PHYSICAL REVIEW A VOLUME 56, NUMBER 3 SEPTEMBER 1997

Dissociative-attachment cross sections for excited and ground electronic states of SO_2

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(Received 3 March 1997)

Absolute cross sections for dissociative attachment of electrons to the ground and electronically excited states have been measured using the relative flow technique. The excited molecules were prepared by laser optical pumping and their fraction was determined from the reduction in the dissociative attachment signal from the ground state. The cross sections for the excited state were determined by normalizing to this fraction. The success of this experiment should lead to similar measurements on other molecules.
[S1050-2947(97)02909-0]

PACS number(s): 34.80.Ht, 34.80.Qb, 31.50.+w, 33.20.Wr,

I. INTRODUCTION

Cross sections for dissociative attachment (DA) of low-energy electrons to molecules are very important for modeling low-energy plasmas and various atmospheric processes, pollution control, the physics and chemistry of combustion, and a variety of practical applications. For a large number of molecules these cross sections have been obtained [1] and measurements using improved techniques are still being carried out [2]. However, as in the case of most other collision processes involving excited species, very little has been reported on dissociative attachment to excited molecules. This dearth of information has been due to the difficulties involved in preparing excited species in sufficient number densities. The importance of the dissociative attachment data from excited molecules is enhanced due to the selection rules governing the electron attachment process and the competition between autodetachment and dissociation of the negative-ion resonant state (NIRS). The selection rules [3] allow only specific NIRS to be formed from a given neutral state depending on the symmetry of the initial neutral state plus electron system and the NIRS. As a result, electronic excitation of the neutral state to a different symmetry could open up new channels as seen in the measurements on O_2 [4]. The competition between autodetachment and dissociation of the NIRS causes several orders of magnitude change in cross sections for DA as a function of vibrational or rotational excitation [5,6]. Thus the presence of excited molecules could drastically modify a plasma environment through the enhancement in dissociative-attachment cross sections.

DA studies from vibrationally excited SF_6 [7], Li_2 [8], and Na_2 [6] produced by optical pumping and from vibrationally excited HCl and HF produced by laser photodissociation [9] have been reported. Measurements involving electronic excitation of the neutral state by optical pumping have been done on NO [10], C_6H_5SH [11], SO_2 [12], and NO, H_2, and D_2 [13]. Electron attachment to laser irradiated H_2 [14] and triethylamine [15] has been carried out recently. However, these measurements have been qualitative in nature and no absolute cross sections have been reported from specific excited states except for an estimation of the cross section for the long-lived O_2 $(^1\Delta_g)$ produced by microwave discharge [4]. In fact, in most measurements involving lasers, the term ‘‘laser-enhanced dissociative attachment’’ has been used and as the name suggests these have focused on the qualitative enhancements in the dissociative-attachment cross sections.

Laser-enhanced dissociative attachment to SO_2 has been reported earlier [12]. These measurements were carried out by exciting the SO_2 molecules with 308-nm radiation from a XeCl excimer laser and observing the formation of ions using a quadrupole mass spectrometer. Since a pulsed laser was used for excitation, the ions formed from the laser-excited molecules were distinguished by their time of flight (TOF) through the quadrupole mass spectrometer. These measurements showed the appearance of a new peak in the O^- intensity that was shifted down approximately by the laser photon energy from one of the two peaks observed from ground-state molecules. These measurements were qualitative in nature, even though an estimate of the cross sections for the excited state was found to be two orders of magnitude larger than those from the ground state.

We have recently used dissociative attachment to electronically excited SO_2 as a tool to identify the resonances observed from SO_2 as well as to characterize the excited neutral state itself [16]. In this paper, we present the results of the measurement of absolute cross sections for this excited electronic state along with those for the ground state. The measurements on the ground state have been necessitated by the disparity existing in the results reported so far.

II. APPARATUS AND METHOD OF MEASUREMENT

The measurements were carried out in a triple-crossed beam geometry in which a pulsed beam of laser excited the molecules in an effusive beam. A pulsed electron beam intersected this effusive beam immediately following the laser pulse. The ions produced were extracted by a pulsed electric field into a multielement time-of-flight mass spectrometer (TOFMS) and detected by a channel electron multiplier. The schematic of the experimental arrangement is shown in Fig. 1 along with a schematic of the pulsing sequence. This experimental arrangement is similar to what has been used earlier for the measurement of partial cross sections for ioniza-

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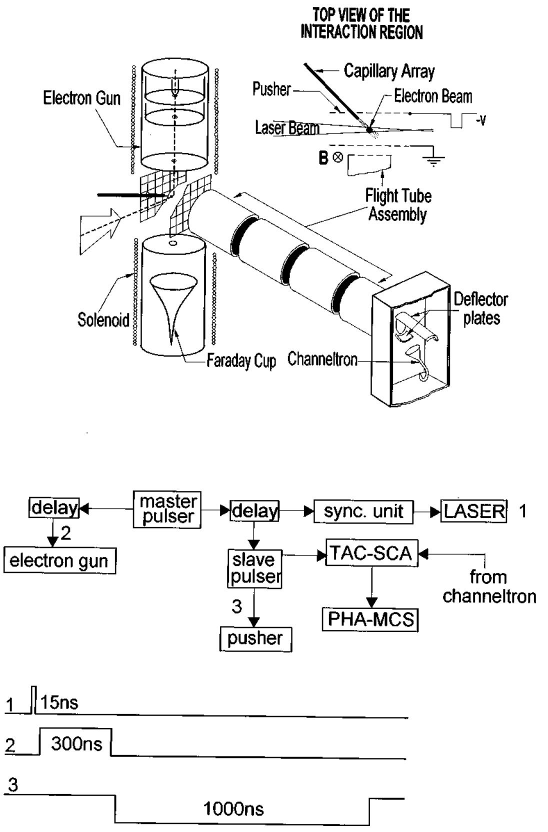

FIG. 1. Schematic of the experimental arrangement. TAC-SCA is time to amplitude converter with single channel analyzer and PHA-MCS is the pulse height analyzer with multichannel scalar.

tion of and dissociative attachment to molecules by electron impact [17], the only modification being the provision to incorporate the laser beam.

The electron gun was of Pierce geometry with a heated tungsten filament producing the electrons. A magnetic field along the axis of the electron gun was used to collimate the beam. The gun was pulsed by initially cutting of the current by an appropriate bias on the grid and over riding it with a few volts pulse of subnanosecond rise time. The width of the electron pulse could be controlled by the width of the pulse applied to the grid. In the present measurements a width of 300 nsec was found to be optimum. The electron-beam current was measured using a Faraday cup beyond the interaction region. The time-averaged current during measurements was about 200 pA.

The effusive molecular beam was produced by flowing the gas through a capillary array, the tip of which was kept 3 mm away from the interaction region. The electric field used to extract the ions was produced between two fine molybdenum wire meshes mounted symmetrically on either side of the interaction region. The TOFMS was made of four cylindrical tubes forming an electrostatic lens assembly designed to transport even relatively divergent beams to the ion detector. The directions of the electron beam, the laser beam, and the TOF tube axis were in mutually perpendicular directions. The axis of the capillary array made an angle of 45° with respect to both the laser beam and the TOF tube axis. This electron collision system based on a pulsed-electron-beam and pulsed-ion-extraction technique coupled to a multielement time-of-flight tube has been found to be the most suitable apparatus for making accurate measurements of cross sections without discriminating against the mass to charge ratio and the initial kinetic energies and angular distribution of the ions. The performance of the present apparatus has been checked and found to be satisfactory against various systematic errors as described elsewhere [17]. However, a summary is given below for the sake of clarity.

Measurement of partial ionization cross sections necessitates the use of a mass spectrometer to distinguish various ionic species. This makes the measurement of absolute cross sections almost impossible. This has been circumvented by the use of a calibration procedure using a standard atom or molecule of known cross section. The relative flow technique [18,19] has been established to be quite reliable for this purpose. The critical aspect of this calibration procedure is the comparison of the relative intensities of the species of interest with that of a standard species of known cross section. For example, the cross section for the formation of SO^- from SO_2 could be determined using the cross section for the formation of O^- from O_2 based on the equation

$$\sigma(SO^-/SO_2)=\sigma(O^-/O_2)\times\frac{N(SO^-)F(O_2)M_{O_2}^{1/2}I_e(O_2)K(O^-)}{N(O^-)F(SO_2)M_{SO_2}^{1/2}I_e(SO_2)K(SO^-)}, \tag{1}$$

where N is the number of ions collected for a specific time, M is the molecular weight of the parent molecules, F is the flow rate, I_e is the electron current, σ is the cross section, and K is the detection efficiency, which is a product of the efficiency with which ions are extracted from the interaction region, their transmission through the mass spectrometer, and finally the efficiency with which they are detected. The overall efficiency as a function of the mass to charge ratio could be written as

$$K(m/e)=k_1k_2k_3, \tag{2}$$

where k_1 is the efficiency of extraction from the interaction region, k_2 is the efficiency of transmission through the mass analyzer, and k_3 is the efficiency of detection of the ion by the particle detector. In practice, it is difficult to isolate k_1, k_2, and k_3 and one measures only K. k_1 is independent of the mass to charge ratio, but depends on the initial kinetic energies and angular distributions of the fragment ions. k_1 could be made independent of these by applying a large enough extraction field in the interaction regions so that all the ions are extracted into the mass spectrometer independently of the kinetic energies and angular distributions. The effect of such extraction fields on the electron beam could be eliminated only by pulsing the electron gun and the extraction field without any temporal overlap.

The transmission in the mass analyzer k_2 is independent of m/e in a time-of-flight spectrometer unlike in the case of a quadrupole mass spectrometer. However, k_2 could depend on the initial kinetic energies and angular distribution of the ions in the following way. Depending on the kinetic energies and angular distributions, the ions extracted from the interaction region will have finite divergence at the entrance of the mass spectrometer. In order to transport these ions to the detector without loss, one needs to use an electrostatic focusing lens assembly. This could be achieved by using the mass

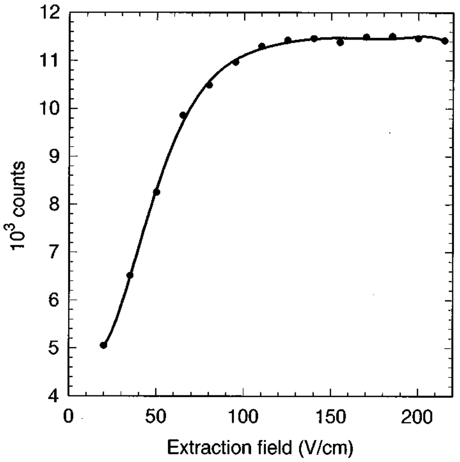

FIG. 2. Number of ions extracted as a function of the extraction field.

spectrometer itself as a focusing assembly. Thus, in the present case, the flight tube of the TOF spectrometer is made of four separate elements and biased in such a way that the divergent beam of ions entering it is focused at its exit where the detector is mounted. This lens system was designed using the SIMION program [20] by taking into account worst-case kinetic energies and angular distributions and optimum extraction fields. Thus, by the appropriate choice of a multielement TOFMS we could make k_2 independent of m/e and initial kinetic energies and angular distributions.

The detection efficiency k_3 of the ions by the channel electron multiplier has been found to depend on the velocity with which the ions strike the detector surface. Thus, for a given acceleration, ions of smaller m/e will have larger detection probability [21]. In the case of measurements on positive ions, $K(m/e)$ can be determined using cross sections for the formation of singly charged ions from their respective noble-gas atoms in the mass range from 4 to 132, by the relative flow technique [22]. But so far it has not been possible to apply it to the negative ions due to the unavailability of accurate cross sections in a wide m/e range. The only way to take care of the m/e dependence of K through k_3 is by increasing the nose-cone voltages to such levels that there is saturation in the detection efficiency. This procedure was employed in the present experiment.

Measurements were carried out on the extraction efficiency of ions as a function of the extraction field. The results of these measurements are shown in Fig. 2 for the case of O^- from O_2. It may be noted that beyond a field strength of 120 V/cm, the extraction efficiency saturated. We also carried out measurements on the detection efficiency of the channel electron multiplier as a function of the nose-cone voltage by keeping the bias across it constant. The results of these measurements for various ions of interest in the present case are shown in Fig. 3. It is seen that beyond 1200 V, the detection efficiency showed saturation.

The XeCl (308-nm) excimer laser (LPX 240i, Lambda Physik) used for preparing the molecules in the excited state was operated at a pulse repetition rate of 300 Hz. The temporal profile had a half-width of about 14 ns. The beam was transported to the interaction region using a pair of mirrors and focused by a plano convex lens of focal length 500 mm. The laser pulse interacted with the molecular beam, exciting a good fraction of the SO_2 molecules to the $\tilde{B}^1B_1$ state. A few tens of nanoseconds after the laser pulse, the pulse of electrons were put on for about 300 ns. Soon after (about 20 ns) the departure of the electron beam from the interaction region, a 200-V pulse of 1-μs duration was applied to the pusher plate of the ion extraction assembly. The time jitter in the laser pulsing was minimized by using a synchronizing unit. The ions entering the TOF tube assembly were focused at the exit of the assembly and detected by the channel electron multiplier mounted off axis and operated in the pulse counting mode. The TOF spectra were recorded using a time-to-amplitude converter (TAC) and a pulse height analyzer (PHA). The count rate of a particular ion versus the incident electron energy (excitation function) was obtained by selecting the appropriate time window in the TAC and storing the data using a general purpose interface bus based data acquisition system that also controlled the digital power supply used for defining the electron-beam energy. This data acquisition system ensured simultaneous monitoring of the electron-beam current, the pressure behind the capillary array (which determines the pressure in the interaction region), and the intensities of all the ionic species of interest. This helps in correcting the excitation functions for the possible variation in current and target density and also the collection of several excitation functions simultaneously, thereby reducing the data acquisition time considerably.

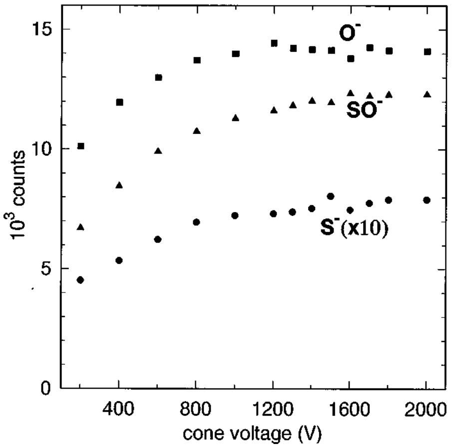

FIG. 3. Number of ions detected as a function of the voltage on the nose cone of the channeltron for negative ions of interest in the present experiment. The voltage across the channeltron is kept constant.

The absolute cross sections for the ground-state SO_2 were obtained by using the relative flow technique as given by Eq. (1) using the accurately known cross section for formation of O^- from O_2 [23]. During the experiment, we found that it was very difficult to measure the flow rates of SO_2 accurately. Hence we used the simplified version of the relative flow technique applicable to low pressures [19] in which the pressures behind the capillary array are used instead of the flow rates. The absolute pressure behind the capillary array was measured using a capacitance manometer (MKS Baratron).

In order to obtain the cross sections for the excited-state molecules, it is necessary to obtain their number density relative to that of the ground-state molecules. This was done in the following way. Mass spectra were collected at the elec-

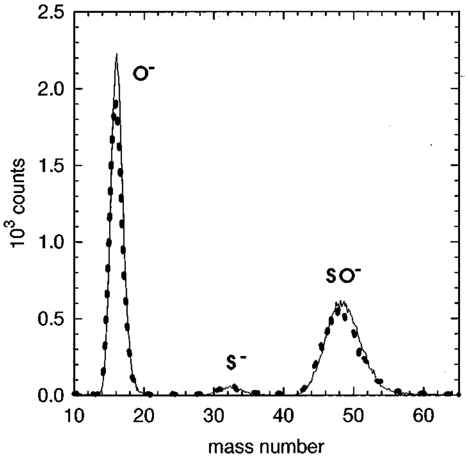

FIG. 4. Time-of-flight spectra of negative ions at the electron energy of 4.6 eV with (dotted line) and without (continuous line) laser excitation.

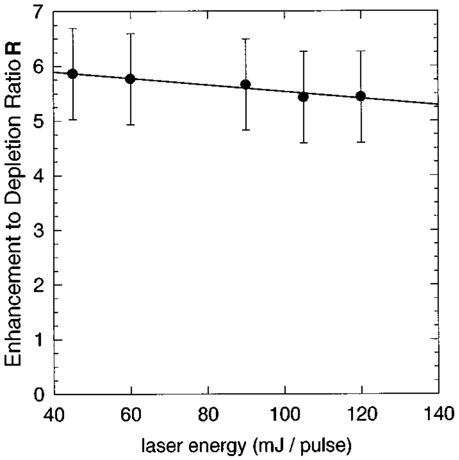

FIG. 5. Ratio R of the number of O^- ions formed from the excited state to the reduction in the number of ions from the ground state. The error bars represent the statistical error.

tron energies corresponding to the peaks in the dissociative-attachment spectrum with and without the laser beam, keeping all other parameters such as the gas pressure and the electron-beam current constant. One such set of spectra obtained at an incident electron energy of 4.6 eV is shown in Fig. 4. From the figure it may be noticed that the TOF spectra taken with the laser excitation has a lower count rate compared to that taken without the laser. This could only be due to a reduction in the number of molecules in their ground state due to the laser action since at the electron energy used, attachment occurs only to the ground-state molecules. Using the difference in the intensities of the two cases, we calculated the percentage depletion of the target molecules due to laser excitation. As expected, this depletion was independent of whether we used O^- or SO^- for the analysis. We also repeated the measurements at the 7-eV peak seen from the ground state and obtained identical results. As the experiments were done in a single-photon absorption regime and the lifetimes of the excited state involved are much larger than the time interval between the laser and electron pulses, this depletion had to manifest as the fraction of molecules in the excited state. Using this fraction, which was within 0.1–0.15 depending on the spatial overlap of the electron and laser beams, the cross sections for the excited states were determined.

The possibility that multiphoton processes could contribute to the depletion from the ground state was investigated the following way. To begin with, the focal point of the laser-beam optics was kept away from the interaction region to reduce the probability of multiphoton processes and also to provide larger interaction volume among the three beams. The laser spot size at the interaction region was estimated to be $0.7\times 2\ \mathrm{mm}^2$. Mass spectra were obtained at the energies corresponding to the peaks in the attachment cross sections from ground-state and excited-state molecules at a number of laser energies starting from 45 mJ/pulse to 120 mJ/pulse. Using the intensities of the ions obtained from the mass spectra, it was found that the ratio of the number of negative ions from the excited state to the reduction in the number of ions from the ground state was almost constant. The results are plotted in Fig. 5 as a function of the laser energy. It is found that as the laser energy is increased from 45 mJ to 120 mJ, the above ratio decreases by a small amount within error limits. This may be due to a small amount of depletion from the ground state due to a two-photon process leading to dissociation [24]. We have corrected for this variation by extrapolating to the zero laser energy limit.

The change in path length of the electrons due to helical motion in the confining magnetic field could contribute significantly to the error at very low electron energies [25]. As the attachment from the excited state occurs at very low energies it was felt necessary to correct for it. The actual path length L that an electron traverses when it moves across a length l along the direction of the electron beam is given by

$$L=\frac{l}{\sqrt{1-\frac{v_\perp^2}{v^2}}}=\frac{l}{\sqrt{1-\frac{e^2B^2r_L^2}{v^2}}}, \tag{3}$$

where e is the electronic charge, B is the magnetic field, r_L is the radius of the interaction region, v is the speed of the electron, and $v_\perp$ is the speed perpendicular to the direction of the beam. The electron beam emerged from the gun through an aperture 1 mm in diameter and this was taken as the diameter of the interaction region. The magnetic field at the interaction region was 25 G. Using these parameters, the correction needed in the electron-beam path length was computed and the final cross sections corrected accordingly.

III. ERRORS AND THEIR ESTIMATION

The uncertainty in the present measurements arise from the calibration technique, statistical uncertainties, contributions due to the relatively poor electron energy resolution, and uncertainty in the measurement of electron-beam current. The errors due to incomplete collection of ions arising from the dissociation process, their mass analysis, and detection have been eliminated by the appropriate use of high extraction fields, the use of a multielement TOFMS that focuses the ions on to the detector, and appropriate use of detector voltages. The maximum error arising from the detection of the ions is estimated to be 5%. The cross section for O^- from O_2 used for calibration has an uncertainty of

10% [26]. The uncertainty in the pressure measurements is 5%, statistical errors from counting 3%, and the reproducibility of the excitation function 5%. Poor electron energy resolution could lead to an underestimation of the cross section at the resonant peaks. We find that the half-width of the O^- peak at 4.3 eV is about 1.3 eV, compared to the 1.25 eV reported by Spyrou *et al.* [27] and 1 eV by MacNeil and Thynne [28]. Thus the present results at the peaks may be underestimated by a small amount, the estimate of which has not been made. Excluding this, the overall root-mean-square uncertainty in the data for ground-state molecules is less than 15%.

For the cross sections from the excited state, the major contributing factor is the uncertainty in the determination of the fraction of molecules in the excited state. This fraction was determined by measuring the reduction in intensity of the molecules in the ground state at their dissociative-attachment peaks. This may have a systematic contribution due to some of the molecules being excited to states other than the one of interest to us due to multiphoton processes or due to decay of the excited state to a lower state. Measurements to check the presence of multiphoton processes have been described above. A small correction though within the experimental errors was found and has been applied to the final data. The decay to other low-lying states was investigated by making the measurements as a function of delay between the laser pulse and the electron pulse. It was found that within statistical errors the intensity of the negative ions due to the excited state was proportional to the depletion of molecules from the ground state, independent of the delay between the laser pulse and the electron pulse. The upper limit on the uncertainty in the fraction of molecules in the excited state was estimated to be 10%.

As the attachment from the excited state occurs at very low electron energies, the necessary correction for the path length was applied. We estimate a maximum uncertainty of 5% in this procedure. Thus considering all possible sources of errors, including 15% uncertainty in the cross section for the ground state, we find that the cross sections from the excited state have an uncertainty of 20%.

IV. RESULTS AND DISCUSSION

A. Ground state

Qualitative information on dissociative attachment to SO_2 molecules in the ground state has been found to be in good agreement among various reports [27,29–31]. The dissociative attachment has been found to produce O^-, S^-, and SO^-, each having two major features in their partial cross sections. The first one, which is the stronger of the two for all three fragment ions, is a peak centered between 4 eV and 5 eV. The second one appears as a strong peak in the case of O^- at slightly above 7 eV, but weakly in the case of S^- and SO^-. In addition, there appears to be a small peak centered around 9 eV in the S^- cross sections [29]. Using the selection rules for dissociative attachment and a comparison of the dissociative attachment from the ground state and excited state, the two prominent features seen from the ground state have been identified as due to $^2A_1$ and $^2B_2$ negative-ion resonant states, respectively, in increasing order of energy [16] (see also the discussion given below). Based on the selection rules, the symmetry of the resonant structure seen at 9 eV may be one of $^2A_1$, $^2B_1$ or $^2B_2$.

The partial and total cross sections for the formation of O^-, S^-, and SO^- from the ground state and excited state of SO_2 are shown in Fig. 6. The cross sections at the peaks for attachment to the ground state are given in Table I along with other reported results. Our results are qualitatively in good agreement with the earlier data, including the small peak observed by Orient and Srivastava [29] in the S^- cross sections at 9 eV. As seen from the table, the cross sections reported by various groups have shown a large variation, even in the relative intensity of various ions. Both Orient and Srivastava [29] and Spyrou *et al.* [27] observed SO^- to have the highest cross section, whereas Čadež *et al.* [30] estimated the maximum SO^- cross section to be less than one-third of O^- cross section. The partial and total cross sections at the major resonant peak reported by Spyrou *et al.* is about a factor of 3 smaller than those measured by Orient and Srivastava. The latest measurements on total cross sections by Wan *et al.* [31] is about half of those obtained by Orient and Srivastava, but are higher than those reported by Spyrou *et al.* and Čadež *et al.* by about 35% and 40%, respectively, at the 4.6 eV peak and 90% and 30%, respectively, at the 7.2 eV peak. It may be noted that the total cross sections obtained by Spyrou *et al.* using the swarm-beam technique are lower than their crossed-beam measurements. The swarm data of Rademacher *et al.* [32] give total cross sections in agreement with the results of Spyrou *et al.* and by Čadež *et al.* for the peak at 4.6 eV.

The partial cross sections measured by us do not show any overall agreement with either the results of Orient and Srivastava or Spyrou *et al.*, though it appears that our O^- data are in agreement with those of Orient Srivastava within the combined experimental errors and the SO^- data are in very good agreement with those of Spyrou *et al.* However, the relative cross sections of SO^- are smaller than those of O^- in our case as compared to the data from these two reports where they observed larger SO^- intensities. Another feature of the present results is the relatively larger cross sections at the second peak for all the ions as compared to those of Orient and Srivastava and Spyrou *et al.* The total cross sections obtained by us are in agreement with the latest data of Wan *et al.* at both the resonant peaks within experimental errors. This gives further credence to the accuracy of the present partial cross sections.

Spyrou *et al.* have attributed the difference between their data and those of Orient and Srivastava as due to possible discrimination against higher energy O^- from O_2 used by the latter group for normalizing the cross sections to absolute values. It is indeed possible that ions of larger kinetic energy may not be detected if sufficient extraction fields are not employed. However, Orient and Srivastava seem to have paid due attention to this aspect. The larger values obtained by them may be attributed to another source of systematic error. It has been found that flow rate measurements on SO_2 for calibration by relative flow technique gives relatively low values and hence larger cross sections. The measurements by Orient and Srivastava employed the relative flow method for normalization and hence may have overestimated the cross sections. It may be noticed that in the present measurements we used the *relative pressures* instead

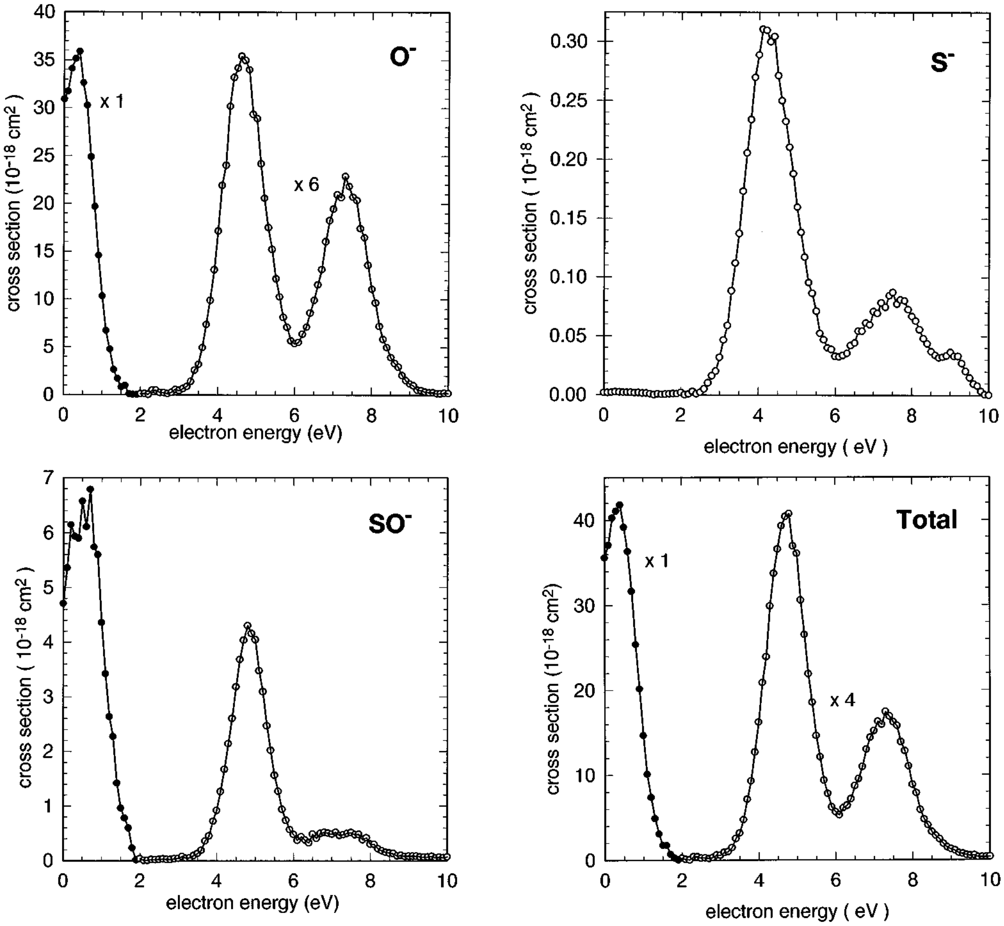

FIG. 6. Partial and total dissociative-attachment cross sections from ground and excited states of SO_2. The filled circles represent the cross sections from the excited ($\widetilde{B}\,^1B_1$) state and the open circles from the ground ($\widetilde{X}\,^1A_1$) state, respectively. The values for the ground state have been multiplied by a factor of 6 in the case of O^- cross sections and a factor of 4 in the case of total cross sections as marked in the respective figures: (a) O^-, (b) SO^-, (c) S^-, and (d) total.

of the relative flow for normalization of the cross sections. It appears that the cross sections obtained by Spyrou *et al.* for the formation of O^- is too low. The relatively large cross sections for SO^- as compared to O^- observed by them as well as Orient and Srivastava may be due to differences in the detection efficiencies of the channel electron multiplier for F^- and O^-, which were used as standards in the respective experiments, as compared to that for SO^-.

B. Excited state

The cross sections for attachment to the excited state are given in Fig. 6 along with those for the ground state. Dissociative attachment to the excited SO_2 produced by irradiation of a XeCl excimer laser at a wavelength of 308 nm was observed by Jaffke *et al.* [12]. Our recent measurements [16] have confirmed their observation of a different resonant peak. Unlike that from the ground state, the cross sections for the formation of O^- and SO^- from the excited state appear to have only one peak each. These are shifted down by approximately 4 eV with respect to the first peak seen from the ground-state molecules and corresponds to the energy of the photons used to excite the molecules. The absence of a second peak in the dissociative attachment to the excited molecules was interpreted in terms of the selection rules for electron attachment and was used to identify the resonant attachment peak seen at 7.4 eV from the ground-state molecules as a $^2B_2$ state. This and the results of molecular-orbital calculations helped in assigning the $^2A_1$ symmetry to the resonance seen from the excited state as well as from the ground state. In addition, it was also possible to identify the exact nature of the excited state. Previous spectroscopic data had identified the excited state as $\widetilde{B}\,^1B_1$. It was found to be strongly perturbed by neighboring rovibrational levels from $\widetilde{A}\,^1A_2$, $\widetilde{X}\,^1A_1$, and $\widetilde{a}\,^3B_1$ states. Using the selection rules and the dissociative-attachment data from the ground and excited states we were able to eliminate the $\widetilde{A}\,^1A_2$ and $\widetilde{X}\,^1A_1$ states as possible perturbers at the excitation wavelength of 308 nm. Thus the excited neutral state is a $\widetilde{B}^1B_1$ state with a possible admixture of a $\widetilde{a}^3B_1$ state [16].

The cross section for the formation of O^- from the excited state has a peak at 0.4 eV with a value 36×10^{-18} cm^2. The SO^- cross section peaks at 0.6 eV with a value 6.6×10^{-18} cm^2. Jaffke *et al.* [12] had estimated the cross section for the formation of O^- to be about 175 times larger from the excited state as compared to that from the ground

TABLE I. Dissociative attachment cross sections for ground state of SO_2. The indices a and b for Ref. [27] represent beam data and swarm-beam data, respectively. The peak positions are in units of eV and the cross sections (σ) are in units of 10^{-18} cm^2. The uncertainties, whenever available in the respective cross sections, are given in *italics*.

	Ref. [29]		Ref. [27]^a		Ref. [27]^b		Ref. [32]		Ref. [30]		Ref. [31]		Present	
Ion	E_{peak}	σ	E_{peak}	σ	E_{peak}	σ	E_{peak}	σ	E_{peak}	σ	E_{peak}	σ	E_{peak}	σ
O^-	4.3	8.08	4.55	2.46					4.8	4.44			4.6	5.9
		±1.61								*±0.36*				*±0.89*
	7.1	2.68	7.3	1.27					7.4	2.44			7.2	3.7
		±0.54								*±0.20*				*±0.55*
S^-	4.0	0.313	4.2	0.17					4.4	0.136			4.2	0.3
		±0.626								*±0.011*				*±0.05*
	7.5	0.036	7.4	0.044									7.4	0.08
		±0.007												*±0.012*
	8.9	0.03											9.0	0.035
		±0.006												*±0.005*
SO^-	4.7	10.98	4.85	4.11					4.8	1.4			4.8	4.3
		±2.20								*±0.11*			4.6	*±0.65*
	7.3	0.51	7	0.41					7.4	0.072			7.3	0.5
		±0.10								*±0.006*				*±0.08*
Total	4.5	17.55	4.7	6.44	4.7	4.6	5.0	5.5	4.7	6.21	5	8.7	4.6	10.2
		±3.51								*±0.50*		*±1.31*	4.6	*±1.53*
	7.1	3.11	7.3	1.72					7.4	2.53	7.4	3.3	7.2	4.3
		±0.62								*±0.20*		*±0.50*		*±0.65*

state. Our measurements show that the enhancement is about a factor of 6 only. SO^- shows an enhancement of about 50%. The presence of S^- was noticed in the dissociative attachment to excited molecules. However, it was too weak to make any meaningful measurements.

It is interesting to compare the cross sections for the excited state with the resonance at 4.6 eV from the ground state as a function of the electron energy since the negative-ion resonance formed in both cases are identical. For an s-wave electron capture, the cross section changes as $1/E$. This may be expected to manifest in the dissociative-attachment cross sections if the internuclear separations of the two neutral states are identical. The sum of the cross sections for the formation of O^- and SO^- from the excited state peaks at 0.4 eV with a value of 4.2×10^{-17} cm^2. As compared to this, the corresponding cross section from the ground state is 10.2×10^{-18} cm^2 at an energy of 4.6 eV. Based on this, it appears that the $1/E$ relationship holds within a factor of 2. This is in conformity with Christophorou *et al.* [1], who have shown, using data on a variety of molecules, that the cross sections decrease as the resonant energy increases.

V. APPLICATION OF THE PRESENT TECHNIQUE TO OTHER EXCITED STATES

The excited state of SO_2 for which the measurements are carried out is known to have a lifetime in the range 50–530 μs [33]. This long lifetime prevents the decay of the excited molecules to a lower level before the electron pulse interacts with them. In the current set up the time difference between the laser pulse and the electron pulse is in the range of tens of nanoseconds and the width of the electron pulse is 300 ns. Thus, in the present measurements the excited state had a reasonably good number density. The large lifetime also ensured that this state decayed very little to any other low-lying excited electronic state or higher vibrational levels of the ground electronic state. Thus we did not have to tackle the difficulties arising from the presence of more than one excited state.

In principle, the present technique could be used to any excited state irrespective of its lifetime, provided its number density is sufficient. It should be possible to reduce the time difference between the end of the laser pulse and the electron pulse to a few nanoseconds. However, this may not be of much help since in the present measurement the width of the electron-beam pulse is the limiting factor. Though it is possible to reduce the width of the electron-beam pulse to a few nanoseconds, the corresponding reduction in the signal will make the experiment almost impossible. In order to have a sufficient signal it is necessary to have a sufficient number density in the excited state for a time of the order of 0.1 μs, which is typically the duration of the electron pulse we could operate with the present arrangement. Thus, in practice, this technique may be limited to those states with lifetimes in the range of 100 ns and above. This limit may be reduced further if the experiment is modified to operate at larger repetition rate using appropriate lasers. Apart from the reduction in the number density, the short lifetime of the excited state may lead to other difficulties, depending on the level to which it decays.

The present technique to determine the absolute cross sections is applicable to cases where it is possible to clearly distinguish the dissociative attachment signals from various states as a function of the electron energy. In order to determine the fraction of molecules in the excited state it is essential that the contribution from the excited state does not overlap with at least some section of the excitation function for the ground state. The population of higher vibrational levels of the ground electronic state due to the short lifetime of the excited state is a possible situation where this technique may run into difficulty due to overlap of signals, considering the relatively poor electron energy resolution.

Another difficulty that may arise due to the short lifetime of the excited state is the population of three states at a given time. If the lower excited state gives rise to a dissociative-attachment signal separated from that of the ground state, measurements may still be made by delaying the electron-beam pulse such that the upper excited state is completely decayed. The relative number density of the resulting two component mixture can be determined as in the present case to obtain the cross section of the lower excited state. This procedure could then be iterated to a three-component mixture with almost no time delay to determine the relative number density and the corresponding cross sections for the higher state initially formed by photoabsorption. However, this method may fail if the lower excited state does not give rise to any dissociative attachment.

Thus it appears that the present technique is best suited for those states with relatively large lifetime (microsecond range) and may be used for states with short lifetimes (100 ns range) in specific situations with appropriate modifications. From the point of view of applications to various plasmas, the states with larger lifetimes are important and there exist a large number of such states belonging to various molecules.

VI. CONCLUSION

A combination of a pulsed electron beam and pulsed laser beam along with a multielement TOFMS with special emphasis on the collection and detection of all the ions independent of the kinetic energies and angular distributions has been used to determine the cross sections for dissociative attachment of electrons to electronically excited SO_2 molecules. Absolute partial cross sections for the formation of O^-, S^-, and SO^- from the ground-state molecules were determined using the relative flow technique, as the existing data on these show large disparities. The total cross sections obtained from the partial cross sections were found to be in agreement with the latest total attachment data. The absolute partial cross sections for the excited molecules were determined by measuring the fraction of molecules in the excited state using the dissociative-attachment signal from the ground state. The partial cross sections for O^- from the excited state are found to be a factor of 6 larger than those from the ground state, whereas the cross sections for SO^- show an enhancement of about 50%. Though S^- from the excited state was observed, the signal was too weak to make any useful measurements. The success of the experiment opens up the possibility of carrying out similar measurements on the excited states of a variety of molecules.

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