Dissociative electron attachment to SO$_2$ near 7.5 eV resonance and axial-recoil approximation

Irina Jana$^1$, Sumit Naskar$^2$ and Dhananjay Nandi$^1$

$^1$Department of Physical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur-741246, India
$^2$Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur-741246, India
E-mail: ij14rs047@iiserkol.ac.in

Abstract. We present experimental results for dissociative electron attachment to sulfur dioxide near the 7.5 eV resonance. The dissociation channels leading to O$^-$, S$^-$ and SO$^-$ ions formation have been investigated with a velocity map imaging technique. While the O$^-$ and SO$^-$ ions formed by dissociative electron attachment show angular distributions characteristic to a combination of $A_1+B_2$ symmetry, the S$^-$ ions show angular distributions resulting from changes in the orientation of the dissociating bond due to bending mode vibrations implying the failure of axial-recoil approximation.

1. Introduction

Chemical reactions initiated by collisions with low-energy electrons play an important role in atmospheric chemistry, astro-chemistry, synthetic chemistry, and biology, amongst other areas. Understanding the mechanisms of these reactions in detail offers new insight into a range of vital physical and chemical processes, ranging from the breaking of a single chemical bond all the way through to complex multi-step processes. Low-energy electron attachment to molecules resulting in the formation of a temporary negative ion (TNI) and then dissociation of the TNI into negative ion and neutral fragments is known as dissociative electron attachment (DEA). Since the path-breaking works of Chandler and Houston [1] and Eppink and Parker [2], it is a well-known practice to measure the complete scattering distribution of the resulting negative ion fragment using the velocity-map ion imaging (VMI) technique [3, 4]. VMI combines time-of-flight mass spectrometry with imaging, separating ions of different mass and mapping their velocity distributions onto a position sensitive detector. Having controlled the initial velocity of the reactants and measured the final velocities of the products, one can ‘join the dots’ to learn about the forces and energetics that drive the chemical reaction under study. The kinetic energy and angular distribution of the negative ion fragments can thus be revealed from the velocity map images. Such experiments yield great insight into the physics underlying chemical reactivity [5, 6, 7, 8].

DEA to SO$_2$ produces three negative fragment ions O$^-$, S$^-$ and SO$^-$ at two resonances near 4.5 and 7.5 eV incident electron energies [9]. We report here DEA to SO$_2$ for the formation of O$^-$, S$^-$ and SO$^-$ ions close to the second resonance near 7.5 eV. According to the axial-recoil approximation, the symmetry of the TNI can be found from the negative
ions’ velocity-mapped images provided the molecule does not rotate or undergo any structural changes before the dissociation of the TNI into respective negative and neutral fragments takes place. Thus, the negative fragment ion retains the information on the orientational dependence of the electron capture process [10]. This methodology can be used to extract the angular distribution information, related to partial waves s, p, d,... in the attachment process, by fitting the experimental data with the theoretical formula given by O’Malley and Taylor and Azria et al. [11, 12]. However, this methodology completely fails in the absence of the axial-recoil approximation thus making it impossible to extract information about the symmetry of the TNI.

It can be noted from the existing literature that for some molecules, such as CO$_2$, the axial-recoil approximation can be seen to fail implying a strong nonaxial recoil effect due to the bend and stretch contributions to the dissociation dynamics [13, 14]. CO$_2$ is known to have a 4 eV shape resonance and 8 eV Feshbach resonance. The negative fragments ions’ angular distributions around both the 4 and 8 eV resonances are observed to show remarkable difference from the axial-recoil prediction giving a clear evidence of an axial-recoil approximation breakdown.

In this article we report DEA studies to SO$_2$ around the second resonance at 7.5 eV for O$^-$, S$^-$ and SO$^-$ ions to present an interesting case where the axial-recoil approximation is seen to be valid and failing simultaneously for the same molecule depending on the negative ion fragment produced after the dissociation. The O$^-$ and SO$^-$ fragments are known to be produced from the asymmetric stretching of the molecule. The S$^-$ ions, on the other hand, come from symmetric stretching simultaneously accompanied by symmetric bending with O$_2$ produced as the neutral counter-part [15].

2. Experimental apparatus
The experimental technique has been described in detail previously, so we will provide only a brief overview here [16, 17, 18]. The momentum of the final-state anionic fragments O$^-$, S$^-$ and SO$^-$ following DEA to SO$_2$ molecules were measured using a velocity slice imaging negative ion spectrometer. A gaseous target beam is effused from a narrow stainless steel capillary to intersect with a magnetically collimated electron beam pulsed at 10 kHz repetition rate forming a ‘Newton sphere’ of negative ions. The electron energy spread is typically 0.8 eV full width at half maximum. Ion focusing optics within the ion spectrometer allows the effective interaction and ion momentum images are recorded from a MCP-based position- and time-sensitive detector to an event list, so two-dimentional momentum distributions and time-of-flight information can be determined for a full 2π solid angle of detection. The central slice of the Newton sphere is selected for a time-window of 50 ns containing complete kinematic information of the negative

Figure 1. Time-sliced images for (a) O$^-$, (b) S$^-$ and (c) SO$^-$ ions at 7.5 eV incident electron energy. The incident electron beam is from left to right as shown by the arrow for all the figures.
ions. The kinetic energy distributions are obtained by integrating the ion counts over the entire ejection angle of the negative ion fragments and plotting them as a function of ion kinetic energy. On the other hand, the angular distributions are obtained by integrating the ion counts for a small ejection angle range $\theta$ to $\theta + d\theta$ of the ion fragments and plotting them as a function of ejection angle.

3. Results and discussion

The measured $O^-$, $S^-$ and $SO^-$ time-sliced velocity distributions for 50 ns width at 7.5 eV incident electron energy are shown in figure 1. All the images show an almost uniform central blob, with the diameters varying according to the respective kinetic energies of the negative ion fragments.

![Figure 2](image-url)

**Figure 2.** The calculated optimized ground state geometries of: (a) SO$_2$ and (b) SO$_2^-$ ion both showing the C$_{2v}$ symmetry.

![Figure 3](image-url)

**Figure 3.** Depiction of computed vibration modes for SO$_2$ molecule. (a) and (b) represent symmetric stretching mode; (c) and (d) represent symmetric bending mode; (e) and (f) represent anti-symmetric stretching mode. The arrow denotes the dipole derivative unit vector in all the cases.

The ground state geometries of SO$_2$ and SO$_2^-$ molecules optimized with Möller-Plesset perturbation theory up to second order (MP2) using aug-cc-pVQZ basis set to obtain a stable structure using the Gaussian 09 program package are shown in figure 2 [19]. The neutral SO$_2$ molecule has C$_{2v}$ symmetry with a S-O bond length of 1.45 Å and 119.20$^\circ$ O-S-O bond angle in the optimized state (figure 2 (a)) [20]. After the attachment of an electron, the anion retains C$_{2v}$ symmetry but the S-O bond length increases by 0.07 Å while the O-S-O bond angle decreases.
by $5.10^0$ (figure 2 (b)) [16]. The three normal modes of vibration: symmetric stretching ($\nu_1$), symmetric bending ($\nu_2$) and asymmetric stretching ($\nu_3$) for SO$_2$ are shown in figure 3. It can be inferred from figure 3 that the symmetric stretching will give rise to S$^-$ fragment formation. As the stretching may produce S$^-$, it has to be followed by the bending mode simultaneously such that the O-atoms can come close enough to form O$_2$. The same will be true for the formation of O$_2^-$ fragment which has a very low cross-section as compared to S$^-$ and hence is generally not reported [15]. The antisymmetric stretching mode alone may result in the formation of O$^-$ and SO$^-$ negative ions [15]. Thus, the dissociation (recoil) axis must rotate between the time of electron attachment to the neutral target molecule and subsequent dissociation of SO$_2^-$ for the production of S$^-$ fragment. This structural change in the TNI undergoing bending mode vibration into S$^-$ + O$_2$ fragments results in failure of the axial recoil approximation. On the other hand, the axial recoil approximation is valid for the production of O$^-$ and SO$^-$ fragments.

Using this approximation, the symmetry of the TNI can be found provided the symmetry of the neutral molecule and the angular distribution of the negative ion fragment is known by following the methodology of O’Malley and Taylor and Azria et al. [11, 12]. The general equation for describing angular distribution was given by Tronc et al. [21] which was then modified for polyatomic molecules by Azria et al. [12].

![Figure 4](image-url)

**Figure 4.** Angular distribution data along with necessary fits for $A_1$ to $A_1+B_2$ transition for O$^-$, S$^-$ and SO$^-$ ions for 7.5 eV incident electron energy at the second resonance.

The measured angular distribution for O$^-$, S$^-$ and SO$^-$ ions are shown in figure 4. The fit corresponding to $A_1$ to $A_1 + B_2$ transition is also shown in figure 4 with solid lines for O$^-$ and SO$^-$ ions only. Indeed, as mentioned before, the S$^-$ cannot be fitted due to the failure in axial recoil approximation. Equations for $A_1$ to $A_1 + B_2$ transitions due to a combination of (s + p + d)- partial waves showing the scattering intensities coming to play for the $C_{2v}$ point group are explained in details by Jana and Nandi [16].

Time-dependent density functional theory (TD-DFT) calculations are carried out to get the theoretical vertical energy values and symmetries of corresponding excited states for the SO$_2^-$ molecule lying within the Franck-Condon region. Then the symmetry states lying near the second resonance observed in the range 7.0 - 7.6 eV by different groups [7, 8, 16, 17] and having symmetries with considerable value of oscillator strength (f) are noted. The table showing the symmetry states for the two resonances with considerable f-value are shown in table 1 in order of descending f-value.
Six symmetry states can be observed with high f-values and are reported in Table 1. Amongst these, four are $B_2$ and two are $A_1$ symmetry states. From this observation, it can be concluded that the second resonance occurs due to an $A_1$ to $A_1 + B_2$ transition. This result matches excellently with the recent experimental works on DEA to SO$_2$ [16, 17].

### Table 1. Symmetry states of excited TNI with corresponding oscillator strengths in descending order which are expected to contribute to DEA to SO$_2$ from TD-DFT calculations with SO$_2$ ground state optimized geometry with the aug-cc-pVQZ basis and B3LYP exchange-correlational functional.

| Energy range (eV) | Symmetry of TNI | Oscillator strength (f) | Ref[16] |
|------------------|-----------------|-------------------------|--------|
| 7.0 - 7.6 eV     | $A_1$           | 0.0516                  |        |
|                  | $B_2$           | 0.0445                  | $A_1 + B_2$ |
|                  | $B_2$           | 0.0383                  |        |
|                  | $B_2$           | 0.0319                  |        |
|                  | $A_1$           | 0.0240                  |        |
|                  | $B_2$           | 0.0111                  |        |

4. Conclusion

We have performed DEA to SO$_2$ at the second resonance at 7.5 eV incident electron energy. Although the neutral molecule and the TNI both have $C_2v$ symmetry, from the normal vibration modes it is clear that O$^-$ and SO$^-$ ions are formed keeping the angle between the dissociation axis of the molecule and incident electron beam direction the same as that of the TNI, thus validating the axial recoil approximation. On the other hand, the S$^-$ ion formation takes place with a rotation of the molecular dissociation axis resulting in a complete failure of the axial recoil approximation. Thus the axial recoil approximation can be seen to be validated and failed simultaneously for the same molecule with regards to the fragment ions formed. Also, the analysis of the angular distributions of O$^-$ and SO$^-$ ions and TD-DFT calculations show that the 7.5 eV peak is formed predominantly due to the $A_1$ to $A_1 + B_2$ transition.

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