Dissociation dynamics of transient anion formed via electron attachment to sulphur dioxide (SO₂)

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Synopsis: We have investigated the dynamics of dissociative electron attachment to sulfur dioxide (SO₂) using velocity slice imaging (VSI) technique. The symmetric dissociation of the transient parent anion results in S⁻ formation whereas its asymmetric dissociation results in the O⁻ and SO⁻ channels. We clearly see the competition between bending and stretch mode of vibrations of the parent anions in S⁻ formation whereas the stretch modes dominate in the other two ions production.

Very little is known about the excited anion states of sulphur dioxide (SO₂) in spite of their importance in atmospheric chemistry and industrial pollution. Dynamics of dissociative electron attachment (DEA) may provide some information about the excited states of the anions formed by electron attachment. We have studied the DEA dynamics for SO₂ in terms of angular distribution and kinetic energy distribution of the fragment anions using velocity slice imaging [1].

DEA to SO₂ is known to produce O⁻, S⁻ and SO⁻. Among all of the observed ions, the most dominant are O⁻ which peaks at 4.6 eV and 7.2 eV, S⁻ peaking at 4.2 eV, 7.4 eV and 9 eV and the SO⁻ peaking at 4.8 eV and 7.3 eV. We have recorded the momentum images for these ions across all these peaks.

Since the three-body fragmentation thresholds to form S⁻ or O⁻ are above 9 eV, the observed formation of these ions is due to two-body dissociation. The momentum images obtained for S⁻ channel show very little kinetic energy release. This implies that the excess energy appears as the internal excitation of the O₂ fragment. This excitation is found to increase with electron energy indicating the interplay between the bending and stretch mode vibrations in the parent anion. For electron energies beyond 4.8 eV, O₂ can also be formed with electronic excitation. However, even for that channel the excess energy appears as the vibrational excitation of O₂.

The KER spectra obtained for the O⁻ channel clearly indicates internal excitation of SO. This internal excitation may appear in its rotational and vibrational motion. The rotational excitation of SO is a consequence of the asymmetric two body fragmentation of the resonant state. It is found that the internal excitation of the SO increases with the electron energy. Our analysis of the results indicates the dominance of both symmetric and asymmetric stretch modes of vibration over the bending mode in the parent anion. We draw similar conclusion for the SO⁻ channel as well. Though both O⁻ and SO⁻ channels have very similar dynamics, we note a clear distinction between the two. In the O⁻ channel the SO fragment can store considerable amount of energy as internal excitation, while in the SO⁻ channel this is limited by the electron affinity of SO which is 1.1 eV only. This may explain the lower value of the ratio of absolute cross sections of SO⁻ and O⁻ at the 7.3 eV peak as compared to that at 4.8 eV.

References
[1] D. Nandi et al. 2005 Rev. Sci. Instrum. 76 053107