Dissociative attachment of electrons to excited molecules

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Abstract. The development and the first results from an experiment to carry out dissociative attachment to excited molecules are discussed. A brief summary of the relevance and status of such measurements are given. Apart from measuring the absolute cross sections from excited and state selected SO_2 molecule, we have been able to characterize the negative ion resonances using the excited state dissociative attachment. In addition, the state specificity of the electron attachment process has been used to derive information on the excited neutral state itself which has not been possible using optical spectroscopy. The applicability of this technique to other species are also discussed.

1. Introduction

Dissociative attachment is a dominant process in the low energy electron-molecule interactions. This process is characterized by the resonant interaction of the electron with the molecule resulting in an unstable negative ion and its subsequent dissociation into neutral and negative ion fragments before it could decay through the ejection of the extra electron. Thus dissociative attachment has been used as a probe for studying negative ion resonant states (NIRS) in molecules. In addition, the two modes of decay of the negative ion resonant state, one through the electronic process (autodetachment) and the other through the nuclear motion (dissociation), makes the dissociative attachment process an ideal ground for investigating the coupling between the electronic and nuclear degrees of freedom. From a practical point of view, cross-sections for dissociative attachment of low energy electrons to molecules are very important for modelling 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 dissociative attachment data from vibrationally and electronically excited molecules are all the more important due to the large changes in cross sections as a function of the vibrational levels and the selection rules for electron capture depending on symmetry properties respectively.

2. Dissociative attachment to vibrationally excited molecules

Increase in the dissociative attachment cross sections as a function of temperature of the target molecules was observed quite some time back. Measurements on this aspect have been carried out by a number of workers starting from Hickam and Berg [3] using both electron beam techniques [4] and swarm techniques [5]. Excellent reviews of these studies along with other aspects of dissociative attachment and negative ions has been given by Christophorou *et al* and Massey [1, 6]. The theoretical treatment of the enhancement in the cross sections in dissociative attachment as a function of temperature was given by O'Malley [7]. His work on O_2 showed that excitation of vibrational levels as a function of temperature was responsible for this observed behaviour. Even though he ignored rotational excitation, he could predict the threshold, magnitude, width, and energy position of the resonance accurately, thus showing the effect of rotational excitations to be negligible.

A schematic of the dissociative attachment process is shown in figure 1 for the case of a molecule *AB*. When an electron of specific energy, *E*, interacts with the molecule, it gets captured forming the resonance. The energy range in which the electron gets captured is limited by the Franck–Condon overlap between the neutral state and the negative ion resonance. This resonance may decay by electron ejection or through dissociation as the potential energy surface is not bound along the internuclear axis between *A* and *B*. The electron detachment occurs all along the curve till the internuclear separation corresponding to the distance R_c, beyond which the resonance cannot decay through electron ejection (also called autodetachment). It is important to point out that the negative ion resonance need not necessarily be a repulsive state. It may have a minimum in its internuclear potential, in which case dissociative attachment may or may not happen
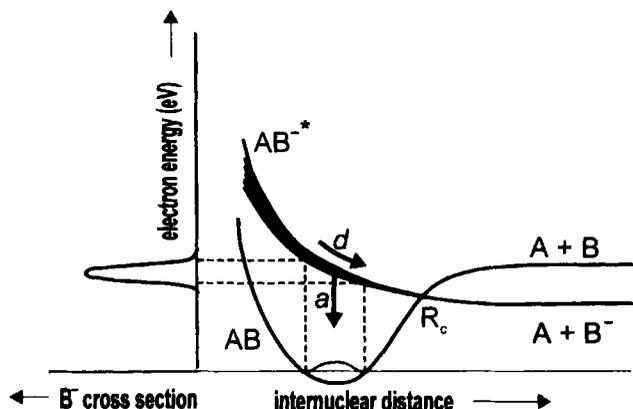
Figure 1. Schematic of the dissociative attachment process for a molecule *AB*. The two vertical dashed lines defines the Franck-Condon region of the internuclear separation in which the negative ion resonance, AB^{-*} is formed. The two horizontal dashed lines denotes the range of electron energy in which the electron is captured. 'd' shows the dissociation decay channel and 'a' shows the autodetachment decay channel of the resonance. R_c is the internuclear distance beyond which autodissociation is not possible and the resonance necessarily decays through the dissociation channel.

depending on whether the electron capture leads to the continuum or bound part of the curve. If it is bound against dissociation, the only mode of its decay is through electron ejection. The dissociative attachment cross section, σ_{DA} can be written as the product of the cross section σ_c for the electron capture resulting in the formation of the negative ion resonance and the 'survival probability', p. p is the probability that the negative ion resonance will decay via dissociation

$$\sigma_{DA}(E) = \sigma_c(E)p(E), \tag{1}$$

where E represents the incident electron energy. The capture cross section, σ_c depends on the symmetry properties of the neutral molecule and the negative ion resonance and their Franck–Condon overlap. p depends on the mean lifetime of the resonance due to auto-detachment and the separation time of the dissociation fragments. Thus the dissociative attachment cross section is strongly dependent on the competition between the two modes of decay of the resonance, viz., autodetachment and dissociation. The survival probability can be explicitly written as [7–10]
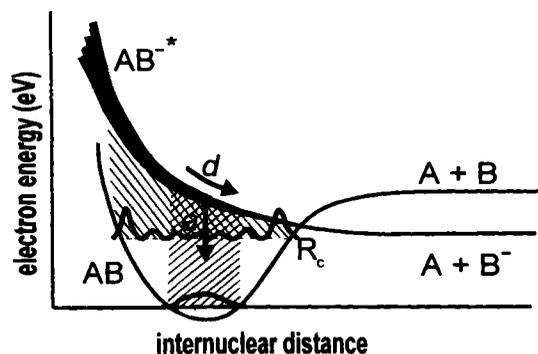
$$p(E) = \exp\left(-\int_{R_E}^{R_c} \frac{\Gamma_a(R)}{\hbar v(R)}\, dR\right) \approx \exp\left(-\frac{\tau_s}{\bar{\tau}_a}\right), \tag{2}$$

where Γ_a is the autodetachment width, R_E is the internuclear separation at which the electron is captured, R_c is the internuclear separation beyond which autodetachment is not possible, and $v(R)$ is the relative velocity of separation of the dissociating fragments. τ_s is the time needed for AB^{-*} to separate from R_E to R_c given by

$$\tau_s = \int_{R_E}^{R_c} \frac{dR}{v(R)} \tag{3}$$

and

$$\bar{\tau}_a = \frac{\hbar}{\bar{\Gamma}_a} \tag{4}$$

Figure 2. Schematic of the dissociative attachment from a vibrationally excited molecule AB. The two shaded regions show Franck–Condon regions corresponding to the zeroth vibrational level and a high-lying vibrational level. Other symbols are the same as in figure 1.

is the mean autodetachment lifetime of AB^{-*} with $\bar{\Gamma}_a$ being the average autodetachment width.

From the expression for $p(E)$ it is evident that as R_E becomes closer to R_c, τ_s decreases and $p(E)$ increases exponentially. When the neutral molecule is vibrationally excited, depending on the Franck–Condon factor, electron capture occurs at distances R_E which are closer to R_c (see figure 2). The corresponding τ_s would be smaller resulting in several orders of magnitude increase in $p(E)$ and σ_{DA}.

## 3. Dissociative attachment to electronically excited states and selection rules

The anisotropy in the angular distributions of negative and positive fragment ions produced by electron impact on molecules were attributed by Dunn [11] due to selection rules arising from symmetry constraints. He argued that since the interaction potential is a scalar sum of Coulomb terms, any symmetries existing prior to the collision must be preserved. For the dissociative attachment case, the incident plane wave represented by $e^{i\mathbf{k}\cdot\mathbf{r}}$ is symmetric with respect to all rotations about $\mathbf{k}$ and with respect to reflections in planes containing $\mathbf{k}$. If the target molecule happens to have its internuclear axis aligned along $\mathbf{k}$ at the time of collision, depending on its electronic state the molecule has definite symmetries with respect to these operations. Since the symmetries of the entire system before and after collision has to be conserved, in order to have nonvanishing transition probability, the final molecular ion state must possess the same symmetries with respect to these two operations. Following these arguments he worked out the selection rules for dissociative attachment to diatomic molecules as a function of their orientation with respect to the electron momentum vector $\mathbf{k}$. These selection rules has been used in identifying negative ion resonances and the angular distributions of the fragment negative ions in several situations [1, 6]. More importantly, based on the selection rules, one could visualize that if the symmetry of the molecule is changed through electronic excitation, it could capture electrons leading to negative ion resonances which were not allowed to be formed from the ground state. This aspect has been highlighted by the work on O_2 $\tilde{a}\,{}^1\Delta_g$ by Belic and Hall [13] in which they observed two new negative ion resonances that could not be formed from the ground state $\tilde{X}^3\Sigma_g^-$. Bottcher and Buckley [14] has done calculations which shows that dissociative attachment to excited molecular hydrogen in $\tilde{c}^3\Pi_u$ metastable state could produce substantially larger quantities of H^- as compared to dissociative attachment from the low vibrational levels of the ground electronic state $\tilde{X}^1\Sigma_g^+$ of H_2. This may have a strong bearing on the H^- production in hydrogenic plasmas when substantial numbers of the $\tilde{c}^3\Pi_u$ metastable H_2 molecules are present.

4. Experiments on excited molecules

4.1 *Excitation of molecules*

Preparing excited molecules in a specific state in sufficient number densities is the biggest challenge to collision experiments on excited states. As discussed above experiments have been conducted by heating the target gases, leading to the formation of rotationally and vibrationally excited molecules. Heating populates various levels according to
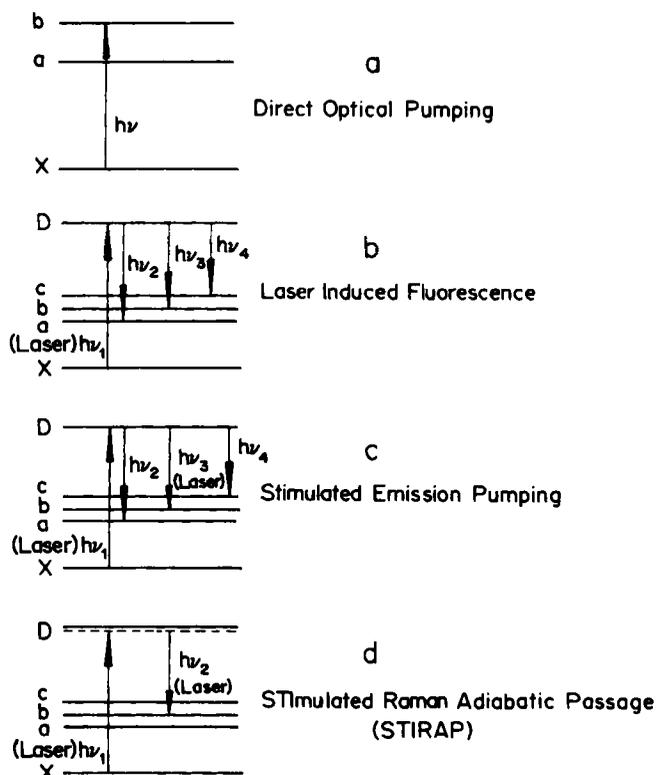
Figure 3. Schematic of various optical pumping techniques used for creating excited states. X is the ground state and the letters a, b, c and d are excited levels.

Boltzman distribution. DC, RF or microwave discharges have been used for producing molecules in excited states. But here again a mixture of states are populated. However microwave discharge has been used to produce a rather clean mixture of the excited metastable level $O_2\tilde{a}$ ($^1\Delta_g$) with O_2 molecules in the ground state for various collision experiments [12, 13, 15].

The development of high power and tunable lasers have opened up the possibility of using optical pumping techniques for preparation of excited molecules in sufficient number densities. A variety of schemes have been used in this respect. The first one is the simple optical excitation in which the ground state molecules are excited by photo-absorption to a higher level (figure 3a). This technique is useful for populating excited electronic states or a very low lying vibrational level of the ground electronic state. If the higher electronic state formed on photoabsorption is short-lived it may decay back to any of the lower levels through fluorescence (laser induced fluorescence or in short LIF) as shown in figure 3b. In the case of molecules, the LIF process leads to the population of a mixture of vibrational levels of the lower electronic state to which fluorescence occurs depending on the Franck–Condon overlap of the excited state with the lower state and in many cases this process has been used to populate higher vibrational levels of the ground electronic state. More efficient and selective population of the vibrational levels may be

achieved by using a second laser beam to stimulate the emission to a particular vibrational level after excitation to the upper electronic state occurs (figure 3c). This process called stimulated emission pumping may be able to transfer as much as a few tenths of the population from the ground vibrational level to a higher vibrational level. The most sophisticated technique used for transfering population to a higher level is the STImulated Raman Adiabatic Passage (STIRAP) [16]. This technique shown in figure 3d is capable of transfering almost the entire population to a specific excited state and has been used in creating excited vibrational level populations in Na_2 [16], NO [17], and SO_2 [18].

DA studies from vibrationally excited SF_6 [19], Li_2 [20] and Na_2 [16] produced by optical pumping and from vibrationally excited HCl and HF produced by laser photo-dissociation [21] have been reported. Measurements involving electronic excitation of the neutral state by optical pumping have been done on NO [22], C_6H_5SH [23], SO_2 [24] and NO, H_2 and D_2 [25, 26]. Electron attachment to laser irradiated H_2 [27] and triethylamine [28] 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. In fact, in most measurements involving lasers, the term 'laser enhanced dissociative attachment' has been used and as the name suggests these have been focused on the qualitative enhancements in the dissociative attachment cross sections.

From the above discussions it is clear that there has not been much success in studying dissociative attachment to excited molecules in a systematic way. Also a method to measure absolute cross sections for dissociative attachment from excited molecules has not been worked out yet. Considering this, we have initiated a programme to study dissociative attachment to excited molecules. In the following sections we describe our experiments and the results obtained on dissociative attachment to electronically excited SO_2 molecules.

4.2 *Experiment on SO_2*

The combination of a pulsed electron beam and pulsed ion extraction technique in conjunction with a segmented time-of-flight spectrometer has been found to be ideal for measuring absolute cross sections in dissociative attachment and ionization experiments using electron impact [29, 30]. The basic philosophy in such an apparatus is to collect all the fragment ions which are likely to be produced with kinetic energies of several electron volts using fairly large electric fields and transport them to a detector through a mass spectrometer without discrimination against their mass to charge ratios and initial kinetic energies and angular distributions. The ion extraction field required to collect all the ions is generally very large (typically, about 100 V/cm). Such a large field could be employed only by having it in a pulsed form and out of phase with the electron beam pulse so that the electron beam does not get affected by it. The appropriately designed segmented time-of-flight spectrometer acts as an electrostatic lens assembly transporting without loss, rather divergent beam of ions entering it to the detector.

This technique of pulsed electron, pulsed ion extraction is ideal for studying excited states as the high power lasers that could be used for excitation are pulsed in nature. In our experiment so far we have used a pulsed excimer laser. However the provision exists for using the excimer laser to pump a tunable dye laser with frequency doubling facility which in turn could be used to produce the excited states. The measurements were carried
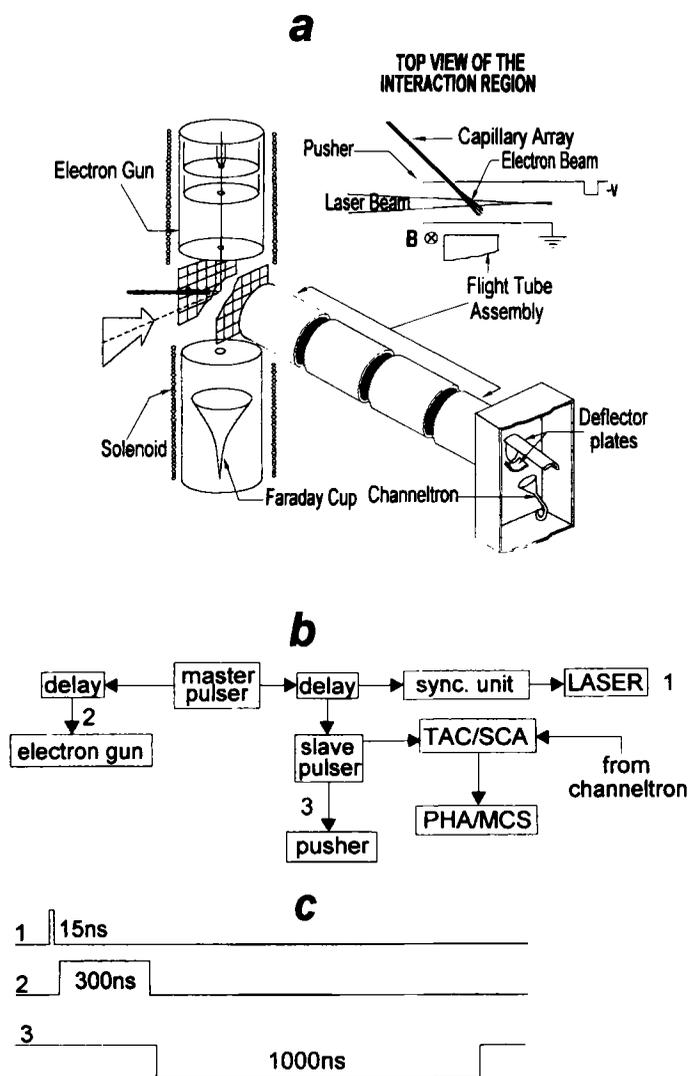
Figure 4. Schematic of the experiment for dissociative attachment to excited molecules. a: The experimental set up. b: The pulse control and data acquisition electronics. The computer control of the experiment including electron energy scan control and the details of the data acquisition are not shown. TAC/SCA represents the time to amplitude converter and single channel analyser and PHA/MCS represents the pulse height analyser and multi-channel scaler. c: The pulse sequence. The numbers 1, 2, and 3 corresponds to those in 'b'.

out in a triple crossed beam geometry in which the pulsed beam of laser excited the molecules in an effusive beam. A pulse of electrons intersected this effusive beam immediately (within a few tens of nanoseconds) following the laser pulse. The ions produced were extracted by a pulsed electric field into a multi-element time-of-flight mass spectrometer (TOFMS) and detected by a channel electron multiplier. The schematic of

the experimental arrangement is shown in figure 4. The details of the experiment and the measurement procedures could be found elsewhere [31].

4.3 *Selection rules and resonances in SO_2*

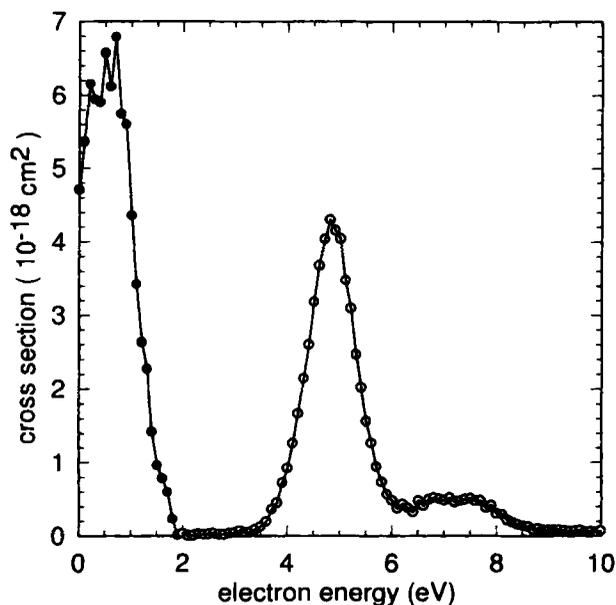Dissociative attachment to SO_2 in its ground state has been found to produce O^-, S^-, and SO^-. Of these O^- and SO^- channels have relatively large cross sections as compared to S^- channel [32]. Two major resonant features have been observed in all these ion channels, one between 4 and 5 eV and the second one slightly above 7 eV. Since the resonances appear in all the three channels approximately at the same energies, it is believed that all the three ionic channels arise from the same two resonances observed at these two energies. There exist no further information on the nature and symmetry of these resonances.

Our results on the cross-sections for the formation of O^- and SO^- from the excited state are given in figures 5 and 6 respectively along with those from the ground state. The formation of S^- from the excited state was too weak to make any reliable measurements. It is found that the resonance attachment to the excited state gives rise to new peaks in the O^- and SO^- data at electron energies shifted approximately by 4 eV from the first peak observed from the ground state molecules. The laser enhanced dissociative attachment by Jaffke *et al* [24] have made a similar observation.

The most noteworthy part of the results is the absence of a second peak due to dissociative attachment to the excited state. One would expect to see additional peaks at about 3 eV in both the O^- and SO^- data due to DA to the excited molecules corresponding to that seen at about 7 eV from the ground state. It may be argued that the
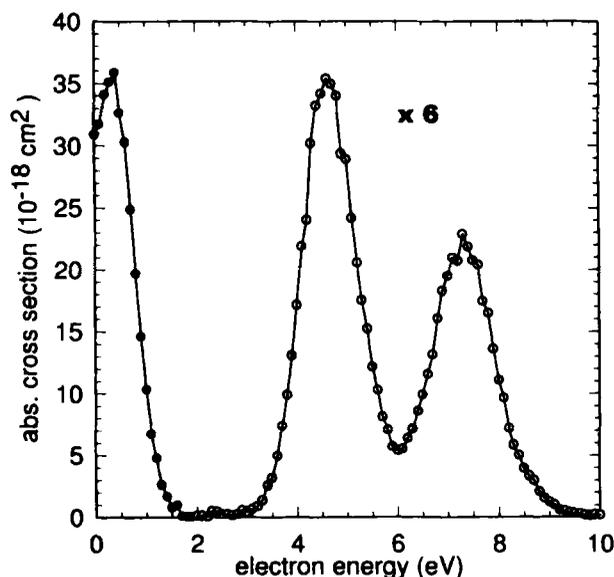

Figure 5. The dissociative attachment cross sections for the formation of O^- from ground and excited states of SO_2. The filled circles represent the cross-sections from the excited ($\tilde{B}^1B_1$) state and the open circles from the ground ($\tilde{X}^1A_1$) state respectively. The values for the ground state have been multiplied by a factor of six.

Figure 6. The dissociative attachment cross sections for the formation of SO$^-$ from ground and excited states of SO$_2$. The filled circles represent the cross-sections from the excited ($\tilde{B}\,^1B_1$) state and the open circles from the ground ($\tilde{X}\,^1A_1$) state respectively.

absence of the above peak from the excited state is due to small 'survival probability' (see eq. (2)) of the NIRS. However, as the excited neutral states will be in higher vibrational levels, the NIRS formed from them should have larger survival probability, leading to larger dissociative attachment cross sections. Thus the absence of the peak has to be attributed to selection rules governing the electron capture process. An analysis of this based on the selection rules helped not only to identify the negative ion resonance but also to characterize the excited neutral state itself, which has not been possible by high resolution optical spectroscopy [33].

Using the general rule laid out by Dunn [11], we worked out the selection rules for dissociative attachment to SO$_2$ which has a C_{2v} symmetry, taking into account all possible orientations of the molecule with respect to the momentum vector of the incident electron as discussed below. In the laboratory frame, the molecules are randomly oriented and the incident electron momentum vector is fixed. In order to get the selection rules we consider three mutually perpendicular orientations of the molecule with respect to the electron momentum vector k. These are shown in figure 7. In the first case, the molecule is in the xy-plane with its symmetry axis oriented in the direction of k. Thus the initial system of electron plus molecule has a C_{2v} symmetry. The symmetry operations relevant to the C_{2v} group are a rotation through 180° about k and reflections in the plane of the molecule and the plane containing k normal to the plane of the molecule. In order to have nonzero transition probability to the negative ion state, the initial molecular state and final negative ion resonant state should have the same symmetry with respect to these operations. Using the character table for C_{2v} group we find that the selection rules for this
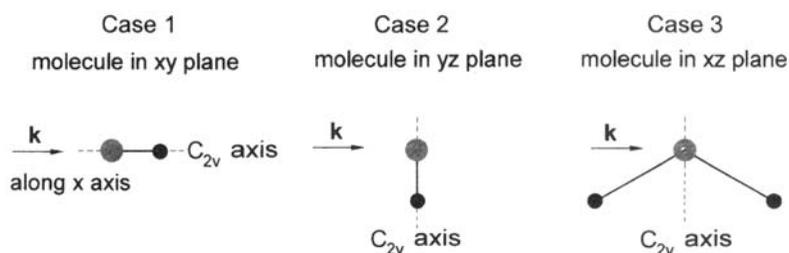
Figure 7. Three cases of mutually perpendicular orientations of a molecule of C_{2v} symmetry with respect to the incident electron momentum vector **k** considered for determining the selection rules for the formation of negative ion resonance.

particular orientation of the molecule with respect to **k** are $A_1 \leftrightarrow A_1$, $A_2 \leftrightarrow A_2$, $B_1 \leftrightarrow B_1$ and $B_2 \leftrightarrow B_2$.

In the second case, the molecule is oriented with its plane normal to **k**. In this case the electron-molecule system has C_s symmetry. The symmetry operation relevant to this system is the reflection in the plane containing **k** and normal to the plane of the molecule. The selection rules in this case works out to be $A_1 \leftrightarrow A_1$, B_2; $A_2 \leftrightarrow A_2$, B_1 with similar rules for B_1 and B_2 states. In the third case, the molecule is oriented in such a way that **k** lies in its plane, but normal to the symmetry axis of the molecule. In this case again the electron-molecule system has a C_s symmetry, with the lone symmetry operation of reflection in the plane of the molecule. The selection rules corresponding to this are seen as $A_1 \leftrightarrow A_1$, B_1; $A_2 \leftrightarrow A_2$, B_2 etc. The selection rules for all the three orientations are given in table 1. In the case where molecules are randomly oriented and measurements are made without any angular discrimination as in our case, the selection rules will be the union of all the three cases and are given in table 2.

From table 2 we see that if the initial state of the neutral is a B_1, the NIRS cannot be a B_2 and vice versa. Similar restrictions exist between A_1 and A_2. All other combinations are possible. As a result, any NIRS which is a B_2 is accessible only from A_1, A_2 and B_2 states of the neutral and not from a B_1 state. This readily explains why the second resonant peak is not accessed from the excited state which is a B_1 but is accessed from the ground state which is an A_1 and identifies the NIRS as a B_2 state. Thus we are able to characterize the NIRS using selective excitation of the neutral, without recourse to angular distribution measurements. Once we are able to characterize the resonance observed above 7 eV, based

Table 1. Selection rules for resonant attachment of electrons for the three mutually perpendicular orientations of the molecules of C_{2v} symmetry.

| Neutral state | NIRS | | | |
	A_1	A_2	B_1	B_2
A_1	a—a—a	n—n—n	n—n—a	n—a—n
A_2	n—n—n	a—a—a	n—a—n	n—n—a
B_1	n—n—a	n—a—n	a—a—a	n—n—n
B_2	n—a—n	n—n—a	n—n—n	a—a—a

a: Allowed, n: Not allowed. Case 1 is on the left, case 2 is the middle and case 3 on the right (see text for description of the three cases).

Table 2. The selection rules for resonant attachment of electrons with randomly oriented molecules like SO_2 with C_{2v} symmetry.

| Neutral state	NIRS			
	A_1	A_2	B_1	B_2
A_1	a	n	a	a
A_2	n	a	a	a
B_1	a	a	a	n
B_2	a	a	n	a

a: Allowed, n: Not allowed.

on quantum chemical calculations and the selection rules discussed above, it was possible to assign the resonance observed at lower energy as a $^2A_1$ state [33].

An unexpected, but rather straightforward result which came out of this experiment was the characterization of the excited neutral state itself. The optical excitation of SO_2 from the ground state by 308 nm laser radiation leads to the Clements' bands [34,35]. This band shown in figure 7 has been characterized by some very unusual properties. Dipole selection rules allow excitation only to the $\tilde{B}\ ^1B_1$ state. However, no signature of any vibrational bands of $\tilde{B}\ ^1B_1$ has been observed yet. What is observed are the finger-like bands with anomalous intensity pattern (Clement's bands). This band structure has been explained as due to a $\tilde{A}\ ^1A_2$ state which vibronically couples strongly with $\tilde{B}\ ^1B_1$ [36,37]. The only signature of the $\tilde{B}\ ^1B_1$ state is the quasi continuum-like structure underlying the Clements' bands. Also fluorescence measurements from this state has shown anomalously large lifetime [38]. This and the absence of any clear vibrational bands due to $\tilde{B}\ ^1B_1$ has been explained as due to strong mixing with closely spaced high
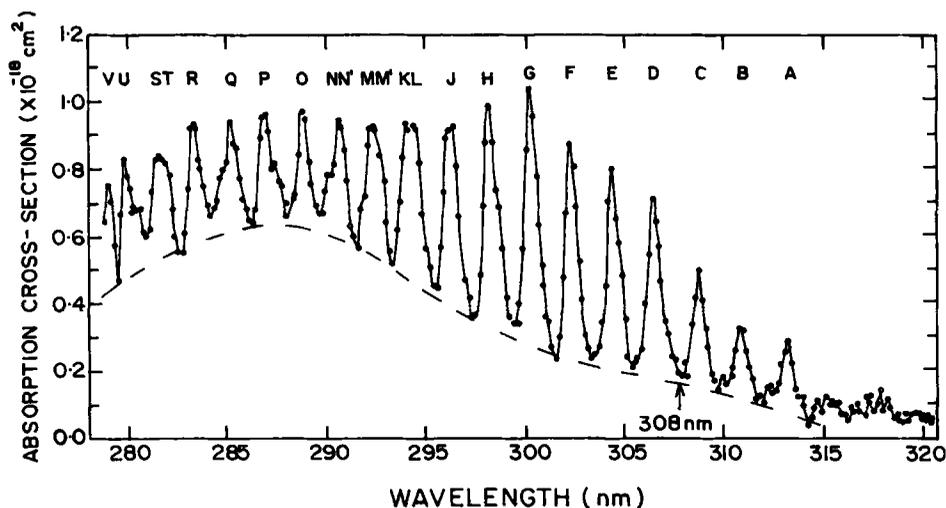
Figure 8. Photoabsorption cross section of SO_2 in the region of the Clements' bands [35]. The dashed line has been drawn to show the underlying continuum below the finger-like band structures marked alphabetically. The arrow indicates 308 nm at which the molecules are excited using the XeCl excimer laser.
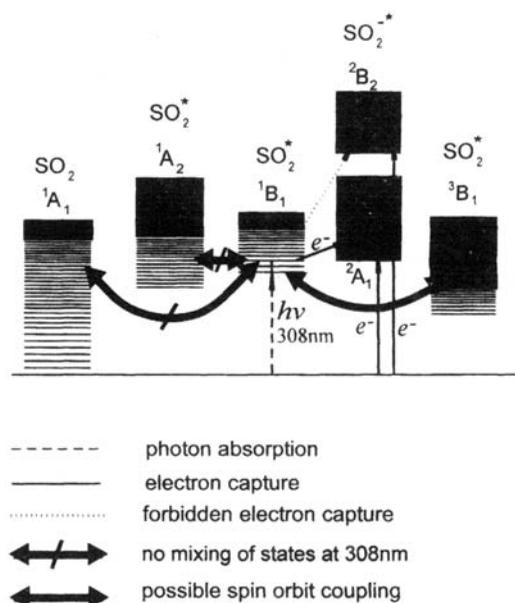
Figure 9. Schematic representation of the conclusions on the dissociative attachment to the excited ($\tilde{B}\,^1B_1$) state and the ground ($\tilde{X}\,^1A_1$) state based on measurements and selection rules. The horizontal line at the bottom represents the $v = 0$ vibrational level of the ground electronic state $^1A_1$. The $^1B_1$ state is reached by absorption of the 308 nm photons. The figure shows that electron attachment to the ground state leads to two negative ion resonances, $^2A_1$ and $^2B_2$ of SO_2^{-*}. However electron attachment to the excited $^1B_1$ state leads to only the $^2A_1$ resonance. The absence of the $^2B_2$ resonance in the excited state dissociative attachment overrules possible mixing of the high-lying vibrational levels of the $^1A_1$ state and the $^1A_2$ state with the $^1B_1$ state. See text for details.

lying states of the ground state $\tilde{X}\,^1A_1$ through vibronic interaction (Renner–Teller coupling) and with $\tilde{a}\,^3B_1$ state through spin orbit interaction [36, 39]. Thus based on the existing spectroscopic data, excitation by 308 nm photons leads to a state which is a mixture of $\tilde{B}\,^1B_1$, $\tilde{A}\,^1A_2$, $\tilde{X}\,^1A_1$ and possibly $\tilde{a}\,^3B_1$ states. However, if $\tilde{A}\,^1A_2$ and $\tilde{X}\,^1A_1$ were present in the admixture, we would expect to see a second peak in the resonance attachment from the excited molecule as the selection rules do not overrule the attachment process from these states to form a $^2B_2$ NIRS. Since we do not see such a process, we have to conclude that the state excited by the 308 nm radiation does not have any $^1A_2$ or $^1A_1$ characteristics but is only B_1 in nature. The absence of vibronic mixing between the $^1A_2$ and the $^1B_1$ states at 308 nm excitation may be due to the fact that the rovibrational levels of the $^1B_1$ state is far removed from the rovibrational levels of the $^1A_2$ state. This is supported by the fact that the absorption at 308 nm lies right in the valley between the Clements' C and D bands [34, 36] (see figure 8). The observation, that the excited state does not have any $^1A_1$ characteristic leads us to the conclusion that the quasi continuum nature seen for the $\tilde{B}\,^1B_1$ is entirely due to mixing with the $\tilde{a}\,^3B_1$ state. A schematic representation of these results is given in figure 9.

4.4 *Absolute cross sections*

The absolute cross-sections for the ground state SO_2 were obtained by using the relative flow technique [40] using the accurately known cross-section for formation of O^- from O_2 [41]. In order to obtain the cross-sections for the excited state molecules, it was necessary to obtain their number density relative to that of the ground state molecules. This was done by measuring reduction in the dissociative attachment signal due to molecules in the ground state when the laser is put on. As the experiments were done in 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 to 0.15 depending on the spatial overlap of the electron and laser beams, the cross-sections for the excited states were determined. A host of several other careful measurements were necessary in determining the absolute cross sections. These were related to the possible presence of multi-photon processes and ion extraction and detection efficiencies [31]. The overall uncertainty in the cross section from the excited state was estimated to be 20%.

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* [24] 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 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.

5. 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 of 50 to 530 µs [42]. 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 nanoseconds. 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 sufficient signal it is necessary to have 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 nanoseconds 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. Population of higher vibrational levels of the ground electronic state due to 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 which 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 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 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 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 do not give rise to any dissociative attachment.

Thus it appears that the present technique is best suited for those states with relatively large lifetime (μsecond range) and may be used for states with short lifetimes (100 nanosecond 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. Dissociative attachment to excited state of CS_2 molecule [43] has already been carried out and similar measurements on other molecules are in progress.

The method described here may also be useful in carrying out dissociative attachment measurements on radicals which could be produced by photodissociation. In addition, this technique opens up the possibility of carrying out measurements on positive ion production from excited and state selected molecules by electron impact as well as investigating the dissociation dynamics of positive and negative ions as a function of their initial geometries.

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