Title

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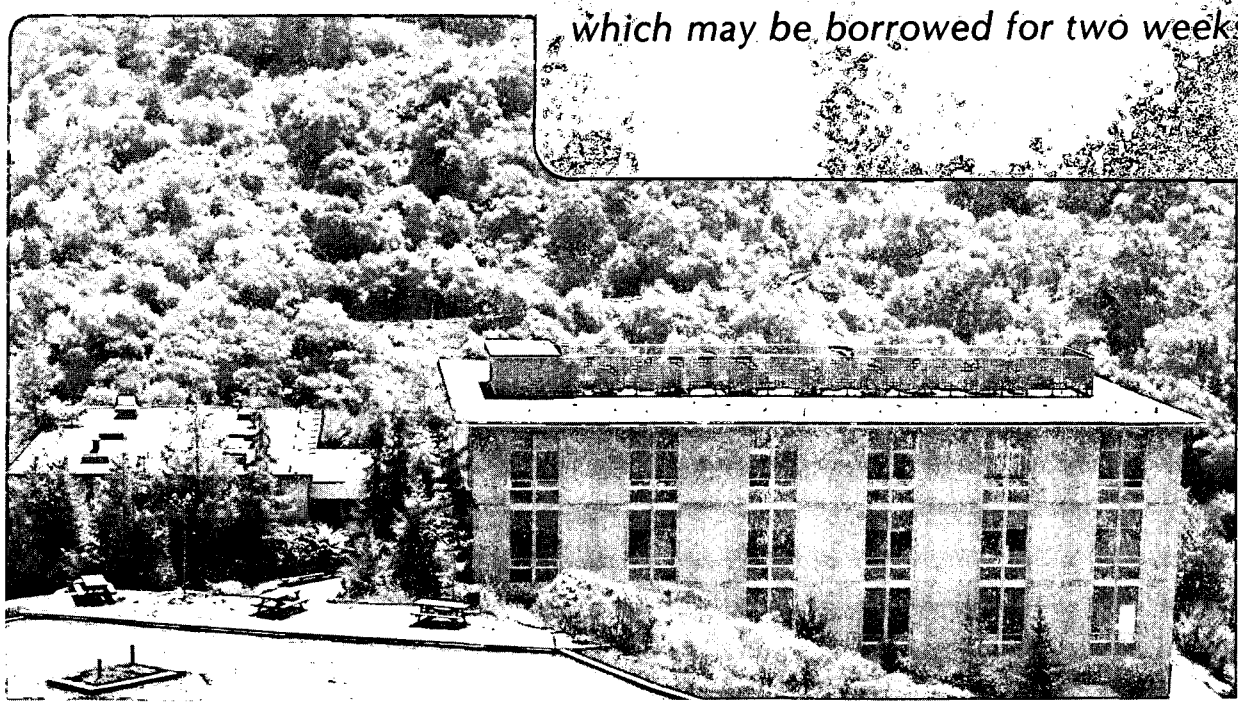

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MOLECULAR BEAM PHOTOELECTRON SPECTROSCOPY OF SO_2: GEOMETRY, SPECTROSCOPY, AND DYNAMICS OF SO_2^+

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ABSTRACT

We have reinvestigated the HeI (584A) photoelectron spectroscopy of SO_2 using a supersonic molecular beam. Improved resolution and rotational cooling allow us to observe new features and to resolve explicitly the vibrational structure in the first six electronic states, in the first three photoelectron bands. The adiabatic ionization potentials (IP's) were accurately determined for all six states. The $\tilde{X}\ ^2A_1$ ground state is assigned to the ν_2 mode exclusively. Irregularity of the vibrational progression on the high IP side was observed for the first time. A potential barrier (to linearity) is proposed to interpret the irregular vibrational spacings in the ν_2 vibration. The barrier height is estimated to be 0.42 eV (3400 cm^{-1}). The complex second band contains two states. Abnormal vibrational structure in the $\tilde{A}\ ^2A_2$ state is explained by the principal excitation of the ν_3 mode. A potential barrier is present in the ν_3 potential surface, so that the ion has an asymmetric equilibrium geometry in this state. The barrier height is estimated to be less than 220 cm^{-1}. A new progression is resolved in the $\tilde{B}\ ^2B_2$ state, which is assigned to be a combination of ν_2 with $2\nu_3$. The ν_2 vibration is observed to be strongly coupled with the ν_3 mode. The true adiabatic IP for the $\tilde{C}\ ^2B_2$ state is determined for the first time, as 15.902 ± 0.003 eV. The dynamics of the ion dissociation in this state is discussed and slow predissociations through the lower lying states are suggested. The $\tilde{D}\ ^2A_1$ and $\tilde{E}\ ^2B_1$ states are subtantially broadened above the first few vibrational levels. Fast predissociations through the $\tilde{C}\ ^2B_2$ state are proposed to account for the spectral diffuseness. A weak band at about 14.6 eV, which had been assigned as a

configuration interaction (CI) satellite band, is found to be a HeI β line (537Å) spectrum of the third band, due to the resolved vibrational structure. A true CI band at about 17.5 eV with resolved vibrational structure is observed. It consists of two ν_1 vibrational progressions, which look like two spin-orbit split components.

I. INTRODUCTION

Many experimental methods have been used to study molecular ions, because of their important role in atmospheric chemistry and physics.[1] Molecular Photoelectron Spectroscopy (PES) is intrinsically concerned with the properties and spectroscopy of molecular ions, and PES has contributed a great deal to our knowledge of these ions. Although rotationally resolved PES is only possible for the lightest diatomic molecules with a conventional photon source (HeI, 584Å),[2] sufficiently high resolution PES can still provide substantial information about the energy levels, geometries, and dynamics of the molecular ions.[3] The nonresonant mechanism of the photoionization process provides access to many electronic states of a molecular ion.

Numerous investigations have been devoted to the SO_2^+ ion, including electron impact,[4] Penning ionization,[5] absorption spectroscopy,[6] photoelectron spectroscopy,[7-13] photoelectron-photoion coincidence spectroscopy,[14,15] photoelectron-fluorescence coincidence spectroscopy,[16] and photoionization mass spectrometry.[17-21] Surprisingly, the high resolution photoelectron spectrum for this ion is still not available, and the spectroscopy of the ion in its various electronic states remains poorly understood. Even the molecular orbital order and the adiabatic ionization potentials in its different states are not completely consistent. In this paper, we report a high resolution HeI photoelectron spectrum of SO_2 using supersonic molecular beams.

Sulfur dioxide in its ground state ($\tilde{X}\ ^1A_1$) is a bent molecule (<OSO = 119.3°), with C_{2v} symmetry.[22] There are seven valence molecular orbitals,[23-26] among which six are known to be accessible to HeI radiation (584A).[7-13] The molecular orbital configuration can be represented as follows, with the bonding characters given underneath each orbital:[23]

$6a_1^2$	$2b_1^2$	$7a_1^2$	$4b_2^2$	$5b_2^2$	$1a_2^2$	$8a_1^2$
S 3s	S-O	S-O	weak	O-O σ_u	weak S-O	S
non-bonding	Π bond	σ bond	S-O bond	+ S-O	Π bond	lone pair
				weak bond		

The $8a_1$ orbital is mainly the sulfur lone pair, which is responsible for the bent geometry of the molecule. The $1a_2$ and $5b_2$ orbitals would be non-bonding based on only s and p orbitals, without considering the sulfur d orbitals. The $6a_1$ orbital is the sulfur 3s lone pair, which is generally not accessible for electrostatic type electron analyzers with HeI (584A) radiation. Therefore, photoionization by HeI can produce six electronic states of the molecular ion.[7-13] The assigned ordering of the states has not been totally consistent. The order given above is generally accepted.[9] However, for example, in a recent tabulation of HeI photoelectron spectra, Kimura et al. gave a different ordering, based on their ab initio assignment.[12]

The early HeI photoelectron spectrum of SO_2^+ was taken by Turner et al.[7], and by Eland and Danby.[8] Three bands were observed. One state was assigned to the first band, which corresponds to the ionization of the $8a_1$ orbital. Two states were assigned to the second and third bands respectively, though Eland and Danby[8] pointed out that one single peak

at 16.67 eV was observed in the third band of their spectrum and proposed that it could arise from a third state in the band. Lloyd and Roberts[9] obtained a higher resolution spectrum of the third band and found that there were indeed three states in the band, which was in agreement with theoretical predictions.[23-26] Potts[11] obtained the low resolution HeI (584A) and HeII (303.8A) spectra of SeO_2 and SO_2, trying to correlate the molecular orbitals in the two molecules. Recently, Holland, Parr, and Dehmer[13] measured the photoelectron asymmetry parameters and branching ratios for SO_2 in the 14-25 eV photon energy range by using synchrotron radiation.

The vibrational structure of the SO_2^+ PE spectrum is rather complicated, except for the first band, which was assigned to the ν_2 mode exclusively. In the second band, the state at higher IP was assigned to the ν_2 mode, but the state at lower IP was assigned in several ways; Turner et al.[7] assigned it by the ν_2 and ν_3 modes, while Eland and Danby[8] used the ν_1 and ν_2 modes. Cederbaum, Domcke, Niessen, and Kraemer[27] called the vibrational structure in this band "a difficult assignment problem" and performed an ab initio many-body calculation on the vibrational structures for the first two bands ($\tilde{X}\ ^2A_1$, $\tilde{A}\ ^2A_2$, and $\tilde{B}\ ^2B_2$ states). The $\tilde{X}$ and $\tilde{B}$ states seemed to be well reproduced with the ν_2 mode only. They used the ν_1 and ν_2 modes to calculate the $\tilde{A}\ ^2A_2$ state. The result was less conclusive, because the experimental spectrum was not well resolved.[7,8] The third band of the spectrum is even more complicated, due both to the heavy overlapping of the last three states and to the band diffuseness.

A molecular beam photoionization study of SO_2 was reported by Erickson and Ng.[20] They obtained the photoionization efficiency (PIE) curves for SO_2^+, SO^+, and S^+. The first IP for SO_2 was accurately determined to be 12.348 ± 0.002 eV. The onsets for the photodissociative ionization processes $SO_2 + h\nu \rightarrow SO^+ + O + e^-$ and $\rightarrow S^+ + O_2 + e^-$ were measured to be 15.953 ± 0.010 eV and 16.228 ± 0.030 eV respectively. They observed a complicated PIE curve for SO_2^+ in the 987-1006 A range corresponding to the first band in the PE spectrum, from which they concluded that "the irregular spacing observed in the PIE curve rules out any simple assignment of the first photoelectron band to the ν_2 bending mode of SO_2^+".

The relaxation of the SO_2^+ ion has also been the topic of several research papers by different coincidence techniques.[14-16] An early photoelectron-photoion coincidence measurement showed that the dissociation of SO_2^+ ion in the third band could not be explained by either a statistical model or a model of direct dissociation.[14] A threshold photoelectron-photoion coincidence study revealed that the S^+ formation occurred only in a very narrow energy range above the threshold.[15] A photoion-fluorescence photon coincidence study of radiative and dissociative relaxation processes in VUV photoexcited SO_2[16] showed that emission from electronic states lying above the dissociation threshold could be observed; that is, the radiative decay was competitive with the nonradiative decay or dissociation.

Although there have been many experimental studies on the SO_2^+ ion, few theoretical studies have been reported.[23,27] There has not been any

recent study. We hope that our high resolution PES study can spur more theoretical work on this ion.

In what follows, we will give in Sec. II a brief account of the experimental technique. The results will be presented in Sec. III. The discussion for the individual state and the summary will be given in Sec. IV and Sec. V respectively.

II. EXPERIMENTAL

The molecular beam photoelectron spectrometer used for this study has been described in detail before.[28] Briefly, the supersonic SO_2 molecular beam was crossed perpendicularly by a photon beam from a rare gas discharge lamp. The electron energy analyzer consisted of a double eletrostatic deflector operated at a pass energy of 1.0 eV, which sampled the photoelectrons at an angle of 90° with respect to both the photon beam and the molecular beam. The complete HeI (584A) photoelectron spectrum of SO_2 (Matheson, Anhydrous Grade, 99.98%), expanded from 200 torr at room temperature through a 100 μm dia. nozzle and skimmed by a 0.9 mm dia. conical skimmer, was recorded with multichannel detection at a resolution of 13 meV FWHM, as measured on Ar^+ ($^2P_{3/2}$).

III. RESULTS

The complete HeI photoelectron spectrum of SO_2 is plotted in Fig. 1, with state labellings shown. The improved resolution and rotational cooling permit the vibrational structure in all the states to be explicitly resolved. Besides the three main bands, two other weak bands at about 14.6 and 17.5 eV are also observed, with resolved vibrational structure. They were assigned as two CI bands in a previous study.[12] An impurity peak of the $\tilde{X}\ N_2^+$ (v=0) is observable in the spectrum at 15.6 eV. The $\tilde{B}\ ^2\Pi_u$ state of N_2^+ should be around 17.0 eV, but the intensity is negligible. Therefore, the SO_2^+ spectrum is not affected. In Table I, the adiabatic IP's of the first six states of SO_2^+ are given and compared with previous measurements where available, and the mean peak positions in all the states are listed in Tables II-VII. Our adiabatic IP for the ground state is in excellent agreement with the value obtained by Erickson and Ng.[20] We note that the first peak in the ground state does not represent the adiabatic IP. As already pointed out by Erickson and Ng, it is a hot band transition. This was confirmed by changing the SO_2 stagnation pressure in the supersonic expansion. From Table II, it is seen that the interval ($515 \pm 3\ cm^{-1}$) between the first and the second peak corresponds exactly to the fundamental ν_2 in the ground state SO_2 ($517.7\ cm^{-1}$).[29] It can be seen from Table I that all the previous PES determinations of the adiabatic IP were actually from the hot band. The onset of the third band represents another interesting situation, where the true adiabatic transition to the $\tilde{C}\ ^2B_2$ state is observed for the first time in the

current spectrum. All previous measurements failed to observe the first peak in this band. The adiabatic IP determined for the $\tilde{C}\ ^2B_2$ state in the present study is 15.902 ± 0.003 eV. As shown in Table I, this value is considerably lower than the previously measured values.

The vibrational assignment and the discussion for the individual states are presented in the next Section.

IV. DISCUSSION

a. The First Band [$\tilde{X}\ ^2A_1$ ($8a_1^{-1}$) state]

The separated spectrum of this band is shown in Fig. 2. The band contains only one state, which is formed by ionizing the outmost $8a_1$ orbital of SO_2. The vibrational structure is completely resolved in Fig. 2. Erickson and Ng[20] observed a rather complicated structure in their PIE curve of SO_2^+, and concluded that it was impossible to make a simple assignment of this band in the PE spectrum to the ν_2 bending mode. However, the well-developed vibrational progression in our spectrum must be ν_2, as assigned in the previous PES spectra.[7,8] The complicated structure that Erickson and Ng observed in the PIE curve may be due to autoionizations. Our derived vibrational intervals, $\Delta G(v_2+1/2)$, are listed in Table II, and are plotted in Fig. 3 as a function of v_2. The vibrational spacings are regular up to $v_2 = 7$, with a positive anharmonicity. A least-squares fit over this range yields the following spectroscopic constants for ν_2: $\omega_e = 404 \pm 1\ cm^{-1}$, $\omega_e\chi_e = 1.5 \pm 0.3\ cm^{-1}$. However, the spacings become irregular above $v_2 = 7$. This suggests that the photoionization transition reaches to the top of the potential barrier (to linearity) in the ν_2 double-well potential. The potential barrier seriously perturbs the vibrational levels around the barrier maximum. Essentially, a frequency halving will be observed far above the barrier maximum, as is the case in H_2S^+ ($\tilde{A}\ ^2A_1$)[30] and the first band of NF_3^+.[31] An irregular vibrational structure will be observed as the transition approaches the barrier maximum. This, in

turn, allows an estimation of the barrier height. If we assume that the $v_2 = 9$ level lies just above the barrier, we estimate the barrier height to be 0.42 eV (3400 cm^{-1}) above the zero point energy. For the counterpart state in O_3^+, Dyke, Golob, Jonathan, Morris, and Okuda[32] observed a complex vibrational structure at the beginning of the band. They estimated a barrier height to be 1880 cm^{-1}. Although their assignment for the onset of the state has been questioned,[20] we believe that the assumption of a potential barrier is reasonable.

b. The Second Band [$\tilde{A}\ ^2A_2$ ($1a_2^{-1}$) and $\tilde{B}\ ^2B_2$ ($5b_2^{-1}$) states]

An expanded spectrum of this band is shown in Fig. 4. It is complex, but the vibrational structure is well resolved. On the high energy side , a ν_2 progression is observed, as assigned before.[7,8] Another progression with weak intensity is also resolved in the current spectrum, which was not observed in previous studies.[7-13] The low energy side of the band is much more complicated. Both the previous experiments[7,8] and theoretical calculations[23,27] agreed that this band contained two overlapping states formed by ionizing $1a_2$ and $5b_2$ orbitals. For the first state ($\tilde{A}\ ^2A_2$), Turner et al.[7] obtained an adiabatic IP of 12.98 eV, while Eland and Danby determined a value of 13.01 eV.[8] At the onset of the band, two small features are resolved in the current spectrum, and the adiabatic IP for the $\tilde{A}\ ^2A_2$ state is measured to be 12.988 ± 0.005 eV. The second state should apparently be the well-developed progression at the high energy side. Turner et al.[7] were not sure where the progression started and did not determine the

adiabatic IP, while Eland and Danby[8] obtained an adiabatic IP of 13.24 eV by assuming that two components of the $\tilde{B}\ ^2B_2$ state overlapped with the $\tilde{A}\ ^2A_2$ state. In our high resolution spectrum, we cannot find any peak or shoulder around 13.24 eV. Instead, we assign the overlapping peak at 13.338 eV as the first component of the $\tilde{B}\ ^2B_2$ state and obtain an adiabatic IP of 13.338 ± 0.004 eV.

The $\tilde{A}\ ^2A_2$ state will be discussed first. This state was not completely resolved before, and no definite assignment is available. Turner et al.[7] used the combination of ν_2 and $2\nu_3$ to assign the spectral features, while Eland and Danby[8] assigned it using ν_1 and ν_2. Cederbaum et al.[22] noticed this "difficult assignment problem" and did a many-body ab initio calculation. They used the vibrational constants reported by Eland and Danby[8] to model a vibrational spectrum. Though this approach produced an irregular vibrational structure, it could not be conclusive, because the experimental resolution was limited (0.035 eV). In fact, it failed to reproduce the small features at the onset of this state that are observed in our spectrum. The spacing between these two weak peaks is 202(13) cm^{-1}. The spacing between the second peak and the third sharp peak is 243(9) cm^{-1}. Neither of these can be ν_1 or ν_2. It is apparent that there are two ν_2 progressions starting at the third peak and at the most intense peak (i.e., at the peaks labeled 002 and 004 in Fig. 4). The spacing between these two progressions is 1467(2) cm^{-1}. This must correspond to $2\nu_3$. Turner et al.[7] did not resolve the first two weak peaks, so they assigned the spacing between the first peak and the most intense peak to be $2\nu_3$ and obtained a $2\nu_3$ value of 1860 cm^{-1}. The ν_3 is an asymmetric vibrational mode, and only the even quantum

levels are vibronically allowed.[33] The intensities of such a vibrational mode are normally very low, unless there is a big change of geometry or vibrational frequency in the ionic state.[33] The unusually intense ν_3 transition in the $\tilde{A}\ ^2A_2$ state here suggests that the $\tilde{A}\ ^2A_2$ state must have been significantly distorted along the ν_3 coordinate. The first two features of the state should be also taken into accunt and they should be two early members of the ν_3 vibration. Therefore, the ν_3 mode has rather erratic vibrational levels, suggesting that a potential barrier exists in the potential surface along the ν_3 coordinate. This potential barrier separates two equivalent unsymmetric SO_2^+ ions with the two S-O bonds being unequal (C_s symmetry). The unusual small spacings of ν_3 at the beginning of the progression is consistent with being around the barrier maximum. Assuming that only the first level is below the barrier maximum, we estimate the barrier height to be less than 202 cm^{-1}. The ion is essentially still symmetric above the ground vibrational state, since the potential barrier is so low that with only one quantum of the vibrational energy the ion can overcome the barrier and vibrate back and forth between the two equivalent unsymmetric configurations separated by the potential barrier. A similar situation was observed in the electronic absorption spectrum of SO_2 for the transition $\tilde{C}^1B_2 \leftarrow \tilde{A}^1A_1$ $[b_1(\pi^*) \leftarrow 1a_2(\pi)]$, where an electron was excited from the $1a_2$ orbital to the b_1 antibonding orbital.[34] The spectrum was very complicated and the interpretation involved assuming a double well potential along the ν_3 coordinate. Therefore, the equilibrium geometry of SO_2 in the $\tilde{C}\ ^1B_2$ state was unsymmetric. A subsequent theoretical treatment[35] yielded the barrier height to be 141 cm^{-1} and the

equilibrium values of the short and long S-O bonds to be 1.491A and 1.639A respectively (compared with 1.4321A for the SO_2 ground state[29]). The calculated energy levels for the ν_3 mode were $1\nu_3$ = 211 cm^{-1}, $2\nu_3$ = 562 cm^{-1}, $3\nu_3$ = 891 cm^{-1}, and $4\nu_3$ = 1249 cm^{-1}, which are comparable to the ν_3 energy levels for SO_2^+ ($\tilde{B}\ ^2A_2$) observed in our spectrum, as seen from Table III. As a matter of fact, Jaffé[36] has treated the nonrigid SO_2 molecule in the $\tilde{C}\ ^1B_2$ state by classical mechanics and reassigned the observed vibrational structure of the $\tilde{C}\ ^1B_2 \leftarrow \tilde{X}\ ^1A_1$ electronic transition by a set of local modes and normal modes. The $\tilde{C}\ ^1B_2$ state of SO_2 and the $\tilde{A}\ ^2A_2$ state of SO_2^+ should have similar properties, since both involve removing an electron from the same orbital ($1a_2$).

The $\nu_3 = 1$ level is a vibronically forbidden transition without any vibronic interaction.[33] Such a transition was also observed in other molecules.[37] The ν_1 mode must also be taken into account in order to make a thorough assignment for this state. The complete assignment is shown in Fig. 4, and the IP's and vibrational intervals are listed in Table III. The $\nu_3 = 3$ transition may also contribute to the broad feature at 13.11 eV.

The assignment for the $\tilde{B}\ ^2B_2$ state is straightforward. Both Turner et al.[7] and Eland and Danby[8] assigned this state with a pure ν_2 vibration. The calculation of Cederbaum et al. with a pure ν_2 mode reproduced this state well.[27] Moreover, their calculated band maximum agrees with our assignment. The derived $\Delta G(v_2+1/2)$ values are listed in Table IV. A least-squares fitting of $\Delta G(v_2+1/2)$ vs v_2 yields the following spectroscopic constants: ω_e = 489 ± 5 cm^{-1}, $\omega_e\chi_e$ = 2 ± 1 cm^{-1}. However, it can be seen from Table IV or Fig. 5 that the vibrational

intervals do not decrease monotonically as a function of v_2 within the experimental uncertainty.

A new progression with relatively low intensity is resolved for the $\tilde{B}\ ^2B_2$ state in Fig. 4. This is another ν_2 progression, which should be a combination of ν_2 with either ν_1 or ν_3. The difference between this progression and the main progression is 1223 cm^{-1}, which cannot be ν_1 (1151.3 cm^{-1} for SO_2[29]). We assign it to be $2\nu_3$ since $1\nu_3$ is normally forbidden.[33] The fact that the ν_3 mode is active suggests that the $\tilde{B}\ ^2B_2$ state is also somehow distorted along the ν_3 coordinate. Since the $\tilde{B}\ ^2B_2$ and $\tilde{A}\ ^2A_2$ states are formed by ionizing $1a_2$ and $5b_2$ orbitals, both of which are originated from the S d-orbital bonding, there is no surprise that the two states have some similar characteristics. They are both distorted along both ν_2 and ν_3 coordinates, and both have very different geometries from the ground state. The $\tilde{A}\ ^2A_2$ state is distorted more along the ν_3 coordinate, and the $\tilde{B}\ ^2B_2$ state is distorted more along the ν_2 coordinate. Therefore, from the Franck-Condon principle, the major vibrational progression should be ν_3 for the $\tilde{A}\ ^2A_2$ state, and ν_2 for the $\tilde{B}\ ^2B_2$ state. However, it is not clear from our spectrum whether the $\tilde{B}\ ^2B_2$ state also has an asymmetric equilibrium geometry like the $\tilde{A}\ ^2A_2$ state. From the fact that the ν_2 mode in the $\tilde{B}\ ^2B_2$ state has an abnormal spacing dependence with v_2, it is clear that the ν_3 mode couples with the ν_2 mode in the $\tilde{B}\ ^2B_2$ state so that the ν_2 mode differs from a normal anharmonic oscillator, as shown in Fig. 5.

c. The Third Band [$\tilde{C}\ ^2B_2$ ($4b_2^{-1}$), $\tilde{D}\ ^2A_1$ ($7a_1^{-1}$), and $\tilde{E}\ ^2B_1$ ($2b_1^{-1}$)]

This band is shown separately in Fig. 6. The spectrum is diffuse at the high IP side, which makes the assignment more difficult. In the early PES studies of SO_2^+, some inconsistency arose about the number of states in the band. Turner et al.[7] and Eland and Danby[8] assigned only two states in their early studies. It was Lloyd and Roberts[9] who first assigned the third state from a higher resolution study. Their assignment was $\tilde{C}\ ^2B_2$, $\tilde{D}\ ^2A_1$, $\tilde{E}\ ^2B_1$, obtained by comparing their experimental evidence with Hillier and Saunders's ab initio SCFMO calculation.[23]

For the $\tilde{C}\ ^2B_2$ state, both ν_1 and ν_2 modes are excited. As pointed out earlier, we observed the true adiabatic transition for this state. This allows us to observe ν_1 up to $v_1 = 8$, which we believe is the complete Franck-Condon region for the $\tilde{C}\ ^2B_2$ state. The derived vibrational intervals, $\Delta G(v_1+1/2)$, are shown in Table V. A least-squares fit of $\Delta G(v_1+1/2)$ vs v_1 yields the following spectroscopic constants for ν_1: $\omega_e = 816 \pm 3\ cm^{-1}$, $\omega_e\chi_e = 3 \pm 0.5\ cm^{-1}$. The average ν_2 value is $365 \pm 3\ cm^{-1}$. The $\tilde{D}\ ^2A_1$ and $\tilde{E}\ ^2B_1$ state are assigned with the ν_1 mode only. It is difficult to make a thorough assignment, and to find the spectroscopic constants for these two states by the routine least-squares fitting method, since the spectrum becomes rather diffuse toward the high energy side. The vibrational spacings which can be determined are listed in Table VI.

The broadened spectrum indicates fast dynamic processes occuring in this band. The dissociation limits of SO_2^+ to form $SO^+ + O$ and $S^+ + O_2$ in their ground states are 15.95 eV and 16.23 eV respectively.[20] These are the only two dissociation channels which can occur in this band. Three

accounts have been given of the dissociation mechanisms for the ion.[14-16] From their threshold photoelectron-photoion coincidence experiment, Weiss, Hsieh, and Meisels[15] observed that S^+ was only formed in a very narrow energy range between 16.334-16.674 eV and that SO_2^+ became fully predissociated above about 16.67 eV in this band. They explained the formation of SO^+ and S^+ by using a vibrational predissociation model in the $\tilde{C}\ ^2B_2$ state. Dujardin and Leach[16] made a photoion-fluorescence photon coincidence measurement and concluded that S^+ could not be formed in the $\tilde{C}\ ^2B_2$ state, but must come from a higher state. They observed fluorescence in coincidence with SO_2^+ in the third band with a small quantum yield.

It has been shown that a high resolution photoelectron spectrum can be useful in understanding the ultrafast dynamics of a molecular ion, through the correlation functions obtained by Fourier transformations of the individual electronic bands in the photoelectron spectrum.[3b,37,38] In the case of the third band of SO_2^+, the strong overlapping of the three electronic states precludes obtaining the correlation functions. However, the dynamical information that a photoelectron spectrum carries does not depend on the correlation functions. In high resolution PES, the instrumental function limits the time scale on which the ultrafast dynamics can be measured. With an instrumental resolution of 13 meV, we obtain an upper limit of 51 fs for this time scale from the time-energy uncertainty principle. In other words, any state with a lifetime shorter than 51 fs will broaden the spectrum. Therefore, the spectral diffuseness signals the presence of ultrafast processes, from which the dynamics can be inferred.

In the third band of SO_2^+, the spectrum becomes considerably broadened above about 16.7 eV, which means the ultrafast dissociation starts around 16.7 eV. The spectrum below 16.7 eV essentially represents the instrumatal resolution, indicating that the states below 16.7 eV have lifetimes longer than 51 fs, that is, the $\tilde{C}$ state is relatively stable as it covers this whole range. This is consistent with the observation of fluorescence from this region of the spectrum, which gave a lifetime of less than 10 ns.[16] This also agrees with Weiss et al.'s experiment,[15] which shows that SO_2^+ is completely predissociated above 16.67 eV.[15] However, it has been observed that the ion does dissociate from the $\tilde{C}\ ^2B_2$ state, and various interpretations[14-16] have been given to the dissociation mechanisms. The ion can not directly dissociate through this state, since that would require the $\tilde{C}\ ^2B_2$ state to have a very shallow potential well.[16] Therefore, the dissociations from the $\tilde{C}$ state have to proceed through the lower lying states, by electronic predissociations. Because SO_2^+ is a small molecule and there is a big $\tilde{C}$-$\tilde{B}$ state energy gap, these predissociations are unfavored. It is these unfavored processes that actually lengthen the lifetime of the state so that the fluorescence is competitive with the predissociations.

The combination of the $SO^+(\tilde{X}^2\Pi) + O(^3P_g)$ product states can lead to twelve states in the C_s molecular symmetry. These twelve states [$3(^{2,4}A')$ and $3(^{2,4}A'')$] can correlate, in the C_{2v} point group, with all four possible species A_1, A_2, B_1, and B_2. We propose that the formation of $SO^+ + O$ occurs through a predissociation by the $\tilde{A}\ ^2A_2$ state, which possesses an asymmetric ground state geometry favorable to the asymmetric dissociation. However, in the formation of $S^+ + O_2$, the

whole molecular symmetry (C_{2v}) is retained, and combination of the products in their ground states yields states of $^{6,\ 4,\ 2}B_2$ symmetry. Therefore, the dissociation to $S^+ + O_2$ must be through a predissociation of the $\tilde{C}\ ^2B_2$ state by the $\tilde{B}\ ^2B_2$ state, which is observed to be strongly deformed along the ν_2 vibration favorable to form $S^+ + O_2$. As Weiss et al. originally[15] proposed, S^+ is produced entirely from the $\tilde{C}\ ^2B_2$ state. From our spectrum, this would explain why S^+ was only observed in a narrow energy range, since it is simply out of the Franck-Condon region of the $\tilde{C}$ state above 16.67 eV.

The $\tilde{D}$ and $\tilde{E}$ states are resposible for the fast dissociations above 16.7 eV, as evidenced by the spectral diffuseness. In the lack of any theoretical calculation, the only dissociation pathway we can suggest would be predissociations through the $\tilde{C}\ ^2B_2$ state, since the spectral feature precludes any direct dissociation model.

d. The CI Bands

Two weak bands which occur at about 14.6 and 17.5 eV were interpreted by Kimura et al. as two CI bands.[12] Vibrational structure is resolved in the current spectrum, as seen from Fig. 1 and Fig. 6. It turns out that the band at 14.6 eV is the HeI β line spectrum of the third band. The band at 17.5 eV must be a true CI band, because the $\tilde{F}\ ^2A_1$ state is at 20.06 eV[9,11] and the β line spectrum would occur at a higher energy. CI bands are well known in the phtoionization of the inner shell electrons for the first and second row molecules,[39] and CI bands in the valence region have been observed in other third row

molecules.[40] The band we observed consists of two ν_1 vibrational progressions which may be two components of a spin-orbit split state. The energies and spacings are listed in Table VII. Autoionization was proposed for this band,[11] but the sharpness of the vibrational structure excludes this possibility.

V SUMMARY

Our high resolution PES study of SO_2 using supersonic molecular beams allows accurate adiabatic IP's for the first six states of SO_2^+ to be determined. The vibrational structure is explicitly resolved in all observed states. The $\tilde{X}\ ^2A_1$ state is assigned to ν_2 vibrations exclusively. A potential barrier is proposed to interpret the irregular vibrational structure on the high energy side. The barrier height for the $\tilde{X}\ ^2A_1$ state is estimated to be 0.42 eV (3400 cm^{-1}). The complex second band contains two states. The abnormal vibrational structure in the $\tilde{A}\ ^2A_2$ state is explained by the distortion motion along the ν_3 coordinate upon photoionization, which makes the ν_3 mode the principal vibration in the state. A potential barrier exists along the ν_3 coordinate, so that the ion has an asymmetric equilibrium geometry. The barrier height for the $\tilde{A}$ state is estimated to be less than 220 cm^{-1}. A new progression is resolved in the $\tilde{B}\ ^2B_2$ state, which is assigned to be the combination of ν_2 with $2\nu_3$. The true adiabatic IP for the $\tilde{C}\ ^2B_2$ state is determined in the first time to be 15.902 ± 0.003 eV. The decay of this state is discussed and predissociations through the lower lying states are suggested. The spectrum above 16.7 eV is much broadened, suggesting that rapid dissociations occur from the $\tilde{D}\ ^2A_1$ and $\tilde{E}\ ^2B_1$ states. Predissociations by the $\tilde{C}\ ^2B_2$ state are proposed.

We believe that more sophisticated calculations are desirable to compare with the experimantal observations, in order to gain a quantitative understanding of the geometry, spectroscopy, and dynamics of the SO_2^+ ion.

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Table I. Adiabatic ionization potentials of the first seven electronic states of SO_2^+ (eV).

	$\tilde{X}\ ^2A_1$	$\tilde{A}\ ^2A_2$	$\tilde{B}\ ^2B_2$	$\tilde{C}\ ^2B_2$	$\tilde{D}\ ^2A_1$	$\tilde{E}\ ^2B_1$	$\tilde{F}\ ^2A_1$
a	12.349(3)	12.988(5)	13.338(4)	15.902(3)	16.339(3)	16.507(3)	
b	12.29	12.98		15.97	16.33		
c	12.30	13.01	13.24	15.986	16.326	(16.7)	
d				15.992	16.324	16.498	20.06
e	12.348(2)						

a. This work.

b. Turner et al. From reference 7.

c. Eland and Danby. From reference 8.

d. Lloyd and Roberts. From reference 9.

e. Erickson and Ng. From reference 20.

Table II. Ionization potentials (eV), vibrational frequencies (cm^{-1}) and the assignment for the $\tilde{X}\ ^2A_1$ state of SO_2^+.

IP	assignment[a]	$\Delta G(v_2+1/2)$
12.2856(7)[b]	2_0^1 hot band	
12.3494(2)	0 0 0	515(3)
12.3995(2)	0 1 0	404.2(0.5)[c]
12.4493(2)	0 2 0	401.8(0.5)[c]
12.4985(2)	0 3 0	396.9(0.5)[c]
12.5474(2)	0 4 0	394.5(0.5)[c]
12.5960(2)	0 5 0	392.1(0.5)[c]
12.6443(2)	0 6 0	389.7(0.5)[c]
12.6923(2)	0 7 0	387.3(1.0)[c]
12.7382(4)	0 8 0	370.3(2)
12.7697(9)	0 9 0	254.1(8)
12.7878(10)	0 10 0	146.0(11)

a. The assignment is labelled with the quantum numbers of ν_1, ν_2, ν_3.

b. The uncertainties of the absolute IP'S are ± 0.003 eV. The smaller uncertainties quoted refer to the relative positions of the transitions, which are used to calculate the uncertainties for the vibrational splittings.

c. Values used in the least-squares fitting.

Table III. Ionization potentials (eV), vibrational frequencies (cm^{-1}) and the assignment for the $\tilde{A}\ ^2A_2$ state of SO_2^+.

IP	assignment[a]	ν_1	$\Delta G(v_2+1/2)$	ν_3
12.9884(21)[b]	0 0 0			
13.0134(21)	0 0 1			202(13)
13.0435(6)	0 0 2			243(9)
13.0873(10)	0 1 2		353(7)	
13.1100(82)	1 0 0	981(60)		
13.1255(98)	1 0 1	904(71)		
13.1436(33)	0 2 2		452(15)	
13.1730(19)	1 0 2	1045(10)		
13.1894(80)	0 3 2		370(60)	
13.2253(6)	0 0 4			1466.8(1.4)[c]
13.2749(6)	0 1 4		400.2(1.6)	
13.3236(23)	0 2 4		393(18)	
13.3569(8)	1 0 4	1062(5)		
13.3730(13)	0 3 4		399(9)	
13.4120(31)	0 4 4		315(12)	

a. The assignment is labelled with the quantum numbers of ν_1, ν_2, ν_3.

b. See (b) in Table II.

c. $2\nu_3$ value.

Table IV. Ionization potentials (eV), vibrational frequencies (cm^{-1}) and the assignment for the $\tilde{B}\ ^2B_2$ state of SO_2^+.

IP	assignment[a]	$\Delta G(v_2+1/2)$	$2\nu_3$
13.3384(12)[b]	0 0 0		
13.3960(7)	0 1 0	465(9)	
13.4578(6)	0 2 0	499(4)	
13.4900(50)	0 0 2		1223(13)
13.5169(7)	0 3 0	477(1)	
13.5503(10)	0 1 2		1245(8)
13.5775(6)	0 4 0	489(1)	
13.6131(31)	0 2 2		1253(24)
13.6360(6)	0 5 0	472(2)	
13.6657(7)	0 3 2		1201(3)
13.6952(6)	0 6 0	478(2)	
13.7279(8)	0 4 2		1213(5)
13.7538(6)	0 7 0	473(2)	
13.7856(7)	0 5 2		1207(5)
13.8113(6)	0 8 0	464(2)	
13.8459(9)	0 6 2		1216(6)
13.8700(7)	0 9 0	474(2)	
13.9059(9)	0 7 2		1227(7)
13.9277(8)	0 10 0	466(2)	
13.9611(14)	0 8 2		1209(10)
13.9826(15)	0 11 0	443(12)	

14.0232(34)	0 9 2		1236(15)
14.0309(20)	0 12 0	390(20)[c]	
14.0800(140)	0 10 2		1229(43)
14.0891(150)	0 13 0	470(45)[c]	

a. The assignment is labelled with the quantum numbers of ν_1, ν_2, ν_3.

b. See (b) in Table II.

c. Values not used in the least-squares fitting.

Table V. Ionization potentials (eV), vibrational frequencies (cm^{-1}), and the assignment for the $\tilde{C}\ ^2B_2$ state of SO_2^+.

IP	assignment[a]	$\Delta G(v_1+1/2)$	ν_2
15.9020(9)[b]	0 0 0		
15.9480(13)	0 1 0		371(10)
16.0012(8)	1 0 0	800(4)	
16.0468(8)	1 1 0		368(4)
16.1011(8)	2 0 0	806(2)	
16.1460(8)	2 1 0		362(2)
16.1999(8)	3 0 0	797(2)	
16.2441(8)	3 1 0		357(2)
16.2983(7)	4 0 0	794(1)	
16.3956(7)	5 0 0	785(1)	
16.4922(10)	6 0 0	779(5)	
16.5860(80)	7 0 0	757(20)[c]	
16.6240(50)	7 1 0		310(46)

a. The assignment is labelled with the quantum numbers of ν_1, ν_2, ν_3.

b. See (b) in Table II.

c. Value not used in the least-squares fitting.

Table VI. Ionization potentials (eV), vibrational frequencies (cm^{-1}) and the assignment for the $\tilde{D}\ ^2A_1$ and $\tilde{E}\ ^2B_1$ states of SO_2^+.

IP	assignment[a]	$\Delta G(v_1+1/2)$[b]	$\Delta G(v_1+1/2)$[c]
[b]16.3393(7)[d]	0 0 0		
[b]16.4523(7)	1 0 0	912(0.7)	
[c]16.5074(8)	0 0 0		
[b]16.5601(8)	2 0 0	869(1)	
[c]16.5949(9)	1 0 0		706(4)
[b]16.6580(60)	3 0 0	790(25)	
[c]16.6858(20)	2 0 0		
[b]16.7415(10)	4 0 0		
[c]16.7813(30)	3 0 0		

a. The assignment is labelled with the quantum numbers of ν_1, ν_2, ν_3.

b. For the $\tilde{D}\ ^2A_1$ state.

c. For the $\tilde{E}\ ^2B_1$ state.

d. See (b) in Table II.

Table VII. Ionization potentials (eV), vibrational frequencies (cm^{-1}) and the assignment for the CI band.

IP	assignment[a]	$\Delta G(v_1+1/2)$[b]	$\Delta G(v_1+1/2)$[c]
[b]17.2575(9)[d]	0 0 0		
[b]17.3783(9)	1 0 0	975(10)	
[c]17.4261(20)	0 0 0		
[b]17.5006(9)	2 0 0	987(5)	
[c]17.5478(10)	1 0 0		982(18)
[b]17.6184(8)	3 0 0	950(5)	
[c]17.6648(10)	2 0 0		944(10)
[b]17.7342(8)	4 0 0	934(14)	
[c]17.7725(10)	3 0 0		869(10)
[b]17.8429(10)	5 0 0	877(7)	
[c]17.8684(20)	4 0 0		774(13)
[b]17.9472(23)	6 0 0	842(19)	
[c]17.9718(13)	5 0 0		834(14)
[c]18.076(10)	6 0 0		840(10)
[c]18.176(20)	7 0 0		808(17)

a. The assignment is labelled with the quantum numbers of ν_1, ν_2, ν_3.

b. For progression 1.

c. For progression 2.

d. See (b) in Table II.

FIGURE CAPTIONS

Figure 1. The complete HeI (584A) photoelectron spectrum of SO_2^+ measured with a resolution of 13 meV and a supersonic molecular beam of SO_2.

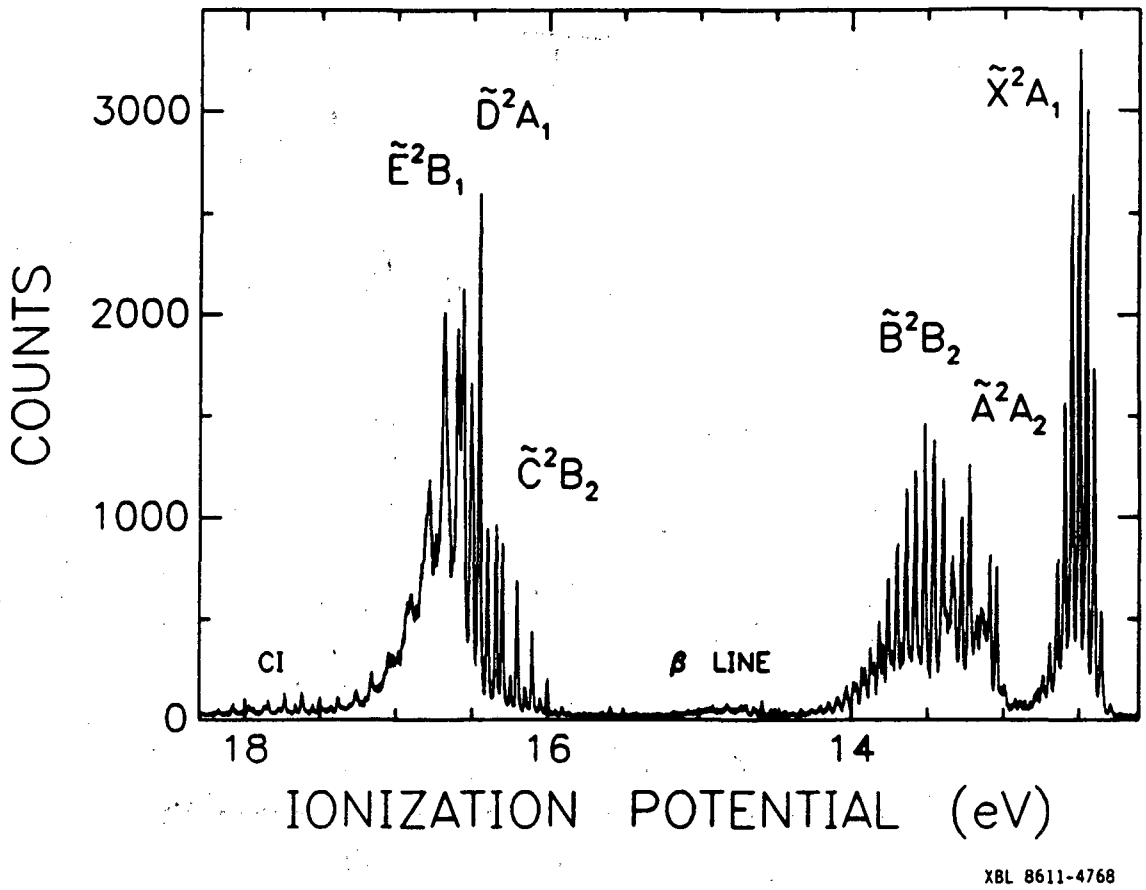
Figure 2. The first band ($\tilde{X}\ ^2A_1$ ground state) of the SO_2^+ HeI photoelectron spectrum and the assignment.

Figure 3. The virational spacing, $\Delta G(v_2+1/2)$, of ν_2 in the $\tilde{X}\ ^2A_1$ state as a function of the vibrational quantum number, v_2.

Figure 4. The second band ($\tilde{A}\ ^2A_2$ and $\tilde{B}\ ^2B_2$ states) of the SO_2^+ HeI photoelectron spectrum and the assignment.

Figure 5. The vibrational spacing, $\Delta G(v_2+1/2)$, of ν_2 in the $\tilde{B}\ ^2B_2$ state as a function of the vibrational quantum number, v_2.

Figure 6. The CI band and the third band ($\tilde{C}\ ^2B_2$, $\tilde{D}\ ^2A_1$, and $\tilde{E}\ ^2B_1$ states) of the SO_2^+ HeI photoelectron spectrum and the assignment.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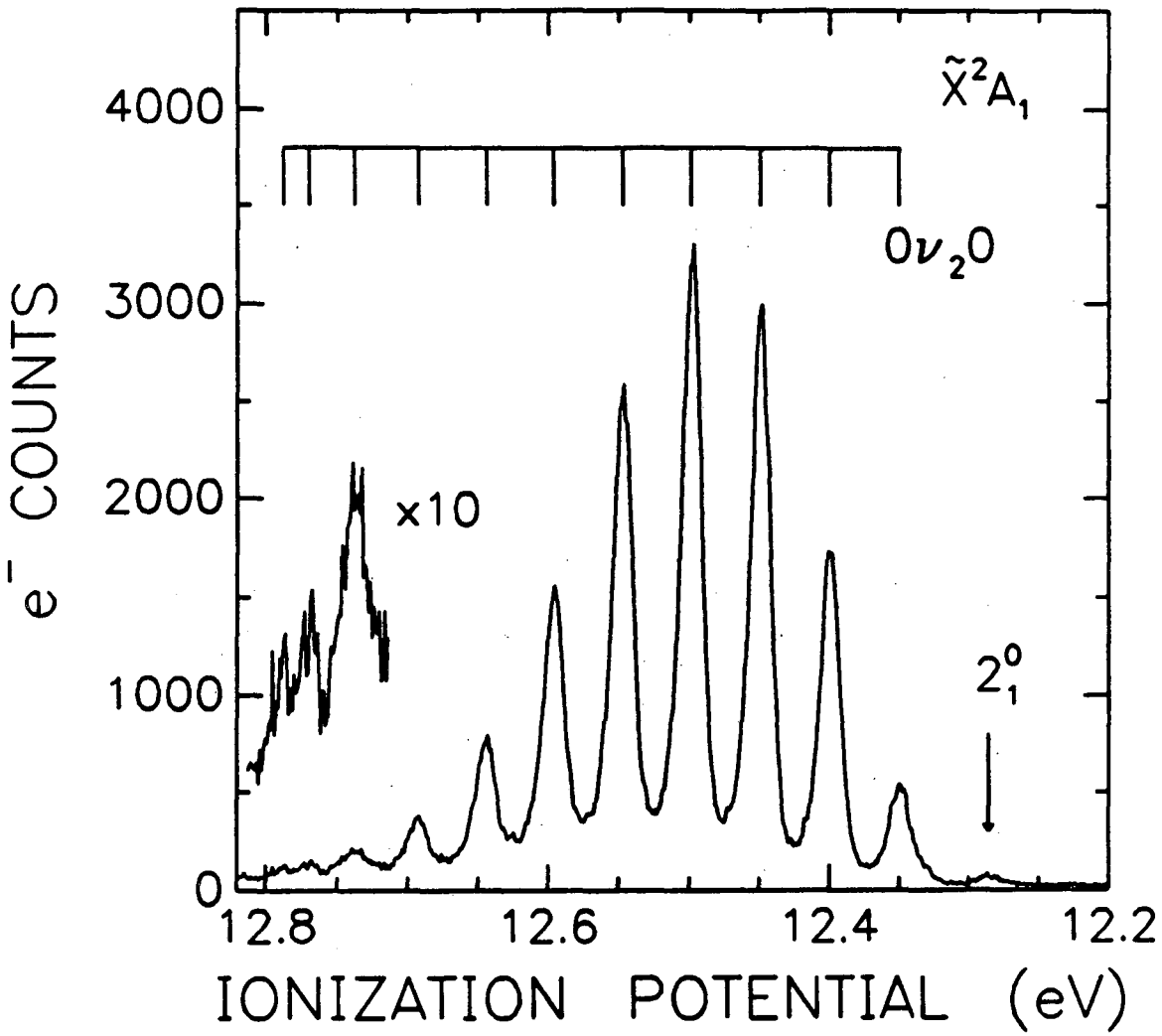
$\tilde{B}^2B_2$
$\tilde{A}^2A_2$
$\tilde{X}^2A_1$
CI
β LINE
18
16
14
IONIZATION POTENTIAL (eV)
XBL 8611-4768

Fig. 1



XBL 8611-4769

Fig. 2

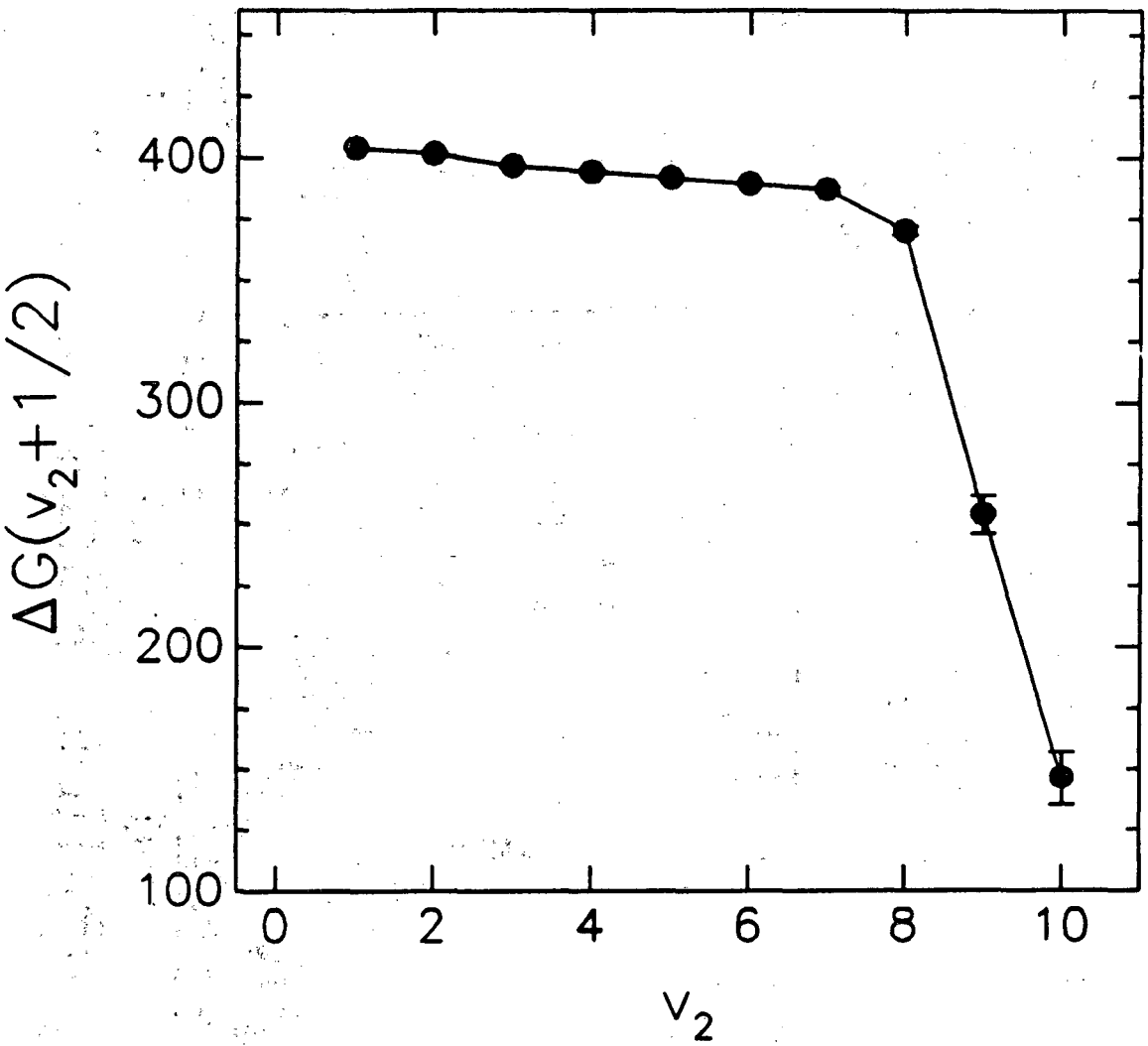
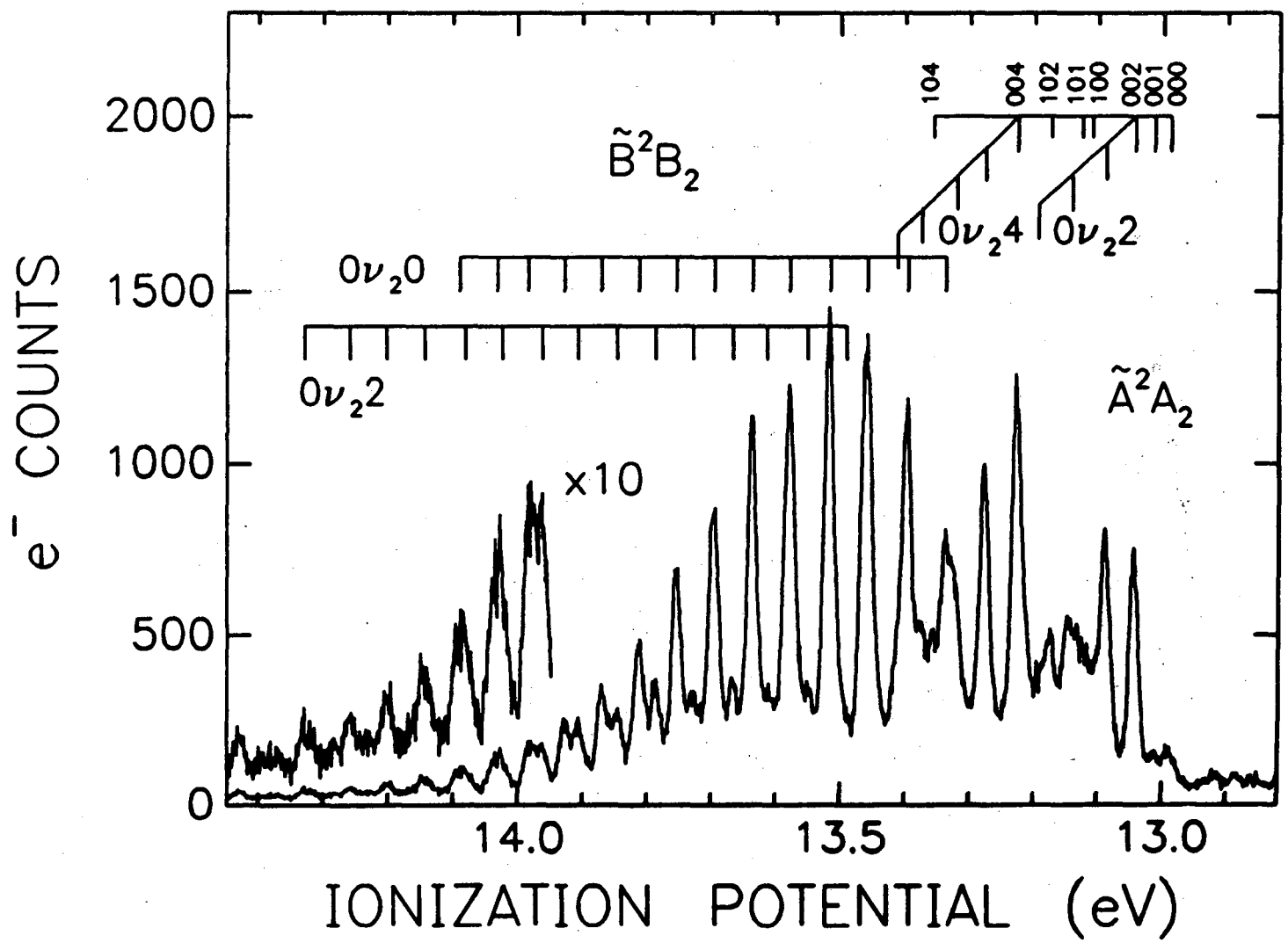
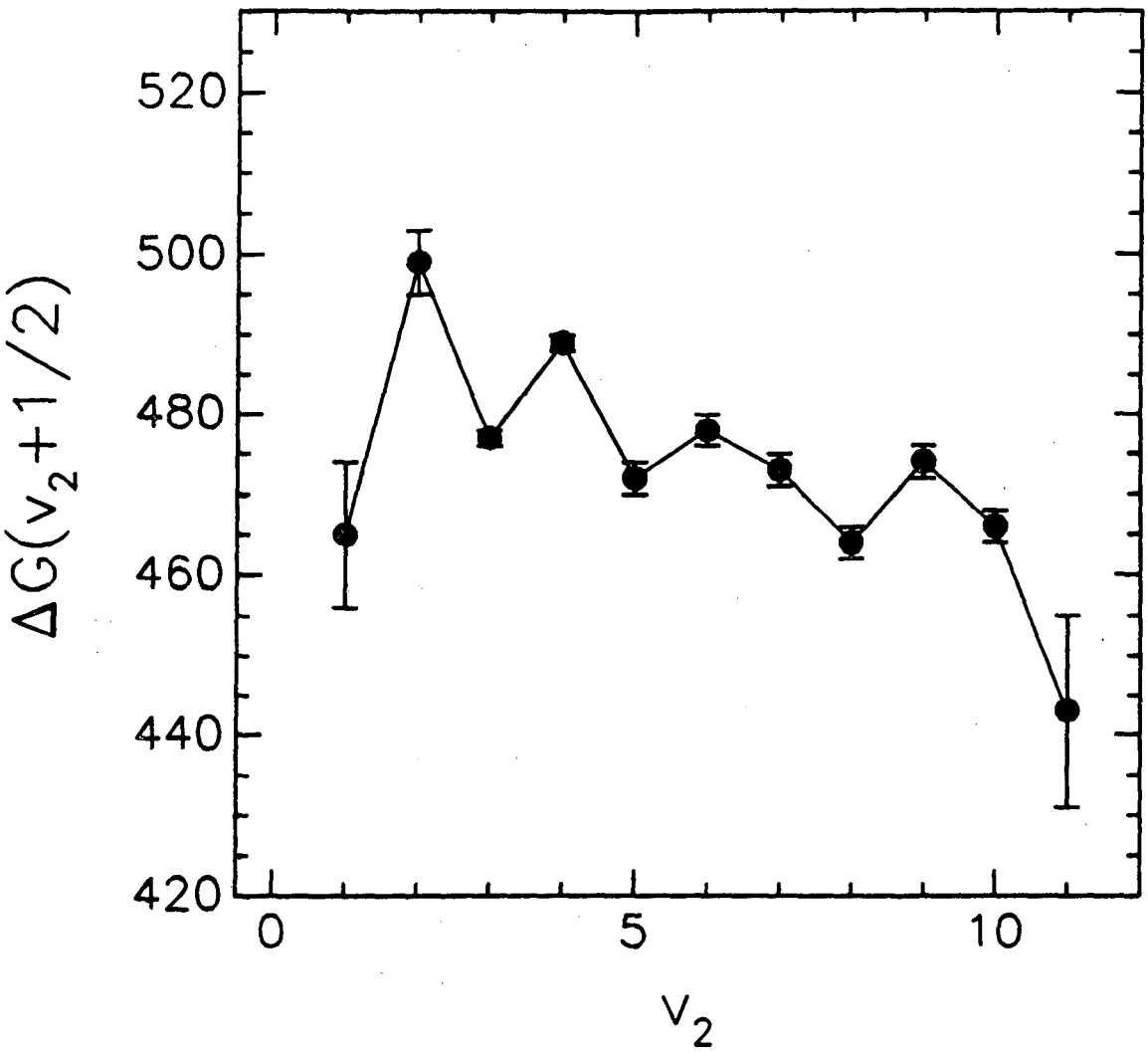


Fig. 3



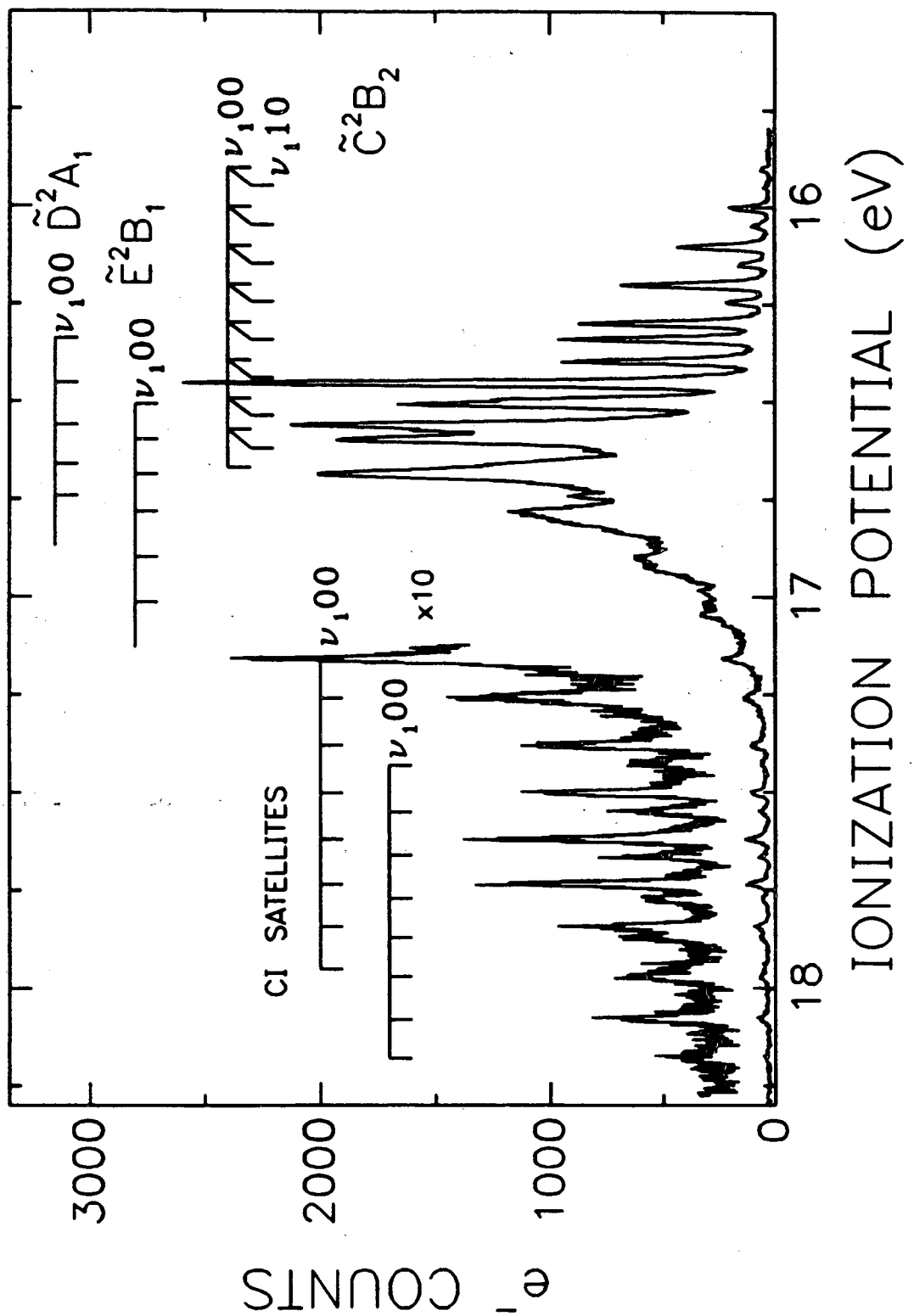
XBL 8611-4771

Fig. 4



XBL 8611-4772

Fig. 5



XBL 8611-4773

Fig. 6

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