

Theory of low-energy electron attachment to molecules and clusters

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Low-energy electron attachment to molecules typically goes through formation of a temporary negative-ion state. The excess energy might be released then in the form of kinetic energy of neutral and anionic fragments. In this case we have a dissociative attachment (DA) process. In large systems, like polyatomic molecules and clusters, the temporary negative ion can be stabilized by coupling of electron motion with vibrational degrees of freedom (or electron-phonon coupling). The DA case has been relatively well studied theoretically, although completely ab initio calculations are still available only for diatomics. The second (nondissociative) case is much more challenging to the theory. However, some features of this process can be understood by using model approaches.

For theoretical description of DA processes we use the resonance R-matrix theory [1] which allows us to obtain DA cross sections in terms of few parameters, the R-matrix pole and the surface amplitude as functions of the internuclear separation. These parameters are adjusted to reproduce experimental or ab initio data on other resonance processes, e.g., resonance elastic scattering or vibrational excitation.

The following important features in DA have been investigated by this method:

1. Vibrational Feshbach resonances [2,3]. These resonances occur due to a temporary capture of the incident electron by the long-range field of a vibrationally excited molecule. Very pronounced vibrational Feshbach resonance was detected experimentally in methyl iodide [2] below the first threshold for excitation of the symmetric stretch vibrations. Higher thresholds are free of the resonances but exhibit pronounced threshold cusps.
2. Low-energy behavior of exothermic DA. This behavior is controlled by the long-range interaction between the incident electron and the target molecule. For non-polar molecules the energy dependence is given by the Wigner law which should be modified in the case of polar targets. The absolute value of the cross

section is often consistent with the Vogt-Wannier [4] or extended Vogt-Wannier [5] theory for the capture of a charged particle into a polarization well.

3. The temperature dependence of the DA cross sections. This dependence is particularly strong in methyl chloride and methyl bromide [3].
4. The influence of environment, particularly surface and condensed matter effects in DA [6].

In case of electron attachment to clusters we have been concentrating on studies of the influence of the cluster environment on vibrational Feshbach resonances. For CO₂ and N₂O clusters the polarization interaction between the electron and the cluster leads to a red shift in the resonance position [7] but the resonance width does not change substantially. In contrast, cross sections for DA to methyl iodide dimers and trimers exhibit substantial broadening of the vibrational Feshbach resonance [8]. This effect can be successfully described by the resonance R-matrix theory which takes into account a modification of the long-range part of the electron-molecule interaction due to the cluster environment.

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