Bimodel distribution of vibrationally excited states in NO via DEA to NO_2

Krishnendu Gope * [1], Vaibhav S. Prabhudesai * [2], and E. Krishnakumar* [3]

* Dept. Nuclear and Atomic Physics, Tata Institute of Fundamental Research, Colaba, Mumbai 400005, India,

Synopsis: We have carried out a study of the dynamics of the dissociative electron attachment to NO_2 using velocity slice imaging technique. The kinetic energy release (KER) distributions obtained from the O^- momentum images indicate that the neutral fragment NO ($X^2\Pi$) is being produced with two different sets of vibrational populations peaking at v=4 & v=13 respectively, at an electron energy of 4.2 eV. This unique feature may arise from the crossing of two different potential energy surfaces of NO_2^- ion at larger bond lengths.

Nitrogen dioxide (NO_2) is an important pollutant gas in the earth's atmosphere and its anions play important role in the atmospheric chemistry. However, due to computational difficulties very little is known about the excited anion states of this molecule. Studying the dissociative electron attachment (DEA) dynamics is one possible approach to unravel the properties of some of the excited anion states. Here we report the study of dynamics of DEA to NO_2 using velocity slice imaging technique [1].

O^- formation from DEA to NO_2 is known to peak at 1.7 eV, 3.2 eV and 8.5 eV. We have recorded the momentum images of this fragment anion across these peaks. The momentum image obtained for the first peak appears as an isotropic blob as very little excess energy is available in the system due to energy threshold of this channel (Table 1). The size of this blob increases with electron energy up to 3.2 eV beyond which two distinct momentum distributions start appearing (Fig. 1). The first two peaks in the DEA are at electron energies well below the threshold for the three body dissociation channel (Table 1). This implies that the O^- formation at these energies is arising solely from the two body dissociation. One characteristic of the terminal atom ejection is the rotational excitation of the diatomic fragment due to momentum conservation. Besides, depending on the dissociation path which is the character of the parent anion potential energy surface, the NO fragment may also be formed with vibrational excitation. Such energy partitioning can be observed in the kinetic energy of the O^- channel. The initial increment in the size of the O^- image is found to be indicating such internal excitation of the NO fragment.

However, the momentum images obtained at 4.2 eV electron energy exhibit two distinct structures; an outer ring and an inner blob. The NO fragment at this electron energy is necessarily formed in its electronic ground state (Table 1). This implies that the two momentum distributions observed in the O^- channel correspond to two distinct vibrational distributions of the NO fragment. This can be seen from the KER spectra of the O^- fragment (Fig. 2) where at 4.2 eV electron energy the NO vibrational excitation peaks at v=4 and v=13.

Table 1. Dissociation channels of DEA to NO_2

No	Dissociation Limit	Threshold
1	$O^- + NO(X^2\Pi)$	1.65 eV
2	$O^- + NO(a^4\Pi)$	6.5 eV
3	$O^- + N(^3P) + O(^3P)$	8.18 eV

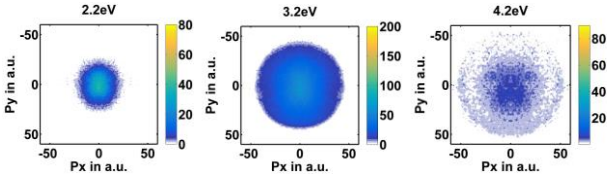

Figure 1. Momentum image of O^- from NO_2 at 2.2 eV, 3.2 eV and 4.2 eV electron energies.

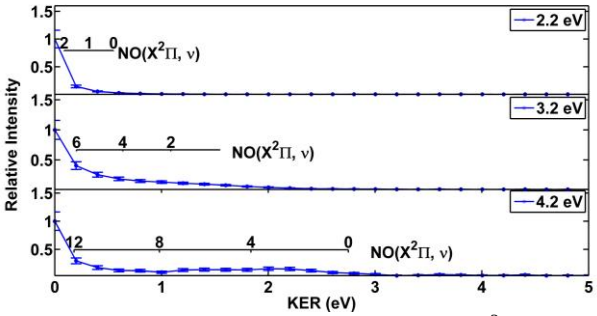

Figure 2. Kinetic energy release of $O^- + NO(X^2\Pi)$.

Such dynamics can be a manifestation of crossing of two different potential energy surfaces of NO_2^- ion at larger bond lengths.

References

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

[1] E-mail: gope.krishnendu@gmail.com
* [2] E-mail: vaibhav@tifr.res.in
[3] E-mail: ekkumar@tifr.res.in