Dissociative electron attachment to CO molecule probed by velocity slice imaging technique

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Abstract. We have studied dissociative electron attachment to CO molecule using the well-established velocity slice imaging spectrometer. We have conclusively determined the symmetries of the TNI states involved in both the channels producing \( \text{O}^- \) ions. In contrast to a recent report, we observed additional forwards lobes in the angular distribution data and we claim there is no need to invoke coherent interference between different states as introduced previously. Recent R-matrix calculations and momentum imaging study by other groups strongly support our claims.

1. Introduction

Low-energy electron-molecule collision leading to dissociative electron attachment (DEA) is an important process from the fundamental as well as the application point of view. DEA is a two-step resonant process resulting in a final anionic and neutral fragments from a parent neutral molecule via an intermediate temporary negative ion (TNI) state. DEA study of molecules are important starting from electrical discharges, atmospheric chemistry, interstellar medium chemistry, radiation induced damage of living cell and biologically important molecules [1].

Carbon monoxide (CO) is a simple but important heteronuclear diatomic molecule. But only few studies on DEA to CO exist in literature may be due to the killing nature of the molecule. DEA to CO has mainly two possible channels for \( \text{O}^- \) production with energy threshold 9.62 and 10.88 eV and are shown by equation (1) and (2) respectively [2]:

\[
e^− + \text{CO}(^1\Sigma^+) \rightarrow \text{CO}^− \rightarrow \text{O}^−(^2P) + \text{C}(^3P) \tag{1}
\]

\[
e^− + \text{CO}(^1\Sigma^+) \rightarrow \text{CO}^− \rightarrow \text{O}^−(^2P) + \text{C}^*(^1D) \tag{2}
\]

Accurate measurements [2, 3, 4] of attachment cross-section function, onsets and structures using a highly monochromatic electron beam clearly demonstrated the presence of two possible channels for the formation of \( \text{O}^- \). However, the symmetry of the TNI states involved was unresolved. Only one angular distribution measurement over limited angular range by Hall et al. [5] concluded a TNI state with \( \Pi \) symmetry is responsible for both the processes. In the recent times, the momentum imaging techniques [6, 7, 8] have been used to understand the complete dynamics in DEA to CO molecule.

In contrast with ref. [5], Tian et al. [6] reported that for 10 eV incident electron energy two states with \( \Sigma \) and \( \Pi \) symmetries are involved but, for 10.6 eV three TNI states, \( \Pi, \Delta \) and \( \Phi \), with coherent interference between them are present. The authors introduced coherent interference
between the different TNI states to explain the non-existence of the forward lobes in their angular distribution data. To address these issues we have studied DEA to CO [7] using velocity slice imaging (VSI) spectrometer [9]. From the kinetic energy distribution measurements we have identified both the processes (equation (1) & (2)) leading to $O^-$ formation and from angular distribution we observed primarily a $\Sigma$ state is responsible for both the channels. We also have observed that there is no need to invoke the coherent interference between different states as suggested by Tian et al.

A third channel has also been recently reported by Wang et al. [10] and Gope et al. [8] with threshold energy of 12.30 eV:

$$e^- + CO(1\Sigma^+) \rightarrow CO^- \rightarrow O^-(2P) + C^*(1S)$$

(3)

2. Experimental method

The experiments were carried out using a VSI spectrometer, similar to [9] with minor modifications and some details of the set-up can be found in the previous report [11]. In brief, the experiments were performed in an ultra-high vacuum condition (with a base pressure better than $10^{-9}$ mbar order), where a magnetically collimated pulsed electron beam was made to interact perpendicularly with an effusive molecular beam in the interaction region of a three-field time of flight spectrometry based velocity map imaging (VMI) spectrometer. In VMI spectrometer the ions created with a given velocity in the interaction region are mapped to a single point on a two dimensional position sensitive detector. In the present set-up a combination of microchannel plates (MCP) and a delay-line based hexanode have been used to record the x-, y- position along with the time-of-flight (t) of each ions hitting the detector. From the recorded time and position informations one can obtain the mass of the ions, cross-section and angular distribution as well as kinetic energy distribution.

3. Results and Discussions

The detailed dynamical studies using imaging techniques have been recently published in [6, 7, 8]. Here we will discuss the complete understanding based on the above three reports. Here our main emphasis will be the existence of forward lobe in the angular distribution and thus there is no need to invoke coherent interference between different TNI states involved in the process. In Figure 1 two representative central sliced images of $O^-$ are shown: (a) image taken at 9.5 eV and (b) at 11.5 eV. The incident electron beam direction is from left to right and passing through the centre of each image. A distinguishable change in the VSI pattern can be observed while changing the incident electron energy from 10 to 10.5 eV, due to involvement of the process.

Figure 1. Velocity slice images of $O^-$ ions produced from CO for (a) 9.5 and (b) 11.5 eV. The electron beam direction is from left to right and passing through the centre of the images. Graphs have been taken from [7].
The kinetic energy and angular distribution of the $O^-$ ions can be obtained from such slice images.

The kinetic energy (KE) distributions showed (Figure 2) a single peak around zero eV for lower energy and for 10.5 eV onwards two peaks are present. Upto 10 eV, the single low energy peak in KE distribution corresponds to the process I. Above 10 eV, the higher and lower energy peaks in the KE distributions correspond to the process I and process II, respectively. The threshold energies determined from the most probable kinetic energies obtained from KE distribution resulted 9.46 eV and 10.2 eV for the process I and process II, respectively. Within the experimental uncertainty these values match well with the previously reported values of 9.62 and 10.88 eV [5].

The angular distribution of the ions created due the processes I and II are measured separately. Figure 3 (a) shows the measured angular distribution taken at different incident electron energies for the process I and (b) represents the fitting for extracting the TNI states involved in the process I. The symmetry of the TNI states involved in the process can be obtained by fitting the angular distribution using the expression given by Tronc et al. [12]

$$I(\theta) \sim \sum_{|\mu|} \left| \sum_{l=|\mu|} a_l Y_{l,\mu} e^{i\delta_l} \right|^2.$$  \hspace{1cm} (4)

Where, $a_l$’s are energy dependent expansion coefficients and $Y_{l,\mu}$ are the spherical harmonics, $\mu = |\Lambda_f - \Lambda_i|$, where $\Lambda_i$ and $\Lambda_f$ are the projection of the electronic orbital momentum along the molecular axis for the initial and final molecular (TNI) states, respectively. The summation over $\mu$ takes care of the involvement of the different states in the process and the $\delta_j$s are the phase differences between the partial waves with respect to the lowest one involved.

The ground state of neutral CO molecule is of $1\Sigma^+$ symmetry. The angular distribution data have been fitted with three different model considering $\Sigma \rightarrow \Sigma$, $\Sigma \rightarrow \Pi$ transition to a single final state and $\Sigma \rightarrow \Sigma + \Pi$ transition to two final states. The angular distribution data along with the fitted curves for the ions created due to 11 eV energy incident electron impact via process I is shown in Fig. 3 (b). From the fittings we observed for the process I, a $\Sigma$ state is always present, contribution of a $\Pi$ state increases with increasing incident electron energy and before 10.5 eV contribution of the $\Pi$ state is vanishingly small. For process II, only one TNI state with $\Sigma$ symmetry is present. This is in contrast with previous report of Hall et al. [5], where, based on angular distribution data measured over a limited angular range the authors assigned
involvement of a Π state for both the processes. In a recent study, Tian et al. [6] reported two TNI states with Σ and Π symmetries are involved for 10 eV and for 10.6 eV three TNI states with Π, Δ and Φ symmetries are involved. The authors observed the absence of two small forward lobes around 30° and 330° and concluded the presence of coherent interference between different TNI states. But, in the current studies we observed presence of the two small forward peaks (Figure 3) for the ions created due to process I and concluded that the coherent interference is not present. In a recent R-matrix calculation Dora et al. [13] observed the presence of only a single Σ resonant state around the studied energy range. Furthermore, in recent momentum imaging studies Gope et al. [8] also observed the involvement of Σ and Π TNI states and absence of coherent interference. These two studies strongly support our observations and conclusions.

4. Conclusions
We observed primarily a Σ TNI state responsible for the DEA to CO for both the processes I and II. In addition a minor energy dependent contribution of a Π state is involved for process I. We also conclude that there is no need to invoke coherent interference between different states.

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References
[1] Illenberger E and Momigny J 1991 Gaseous molecular ions (Steinkopff-Verlag, Heidelberg)
[2] Chantry P J 1968 Phys. Rev. 172 125
[3] Rapp D and Briglia D D 1965 J. Chem. Phys. 43 1480
[4] Deniff G, Muigg D, Stamatovic A and Briglia D D 1965 J. Chem. Phys. 43 1480
[5] Hall R I, Čadež I, Schermann C and Tronc M 1977 Phys. Rev. A 15 599
[6] Tian S X, Wu B, Dia Lei, Wang Y -F, Li, H -K, Zeng X -J, Luo Y and Yang J 2013 Phys. Rev. A 88 012708
[7] Nag P and Nandi D 2015 Phys. Chem. Chem. Phys. 17 7130
[8] Gope K, Tadare V, Prabhudesai V S, Mason N J and Krishnakumar E 2016 Eur. Phys. J. D 70 134
[9] Nandi D, Prabhudesai V S, Krishnakumar E and Chatterjee A 2005 Rev. Sci. Instrum. 76 053107
[10] Wang X -D, Xuan C -J, Luo Y and Tian S X 2015 J. Chem. Phys. 143 060101
[11] Nag P and Nandi D 2016 Meas. Sci. Technol. 26 095007
[12] Tronc M, Fiquet-Fayard F, Schermann C and Hall R I 1977 J. Phys. B 10 305
[13] Dora A, Tennyson J and Chakrabarti K 2016 Eur. Phys. J. D 70 197