cross sections (Marr & West 1976) with those actually observed.

The procedure of first determining β and then the integrated counts in each of the vibrational components was followed for several wavelengths throughout the resonance region. It was possible to determine the 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 $X^2\Sigma^+$ 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 ionization 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 with emission line sources.

3. RESULTS AND DISCUSSION

The potential energy curves of CO and CO^+ relevant to the experiment described here are shown in figure 3. When photons of 72.550 nm (17.09 eV) energy are incident on ground state CO molecules, the first ($n = 3$) member of the Rydberg series approaching the $B^2\Sigma^+$ state of CO^+ and associated with the transition



is excited. The $v = 0$ vibrational component of the neutral excited state denoted by CO^* is drawn on the figure. In the absence of experimental evidence to the contrary, we make the assumption that the autoionizing state has the same potential shape and internuclear separation as the $B^2\Sigma^+$ state. Autoionization from this excited state will lead to one of two final ion states ($X^2\Sigma^+$ or $A^2\Pi$) with almost equal probability. (The probability of ionization is about 83 % according to Samson & Gardner (1976).) The net effect of the interaction, however, is to produce a high- q resonance 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 resonance region since the presence of the autoionizing state 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

In figure 4 the vibrational branching ratio for the $\text{CO}^+ X^2\Sigma^+$ state is plotted as a function of wavelength in the vicinity of the $n = 3$ resonance. The wavelength where the cross section reaches a maximum is indicated by the arrow. This resonance has been observed by Plummer *et al.* (1977) using p.e.s. and synchrotron radiation but they did not study it in detail or give branching ratios between the $X^2\Sigma^+$ and $A^2\Pi^+$ states. Results obtained by Gardner & Samson (1978) using a discrete line

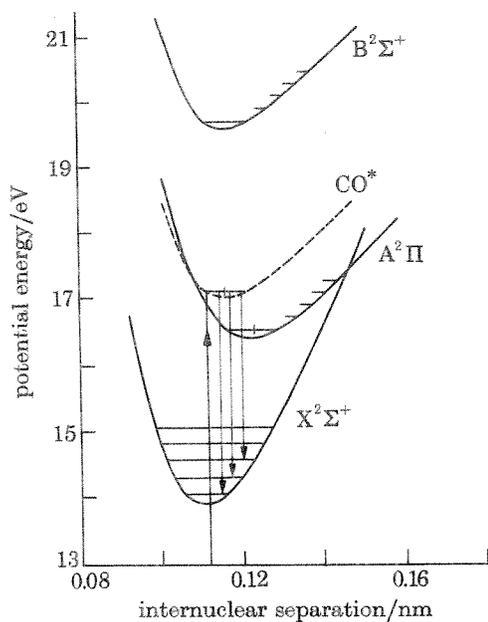


FIGURE 3. The relevant potential energy curves of the CO⁺ molecule: X²Σ⁺; A²Π; B²Σ⁺. The $n = 3$ Rydberg state converging to the B²Σ⁺ limit is denoted by CO*. The upward arrow indicates the initial excitation, the downward arrows the various possible channels as exemplified by figure 2.

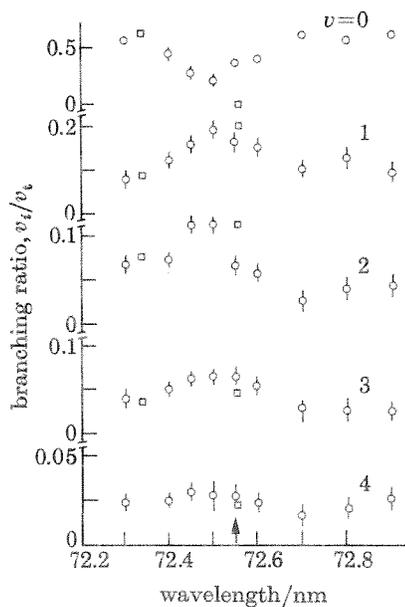


FIGURE 4. Vibrational branching ratios as a function of wavelength, for the X²Σ⁺ state in CO⁺, relative to the total (Σv) cross section in the region of the $n = 3$ member of the series of resonances converging to the B²Σ⁺ state of CO⁺. Data are from: \circ , this paper; \square , Gardner & Samson (1978). The vertical arrow denotes the resonance maximum.

source are shown for the two wavelengths that occurred in the region of overlap. The agreement with the present data at 72.336 nm is quite good and a second point at 73.093 nm (not shown) is consistent with the present data. Coincidentally, a discrete line occurs at the resonance absorption maximum (72.555 nm), and the branching ratios obtained for that line differ from the present data. This disagreement is due in part to the fact that, with a monochromator bandpass of 0.08 nm, the present experiment samples regions where the ratio is rapidly varying.

TABLE 1. COMPARISON OF RELATIVE INTENSITIES OF VIBRATIONAL LEVELS WITH COMPUTED F.C. FACTORS

relative intensity for decay to $\text{CO}^+(\text{X}^2\Sigma^+)$				F.C. factor $\text{CO}^+(\text{X}^2\Sigma^+)$ $\leftarrow\text{CO}(\text{X}^1\Sigma^+)$ 'off'	F.C. factor $\text{CO}^+(\text{B}^2\Sigma^+)$ $\leftarrow\text{X}^2\Sigma^+$ 'on'
$I(72.336 \text{ nm})$ 'off' resonance	$I(72.555 \text{ nm})$ 'on' resonance	$I(73.093 \text{ nm})$ 'off' resonance	$I(73.093 \text{ nm})$ 'on' resonance		
100.0†	100.0‡	100.0†	100.0‡	100.0§	100.0
10.3	10.1	24.0	40.8	8.5	63.8
8.5	9.6	9.6	22.8	1.9	19.5
5.1	4.4	7.3	9.0	—	4.0
3.1	—	3.8	4.0	—	0.6

relative intensity for decay to $\text{CO}^+(\text{A}^2\Pi^+)$			F.C. factor $\text{CO}^+(\text{A}^2\Pi^+)$ $\leftarrow\text{CO}(\text{X}^1\Sigma^+)$ 'off'	F.C. factor $\text{CO}^+(\text{B}^2\Sigma^+ \leftarrow \text{A}^2\Pi^+)$ 'on'
$I(72.336 \text{ nm})$ 'off' resonance	$I(72.555 \text{ nm})$ 'on' resonance	$I(73.093 \text{ nm})$ 'off' resonance		
61.3‡	100.0‡	26.9‡	37§	100.0
76.2	91.7	51.9	82	75.8
80.2	64.8	100.0	100	38.8
100.0	6.0	(not excited)	89	16.6

† Present data. ‡ Data of Gardner & Samson (1978). § Data of Albritton *et al.* (1980).
|| Data of Nicholls (1962).

The data in figure 4 suggest that the largest change in the ratio occurs at a wavelength slightly shifted from the absorption maximum. It is interesting to note that the relative intensity of the $v = 0$ component *decreases* in the neighbourhood of the resonance maximum, while the total cross section is increasing. Gardner & Samson's (1978) data suggest an even smaller relative intensity for the $v = 0$ component at this point. Also of interest in figure 4 is that the effect of the resonance becomes less pronounced as v increases. For the $v = 4$ component there is almost no change in relative cross section. The minimum in the potential curve of the $\text{X}^2\Sigma^+$ state of CO^+ occurs at about the same equilibrium internuclear separation as that of the $\text{X}^1\Sigma^+$ state of CO and so the theoretical F.C. overlap for the $v = 0$ to $v = 4$ levels is virtually zero (Wachs 1964, Albritton *et al.* 1980). Experimentally, however, the $v = 4$ level contains about 2% of the band intensity.

According to the ideas of Smith (1970) and Bahr *et al.* (1971, 1972), in the region

of an absorption-type (high- q) resonance, the (relative) vibrational intensities should be proportional to the F.C. factors between *intermediate* state and final ionic state. Off resonance, the intensities should be proportional to the F.C. factors between the ground states of the neutral and ionic states. Since the autoionizing resonance studied here has a high q -value, the comparison shown in table 1 may therefore be valid. The table shows 'on'-resonance and 'off'-resonance data from Gardner & Samson (1978) and the present work for decay into both the $X^2\Sigma^+$ and the $A^2\Pi^+$ states of CO^+ . The data clearly indicate that more vibrational channels are excited than would be suggested by the magnitude of the 'direct' F.C. factors. However, the F.C.-factors between the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of CO^+ represent the 'on'-resonance data much better. As mentioned earlier, we make the

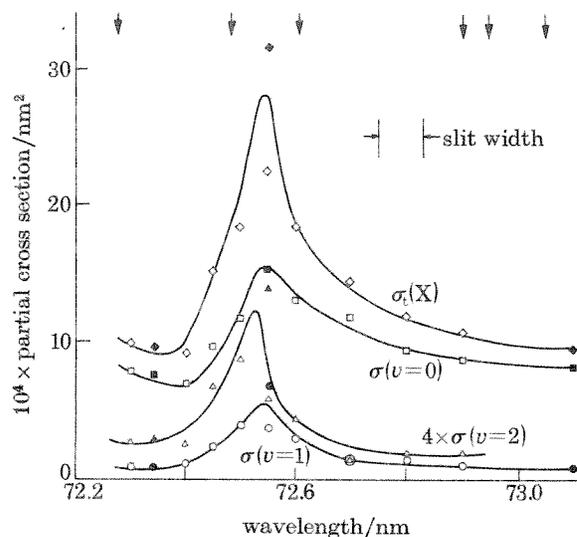


FIGURE 5. The partial cross sections, as a function of wavelength, for the $v = 0$, $v = 1$ and $v = 2$ levels, and the total cross section of the $X^2\Sigma^+$ state of CO^+ . \diamond , Total cross section; \square , $v = 0$; \circ , $v = 1$; \triangle , $v = 2$. Data from Samson & Gardner (1976) and Gardner & Samson (1978) are shown by the solid symbols. Vertical arrows indicate close-lying weak Rydberg states.

simplifying assumption that the intermediate autoionizing state has the same potential shape and internuclear separation as the ionic state with which it is associated – the $B^2\Sigma^+$ state.

The effect of the resonance can be seen more dramatically if one examines the decay into the $A^2\Pi^+$ state of CO^+ . 'Off' resonance the intensity peaks at $v = 2$ or 3, corresponding to the appropriate F.C. distribution between the states CO^+ ($A^2\Pi^+$) and $CO(X^1\Sigma^+)$, whereas 'on' resonance the distribution corresponds more closely to the F.C. distribution (Nicholls 1962) between the CO^+ states $B^2\Sigma^+$ and $A^2\Pi^+$. In the light of recent extensions of the basic ideas (Raoult *et al.* 1981) on the effect of autoionizing resonances on vibrational intensity distributions, we do not wish

to promote the simplistic approach but note that it may serve to make the physical processes more transparent.

Before considering the evaluation of partial cross sections, we note what appears to be an inconsistency between the Gardner & Samson (1978) data and that of Ogawa (1972). The latter spectroscopic data place the $v = 3$ vibrational level of the $A^2\Pi^+$ state of CO^+ at 72.45 nm and yet Gardner & Samson observe the $v = 3$ level in their photoelectron spectrum at 72.555 nm. If their $v = 3$ p.e.s. peak (2.5% of the total) is real, then either the emission line is not at 72.55 nm or the $v = 3$ state is not at 72.45 nm.

The branching ratios and partial cross sections in CO have been measured by using discrete line sources (Samson & Gardner 1976, Gardner & Samson 1978), continuum sources (Bahr *et al.* 1971, 1972, Plummer *et al.* 1977) and small-angle scattering with electrons in the kiloelectron volt energy range (Hamnett *et al.* 1976). In figure 5 are plotted the present partial cross section results for leaving the CO^+ molecular ion in the $v = 0, 1$ and 2 levels of the $X^2\Sigma^+$ state, along with the 'total' cross section σ_t . The cross sections were made absolute by normalizing to the partial cross section of Samson & Gardner (1976) at 72.336 nm. In the figure, this point and two other points that lie in the resonance region are denoted by the appropriate closed symbol. The agreement with the 73.093 nm emission line is good, but the disagreement at the resonance peak reflects in part the lack of spectral resolution in the experiment described here as well as an additional small underestimation of the total curve due to our omission of levels greater than $v = 5$. (The bandpass of 0.08 nm is indicated on the figure.)

Vertical arrows at the top of the figure indicate the position of weaker Rydberg series members converging to the different vibrational levels of the $A^2\Pi^+$ state of CO^+ . Although the resonance decays to the $X^2\Sigma$ and $A^2\Pi^+$ states with about equal probability, these high Rydberg series members do not seem to perturb the decay channels significantly. The resonance in the X-channel has a typical Fano-type profile. The asymmetry seems to reverse (negative to positive q) as v increases but the data are not of sufficient quality for us to be definite on this point.

3.2. Angular distributions

The theoretical framework for calculating the asymmetry parameter, β , has evolved during the past decade (Cooper & Zare 1969; Dill & Fano 1972; Chang 1978; Dehmer *et al.* 1979; Raoult *et al.* 1981). Few detailed calculations dealing with the variation in β through autoionizing resonances exist (Dill 1972, 1973; Taylor 1977). The multiple scattering model has been applied successfully to shape resonances in molecules (Dehmer *et al.* 1979), where the strong dependence of the resonance profile on the internuclear distance invalidates the F.C. separation and shows up as large variations in the angular distribution for electrons associated with the different vibrational channels of the resulting molecular ion.

In figure 6 are shown the results for β in the wavelength range of the $X^1\Sigma^+ \rightarrow (B^2\Sigma^+) 3p\pi$ Rydberg state of CO. Each vibrational channel from $v = 0$ to $v = 4$ is

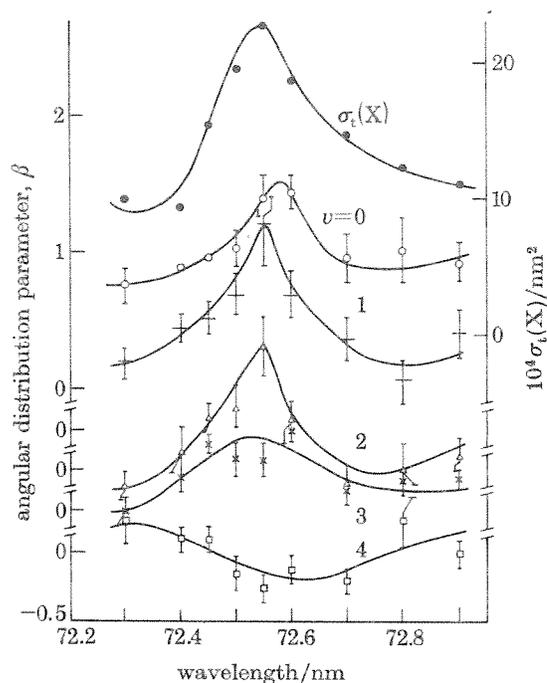


FIGURE 6. The asymmetry parameter, β , as a function of wavelength, for the $v = 0$ to $v = 4$ levels of the $X^2\Sigma^+$ state of CO^+ . The total $X^2\Sigma^+$ cross section is shown at the top of the figure (associated with the right-hand ordinate). The various β -curves are displaced downwards by 0.3β as v increases. Error bars denote the estimated probable error. Meaning of symbols: \circ , $v = 0$; $+$, $v = 1$; Δ , $v = 2$; \times , $v = 3$; \square , $v = 4$.

plotted and to avoid confusion is displaced downwards by 0.3β as v increases. For comparison, the total cross section for the X-channel is also plotted, its values being indicated by the right-hand ordinate. The data points on the various curves are connected simply to aid the eye. The error bars in the figure are estimated probable errors. Other than data taken at 58.4 nm (21.21 eV) (Hancock & Samson 1976), no vibrationally resolved values of β have been published for CO. The closest measurement is that of Holmes & Marr (1980) at 18 eV with a band-integrated value of $\beta = 0.87 \pm 0.02$. In the wings of the resonance at 72.3 nm we obtain a value of 0.66 ± 0.15 for the value of β , weighted by the relative intensity of each of the vibrational levels.

The major qualitative feature is clearly demonstrated in figure 6. The magnitude of β for the lower vibrational levels varies over a large range and tends to peak at the resonance maximum, whereas for the $v = 4$ level β varies much less and in fact becomes slightly negative.

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REFERENCES

- Albritton, D. L., Schmeltekopf, A. L. & Zare, R. N. 1980 *Diatomic intensity factors*. New York: John Wiley. (To be published.)
- Baer, T., Guyon, P. M., Nenner, I., Tabché-Fouhaille, A., Botter, R., Ferreira, L. F. A. & Govers, T. R. 1979 *J. chem. Phys.* **70**, 1585-1592.
- Bahr, J. L., Blake, A. J., Carver, J. H., Gardner, J. L. & Kumar, V. 1971 *J. quant. Spectrosc. radiat. Transfer* **11**, 1839-1852.
- Bahr, J. L., Blake, A. J., Carver, J. H., Gardner, J. L. & Kumar, V. 1972 *J. quant. spectrosc. radiat. Transfer* **12**, 59-73.
- Bardsley, J. N. 1968 *Chem. Phys. Lett.* **2**, 329-332.
- Carlson, T. A. & Jonas, A. E. 1971 *J. chem. Phys.* **55**, 4913-4924.
- Chang, E. S. 1978 *J. Phys.* B **11**, L293-L296.
- Codling, K., Parr, A. C., Ederer, D. L., Cole, B. E., Stockbauer, R., West, J. B. & Dehmer, J. L. 1981 *J. Phys.* B. **14**, 657-666.
- Cole, B. E., Ederer, D. L., Stockbauer, R., Codling, K., Parr, A. C., West, J. B., Poliakoff, E. D. & Dehmer, J. L. 1980 *J. chem. Phys.* **72**, 6308-6310.
- Collin, J. E. & Natalis, P. J. 1969 *Int. J. Mass. Spectrom. Ion Phys.* **2**, 231.
- Cooper, J. W. & Zare, R. N. 1969 *Lectures in theoretical physics*, vol. 11C, p. 317. New York: Gordon and Breach.
- Dehmer, J. L., Dill, D. & Wallace, S. 1979 *Phys. Rev. Lett.* **43**, 1005-1008.
- Dehmer, P. M. & Chupka, W. A. 1978 *Argonne natl Lab. Rep.* ANL-78-75, 10-12.
- Dill, D. 1972 *Phys. Rev.* A **6**, 160-172.
- Dill, D. 1973 *Phys. Rev.* A **7**, 1976-1987.
- Dill, D. & Fano, U. 1972 *Phys. Rev. Lett.* **29**, 1203-1205.
- Doolittle, P. H. & Schoen, R. I. 1965 *Phys. Rev. Lett.* **14**, 348-349.
- Ederer, D. L., Cole, B. E. & West, J. B. 1980 *Nucl. Instrum. Meth.* **172**, 185-190.
- Eland, J. H. D. 1980 *J. chem. Phys.* **72**, 6015-6019.
- Fano, U. 1961 *Phys. Rev.* **124**, 1866-1878.
- Gardner, J. L. & Samson, J. A. R. 1978 *J. Electron. Spectrosc. rel. Phen.* **13**, 7-15.
- Hamnett, A., Stoll, W. & Brion, C. E. 1976 *J. Electron. Spectrosc. rel. Phen.* **8**, 367-376.
- Hancock, W. H. & Samson, J. A. R. 1976 *J. Electron. Spectrosc. rel. Phen.* **9**, 211-216.
- Holmes, R. M. & Marr, G. V. 1980 *J. Phys.* B **13**, 945-950.
- Madden, R. P. 1980 *Nucl. Instrum. Meth.* **172**, 1-8.
- Marr, G. V. & West, J. B. 1976 *Atom. Data nucl. Data Tables* **18**, 497-508.
- Mies, F. H. 1968 *Phys. Rev.* **175**, 164-175.
- Nicholls, R. W. 1962 *Can. J. Phys.* **40**, 1772-1783.
- Ogawa, M. & Ogawa, S. 1972 *J. molec. Spectrosc.* **41**, 393-408.
- Parr, A. C., Stockbauer, R. L., Cole, B. E., Ederer, D. L., Dehmer, J. L. & West, J. B. 1980 *Nucl. Instrum. Meth.* **172**, 357-361.
- Parr, A. C., Ederer, D. L., Cole, B. E., West, J. B., Stockbauer, R., Codling, K. & Dehmer, J. L. 1981 *Phys. Rev. Lett.* **46**, 22-25.
- Plummer, E. W., Gustafsson, T., Gudat, W. & Eastman, D. E. 1977 *Phys. Rev.* A **15**, 2339-2355.
- Price, W. C. 1968 *J. molec. Spectrosc.* **4**, 221.
- Racault, M., Jungen, Ch. & Dill, D. 1981 *J. chem. Phys.* (To be published.)
- Samson, J. A. R. & Gardner, J. L. 1976 *J. Electron. Spectrosc. rel. Phen.* **8**, 35-44.
- Smith, A. L. 1970 *Phil. Trans. R. Soc. Lond.* A **268**, 169-175.
- Stockbauer, R., Cole, B. E., Ederer, D. L., West, J. B., Parr, A. C. & Dehmer, J. L. 1979 *Phys. Rev. Lett.* **43**, 757-761.

Taylor, K. T. 1977 *J. Phys. B* **10**, L699-L704.

Wachs, M. E. 1964 *J. chem. Phys.* **41**, 930-936.

West, J. B., Codling, K., Parr, A. C., Ederer, D. L., Cole, B. E., Stockbauer, R. & Dehmer, J. L. 1981 *J. Phys. B.* **14**, 1791-1801.