

THEORETICAL STUDIES OF DISSOCIATIVE ATTACHMENT: FROM GAS PHASE TO CONDENSED PHASE

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Negative-ion resonances in low-energy electron-molecule scattering can drive the dissociative electron attachment processes. We discuss two approaches to the theoretical description of dissociative attachment: the Feshbach projection-operator method and R-matrix method. Theoretical results were obtained for several diatomic and polyatomic molecules in the gas phase. We extend also the semiempirical R-matrix theory to describe dissociative attachment to clusters and to molecules in a condensed phase. The results of our calculations show good agreement with experimental data.

Introduction

The dissociative electron attachment (DEA) is a two-step process in which electron attaches to a molecular target to form a temporary negative ion that subsequently dissociates into a neutral and a stable anionic fragment. This process is associated with intense energy exchange between electronic motion and nuclear motion. The fact that this can occur, in spite of the small value of the ratio of the electron mass to the nuclear mass, makes the physics of this process particularly interesting. At the same time the large rates of these processes make them important in technology, environmental applications, astrophysics and atmospheric physics.

In spite of importance of DEA reactions, they are poorly studied theoretically. Theoretical calculations still cannot be performed routinely like in the area of electron-atom and electron-molecule (non-reactive) collisions, and there are many examples where we have not achieved even qualitative understanding of DEA processes. The situation becomes even more complicated when the DEA process is affected by environment, like in the case of DEA to clusters and adsorbates, and molecules embedded in a condensed medium.

The present paper discusses recent theoretical advances in studies of DEA reactions. We will start with a relatively simple diatomic case, and then will turn to polyatomics and clusters. Finally, we will discuss condensed-matter effects in DEA.

Diatomic molecules

The nuclear motion in the resonance state is described by the Schroedinger equation with a non-local complex potential [1] which results from the Feshbach projection-operator formulation of the scattering problem. This potential can be constructed by using the amplitude for the electron capture from the continuum into the discrete resonance state. However, there are several principal and computational difficulties in solving the equation with the non-local potential. Therefore, at the early stages of theoretical development researchers were using the local approximation [2,3].

An accurate approach [4,5] which fully incorporates the non-local effects, is based on the discretization of the vibrational continuum using the Lanczos or Schwinger-Lanczos discretization method.

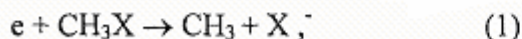
An alternative approach [6] uses the quasiclassical representation of the non-local

complex potential. It is natural in this problem because the nuclear motion is essentially quasiclassical, and its accuracy was shown to be very high. The quasiclassical approach was recently applied to *ab initio* calculations of DEA to H₂ and HF molecules [7]. Both targets attach electrons at low energies, but with very small cross sections of the order of 10⁻²⁰ cm². However the cross section grows strongly if the molecule is vibrationally and/or rotationally excited. This effect for the molecular hydrogen was satisfactorily described by the local version of the resonance theory [8]. More accurate results were provided by the non-local calculations [9,10]. A pronounced temperature effect, confirming experiment [11], was recently found for HF [10].

In summary, the resonance theory has become an efficient tool for calculation of DEA process, and we are in a position to do *ab initio* calculations for several diatomic molecules in their ground states and rotationally and vibrationally excited states.

Polyatomic molecules and clusters

Ab initio methods are still quite difficult to implement for polyatomics, therefore in this case we use a semiempirical version of the resonance theory based on the single-pole approximation for the R matrix [12]. R-matrix parameters are determined from the potential energy curves and from available experimental data on vibrational excitation or DEA. Like in the projection-operator approach, the nuclear dynamics can be treated in the quasiclassical approximation [13]. This approach turned out to be quite successful for description of DEA to methyl halides



where X stands for Cl, Br, or I. In addition to approximations, listed above, we assume that only one vibrational mode, C-X symmetric stretch, participates in the process. The calculated cross sections for the process (1) [14] vary in enormous range from virtually

unmeasurable 10⁻²³ cm² for CH₃Cl at room temperature to 10⁻¹⁴ cm² for CH₃I.

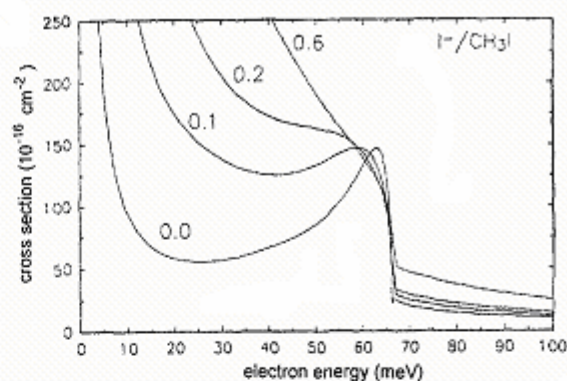


Fig. 1. DEA to CH₃I. Numbers near the curves indicate the solvation energy in eV.

Another interesting feature of these cross sections is a sharp peak near the vibrational excitation threshold which was first experimentally detected for CH₃I [15] and interpreted as the vibrational Feshbach resonance associated with the temporary capture of the incident electron into the long-range field of the vibrationally excited molecule. In Fig. 1 we present the DEA cross sections for methyl iodide calculated with anion curves shifted downwards by different amounts. We showed recently [16] that this shifting allows us to describe the solvation effects in DEA to clusters. Calculations show that for higher solvation energies vibrational Feshbach resonance disappears. This is confirmed by experimental observations of DEA to methyl iodide clusters [16].

Very sharp vibrational Feshbach resonances were recently found [17,18] in the process of electron attachment to N₂O and CO₂ clusters. The resonances occur at energies below those of the vibrational excitation energies of the neutral clusters. The red shift rises with increasing cluster size by about 12 meV per unit for CO₂, and with much smaller rate for N₂O. These observations were explained by simple model calculations for the size dependent binding energies which incorporate the strong polarization attraction between the electron and the cluster.

Condensed-matter and surface effects

Polarization of the medium strongly affects DEA to physisorbed molecules and molecules embedded in medium. This effect is similar to the solvation effect in electron attachment to clusters discussed above. Two series of experiments [19-21] on DEA to CH_3Cl and CF_3Cl molecules were recently performed: in the first molecules were physisorbed on a film of rare-gas atoms, and in the second a layer of molecules was sandwiched between two films. In the first case the surface effect can be simply incorporated by lowering the negative-ion curve by the amount of polarization energy of a point charge on the dielectric surface. The results of this calculation for CF_3Cl are presented in Fig. 2. R-matrix parameters were taken from the gas-phase model [22]. Good agreement with experiment is observed both for the absolute magnitude cross section and the shape of the energy dependence. The case of CH_3Cl is more difficult because the DEA cross section in the gas phase is very small, and the results are very sensitive to details of the theoretical model. Nevertheless, calculations [19,21] are able to reproduce the major feature of DEA to CH_3Cl : enormous increase of the cross section (by almost six orders of magnitude) due to polarization of the medium.

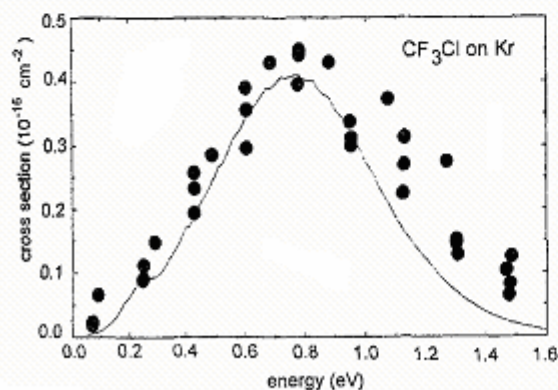


Fig. 2. DEA to CF_3Cl condensed on a Kr surface.
Solid curve – theory;
circles – experimental data [20].

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References

1. W.Domcke, *Phys. Rep.* **208**, 97 (1991).
2. T.F.O'Malley, *Phys. Rev.* **150**, 14 (1966).
3. J.N.Bardsley, *J. Phys. B* **1**, 349 (1968).
4. C.Mundel, W.Domcke, *J. Phys. B* **17**, 3593 (1984).
5. H.D.Meyer, J.Horacek, L.S.Cederbaum, *Phys. Rev. A* **43**, 3587 (1991).
6. S.A.Kalin, A.K.Kazansky, *J. Phys. B* **23**, 4377 (1990).
7. G.A.Gallup, Y.Xu, I.I.Fabrikant, *Phys. Rev. A* **57**, 2596 (1998).
8. J.M.Wadehra, J.N.Bardsley, *Phys. Rev. Lett.* **41**, 1795 (1998).
9. M.Cizek, J.Horacek, W.Domcke, *J. Phys. B* **31**, 2571 (1998).
10. Y.Xu, G.A.Gallup, I.I.Fabrikant, *Phys. Rev. A* **61**, 052705 (2000).
11. M.Allan, S.F.Wong, *J. Chem. Phys.* **74**, 1687 (1981).
12. A.M.Lane, R.G.Thomas, *Rev. Mod. Phys.* **30**, 257 (1958).
13. I.I.Fabrikant, *Phys. Rev. A* **43**, 3478 (1991).
14. R.S.Wilde, G.A.Gallup, I.I.Fabrikant, *J. Phys. B* (to be published).
15. A.Schramm, I.I.Fabrikant, J. M. Weber, E. Leber, M.-W. Ruf, H. Hotop, *J. Phys. B* **32**, 2153 (1999).
16. J.M.Weber, I.I.Fabrikant, E. Leber, M.-W. Ruf, H. Hotop, *Eur. Phys. J.* (to be published).
17. J.M.Weber, E.Leber, M.-W.Ruf, H.Hotop, *Phys. Rev. Lett.* **82**, 516 (1999).
18. E.Leber, S.Barsotti, I.I.Fabrikant, J.M.Weber, M.-W.Ruf, H.Hotop, *Eur. Phys. J.* (to be published).

19. L.Sanche, A.D.Bass, P.Ayotte, I.I.Fabrikant, *Phys. Rev. Lett.* **75**, 3568 (1995).

20. K.Nagesha, L.Sanche, *Phys. Rev. Lett.* **78**, 4725 (1997).

21. I.I.Fabrikant, K.Nagesha, R.Wilde, L.Sanche, *Phys. Rev. B* **56**, R5725 (1997).

22. R.S.Wilde, G.A.Gallup, I.I.Fabrikant, *J. Phys. B* **32**, 663 (1999).

ТЕОРЕТИЧНІ ДОСЛІДЖЕННЯ ДИСОЦІАТИВНОГО ПРИЛИПАННЯ: ВІД ГАЗОВОЇ ФАЗИ ДО КОНДЕНСОВАНОЇ ФАЗИ

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Резонанси, пов'язані з утворенням негативних іонів при розсіюванні низькоенергетичних електронів на молекулах, можуть спричинити процеси дисоціативного прилипання електронів. Обговорюються два підходи до теоретичного опису дисоціативного прилипання: метод оператора проекції Фешбаха і метод R-матриці. Отримано теоретичні результати для кількох двоатомних і багатоатомних молекул у газовій фазі. Нами також розширено напівемпіричну теорію R-матриці з метою опису дисоціативного прилипання до кластерів і молекул у конденсованій фазі. Результати наших розрахунків добре узгоджуються з експериментальними даними.