Electron exchange between dipole-bound anion and polar molecule and dipole-bound anions dimer formation

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Synopsis We consider collision between a dipole-bound molecular anion and a neutral polar molecule and show that the excess electron can bind two neutral molecules into a dimer. Using a variational approach similar to the Heitler–London model of \( \text{H}^+ \) ion we obtain the energy terms of such a dimer. Their difference determines the cross-section of electron transfer from the anion to the neutral molecule in quasiclassical near-resonant Born–Oppenheimer approximation. We obtain for the cross-section an analytic expression containing the weak (logarythmic) factor depending on the molecular dipole moment, and collision velocity. Our analytic calculations are in a good accordance with the results of a recent experiment.

Dipole-bound anions (DBA) have been attracting great, both experimental and theoretical, interest. Almost any neutral molecule with dipole moment \( d > 2.5 \text{D} \) can form DBA, i.e. bind an extra electron due to its dipole potential. As a rule, the electron is bound in a diffuse orbital with large (about of tens of Angstroms) size and weak (about of tens meV) binding energy, and this fact suggests that DBAs should possess high reactivity.

There are several types of charge-transfer reactions involving DBA. The DBA themselves are formed under collisions of polar molecules with Rydberg atoms which also contain an electron in a diffuse weakly-bound orbital. Another type of charge transfer reactions can be collision between two polar molecules with dipole moments large enough to bind the electron. An example of such charge transfer is the reaction studied in Ref. [1]. The measured cross-section values \( \simeq 10^{-12} \text{cm} \) cannot be predicted using rough hard-sphere approximation. Indeed, it implies the hard-sphere radius \( \simeq 60 \text{Å} \) that is more than twice greater than the mean square radius of the excess electron orbital.

In the same time, the most of theoretical studies of DBA are limited to large-scale ab initio calculations that give only the numerical electron affinity values. Some model-potential calculations, although yielding reasonable results for one-photon photodetachment from DBA [2], are hard to use for description of collisions between DBA and neutral molecules. More simple analytical theories can give the electronic affinity as a function of the DBA dipole moment only numerically and are not able to calculate adequately the cross-sections of charge-transfer reactions.

In Ref. [3] a simple analytical model is proposed which is suitable for description of DBA structure (electronic affinity as a function of the DBA dipole moment) and interactions with photons [4]. After some modifications we apply this model to quantitative study of charge-transfer reactions in collisions of DBA with neutral polar molecules on the basis of quasiclassical near-resonant charge exchange calculation technique of the general collision theory. The obtained simple analytic formula gives good agreement with recent experimental data and contains explicitly the cross-section dependence on the dipole moment of the molecules. We also point out that formation of dimers of such molecules bound by the excess electron is possible. Within our consideration the binding energies and dimensions of such dimers can be adequately estimated. For the dimer of CH\(_3\)CN our estimates yield the binding energy about 2.4 meV.

This work was partially supported by RFBR (grant 07-02-01096a).

References

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