

Electron attachment to molecules in a cluster environment: suppression and enhancement effects

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Cluster and surface environments can strongly influence dissociative electron attachment (DEA) processes. These effects are important in many applications, particularly for surface chemistry, radiation damage, and atmospheric physics. The effects can vary depending on physical mechanisms involved in the process. If the DEA is controlled by a vibrational Feshbach resonance (VFR) due to long-range electron-molecule interaction, surface or cluster environment screens this interaction resulting in the VFR suppression. A remarkable example is DEA to the CH₃I molecule [1]. Very pronounced VFR is observed in DEA to this molecule below the first threshold for excitation of the symmetric stretch C-I vibrations in the gas phase. In addition, there is a very strong enhancement of DEA cross sections at low energies due to the weakly-bound anion state (that is actually a virtual state at the equilibrium geometry due to rotational effects). However, both effects were not observed [2] in DEA to CH₃I on a surface of rare-gas films at cryogenic temperatures.

On the other hand, the surface and cluster environments can cause not only suppression, but also a strong enhancement of DEA cross sections. In many chloro- and chlorofluorocarbons the effect is mostly caused by the downward shift of the anion potential energy curves due to the polarization interaction between the anion in the resonance state and the medium. To describe these effects for clusters, a multiple-scattering theory combined with the nonlocal complex potential theory has been developed [3]. The scattering matrix and the wavefunction for electron scattering in the cluster environment is constructed using the scattering matrix for each individual molecule. Then this wavefunction is used to modify the electron capture amplitude in the presence of a cluster environment [3]. In addition the resonance negative-ion curve is shifted to represent the long-range interaction between the attaching molecule and the cluster

molecules. In small-size cluster the dipolar interaction becomes important, and as a result, depending on the orientation of molecules in the cluster, the shift can be both negative and positive [4]. However, for large-size clusters the polarization interaction takes over, and the shift is dominantly negative.

The results of DEA to molecules in a water cluster environment [3,5] show a new interesting feature: the width of the low-energy shape resonance decreases resulting in a higher surviving probability of the resonance negative ion state and enhancement of the cross section. This phenomenon can be explained by the trapping effects: after autodetachment electron can

be rescattered and recaptured by the attaching molecule. However, the present theory does not trace the fate of the survival anion which can be destroyed due to caging effect and/or other reaction processes. Indeed, in recent experiments [6] with microsolvated uracil and thymine the DEA channels were suppressed, and only intact molecular and hydrated anions were detected.

References

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