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Photoionization Resonance Study of the $\tilde{X}(^2\Pi)$, $\tilde{A}(^2\Pi)$, $\tilde{B}(^2\Sigma^+)$ and $\tilde{C}(^2\Sigma^+)$ States of CS_2^+ and COS^+

by

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NOTKESTRASSE 85 · 2 HAMBURG 52

Photoionization Resonance Study of the $\tilde{X}(^2\Pi)$, $\tilde{A}(^2\Pi)$, $\tilde{B}(^2\Sigma^+)$ and $\tilde{C}(^2\Sigma^+)$ States of CS_2^+ and COS^+ [†]

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ABSTRACT

High resolution photoionization resonance spectroscopy (PIR) has been used to determine vibrational frequencies for the $\tilde{X}(^2\Pi)$, $\tilde{A}(^2\Pi)$, $\tilde{B}(^2\Sigma^+)$ and $\tilde{C}(^2\Sigma^+)$ states of CS_2^+ and COS^+. In the $\tilde{X}$ and $\tilde{A}$ states of CS_2^+, Fermi resonances have been observed and the perturbed v_1 and v_2 frequencies reported for several perturbing combinations for both the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. No Fermi resonances were detected in the other spectra reported here. As in CO_2^+ ($\tilde{X}^2\Pi$), we have found the 010 transition in the ground state of both CS_2^+ and COS^+ to be excited, although this is nominally a forbidden transition. A fifth band in the CS_2^+ spectrum ($\tilde{D}$ state?) has been observed in these threshold studies as it was by photoelectron spectroscopy but at somewhat weaker intensity relative to that of the $\tilde{C}$ state. Finally, ionization potentials and values of the spin-orbit splittings are reported.

INTRODUCTION

In a previous publication / 1 /, results were presented for the high resolution study of CO_2^+ in the $\tilde{X}$, $\tilde{A}$, $\tilde{B}$ and $\tilde{C}$ states as observed by means of photoionization resonance spectroscopy (PIR) / 2-4 /. Because of the occurance of vibronic interactions (Renner-Teller effect) and vibration-vibration interactions (Fermi resonances), the family of ions CO_2^+, CS_2^+ and COS^+ are particularly interesting spectroscopically. They have also been difficult to study in the past. The direct nature of PIR spectroscopy along with the high resolution obtainable have enabled us to measure many of the vibrational frequencies for the first four electronic states of these ions. Because one of the two states involved in the transitions reported in this work is the vibronic ground state of the parent molecule, assigning the spectra is relatively straightforward and leads directly to the determination of the vibrational frequencies of the molecular ion. In addition, degenerate autoionization processes enhance the intensity of several transitions and make some ionic states stand out where otherwise they would not be detected because of a small direct ionization transition probability. Such intensification results when an autoionizing Rydberg state yields electrons of zero energy because the autoionizing level and the level to which it decays are degenerate within the bandpass of the zero energy electron analyser (ca. .003 eV FWHM). A likely example of this phenomenon is the excitation of 010 in the ground states of all three of the molecular ions discussed here. This is a nominally forbidden transition / 5 /. Comparisons are made between the results obtained here and those

found by photoelectron spectroscopy / 6 / and fluorescence studies / 7 /.

EXPERIMENTAL

The experimental setup is the same as that employed previously / 1 /. Briefly, zero energy (threshold) electrons from the photoionization process are detected as the incident photon energy is continuously scanned. Details of the PIR analyser have been published / 2-3 /. The light source used is the storage ring DORIS at the electron synchrotron (DESY) in Hamburg, West Germany. A three meter vacuum ultraviolet scanning monochromator was used to disperse the radiation, at a resolution of 0.15 Å FWHM.

The gases were commercial samples. The COS gas was 97,5 % pure and used directly from the lecture bottle without further purification. The CS_2 was used after redistillation.

RESULTS AND DISCUSSION

The PIR spectra of the $\tilde{X}(^2\Pi)$, $\tilde{A}(^2\Pi)$, $\tilde{B}(^2\Sigma^+)$ and $\tilde{C}(^2\Sigma^+)$ states of CS_2^+ and COS^+ are shown in figures 1-6 and the wavelengths of the peaks are given in Tables 1 and 2. As was the case for CO_2^+ ($\tilde{X}\ ^2\Pi_g$), the adiabatic ionization potentials to both spin-orbit states of both molecular ions studied here are resolved. However, the intensities for the two spin-orbit states are quite different in both molecules, where for purely direct ionization they would be expected to be the same. This suggests that there is a contribution to the $\Omega = 3/2$ photoionization cross section from degenerate autoionization. The constancy of the intensity ratio, about 2:1 for COS^+, further supports this contention. In CO_2^+ the intensities were found to be about equal. The 000 transition in CS_2^+ is similarly affected, but the higher vibrational components are only weakly excited. It should be emphasized that the intensities observed do represent the photoionization cross section at threshold which can be strongly altered by the interaction of direct and autoionizing channels as shown theoretically by Fano / 8 /, Dill / 9 / and others / 10 /. Such interactions lead to an energy dependent photoionization cross section even at wavelengths which are angstroms away from the autoionization peak that is perturbing the photoionization process, and the net photoionization cross section that is observed cannot be thought of as simply the sum of direct and autoionization.

Because of the near equivalence of the energies of the 100 and 020 levels of CS_2^+ ($\tilde{X}$) and the fact that these vibrations

are of the same symmetry species, these states perturb and are shifted away from each other / 11 /. This effect, a Fermi resonance, is clearly observed in the $\tilde{X}$ and $\tilde{A}$ states of CS_2^+ (Fig. 1,2) and leads to values of $2v_2$ which do not represent the $1v_2$ value. As in the case of CO_2, a transition to 010 in CS_2^+ ($\tilde{X}$) is observed. This yields an unperturbed value of v_1 and thus helps in the interpretation of the Fermi resonance (see below). The reason why this transition is excited is not readily explainable. However, the ion spectrum of CO_2 reveals more vibrational structure in the $\tilde{X}$ state region than expected / 12 / and the suggestion has been put forth that the additional vibrational structure results from the autoionization of an excited non-linear valence state of CO_2 / 12,13 /. Such a process could lead to the threshold excitation of the 010 level of the ion. The fact that the 010 excitation is observed in the PIR spectrum of all three molecular ions, CO_2^+, CS_2^+ and COS^+, indicates that some systematic process is taking place, such as the autoionization of a non-linear molecule, or, however, in such photoionization processes at threshold, releasing very slow electrons, the 010 excitation would no longer be strictly forbidden /21/.

In states of linear molecules, the Born-Oppenheimer separation of electronic and nuclear motions is not always a good approximation for the two-fold degenerate bending vibration. In CO_2^+ ($\tilde{X}\ ^2\Pi_g$), the effects of vibronic interactions, the Renner-Teller effect / 14 /, was observed / 1 /. For CS_2^+ and COS^+ the effect was too small to be measured. For CS_2^+ the unperturbed v_2 frequency is found to be 365 cm^{-1} ($^2\Pi_{3/2}$) and 349 cm^{-1} ($^2\Pi_{1/2}$).

For the $^2\Pi_{3/2}$ progression, the peaks at 100 and 02^00 are mixed with a peak at what should be the location of the 02^20 level which would be unperturbed / 11 / i.e. *ca*. 700 cm^{-1}. However, in the $^2\Pi_{1/2}$ progression, two peaks are clearly seen at 646 cm^{-1} and 735 cm^{-1}, corresponding evidently to the perturbed 100 and 02^00 levels respectively. From the interpretation of CS_2^+ ($\tilde{B}$-$\tilde{X}$) fluorescence intensity data / 7 /, the lower of each spin-orbit pair was taken from the intensities observed to be the perturbed v_1 frequency-an assignment that is consistent with our observed value of $1v_2 \simeq 365$ cm^{-1}. The data for the CS_2^+ ($\tilde{X}$) state are given in Tables 3 and 4.

We have found neither a Renner-Teller effect nor a Fermi resonance in the COS^+ ($\tilde{X}\ ^2\Pi$) spectrum (Fig. 4). It does appear, however, that the 010 level is excited as in the case of both CO_2^+ and CS_2^+. This is more visible in the $^2\Pi_{3/2}$ progressions, at about 1103 Å, than in the $^2\Pi_{1/2}$. The assignments for the transition to the COS^+ ($\tilde{X}\ ^2\Pi$) are as shown in Fig. 4 yielding values for all three vibrational frequencies (Table 5). An additional observation is that the intensity relationship between the $^2\Pi_{3/2}$ progressions and those for $^2\Pi_{1/2}$ is not carried through to the 001 transitions, i.e. the two peaks at *ca*. 1083 Å and 1079 Å, which are nearly equal in intensity. The next higher peaks also appear to have approximately equal intensity.

Transitions to the $\tilde{A}(^2\Pi)$ states of CS_2^+ and COS^+ are shown in figures 2 and 5. In CS_2^+ Fermi resonances are again detectable, but no transition to 010 of the $\tilde{A}$ state is seen. We adopt the interpretation / 7 / that for the $\tilde{A}$ state $v_1 > 2v_2$. The (020, 100) interactions have frequencies of 559 cm^{-1} and 622 cm^{-1} for $^2\Pi_{3/2}$ and 572 and 625 cm^{-1} for $^2\Pi_{1/2}$. At (120, 200) the observed frequencies are 1167 and 1306 cm^{-1} for $^2\Pi_{3/2}$ and 1214 and 1343 cm^{-1} for $^2\Pi_{1/2}$. The (220, 300) frequencies ($^2\Pi_{3/2}$) are found to be 1771 cm^{-1} and 1858 cm^{-1}. In no case in the $\tilde{A}$ state was a transition to 02^20 observed; however, unless such a peak was strong, it would tend to be buried in the background. From fluorescence studies / 7 / $2v_2$ and v_1 frequencies of 549 and 612 cm^{-1} were reported for $^2\Pi_{3/2}$ in the $\tilde{A}$ state, essentially the same as those reported here (see Table 4). For (120, 300), the values were 1153 and 1233 cm^{-1} while for (220, 300) 1758 and 1859 cm^{-1} were reported. At the 300 state and above, CS_2^+ *ion* spectra (see Fig. 2) reveal strong autoionization peaks. The influence of the autoionization structure on the PIR curves is minor, as can be seen by comparing the PIR curves with PES results / 6 / which have almost the same intensity distribution indicating the absence of autoionization feed-through. Nevertheless, detailed analysis of the spectra will not be made above the (300) state because of the possible influence of strong, near degenerate autoionization peaks on the energy assignments of the PIR peaks.

The spectrum of transitions to the $\tilde{A}$ ($^2\Pi$) state of COS^+ (Fig. 5) is not as well defined as that for CS_2^+. Because of strong autoionization structure in the COS^+ ion scan and S^+/COS ion scan across the $\tilde{A}$ state, see Fig. 5, the PIR energy assignments are not as certain as they otherwise are. However, the similarity of the COS^+ $\tilde{A}$ PIR spectrum to the corresponding PES spectrum / 6 / indicates that autoionization has had moderate effect on the PIR results. The ionization potential, the spin-orbit splitting and values of v_1 and v_3 we obtained are given in Table 5.

The spectra of the $\tilde{B}(^2\Sigma^+)$ states of both CS_2^+ and COS^+ show little vibrational structure and are in most respects similar to the PES spectra / 6 / except for the higher resolution obtained here. The lack of structure indicates the removal of a non-bonding electron, which is in this case a σ_u electron / 6 /. Finally, the results shown here confirm the interpretation put forth / 15 / that the v_2 mode of the $\tilde{B}$ state of CS_2^+ is not excited in direct ionization, in agreement with the optical selection rules.

The next electron to be ionized, a σ_g electron, should also be non-binding and the CS_2^+ $(\tilde{C}\ ^2\Sigma_g^+)$ spectrum supports this view, showing the strong adiabatic transition and little else. For COS^+, on the other hand, the $\tilde{C}$ band is surprisingly complex, both in the PIR and in the PES spectra / 6 /. No Fermi resonances are detectable, but considerable vibrational structure is evident which is unexpected coming from the removal of a non-bonding electron. Values of all three vibrational frequencies are obtained from the PIR measurements (Table 5). Again, as the $\tilde{X}$ and $\tilde{A}$ states, excitation of the 010 level is evident in the spectrum. The peak at 688.7 Å yields a value of $v_2 = 379\ \mathrm{cm}^{-1}$.

The broad structureless weak peak in the CS_2 PIR spectrum near 730 Å has its counterpart in the PES spectrum / 6 /, but at somewhat weaker relative intensity with respect to the $\tilde{C}$ state; i.e. about 40 times weaker in peak height. The origin of this "$\tilde{D}$" state has been discussed recently / 16 /. Such a peak has not been observed in the PES spectra of the other linear molecules N_2O, COS, or CO_2 / 6 / or in the PIR spectra of CO_2 or COS / 1 /.

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1. PIR spectrum showing the $\tilde{X}(^2\Pi_g)$ state of CS_2^+.
2. PIR spectrum showing the $\tilde{A}(^2\Pi_u)$ state of CS_2^+, and the CS_2^+ ion spectrum across the $\tilde{A}$ state.
3. PIR spectra of the $\tilde{B}(^2\Sigma_u^+)$ and $\tilde{C}(^2\Sigma_g^+)$ states of CS_2^+ and the threshold electron signal of a possible $\tilde{D}$ state.
4. PIR spectrum showing the $\tilde{X}(^2\Pi)$ state of COS^+.
5. PIR spectra showing the $\tilde{A}(^2\Pi)$ and $\tilde{B}(^2\Sigma)$ states of COS^+, and the COS^+ and S^+/COS ion spectra across the $\tilde{A}$ and $\tilde{B}$ state.
6. PIR spectra showing the $\tilde{C}(^2\Sigma)$ state of COS^+.

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Table 1 CS_2 : Threshold electron peaks

	Line Nr.	λ (Å)	Separation from vibr. ground state (cm^{-1})	Designation	
$\tilde{X}$ (${}^2\Pi_g$)	1	1230.4	0	000	${}^2\Pi_{3/2}$
	2	1224.9	365	010	${}^2\Sigma, {}^2\Delta_{5/2}$
	3	1223.6	452	000	${}^2\Pi_{1/2}$
	4	1220.9	633	100	${}^2\Pi_{3/2}$
	5	1220.1	686	020	${}^2\Pi_{3/2}, {}^2\Pi_{1/2}, {}^4\Phi_{3/2}$
	6	1218.4	801	(010	${}^2\Delta_{3/2}, {}^2\Sigma$)
	7	1214.0	1098	100	${}^2\Pi_{1/2}$
	8	1212.7	1187	020	${}^2\Phi_{5/2}, {}^2\Pi_{3/2}, {}^2\Pi_{1/2}$
	9	1209.5	1405		
$\tilde{A}$ (${}^2\Pi_u$)	1	976.0	0	000	${}^2\Pi_{3/2}$
	2	974.8	189	000	${}^2\Pi_{1/2}$
	3	971.3	559	020	$\left.\right\}{}^2\Pi_{3/2}$
	4	970.7	622	100	
	5	969.4	761	020	$\left.\right\}{}^2\Pi_{1/2}$
	6	968.9	814	100	
	7	966.4	1081		
	8	965.6	1167	120	$\left.\right\}{}^2\Pi_{3/2}$
	9	964.3	1306	200	
	10	963.4	1403	120	$\left.\right\}{}^2\Pi_{1/2}$
	11	962.2	1532	200	
	12	961.2	1641		
	13	960.0	1771	220	$\left.\right\}{}^2\Pi_{3/2}$
	14	959.2	1858	a, 300	
	15	957.8	2010		
	16	956.6	2141		
	17	955.5	2261		
	18	954.5	2371		
	19	953.7	2459		
	20	949.8	2889		
	21	948.8	3000		
	22	943.6	3581		
$\tilde{B}$ (${}^2\Sigma_u^+$)	1	856.3	0	000	
	2	851.9	603	100	
	3	844.4	1645	(a)	
$\tilde{C}$ (${}^2\Sigma_g^+$)	1	765.7	0	000	
	2	761.9	651	100	
$\tilde{D}$		ca. 732. Max.			

a: autoionization peak.

Table 3 CS_2^+ Data

A. Vibrational frequencies (cm^{-1})

		Present work			Fluorescence studies (7)			PES (20)		
		ν_1	ν_2	ν_3	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3
$\tilde{X}$	$^2\Pi_{3/2}$	633	365		617	347*	1203			1170 (Ref.6)
	$^2\Pi_{1/2}$	646	349		623	351*	1201			
$\tilde{A}$	$^2\Pi_{3/2}$	622	279*		612	275*		580		
	$^2\Pi_{1/2}$	625	286*		602					
$\tilde{B}$	$^2\Sigma_u$	603				338 (Ref.19)		614		
$\tilde{C}$	$^2\Sigma_g$	651						653		800 (Ref.6)

* $\nu_2 = \frac{1}{2}(2\nu_2)$

B. Adiabatic ionization potentials (IP) and spin orbit splittings (A)

	Present work (IP,A)	Other studies (IP,A) (Ref.)
$\tilde{X}$ $^2\Pi_g$	10.077 eV, 452 cm^{-1}	10.076 eV, 436 cm^{-1} (18); 10.084 eV, 420 cm^{-1} (20); 440 cm^{-1} (7,17)
$\tilde{A}$ $^2\Pi_u$	12.696 eV, 189 cm^{-1}	12.69 eV (6); 12.634 (20); 169 cm^{-1} (17,19); 176 cm^{-1} (7)
$\tilde{B}$ $^2\Sigma_u^+$	14.479 eV	14.47 eV (18); 14.47 eV (6) 14.472 eV (20)
$\tilde{C}$ $^2\Sigma_g^+$	16.192 eV	16.18 eV (18); 16.190 eV (20)

Table 2 COS: Threshold electron peaks

	Line No.	λ(Å)	Separation from vibr. ground state (cm^{-1})	Designation
$\tilde{X}$ ($^2\Pi$)	1	1108.0	0	000 $^2\Pi_{3/2}$
	2	1103.6	360	000 $^2\Pi_{1/2}$
	3	1102.9	417	010
	4	1099.7	681	100
	5	1095.3	1046	100
	6	1091.5	1364	200
	7	1087.0	1744	200
	8	1083.5	2041	001, (300)
	9	1079.2	2409	001, (300)
	10	1075.3	2745	101, (400)
	11	1071.	3118	101, (400)
$\tilde{A}$ ($^2\Pi$)	1	822.4	0	000 $^2\Pi_{3/2}$
	2	821.6	118	(000 $^2\Pi_{1/2}$)
	3	818.1	639	a
	4	817.0	804	(100 $^2\Pi_{3/2}$)
	5	816.3	909	a
	6	811.6	1618	(200 $^2\Pi_{3/2}$)
	7	810.8	1740	(200 $^2\Pi_{1/2}$)
	8	808.9	2029	a
	9	808.3	2121	(001)
	10	806.1	2459	a
	11	803.6	2845	(101)
	12	800.9	3264	(400)
	13	798.2	3687	(201)
	14	796.1	4017	(002)
	15	795.0	4191	a
	16	793.3	4460	a
$\tilde{B}$ ($^2\Sigma^+$)	1	772.8	0	000
	2	770.0	471	010
	3	768.0	809	100
$\tilde{C}$ ($^2\Sigma^+$)	1	690.5	0	000
	2	688.7	379	010
	3	686.1	929	100
	4	680.5	2128	001

a: autoionization peak

Table 5 COS^+ Data

A. Vibrational frequencies (cm^{-1})

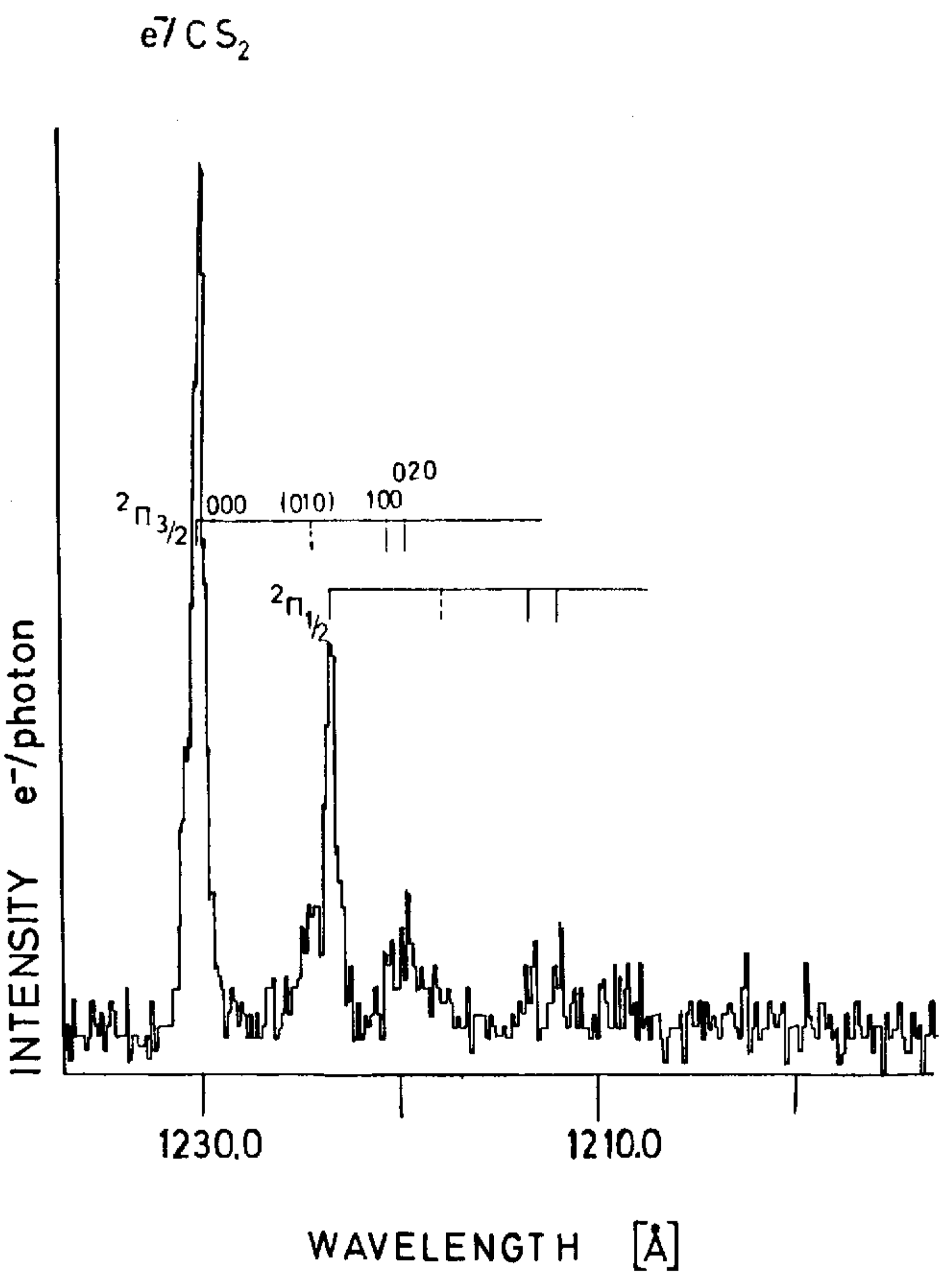
	Present work			PES (6)		
	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3
$\tilde{X}\ ^2\Pi$	685	417	2045	650		2000
$\tilde{A}\ ^2\Pi$	(804)		(2121)	790		2050
$\tilde{B}\ ^2\Sigma^+$	809	471				
$\tilde{C}\ ^2\Sigma^+$	929	379	2128	970	410	2170

B. Adiabatic ionization potentials (IP) and spin orbit splittings (A)

	Present work (IP,A)	Absorption specrtoscopy (18)	PES (6)
$\tilde{X}\ ^2\Pi$	11.190 eV, 360 cm^{-1}		11.189 eV, ~ 350 cm^{-1}
$\tilde{A}\ ^2\Pi$	15.075 eV, 118 cm^{-1}		15.08_0 eV
$\tilde{B}\ ^2\Sigma^+$	16.044 eV	16.04 eV	16.04_2 eV
$\tilde{C}\ ^2\Sigma^+$	17.955 eV	17.93	17.96_0 eV

Table 4 Fermi Resonances observed in CS_2^+

		This work (cm^{-1})	Fluorescence study (7) (cm^{-1})
$\tilde{X}\ ^2\Pi_{3/2}$	010	365	
	100-020	633, 686	617, 695
$\tilde{X}\ ^2\Pi_{1/2}$	010	349	
	100-020	646, 735	623, 703
$\tilde{A}\ ^2\Pi_{3/2}$	020-100	559, 622	549, 612
	120-200	1167, 1306	1153, 1233
	220-300	1771, 1858	1758, 1859
$\tilde{A}\ ^2\Pi_{1/2}$	020-100	572, 625	
	120-200	1214, 1343	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(010)
100
020
²Π1/2
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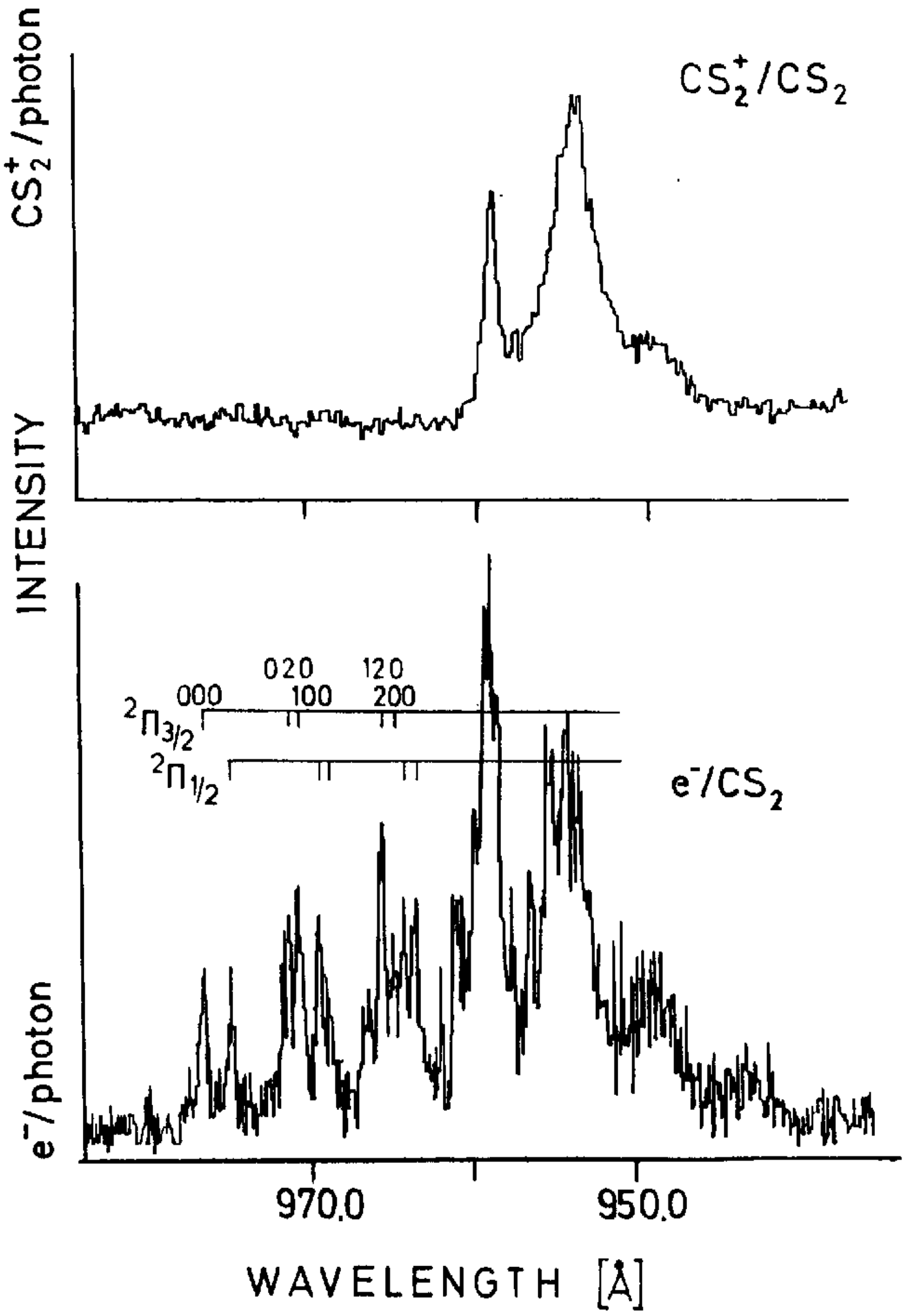
1210.0
WAVELENGTH [Å]

FIG. 1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CS₂⁺/photon
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e⁻/CS₂
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020
100
120
200
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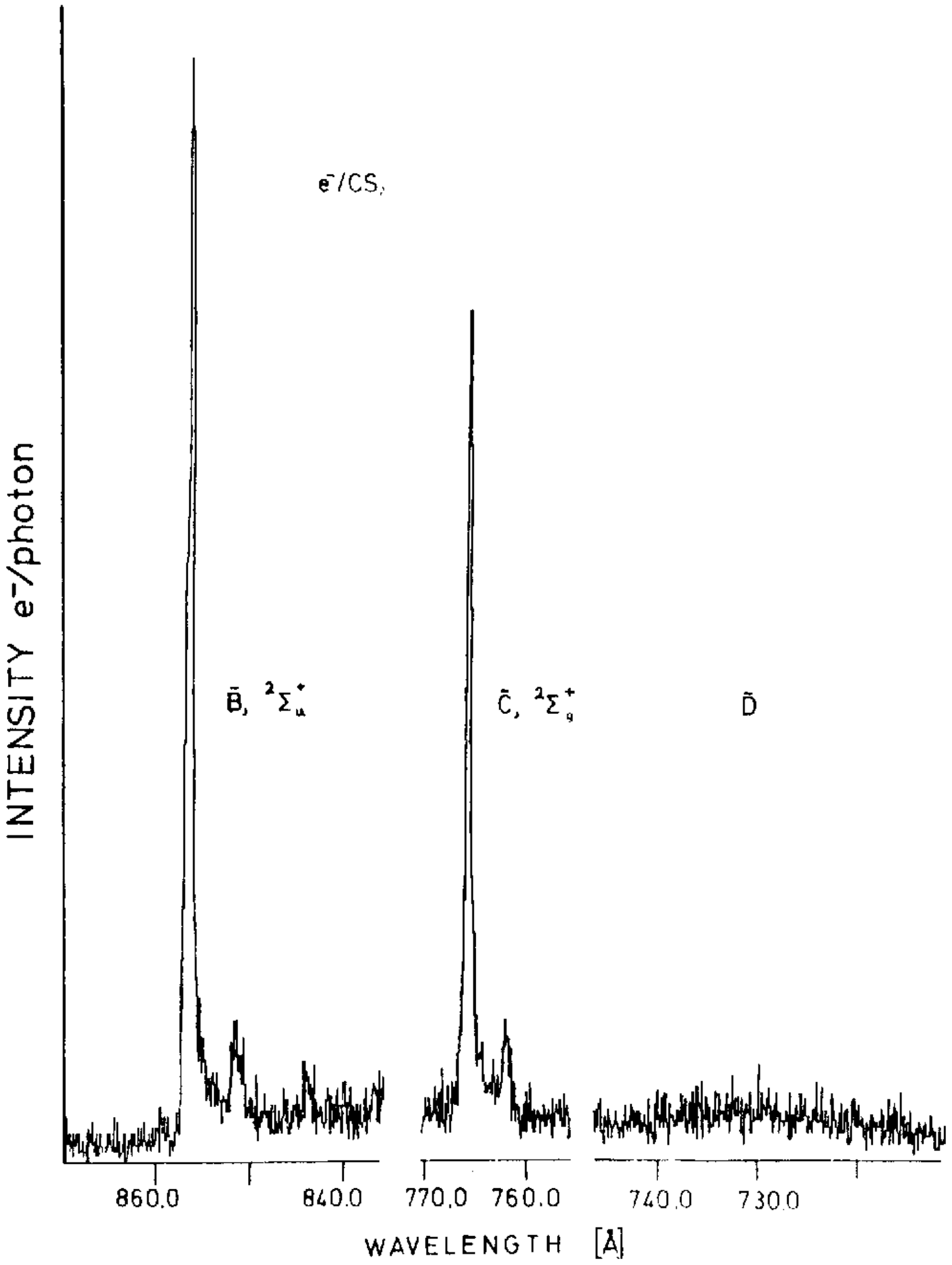
950.0
WAVELENGTH [Å]

FIG. 2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INTENSITY e⁻/photon
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C̃, ²Σ⁺g
D̃
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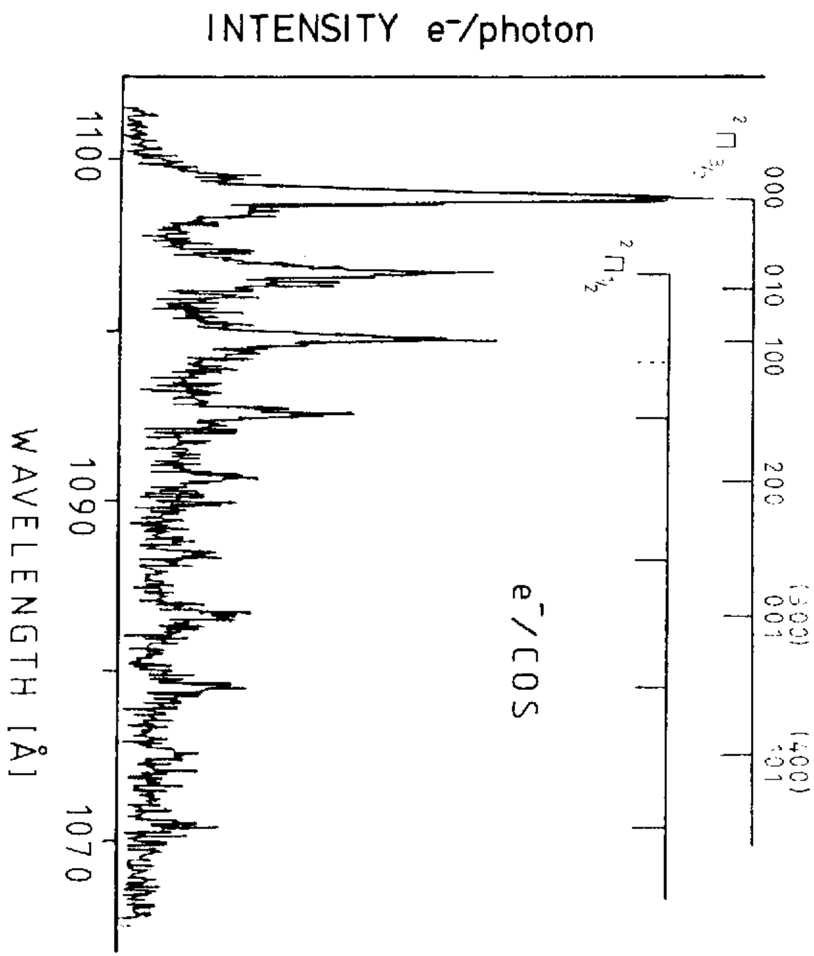
770.0
760.0
740.0
730.0
WAVELENGTH [Å]

FIG.3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WAVELENGTH [Å]
1100
1090
1070
e⁻/COS
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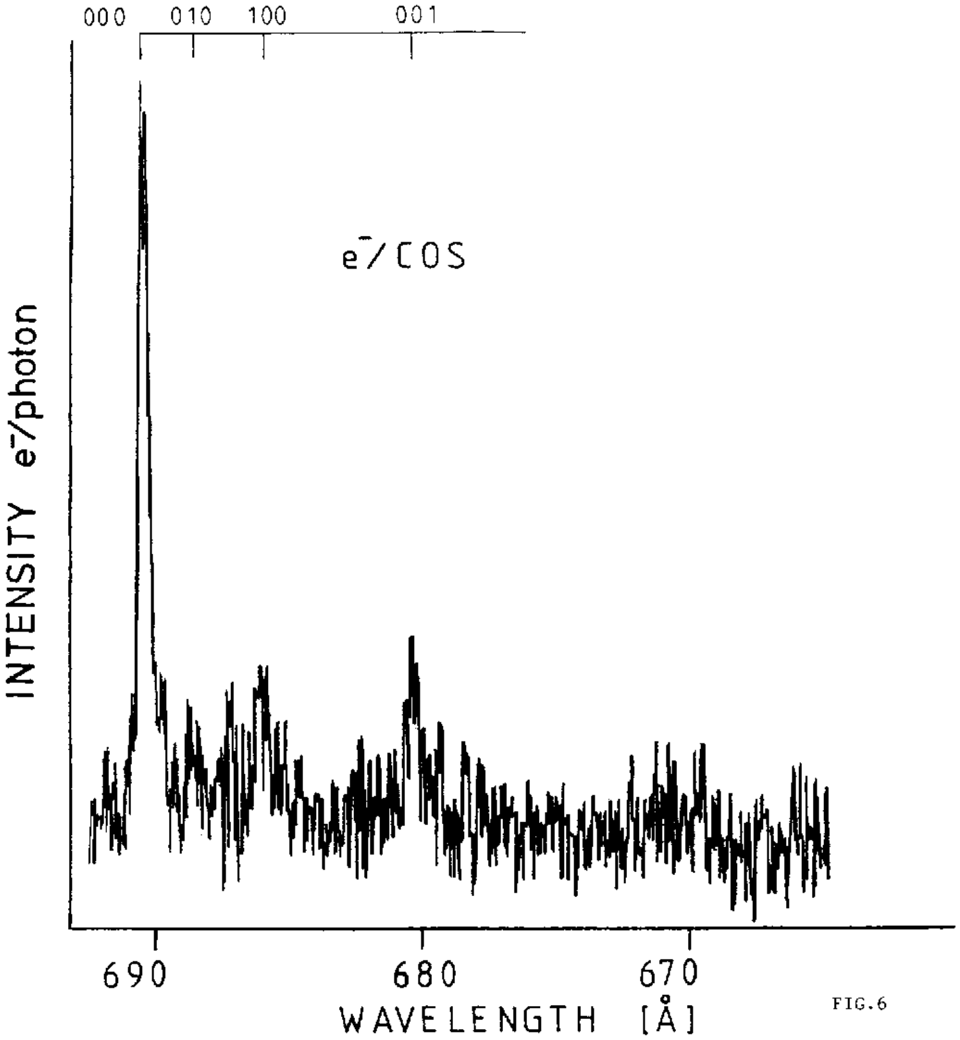
²Π1/2
000
010
100
200
(300) 001
(400) 101

FIG.4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010
100
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e⁻/COS
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680
670
WAVELENGTH [Å]

FIG.6

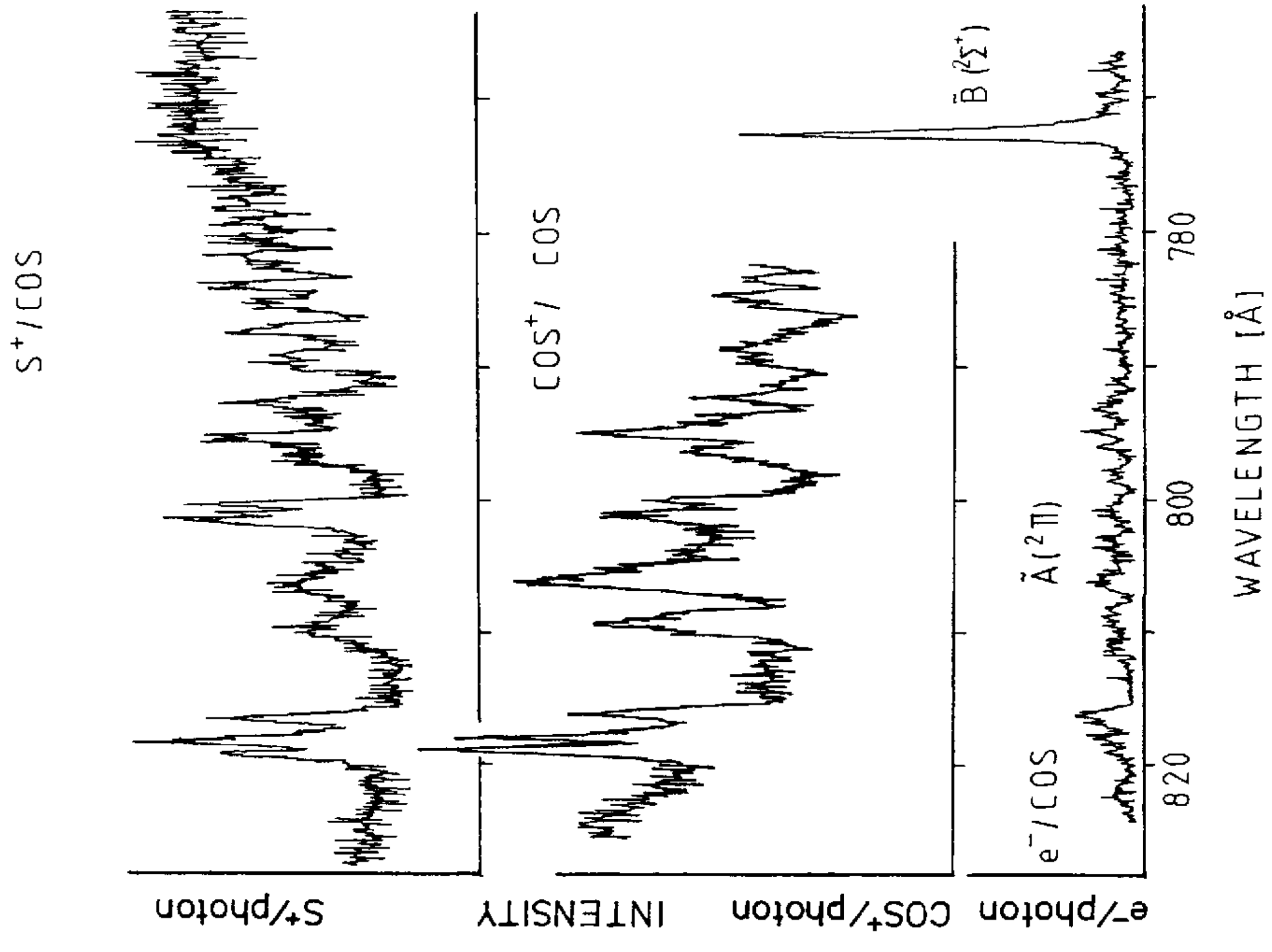
S⁺/COS
S+/photon
INTENSITY
COS⁺/ COS
COS+/photon
e⁻/COS
e⁻/photon
Ã(²Π)
B̃(²Σ⁺)
820
800
780
WAVELENGTH [Å]

FIG.5