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Dissociative electron attachment to electronically excited CS_2

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Dissociative attachment of low-energy electrons to the electronically excited and bent ${}^1B_2$ state of CS_2 is studied. The measurements are carried out in a crossed three-beam geometry in which a laser beam is used to prepare the excited molecules. The absolute cross sections for the formation of S^- and CS^- by dissociative attachment to the ${}^1B_2$ excited state are determined by a measurement of the relative number density in the excited state. Based on the earlier observation of the formation of $S_2{}^-$ from the linear symmetric ground state of CS_2, an increase in the $S_2{}^-$ cross section was expected from the bent excited state. However, $S_2{}^-$ is found to be absent from this state. Possible mechanisms are proposed to explain this counterintuitive result.

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I. INTRODUCTION

Negative-ion resonances in low-energy electron-molecule collisions have been a subject of much attention for the last four decades. The formation and decay of these resonances are very sensitive to the initial conditions of the molecule. This has manifested in several dissociative electron attachment (DEA) experiments from excited states. Most of these measurements have been from vibrationally excited molecules produced by direct heating of the gases while only a few experimental studies have been reported from electronically excited states of molecules.

Despite the need for studying DEA from excited states, the measurements have been relatively few due to the the formidable difficulty of creating the excited states in sufficient number densities. Though a variety of techniques like surface recombination [1], microwave discharge [2], and electron impact [3] have been tried out, conventional heating and optical pumping techniques in some form or other have been the most successful methods for populating excited states for the DEA measurements. Optical pumping has been used in various forms to carry out experiments on vibrationally excited SF_6 [4], Li_2 [5], Na_2 [6], and HCl and HF [7] and electronically excited NO [8], C_6H_5SH [9], SO_2 [10], NO, H_2 and D_2 [11–13], and triethyl amine [14]. Very recently magnetic- and electric-field-induced enhancements in laser-induced anion formation by the attachment of secondary electrons to high Rydberg states of molecules has been reported [15]. All of the above measurements have been qualitative in nature. Moreover, in some of these cases the excited states of neutrals involved were not identified or the measurements have been carried out in conditions where multiple collisions could dominate.

In the present work we report DEA studies from electronically excited CS_2, which is a linear symmetric molecule ($D_{\infty h}$) in its ground electronic state $\tilde{X}\ {}^1\Sigma_g^+$. Like NO_2 and SO_2, CS_2 is a Douglas-type molecule with anomalous lifetimes for its excited state(s), which absorb in the near UV. The DEA to the ground state of CS_2 has been found to give several resonances in the S^- channel, some weak resonances in the C^- channel, and one rather strong resonance each in the CS^- and $S_2{}^-$ channel [16]. Furthermore, it has also been found that $S_2{}^-$ is formed only through a resonance capture unlike other fragment ions which could be formed through polar dissociation as well [16]. The formation of $S_2{}^-$ from CS_2 is a unique process, as the constituent atoms of the negative ion fragment are not directly bonded to each other in the parent neutral molecule. In this particular case, the $CS_2{}^{-*}$ negative-ion resonance state (NIRS) formed by electron attachment to the linear CS_2 molecule goes through a bending process, bringing the two S atoms sufficiently close for bond formation before the two C-S bonds are broken [17]. This leads naturally to the expectation that the neutral CS_2 molecule in an initial state of bending mode vibration or in an electronic state with bent geometry could lead to a strong enhancement in the $S_2{}^-$ channel in DEA. On absorption of the 308 nm radiation, CS_2 gets excited to the bent ${}^1B_2$ state (since this is the equilibrium geometry of the excited state) with C_{2v} symmetry. Thus DEA to this state was thought of as an ideal way of selectively increasing the relative intensity of $S_2{}^-$ ions. Here we report the results of these experiments including absolute cross sections for the formation of S^- and CS^- from the excited ${}^1B_2$ state. Contrary to expectations, we did not find evidence for the formation of $S_2{}^-$ from the bent excited state in these experiments. Probable mechanisms to explain this observation are proposed.

II. EXPERIMENT

The experimental setup and the method of measurement has been discussed in our work on SO_2 [18,19]. For the sake of clarity we give below a summary of the experiment.

The measurements were carried out in a triple-crossed-beam geometry employing a pulsed beam laser, a pulsed electron gun, and an effusive molecular beam formed by a capillary array. A XeCl ($\lambda = 308$ nm) excimer laser (LPX 240i, Lambda Physik) operated at a repetition rate of 300 Hz was used for exciting the molecules. Its temporal profile had a half width of about 14 ns. The beam was transported to the

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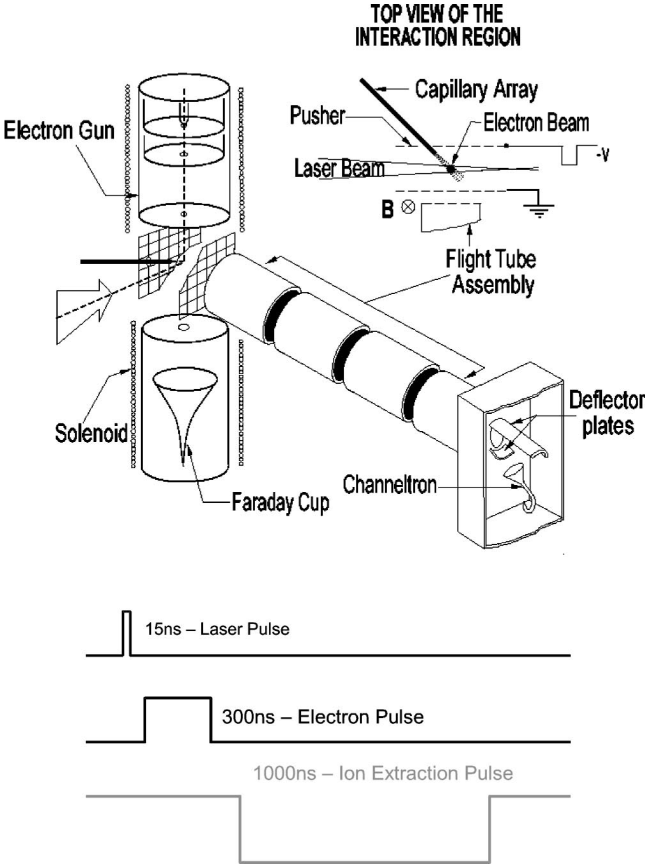

FIG. 1. Schematic illustration of the experimental arrangement. The inset on the top right is a detail of the collision region and the pulsing sequence is illustrated at the bottom.

interaction region using a pair of mirrors and focused by a lens of focal length 500 mm. The laser pulse interacted with the molecular beam, exciting a fraction of the CS_2 molecules to the $^1B_2$ state. The electron beam [300 ns wide and energy resolution of 0.5eV full width at half maximum (FWHM)] intersected the molecular beam within a few tens of nanoseconds after the laser pulse. After the termination of the electron pulse, the ions produced were extracted by the application of a 200 V/cm electric field pulse of 1 μsec duration, to the pusher plate of the ion extraction assembly of a segmented time-of-flight mass spectrometer (TOFMS). As the ion extraction pulse comes into effect only after the termination of the electron pulse, a relatively high electric field could be employed in order to extract all the ions irrespective of their initial kinetic energies and angular distributions without affecting the electron beam. These ions entering the mass spectrometer may still have a reasonable divergence, depending on their initial kinetic energies and angular distributions. The segmented TOFMS acts as a focusing device for these divergent beam of ions while they are transported to the detector without loss, thus making accurate measurements of cross sections possible. The ions were detected by a channel electron multiplier mounted off axis and operated in the pulse counting mode. The schematic of the experimental arrangement is shown in Fig. 1 along with the pulsing sequence. The time jitter and drift in the laser pulsing were minimized by using a synchronizing unit. The performance of this apparatus was evaluated in a similar manner to that reported earlier for dissociative attachment studies from the ground-state molecules [16] and has been discussed in our recent work on excited SO_2 molecules [19].

The TOF spectra were recorded using a time-to-amplitude converter (TAC) and a pulse height analyzer (PHA). In the case of CS_2, the dominant ions formed from the ground-state are S^-, CS^-, and $S_2{}^-$. The count rate for each of these ions versus the incident electron energy (ion yield curve) could be simultaneously recorded by using three TAC's and by selecting the corresponding time windows in each of the TAC's and storing the data using a GPIB-based data acquisition system. This data acquisition system also controlled the digital power supply used for defining the electron beam energy apart from ensuring simultaneous monitoring of the electron beam current and the intensities of all the ionic species of interest. The above arrangement provides accurate compensation of the ion yield curve for the possible variation in current and also the collection of all the ion yield curves simultaneously, thereby reducing the data acquisition time considerably and improving the reliability.

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 achieved by taking the mass spectra at the electron energies corresponding to the peaks in the dissociative attachment spectrum from the ground state with and without the laser beam, keeping all other parameters like the gas pressure and the electron beam current constant. It is noticed that the TOF spectra taken in the presence of the laser have a lower count rate as 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 excitation, since at the electron energy used, attachment occurs only to the ground-state molecules. Using the difference in the ion intensities of the two cases, we calculated the percentage depletion of the target molecules due to laser excitation. Checks were made for signatures of multiphoton excitation and dissociation processes by varying the laser intensity. They did not show significant effects to indicate multiphoton processes. Thus, for all practical purposes, the experiments were done in the single-photon absorption regime. Since the lifetime of the excited state involved is much larger than the combined duration of the laser pulse and the subsequent electron pulse and multiphoton processes are found to be negligible, the observed depletion corresponds to the fraction of molecules in the excited state. Using this fraction, the cross sections for the excited states were determined. The excited-state fraction determination is discussed in greater detail in our recent work on SO_2 molecules [19].

III. ERRORS AND THEIR ESTIMATION

The dominant contribution to the uncertainty in the present measurements arises from the determination of the fraction of molecules in the excited state as compared to that in the ground state. The fraction was determined by measuring the reduction in the DEA signal from the ground state at the electron energy corresponding to the peak cross section for the formation of S^- by collecting the TOF mass spectra and determining the areas under the peaks. The maximum depletion percentage measured by us was in the range of 5–6%. The statistical error in determining this fraction is 50%. Special care was taken to limit this error by collecting data for a large priod of time to improve the statistics as well as repeating the measurements. In addition, there may be a systematic error due to the assumption that multiphoton processes do not contribute to the depletion of molecules from the ground state on laser irradiation. As in the case of SO_2 molecules [19], experiments were conducted as a function of the laser intensity to examine this. However, a trend as a function of laser intensity could not be discerned as the data were dominated by the statistical fluctuation in the depletion measurements. Hence we concluded that the systematic error due to multiphoton processes was much smaller than the statistical error in depletion measurements. Thus the total uncertainty in the measurement of the relative number density is the statistical error mentioned above. The systematic error in the cross sections due to the increase in the path length of the low-energy electrons due to their helical trajectories in the collimating magnetic field [20] was corrected for, taking into account the size of the interaction region. This correction has led to the lowering of the measured value of the cross section close to 0 eV electron energy. Other contributions to the overall error arise due to the uncertainty in the absolute cross sections from the ground state which are used for normalization of the excited-state cross sections. The uncertainty in the ground-state cross sections is 15% [16] of the reported cross section value at the peak. Thus the rms error in the excited-state cross section values is heavily dominated by the measured statistical error in the depletion and works out to be 52% at the peak of the S^- cross section from the excited state. Away from the peak this would be larger, as the statistical error from the measurement of the ion yield curve increases as one moves away from the peak, particularly for the case of CS^-.

IV. RESULTS AND DISCUSSION

DEA to the ground state of CS_2 has been found to produce S^-, CS^-, $S_2{}^-$, and relatively a small quantity of C^-. The S^- cross sections exhibit two strong resonant peaks at 3.6 and 6.2 eV and two relatively weak ones at 7.7 and 9.2 eV, respectively, whereas CS^- and $S_2{}^-$ are found to have one major resonant peak at 6.2 eV [16]. The fact that only S^- has been observed from the resonance at 3.6 eV has been attributed to the minimum energy needed to produce CS^- and $S_2{}^-$ from CS_2 based on thermochemical data. The resonance at 6.2 eV dissociates through the S^-, CS^-, and $S_2{}^-$ channels as has been observed earlier [16].

On irradiation by the 308 nm (4.03 eV) photons, a new peak each was observed in the S^- and CS^- channels. These are shown in Fig. 2. The peak for S^- is centered at 0.5 eV and that for CS^- is centered at 0.7 eV. Both peaks have finite cross section even at 0 eV. The CS^- peak seem to be broader than the S^- peak. The ground-state counts (with laser off) in the present measurements were normalized with the cross section values given in [16] for S^- and CS^-, respectively. The excited-state cross sections were put on an absolute scale using the fraction of molecules in the excited state as measured by the depletion of the DA signal from the ground-state molecules. The absolute values of the cross sections from the excited state at the peaks for S^- and CS^- were 3×10^{-18} cm^2 and 1.7×10^{-19} cm^2, respectively. A tabular summary of cross section values of the DEA fragment ions is presented in Table I. The cross section from the excited state is about an order of magnitude larger as compared to that from the ground state for the S^- channel. However, for the CS^- channel, it is about a factor of 3 larger. In the absence of any information on the potential energy surfaces of the neutral and negative-ion states, it is difficult to say if the observed increase is due to the change in capture cross section, the survival probability, or both.

A surprising result of our measurements was the absence of any S_2^- signal from the excited molecules as shown in Fig. 3. Spectroscopic data on CS_2 [21] show that on absorption of

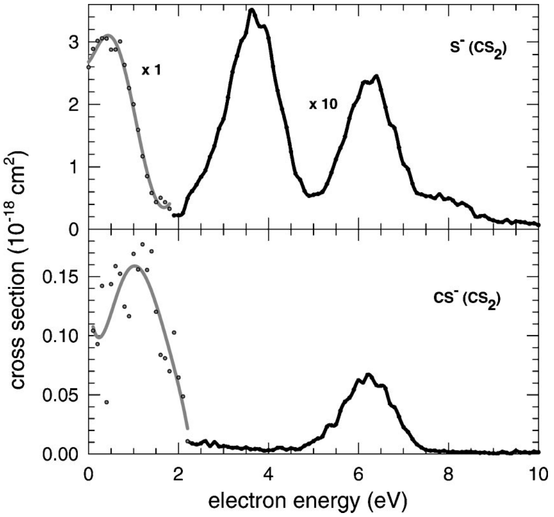

FIG. 2. The S^- and CS^- fragment ion cross sections as a function of incident electron energy. The open symbols indicate the DEA cross section from the excited $^1B_2$ neutral state. The solid symbols represent the ground-state cross sections. In the S^- excitation the DEA signal from the ground state is multiplied by a factor of 10.

TABLE I. DEA cross sections from ground and excited states of CS_2.

Ion	Electron energy at ion peak (eV)	Cross section at ion peak (10^{-18} cm^2)	Initial neutral state
S^-	0.5	3.0	$^1B_2$
	3.6	0.35	$^1\Sigma_g{}^+$
	6.2	0.245	$^1\Sigma_g{}^+$
	7.7	0.04	$^1\Sigma_g{}^+$
CS^-	1.2	0.175	$^1B_2$
	6.2	0.067	$^1\Sigma_g{}^+$
$S_2{}^-$	-	-	$^1B_2$
	6.2	0.025	$^1\Sigma_g{}^+$

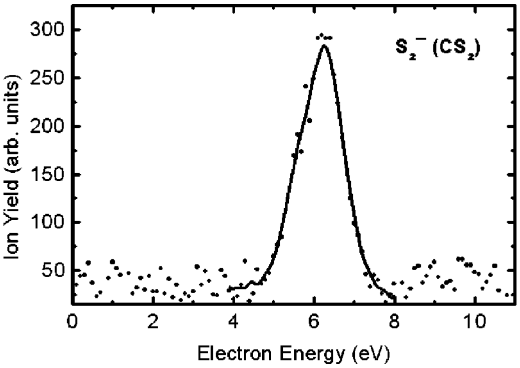

FIG. 3. The S_2^- ion yield curve with the 308 nm laser excitation on. There is no discernible effect of S_2^- negative ion formation from the $^1B_2$ laser excited state.

the 308 nm radiation, the linear symmetric molecule with $D_{\infty h}$ symmetry gets excited to the $^1B_2$ state in bent equilibrium geometry with C_{2v} symmetry. The formation of S_2^- from the ground state (the cross section is as much as a third of the cross section for the formation of CS^-) showed that the negative-ion resonance centered at 6.2 eV may have a bent equilibrium geometry, as the bent geometry facilitates a reduction in the separation between the two S atoms. Considering this, one expects that if the initial neutral state has a bent geometry, a better Franck-Condon overlap to the bent negative-ion state would show an increase in the S_2^- cross sections. It may seem from the ion yield curve shown in Fig. 3 that there is insufficient statistics to detect a peak from the excited state in the S_2^- channel. However, in the present experiment we have made measurements in the mass spectrum mode at several discrete energies below 6.2 eV, where the S_2^- peak from the laser excited state could manifest. These measurements, carried out with a large collection time and thus better statistics, did not show the presence of S_2^- from the excited state.

It may be noted that the threshold for the formation of a $S_2^-(\tilde{X}\ ^2\Pi_g)$ ion from the ground state is 5.2 eV [22,16]. As the energy of the photon used for excitation is 4.03 eV, the threshold for the formation of S_2^- from the excited state will be 1.2 eV. Though we see formation of S^- and CS^- from the excited state beyond 1.2 eV, S_2^- seems to be absent even at higher energies except for the signal from the ground state. Based on energetics, one would have expected to see the formation of S_2^- at about 2.2 eV, assuming that the negative-ion state seen from the ground state is accessible from the excited state and that the Franck-Condon overlap remains energetically the same as in the case of ground-state attachment.

Two possible explanations are given below based on deviations from the above two assumptions in order to explain the observations.

1(a) The electron–excited-molecule interaction potential is considerably different from the interaction potential between the electron and ground-state molecule. The major contribution to the interaction potential arises from the polarizability of the molecule. As the molecule is electronically excited, the polarizability would be modified. The resulting change in the interaction potential would lead to modification of the possible negative-ion resonant states, particularly for the case of shape resonances. This may imply that the negative ion resonance state, accessed from the ground state and the laser excited state, may be completely different. The formation of S_2^- from the ground neutral state requires that the NIRS induce the molecular evolution into simultaneous bending and dissociation. In view of this, one would expect to see evidence of a resonant peak from the excited state in the S_2^- cross section channel at an energy value that is less than 6.2 eV. Additionally the magnitude of the cross section can be expected to be larger if the NIRS is the same in both cases. Thus the absence of the S_2^- ion in the DEA spectrum from the $^1B_2$ laser excited state (with bent geometry) can well imply that the NIRS (seen in the S^- and the CS^- channels) being accessed from excited-state molecules is distinct from the one being accessed from the ground state. This also agrees with the fact that the peak energies seen in the S^- and the CS^- channels do not seem to be energetically related to any of the peaks seen from the ground state through the 4.03 eV photon used for excitation. (b) A possible extension to this argument could be that a different NIRS which is above the 6.2 eV NIRS is accessed from the $^1B_2$ state which correlates to $C(^3P_0)$ and S_2^{-*}. There are two excited states of S_2^- at 2.45 eV ($^2\Pi_u$) and 2.48 eV ($^2\Sigma_u$), respectively. The excited states of S_2^- would be short lived against autodetachment and thus may not be observed.

(ii) The electron capture may be occurring to the same molecular negative ion state, from both the ground $\tilde{X}\ ^1\Sigma_g^+$ state as well as the laser excited $^1B_2$ state. Since the ground state is linear and the excited state bent, an entirely different part of the same NIRS potential energy surface (PES) is being accessed from the ground and electronically excited states. The local area of the PES of the NIRS may be such that the dissociation pathway leading to the formation of the S_2^- ion may not be possible. While this may seem contrary to the initial line of reasoning that motivated this study in the first instance, it cannot be ignored as a possible explanation of the experimental observations. The fact that the peak energies seen in the S^- and the CS^- channels do not seem to be energetically related to any of the peaks seen from the ground state through the 4 eV photon used for excitation may also be attributed to the different region of the accessed PES. However, the present state of our knowledge about CS_2 is such that a more educated statement along this line cannot be made.

V. CONCLUSIONS

We have presented measurements of the DEA cross sections from the electronically excited $^1B_2$ state of the CS_2 molecules. From this state the S^- and CS^- fragment ions are observed. The cross section for the formation of S^- is about an order of magnitude larger than that obtained from the ground state of CS_2. For the CS^- ion the increase is by an aproximate factor of 3. The absence of a S_2^- fragment ion from the excited state only serves to emphasize the pitfalls of simple intuitive reasoning for this complex, multistep phenomenon. We have presented two possible explanations of the observed results. Information on the potential energy surfaces of neutral and negative-ion states of CS_2 are needed for a better understanding of the observed results. Thus future work must be along both experimental and computational and theoretical lines in order to make more definitive statements.

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