Dipolar dissociation dynamics in electron collisions with carbon monoxide

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Synopsis Dipolar dissociation (DD) dynamics of carbon monoxide with electron collision has been studied using velocity slice imaging (VSI) technique. Threshold of the process has been obtained from the ion yield curve. Using the time sliced images kinetic energy and angular distribution have been obtained providing the detailed dynamics involved in the DD process. Two ion-pair states have been identified from the angular distribution measurements.

Low-energy (<100 eV) electron-molecule collision study is an important tool to unlock many unsolved problems in various field of science. Unlike dissociative electron attachment (DEA), dipolar dissociation (DD) process is a non-resonant process where the incident electron transfers (partial or complete) energy to the molecule and leaves it to a super excited state known as ion-pair state. Such ion-pair state then dissociates forming ion-pair as :

$$CO + e^{-} \rightarrow CO^{*} + e^{-} \rightarrow \begin{cases} C^{+} + O^{-} + e^{-} \\ C^{-} + O^{+} + e^{-} \end{cases}$$
 (1)

Due to low C⁻ cross section, only O⁻ dissociation channel is focused here. The threshold value obtained from ion-yield curve is 19.8 eV, which is in good agreement with the previous reports [1]. The velocity sliced images have been taken at five different incident electron energies 25, 30, 35, 40 and 45 eV. Presence of lower and higher kinetic energy (KE) ions throughout the entire energy range of studied confirms two dissociation mechanism [2]. Low KE ions originate through indirect process where the molecule initially excited to a Rydberg state, that crosses the ion-pair state near ion-pair dissociation limit. With increasing electron energy same Rydberg state is accessed throughout and thus low KE energy ions. Higher ion KE peak for 25 eV incident electron energy centred at 1.2 eV whereas, an unchanged KE behaviour around 1.5 eV is observed with increasing incident energy. The initial increase in kinetic energy indicates the direct excitation to the different repulsive part of the ion-pair states in the Franck Condon (FC) region. But as the incident electron energy increases, the states are out of the FC transition window and by partial energy transfer an unchanged KE peak observed. Another possibility is due to involvement of another higher Rydberg state. The position of the ion-pair state can also be located using the KE information. According to conservation of momentum 1.5 eV O⁻ ions will be accompanied by 2 eV C⁺ ions, thus the total KE release sholud be 3.5 eV. The truncated shape seen at the KE distribution for 25 eV incident energy clearly indicates that the ionpair state enters the FC region around that energy. To know the symmetry of associated ion-pair states angular distribution of O⁻ ions for both KE regions are fitted using the formula given by Van Brunt [3]. We conclude that Σ and Π ion-pair states are involved for both dissociation processes. To quantify the result detailed theoretical potential energy curve calculations are needed.



Figure 1. (a) KE distribution of O^- ions and (b) Schamatic diagram to understand the dissociation processes.

References

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