Dissociative electron attachment: threshold phenomena and multimode effects

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Abstract. We present a summary of recent progress on studies of threshold phenomena in low-energy dissociative electron attachment to polyatomic molecules: vibrational Feshbach resonances and threshold cusps. The theoretical approach is based on the resonance R-matrix theory. It allows us to analyze threshold effects in other channels, particularly vibrational excitation. If the molecular long-range field is not strong enough, virtual-state cusps are observed at vibrational excitation thresholds. The second part of the paper illustrates the multimode effects in dissociative attachment using attachment to the CF$_3$Cl molecule as an example. Symmetric stretch C-Cl vibrations $\nu_3$ and symmetric deformation (or so-called “umbrella”) vibrations $\nu_2$ are included. Calculations allow us to study the final-state vibrational distribution in the CF$_3$(\nu_2) fragment.

1. Introduction
Recent progress in studies of dissociative electron attachment (DEA) processes was stimulated by development of new experimental techniques involving electron beams with high energy resolution [1]. This allowed detailed investigation of threshold phenomena in low-energy dissociative electron attachment to diatomic and polyatomic molecules: vibrational Feshbach resonances (VFRs) and threshold cusps. VFRs are similar to Rydberg resonances in the dissociative recombination processes and are due to capture of the incident electron into the long-range field of a vibrationally excited molecule. If the molecular long-range field is not strong enough, virtual-state cusps are observed at vibrational excitation thresholds.

Our approach to describing these phenomena is based on the resonance R-matrix theory [2] which is equivalent to the nonlocal complex potential theory [3]. In the present paper we review recent theoretical results on DEA and vibrational excitation for several halogen-containing molecules.

The theoretical analysis of threshold phenomena is carried out in the approximation including only one symmetric-stretch vibrational mode corresponding to the reaction coordinate. In the second part of the paper we discuss a generalization of the local complex potential theory involving two vibrational modes. This theory is applied to dissociative attachment to CF$_3$Cl molecules in the energy region of the lowest shape resonance of $A_1$ symmetry.

2. Resonance and threshold phenomena
The one-pole R-matrix theory [4] is very well suited for studying resonances and threshold effects in low-energy electron-molecule scattering. A challenging part in this approach is
the calculation of the $R$-matrix surface amplitude generating the resonance width. In most
calculations performed so far (see, e.g. Refs. [5, 6, 7, 8, 9, 10] the surface amplitude was
adjusted empirically in order to reproduce observed vibrational excitation cross sections or
thermal attachment rate coefficients. After this parameter is fixed, structures in DEA and
vibrational excitation can be calculated with high accuracies using the quasiclassical version
[2, 11] of the $R$-matrix theory. The threshold structures are determined by the long-range
electron-molecule interaction which in $R$-matrix theory is included in the logarithmic derivative
of the electron wavefunction in different vibrational channels.

We will illustrate resonance and threshold effects in electron collisions with three polar
molecules which were studied recently experimentally [9, 10, 12]: CF$_3$I, CF$_3$Br, and CH$_3$Br. The
major goal here is to show how the relevant potential energy curves and long-range interaction
influence the DEA and vibrational excitation cross sections, particularly at vibrational excitation
thresholds. A detailed comparison of theoretical results with experimental data was given in
Refs. [9, 10, 12].

The molecules chosen for the present investigation have substantially different dipole moments
at the equilibrium internuclear separation: 0.413, 0.256 and 0.717 a.u. for CF$_3$I, CF$_3$Br and
CH$_3$Br respectively. Their potential energy curves as functions of the C-X (X=I or Br) distance
exhibit the behavior shown schematically in Fig. 1. The C-X distance is the only vibrational
coordinate involved in the present calculations, and it corresponds to the symmetric stretch
vibration $\nu_3$. We show only one curve representing the neutral molecule, and three anion curves
demonstrating major features distinguishing the three cases. All three curves correspond to
exothermic processes. The lowest curve, representing CF$_3$I, crosses the neutral very close to the
equilibrium internuclear separation, therefore the DEA cross section in this case is expected to
be very large in the low-energy region and very weakly dependent on vibrational temperature, in
agreement with earlier observations [13]. No VFRs are expected in this case. The intermediate
case corresponds to CF$_3$Br. The actual anion curve crosses the neutral at the right turning
point for the $\nu_3 = 3$ state [10]. This is a typical case for a strong temperature dependence of
the DEA cross section. One would also expect VFRs in this case if the long-range interaction
were significant like in the case of the CH$_3$I molecule [14]. However, the dipole moment of
CF$_3$Br is too small for VFR formation. In the third case the curve crossing occurs at even
higher internuclear separation corresponding to the right turning point for the $\nu_3 = 5$ state.
Here we expect very low cross sections for attachment to the ground state (or for attachment at
low target temperatures), and the temperature effect should be even stronger than for CF$_3$Br.
Because of the substantial dipole moment of CH$_3$Br, VFRs appear in this case, as was predicted
theoretically [8] and confirmed recently by measurements [12].

Fig. 2 shows the DEA cross sections for these three cases and illustrates the temperature
effect in DEA to CH$_3$Br. For CF$_3$I and CF$_3$Br cusps are observed at the vibrational excitation
thresholds, whereas VFRs are clearly seen in the CH$_3$Br case. Note that due to the thermal
distribution, several vibrational states contribute to the cross section at a given temperature,
therefore one resonance, associated with the $\nu_3 = 4$ threshold, produces several peaks in the
thermally-averaged cross section. The first peak (at 69 meV) is due to attachment from the
$\nu_3 = 3$ state, the second (at 143 meV) due to the $\nu_3 = 2$ state, and the third (at 218 meV) due
to the $\nu_3 = 1$ state. The contribution due to attachment from the $\nu_3 = 0$ state is noticeable at
room temperature, but is suppressed at $T = 600$ K.

Resonances associated with lower thresholds become weaker when going from $\nu_3 = 4$ to $\nu_3 = 1$
[8, 12]. This can be also seen from the vibrational excitation cross sections. In Figs. 3 and 4
we show vibrational excitation from the ground state. The CH$_3$Br cross section is not enhanced
compared to the CF$_3$Br case, although there are VFRs at higher thresholds in the former case
and none in the latter. However, a huge enhancement was predicted [12, 15] for excitation from
excited states of CH$_3$Br. In particular, the cross section for the $\nu_3 = 2 \rightarrow 3$ transition reaches
90 × 10⁻¹⁶ cm² near the threshold [12]. Note that the ν₃ mode in all discussed molecules is infrared active, therefore electron-impact vibrational excitation can also occur directly due to the transition dipole moment. However, in CF₃Br and CF₃I the transition dipole moment is relatively weak. Only in CH₃Br the contribution of the direct excitation is noticeable and equals about 20% of the total cross section near the threshold [12, 15].

Another substantial difference between CF₃Br and CH₃Br is the existence of the broad peak associated with the A₁ resonance in the former case, and its absence in the latter. The vertical attachment energy for CH₃Br, 2.4 eV, is much higher than for CF₃Br, 1.0 eV, and the resonance width grows with the electron energy. In addition, the resonance width increases with the increase of the long-range interaction, as was shown for the hydrogen halides [16]. Therefore in the CH₃Br case the shape resonance is much broader and does not appear in the vibrational excitation cross section.

A large cross section for excitation from the ground vibrational state is observed for CF₃I (Fig. 4).
4). This is because the anion curve crosses the neutral very close to the equilibrium separation, as illustrated in Fig. 1. This relative curve position makes the Franck-Condon factor favorable and enhances the cross section due to the bound/virtual state of the CF$_3$I$^-$ system [17].

Resonances and cusps in the elastic cross sections were discussed in Refs. [12, 15]. An important point worth noting here is that for polar molecules resonances and threshold effects are strongly suppressed in angular-integrated cross sections due to a large contribution of the direct (nonresonant) process. However, the threshold features are well pronounced in differential cross sections at large scattering angles.

3. Multimode effects in DEA to CF$_3$Cl

The calculations presented in the previous section were carried out in the approximation including one vibrational mode corresponding to the reaction coordinate. This is a natural simplification in DEA treatment for polyatomic molecules in view of the tremendous amount of computational work necessary to obtain multidimensional complex potential energy surfaces and the solution of the multidimensional Schrödinger equation for the nuclear motion. Some examples of recent calculations going beyond the 1-dimensional approach are model studies of DEA to CO$_2$ [18] and ab initio calculations of DEA to water [19]. Both calculations were performed within the framework of the local complex potential theory.

Multimode effects in DEA to molecules of the type CX$_3$Y, where Y is a halogen atom, have not been investigated so far. In this section we present the first attempt to study these effects in the process

$$e + CF_3Cl(\nu_2, \nu_3) \rightarrow CF_3Cl^- \rightarrow CF_3(\nu_2) + Cl^-.$$ (1)

Here $\nu_2$ stands for symmetric deformation vibrations (or, so-called “umbrella” mode) The inclusion of only one mode, in addition to the reaction mode $\nu_3$, can be justified by the same reasoning as that given by Shapiro and Bersohn [20] in their studies of photodissociation of CH$_3$I. First, the intermediate negative-ion state of CF$_3$Cl responsible for DEA at low energies has $A_1$ symmetry, therefore degenerate vibrations $\nu_4$, $\nu_5$ and $\nu_6$, having $e$-type, can be excited resonantly only in pairs. Second, the C-F bond length, is very close to that for the anion [21] and the radical CF$_3$. Therefore we can assume that the C-F symmetric stretch mode $\nu_4$ is unlikely to be excited as well. These assumptions are confirmed by measurements of Mann and Linder [22] who observed strong electron-impact vibrational excitation of the $\nu_3$ and $\nu_2$ modes in the $A_1$ resonance region, whereas other modes were not significantly excited.

Inclusion of additional vibrational modes in the description of the attachment dynamics for CF$_3$X is of interest for two reasons. First, it allows us to study the distribution of the internal energy of the fragment, in our case the energy of the umbrella motion in the CF$_3$ radical. This energy can be significant due to, first, a significant Franck-Condon factor for transition between the initial state of CF$_3$X and the excited vibrational states of the intermediate negative ion CF$_3$X$^-$, and, second, due to the final-state interaction between CF$_3$ and X$^-$ redistributing the internal energy of CF$_3$. Studies of Rydberg electron attachment to CH$_3$I, CF$_3$I and CF$_3$Br molecules [23] showed that at high principal quantum number $n$ (or at low electron energies) the major portion of energy released by electron capture appears in translation, indicating insignificance of the internal energy redistribution in the final state. However, at lower $n$ (or higher electron energies) the final-state interaction becomes important [24, 25], although there is no quantitative data, either experimental or theoretical, on the internal energy distribution in the CF$_3$ or CH$_3$ fragment.

The second motivation for DEA studies with inclusion of the umbrella vibrations is the strong sensitivity of the DEA cross section to the initial vibrational state of the target, or to the initial vibrational temperature. The one-mode approximation explains quite well the observed temperature dependence of DEA in electron collisions with methyl halides [8, 26]. However, it fails [7, 27] to give the correct quantitative description of the observed temperature dependence.
of low-energy peak in DEA to CF$_3$Cl. A recent joint experimental and theoretical paper on DEA to CF$_3$Br [10] demonstrates that the DEA rate calculated in the one-mode approximation gives a slower growth at high temperatures than that observed. This indicates that the umbrella mode in perfluoromethyl halides is more important than in methyl halides. This is consistent with the fact that corresponding vibrational quanta are lower in perfluoromethyl halides (e.g., compare 168 meV in CH$_3$Cl and 97 meV in CF$_3$Cl), therefore the excited umbrella mode is more populated there than in methyl halides.

3.1. Coordinates and Hamiltonian
The potential energy surfaces $U^0$ and $U$ for the neutral molecule CF$_3$Cl and the anion CF$_3$Cl$^-$ are represented using two internal coordinates: C-Cl separation $R$, and the distance between the C atom and the plane formed by the F atoms, $r = -R_{CF} \cos \theta$, where $\theta$ is the FCCl angle. At $R \to \infty$ both surfaces are represented in the harmonic form $k(r - r_{ef})^2/2$ for the neutral and $k(r - r_{ef})^2/2 - EA$ for the anion, where $EA$ is the electron affinity of the Cl atom, and $r_{ef}$ is the equilibrium value of $r$ for the radical CF$_3$.

The classical kinetic energy for the nuclear motion in the approximation of two symmetric coordinates can be worked out from the general Hamiltonian for XY$_3$Z molecules [29]

$$ T = \frac{1}{2} \mu \dot{R}^2 + \frac{1}{2} m_{F3} \left( \cot^2 \theta_0 + \frac{m_C + m_{Cl}}{M} \right) \dot{\rho}^2 + \frac{m_{Cl} m_{F3}}{M} \dot{R} \dot{r}, \quad (2) $$

where $M = m_{Cl} + m_C + 3m_F$, $\mu = m_{Cl} m_{F3}/M$, and $\theta_0$ is the equilibrium value of $\theta$. In order to uncouple two motions in this expression, we introduce now the reaction coordinates $\rho$ and $r$ [20], where

$$ \rho = R + \eta r, \quad \eta = \frac{3m_F}{m_C + 3m_F}, \quad (3) $$

and $r$ remains unchanged. The reaction coordinate $\rho$ is simply the distance between Cl and the center of mass of CF$_3$. With the reaction coordinates $\rho$ and $r$ the kinetic energy becomes decoupled [30].

If the initial state of the neutral is not highly excited, we can use the harmonic approximation for $U^0(\rho, r)$ and diagonalize the Hamiltonian $T + U^0$. This gives us the normal frequencies and normal mode coordinates expressed as linear combinations of $\rho - (R_e + \eta r^0_e)$ and $r - r^0_e$.

3.2. Local theory of dissociative attachment
We will employ now the local version [3, 31] of the complex potential theory for DEA. First, the nonlocal calculations are quite complicated even in the one-mode approximation, therefore before we attempt them, it is desirable to get some results using a simpler approach. Second, the $A_1$ shape resonance in CF$_3$Cl occurs at a relatively high energy, 1.83 eV [32], and its width is rather narrow, about 0.6 eV in the Franck-Condon region. This justifies the use of the local theory for CF$_3$Cl.

In Fig. 5 we present comparison of two versions of the theory in the one-mode approximation, nonlocal calculations based on the resonance $R$-matrix approach [7] and the local version. Calculations were done for different initial vibrational quantum numbers $\nu_3$. The comparison confirms our assumption. Both calculations employ the width function $\Gamma(E, R)$ obtained from the semiempirical $R$-matrix theory as described in Ref. [7].

In the one-mode calculations the local (adiabatic) width is represented as $\Gamma(E_r(R), R)$, where $E_r(R) = U(R) - U^0(R)$ is the resonance energy for a given internuclear distance $R$. Its extension to the two-mode case requires additional information on the dependence of the width on the second coordinate $r$. As a first try, we present the two-mode width $\Gamma(E_r(R, r), R, r)$ as a function of $E_r(R, r)$ only.
The basic equation for the nuclear wavefunction $\chi_E(\rho, r)$ in the local approximation has the form [31]

$$[T_\rho + T_r + U(\rho, r) - i\Gamma(\rho, r)/2 - E]\chi(\rho, r) = V(\rho, r)\zeta_i(\rho, r),$$

where $T_\rho + T_r$ is the kinetic energy operator in the reaction-coordinate representation, $V(\rho, r) = [\Gamma(\rho, r)/2\pi]^{1/2}$ is the amplitude for electron capture into the resonance state, and $\zeta_i(\rho, r)$ is the vibrational wave function of the neutral in the initial state.

To solve Eq. (4), we expand $\chi$ in a basis depending on $r$ only [20, 33]. Specifically, we choose eigenfunctions of the Hamiltonian corresponding to the infinite separation of CF$_3$ and Cl (note that $\Gamma(\infty, r) = 0$):

$$(T_r + U^0(\infty, r) - \epsilon_s)\phi_s(r) = 0,$$

where $\epsilon_s$ are corresponding eigenenergies, $\epsilon_s = D + \omega_2'(s + 1/2)$, where $\omega_2'$ is the frequency of the umbrella vibration in free CF$_3$, and $D$ is the C-Cl bond dissociation energy.

Thus, the expansion has the form

$$\chi(\rho, r) = \sum_s \psi_s(\rho)\phi_s(r),$$

where functions $\psi_s(\rho)$ are solutions to the coupled equations

$$(T_\rho + \epsilon_s - E)\psi_s(\rho) + \sum_{s'} U_{ss'}(\rho)\psi_{s'}(\rho) = \lambda_{is}(\rho),$$

where

$$U_{ss'}(\rho) = \int \phi_s(r)[U(\rho, r) - i\Gamma(\rho, r)/2 - U(\infty, r)]\phi_{s'}(r)dr,$$

$$\lambda_{is}(\rho) = \int V(\rho, r)\zeta_i(\rho, r)\phi_s(r)dr.$$

Coupled equations (7) should be solved with the outgoing-wave boundary condition at $\rho \to \infty$ (or exponentially decaying condition for energetically closed channels):

$$\frac{d\psi_s(\rho)}{d\rho} \sim iK_s\psi_s(\rho), \quad \rho \to \infty,$$
where
\[ K_s^2 = 2\mu(E - \epsilon_s). \] (11)

Then the cross section for DA with the formation of the CF\(_3\) fragment in the state \(s\) is
\[ \sigma_s = \frac{2\pi^2}{k^2} \frac{K_s}{\mu} \lim_{\rho \to \infty} |\psi_s(\rho)|^2, \] (12)
where \(k^2/2\) is the initial electron energy.

### 3.3. Results of two-mode calculations

The two-dimensional potential surfaces for CF\(_3\)Cl and corresponding anion were calculated using the second-order Møller-Plesset perturbation theory employing the Dunning’s aug-cc-pVTZ basis set [21, 34]. The anion surface was adjusted in the Franck-Condon region to incorporate the experimental vertical attachment energy for CF\(_3\)Cl [32].

![Figure 6. Dissociative attachment to CF\(_3\)Cl from the ground vibrational state. Numbers near the curves show the vibrational quantum numbers for umbrella vibrations in the final state.](image)

In Fig. 6 we present dissociative attachment cross sections for CF\(_3\)Cl. The total cross section is higher than in the 1-d calculations. Our analysis of the capture amplitudes indicates that the possible reason for this effect is the lower effective resonance width in the 2-d case which leads to a higher survival probability. Of course, this effect strongly depends on the width as a function of the nuclear coordinates, therefore to find out if this effect is real we need ab initio calculations of the 2-d width. Both 1-d and 2-d calculations agree qualitatively with the results of the swarm [35] and beam [36] measurements for the total DEA cross sections. However, these measurements disagree in the absolute value of the peak cross sections by more than a factor of 2 with the beam measurements being closer to our 1-d results and swarm measurements closer to our 2-d results.

The shape of the cross section as a function of electron energy obtained in relative beam measurements of Hahndorf et al [28] agrees approximately with both 1-d and 2-d calculations. However, both theoretical curves decay faster towards lower energies than the experimental curve [28]. On the other hand, the 2-d curve decays slower at higher energies than the 1-d curve which leads to a better agreement with the experiments [35, 36].

The final-state vibrational energy distribution indicates a large contribution of the states with \(\nu_2 = 1, 2, 3\) and 4. This phenomenon is qualitatively independent of the width, and it suggests that the DEA process is an efficient way of exciting vibrational modes in CF\(_3\).
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