

MEASURED AND CALCULATED PARTIAL PHOTOIONIZATION CROSS SECTIONS OF CO BETWEEN 15 AND 40 eV

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ABSTRACT

Vibrationally resolved partial photoionization cross sections of CO have been measured and theoretical partial cross sections have been calculated using the method of Raşeev et al. and the two-step MQDT formulation of Giusti-Suzor and Lefebvre-Brion.

We discuss the physical nature of the shape resonances appearing in the $\epsilon\sigma$ continua and we analyze their vibrational selectivity. A new assignment of the Rydberg series converging to $\text{CO}^+ B^2\Sigma^+$ is suggested and their electronic and vibrational selectivity is discussed.

INTRODUCTION

Molecular photoionization studies have already proven their usefulness in describing the effects of the anisotropic ionic core(s) on the escaping electron (ref. 1). In this communication, we shall deal with a few features of the photoionization spectra of CO. In spite of extensive experimental and theoretical work (ref. 2 to 17), several important questions remain unanswered :

- (i) Shape resonances have been identified in the $X^2\Sigma^+$ and $B^2\Sigma^+$ continua. Few information exists on the $B^2\Sigma^+$ resonance, on its physical nature and its vibrational selectivity. A comparison between the two continua would be instructive.
- (ii) Why doesn't it appear any shape resonance in the $A^2\Pi$ partial cross section ?
- (iii) The assignments of the Rydberg series converging to $B^2\Sigma^+$ differ from one author to another (ref. 13 to 17).

To get a deeper insight in these photoionization processes, we have orienta-

ted our work in two directions. We have measured the vibrationally resolved partial cross sections for the production of $\text{CO}^+ X \ ^2\Sigma^+$ and $\text{B} \ ^2\Sigma^+$ and we have performed calculations of the partial cross sections including the autoionization process.

METHODS

Experimental

Vibrationally resolved partial photoionization cross sections are measured using the pulsed ACO synchrotron radiation at Orsay (France) and the experimental technique described elsewhere by Morin et al. (ref. 18). The resolution of the grazing incidence monochromator is of 1Å. The ejected electrons are detected by a 127° electrostatic analyzer, the energy resolution of which is 7 % of the pass energy, allowing the separation of the vibrational levels of the CO^+ states. Spectra are recorded in the Constant Ionic State (C.I.S.) mode (ref. 3, 18).

Framework of the theoretical methods

The direct photoionization cross sections are calculated using the method developed by Raşeev et al. (ref. 19, 20). The calculation of the continuum wave function describing the motion of the escaping electron in the molecular field of each ionic core ($X \ ^2\Sigma^+$, $A \ ^2\Pi$ and $B \ ^2\Sigma^+$) separately leads to the continuum eigenphases and to the partial cross sections.

This electronic continuum wave function is also used to calculate the autoionization resonances by the two-step MQDT formulation of Giusti-Suzor and Lefebvre-Brion (ref. 21 to 23) : the continuum-continuum interactions are calculated and introduced in a MQDT calculation to obtain the partial cross sections including the autoionization processes.

RESULTS

The high-energy region ($20 \text{ eV} < E < 40 \text{ eV}$).

Fig. 1 displays the continuum eigenphases corresponding to $X \ ^2\Sigma^+ \ \epsilon\sigma$, $A \ ^2\Pi \ \epsilon\sigma$ and $B \ ^2\Sigma^+ \ \epsilon\sigma$. We can see immediately that their behaviour is very similar.

We note that the four partial waves s, p, d and f contribute to each particular eigenchannel as expected for a heteronuclear molecule. This l-mixing is very strong and will have important consequences on the presence of shape resonances.

The eigenphase associated with the f-like eigenchannel (denoted by "f") increases by approximately 0.7 (in units of Π) between $\epsilon_k = 0.35 \text{ a.u.}$ and 0.75 a.u. thus indicating the presence of a shape resonance in each $\epsilon\sigma$ continuum. When increasing, this "f" eigenphase would successively cross the "s+d", "p" and "s-d" eigenphases : a pattern of avoided crossings, which is qualitatively the same for the three continua, results then from the "non-crossing rule" and this gives information on the magnitude of the l-coupling. We can see that the coupling bet-

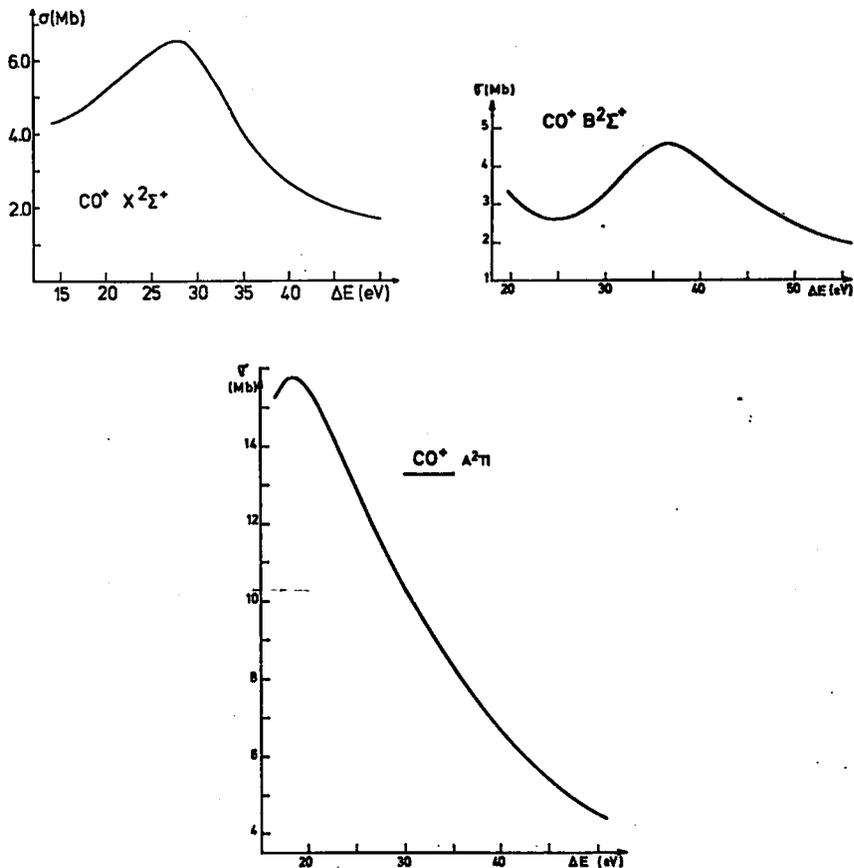


Fig. 2 . Calculated partial vertical photoionization cross sections of CO.

$\langle "p" \pi | \vec{r} | \epsilon "f" \sigma \rangle$. The shape resonance of the $A^2\Pi$ $\epsilon\sigma$ continuum is therefore hidden in the photoionization cross section. The broad peak at threshold results from the $\epsilon\delta$ channel and cannot be interpreted as a shape resonance because of the very smooth variation of the corresponding eigenphases.

The vibrationally resolved cross sections (Fig. 3) show a different behaviour for the $X^2\Sigma^+$ and $B^2\Sigma^+$ ionic states. In the $X^2\Sigma^+$ case, the position of the resonance is shifted to lower energies as v increases whereas in the $B^2\Sigma^+$ case, we do not observe any significant variation. For the $X^2\Sigma^+ \leftarrow X^1\Sigma^+$ transition, the R-centroid values increase as v increases (Table 1) producing a shift of the resonance maximum to lower energies (ref. 10). In the $B^2\Sigma^+ \leftarrow X^1\Sigma^+$ case however, the weak R-centroid variation explains the constancy of the resonance maximum position.

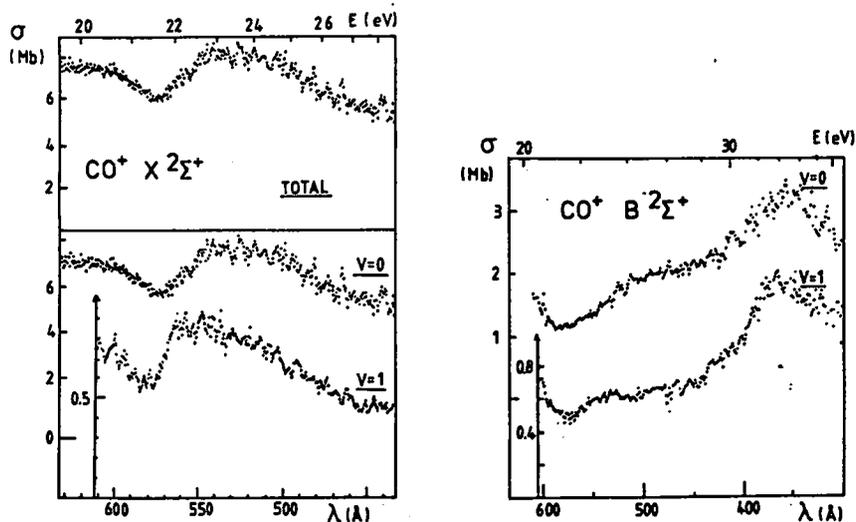


Fig. 3. Vibrationally resolved cross sections for the production of $\text{CO}^+ \text{X } 2\Sigma^+$ and $\text{B } 2\Sigma^+$.

TABLE 1

R-centroid values for transitions from $\text{CO } 1\Sigma^+$

| Final state : | $\text{X } 2\Sigma^+$ | $\text{B } 2\Sigma^+$ |
|---------------|-----------------------|-----------------------|
| v = 0 | 1.126 Å | 1.152 Å |
| v = 1 | 1.302 Å | 1.101 Å |
| v = 2 | 1.810 Å | 1.047 Å |

Electronic autoionization below 20 eV

Among the numerous Rydberg states lying below 20 eV, we have restricted ourselves to a more careful study of those converging to $\text{CO}^+ \text{B } 2\Sigma^+$ in the 680 Å-730 Å region (17-18.4 eV). These states belong to four series called sharp, diffuse, III and IV (ref. 13 to 17). The tentative assignments given by different authors are summarized in Table 2.

Our MQDT calculations are presented in the first part of this section. The second part deals with the experimental vibrational resolved partial cross sections of $\text{CO}^+ \text{X } 2\Sigma^+$.

TABLE 2

Assignments of the Rydberg series converging to $\text{CO}^+ \text{B } ^2\Sigma^+$

| Series | Lindholm 1969 | Betts and McKoy (1971) | Ogawa and Ogawa (1974) | Fock et al. (1980) | This work |
|---------|------------------|------------------------------|------------------------------|-----------------------|----------------------------|
| Sharp | $p\sigma$ | $p\pi$ | $p\pi$ | $p\sigma$ | " p^{π} " |
| Diffuse | $p\pi$ | $p\sigma$ | $p\sigma$ | $p\pi$ | " p^{σ} " |
| III | $s\sigma$ | $s\sigma$ | $s\sigma$ | $s\sigma$ | " $s-d^{\sigma}/d^{\pi}$ " |
| IV | $d\sigma$ | $d\pi$ | $d\sigma/d\pi$ | $d\sigma$ | " $s+d^{\sigma}$ " |

MQDT Results. Fig. 4 displays the calculated total photoionization cross section in the 675 Å-730 Å range. It is compared with the experimental results of Berkowitz (ref. 26).

The reasonably good agreement between the two curves allows us to give the following assignment (Table 2). The sharp $n=3$ peak corresponds to the $3^{\pi}p^{\pi}v=0$ state; the peak at 717 Å is assigned to a superposition of $3^{\pi}p^{\sigma}v=0$ and $3^{\pi}p^{\pi}v=1$. The peak located at 690 Å (series IV) corresponds to " $4s+3d^{\sigma}v=0$ " whereas the structure at 682 Å (series III) results from the superposition of $3^{\pi}d^{\pi}v=0$ and " $4s-3d^{\sigma}v=0$ ".

The l-mixing is particularly important in the case of the $s\sigma$ and $d\sigma$ series. As $(n+1)s\sigma$ and $nd\sigma$ are generally quasi degenerate, they interact strongly giving rise to two new states which can be labeled " $(n+1)s + nd^{\sigma}$ " and " $(n+1)s - nd^{\sigma}$ ".

We summarize now the main results which can be obtained from our calculations of the partial cross sections corresponding to the $X ^2\Sigma^+$ and $A ^2\Pi$ ionic states. The branching ratio of the two peaks located at 726 Å and 717 Å is 0.52 in the X channel and 0.78 in the A channel in good agreement with Plummer et al. (ref. 3) and with our own results. This results from the fact that $3^{\pi}p^{\pi}$ interacts mainly with the X continuum and $3^{\pi}p^{\sigma}$ with the A continuum. The window resonance at 679 Å appears in the two ionic states as well as in the total cross section. In the A channel, it is due to the $3^{\pi}d^{\pi}$ state whereas in the X channel, it is the emission part of the Fano profile corresponding to " $4s-3d^{\sigma}$ ". The physical origin of this window resonance in the A channel is the strong interaction between $3^{\pi}d^{\pi}$, which has a weak oscillator strength and the very intense $A ^2\Pi e^{\pi}d^{\sigma}$ channel. The " $4s+3d^{\sigma}$ " state interacts weakly with both continua, although the calculated interactions are underestimated (see Fig. 4).

A few features remain uninterpreted. The most important is the peak at 722 Å. It has been assigned by Ogawa and Ogawa (ref. 15) to Rydberg states ($n=9,10,11$) converging to $A ^2\Pi v=4$. We shall discuss this point in the following section.

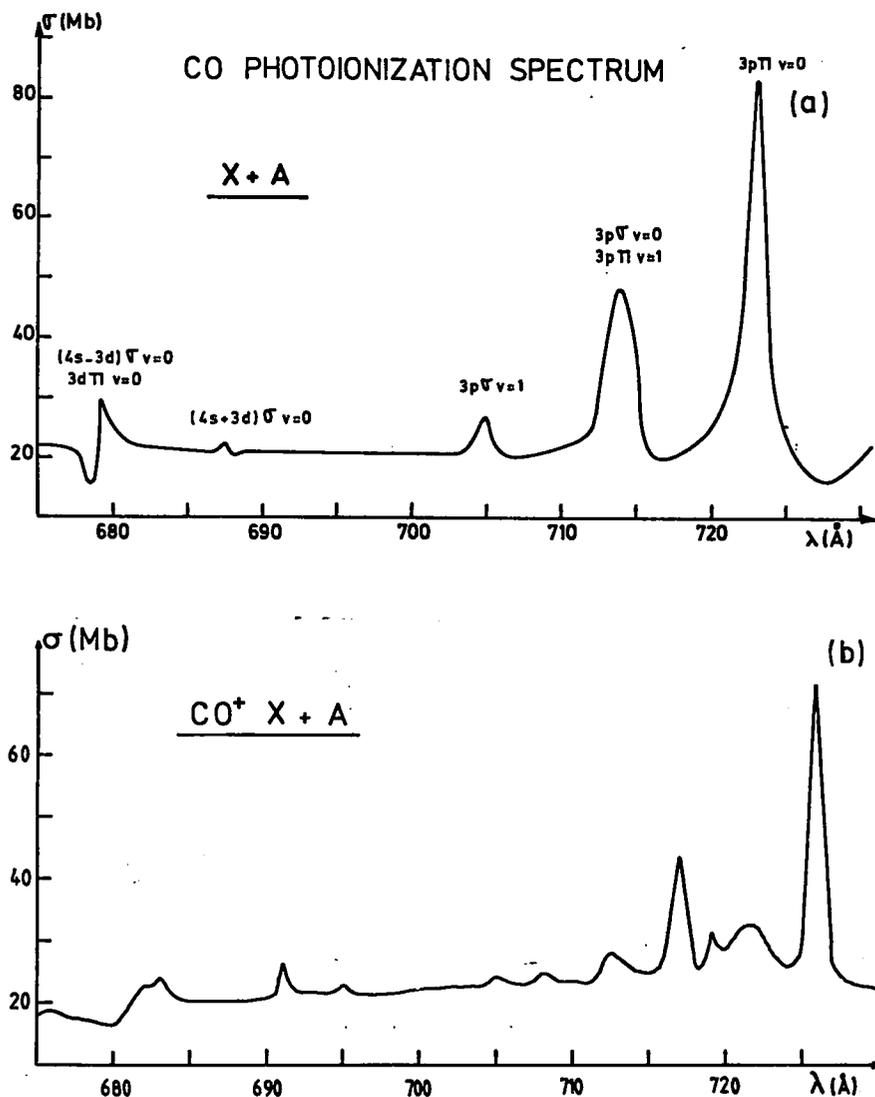


Fig. 4 . Total photoionization cross section of CO. (a) : our MQDT results ; (b) : experimental results of Berkowitz (ref. 26).

Vibrationally resolved cross sections of the $X^2\Sigma^+$ ionic state. Vibrationally resolved cross sections for the production of $\text{CO}^+ X^2\Sigma^+$ are displayed on Fig. 5. The vibrational selectivity can be analyzed in the framework of Smith's theory (ref. 27) : he showed that, within the Franck-Condon approximation, the part of a partial cross section which is due to a lorentzian resonance is proportio-

nal to $|\langle v_0 | v_{\text{Rydb}} \rangle|^2 |\langle v_{\text{ion}} | v_{\text{Rydb}} \rangle|^2$ where $|v_0\rangle$ is the vibrational state of the electronic ground state of the neutral molecule.

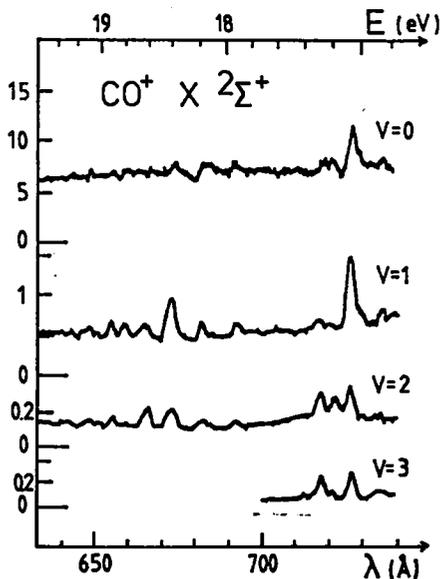


Fig. 5 . Vibrationally resolved partial cross section for the production of $\text{CO}^+ X \ 2\Sigma^+$.

values for odd v . This corresponds exactly to the v -dependence of the 722 Å structure, confirming therefore the interpretation of Ogawa and Ogawa (ref. 15).

CONCLUSION

The physical nature of the shape resonances associated to the three X, A and B ionic states has been qualitatively described. The behaviour of the A $2\Pi \ \epsilon\sigma$ resonance has also been explained : this shows that a shape resonance doesn't always manifest itself by an enhancement of the corresponding cross section.

The comparison between our experimental and theoretical results has allowed a new assignment of the Rydberg states converging to $\text{CO}^+ B^2\Sigma^+$ and a deeper understanding of the partial and vibrationally resolved cross sections.

We thank the technical staff of L.U.R.E. and Laboratoire de l'Accélérateur Linéaire. The "Fonds National de la Recherche Scientifique" of Belgium and the NATO (contract n° 096.82) are gratefully acknowledged for their financial support.

We have observed that the v -dependence of the branching ratio between the two peaks at 726 Å and 717 Å can be roughly reproduced if one assumes that the major contribution to the peak at 717 Å is due to $3^1P^1 \pi v=1$. This confirms our MQDT results.

The Fano profile at 682 Å becomes lorentzian for $v_{\text{ion}} \geq 1$. As v increases, the direct transition moment to the X $2\Sigma^+$ continuum decreases and this results in a tendency to the lorentzian shape.

We have also calculated the $\langle A \ 2\Pi \ v=4 | X \ 2\Sigma^+ v \rangle$ overlap integrals and we have found that these integrals have negligible

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DISCUSSION

DRESSLER - The fact that in this type of molecule the Rydberg s and $d\sigma$ channels unit very strongly has been recognised and described in detail by Ch. Jungen 15 years ago. He also recognised that the presence of this interaction in NO and its absence in H_2 can be related to the presence (or absence) of precursors to the $d\sigma$ orbital in the core of NO (or of H_2 , resp.).

LEYH - The strong s - d mixing in the Rydberg orbitals of the second row diatomic molecules is indeed induced by the contribution to the molecular field of the 5σ orbital (which is a mixture of the s and d partial waves) (C. Jungen, J. Chem. Phys. 53 (1970) 4168). In the present case, the interaction energy for the pair $4s$ - $3d$ (with a $B^2 \Sigma^+$ ionic core), H_{sd} , is equal to 1100 cm^{-1} (N_2 : 970 cm^{-1} , NO : 910 cm^{-1}).

This mixing of the partial waves of the same parity has also been recognised in the continuum wavefunction. We have observed that, provided we had renormalized the Rydberg wavefunctions with the $n^{*3/2}$ scaling factor, the s - d interactions have approximately the same value, below and above the threshold. Moreover, in contrast with the N_2 case, the heteronuclear molecular field couples strongly the partial waves of different parities. The most important interactions takes place between the s - d and p waves (for the pair $4s$ - $3d/4p$, $H_s=990 \text{ cm}^{-1}$). This strong departure from the homonuclear situation has important consequences on the photoionization spectra, even if we consider only the direct photoionization processes.

LEACH - Could you elaborate a little more on the differences and similarities between N_2 and CO Rydberg states and series ?

LEYTH - In the N_2 isoelectronic case, three series converging to $N_2^+ B^2 \Sigma_u^+$ have been identified : the "absorption" series, the "emission" series and a third series appearing as absorption shoulders on the long-wavelength side of the emission series. The work of Raoult et al (J. Phys. B 16 (1983) 4601) has allowed to assign unambiguously these series. If we compare with our results, we see that the N_2 "absorption" series correspond to the series IV in CO (" $s+d\sigma$ "), whereas the "emission" series and the near-by shoulders correspond to the complex series III (" $s-d\sigma/d\pi$ "). the intensities and quantum defects are of the same order of magnitude in the two cases. However, the major features of the CO photoionization spectrum in this region are due to the " $p\sigma$ " and " $p\pi$ " states which are strongly forbidden in the N_2 case (g - u selection rule). This emphasizes once more the strong heteronuclear nature of the CO molecular field.

CHUPKA - Has any one made photoelectron angular distribution studies in this region ?

LEYH - Up to now, only Ederer et al (Proc. R. Soc. Lond. A378 (1981) 423) have made detailed measurements of the β parameter in the region of the R_B states. They have however restricted themselves to the sharp $n=3$ ($3p\pi$) resonance : they have observed an increase of the β value at the position of the resonance for $v_{ion} = 0-3$ and a decrease of $v_{ion} = 4$. In order to complete our work on the partial and vibrationally resolved photoionization cross sections, we intend now to make a detailed study (both experimentally and theoretically) of the photoelectron angular distributions between 675 \AA and 730 \AA .