

Nonadiabatic Chemical Reaction Triggered by Electron Photodetachment: An *Ab Initio* Quantum Dynamical Study

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Dynamics following electron photodetachment in a complex of a chloride anion with ammonia is explored by a combination of electronic structure and quantum dynamical methods. This system serves as a prototype for investigating a hitherto unexplored class of chemical reactions—nonadiabatic proton transfer triggered by a detachment of an electron. All the reactive and nonreactive channels of this process are characterized and the respective quantum yields are presented.

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Chemical reactions triggered by electronic excitation of light absorbing molecules play an important role in nature, prominent examples being the primary processes of photosynthesis or vision. The term photochemistry is generally used to encompass natural or technological reactions initiated by an optical excitation of a chromophore from the ground state to a discrete excited electronic state. However, using radiation with a sufficiently short wavelength (typically in the UV region) valence electrons in molecular systems can also be excited to the dissociative continuum. While in most cases electron photodetachment is a nonreactive process, for properly selected systems chemistry can take place via the so-called transition state spectroscopy [1,2].

It has been shown by photoelectron spectroscopy measurements as well as by *ab initio* quantum chemistry and quantum molecular dynamics calculations that photodissociation, which is the simplest photochemical reaction, follows photodetachment of the most weakly bound electron in anionic complexes, such as $(XHY)^-$, where X and Y represent halogen atoms [3–7]. Moreover, calculations indicate that also more complex processes, such as exchange or proton transfer reactions, can follow the preparation of a ground state neutral complex from an anionic precursor by electron photodetachment [8,9]. All these chemical processes occur on a single electronic surface (i.e., the neutral ground state) and are, therefore, electronically adiabatic.

What happens if the molecular system is prepared in an excited rather than ground state by electron photodetachment? Such an excited electronic state has been prepared and its vertical detachment energy characterized, e.g., by photodetachment from a $Cl^- \cdots NH_3$ complex [10–12]. While the neutral ground state lies 4.0 eV above the anion, a threshold photon energy of 6.45 eV is necessary to create an excited charge-transfer state $Cl^- \cdots NH_3^+$ (experimental values for vertical transitions from Ref. [10]). What is the chemical dynamics following the preparation

of this charge-transfer state by vertical electron photodetachment from the anionic precursor and which electronic states get involved?

In order to provide an answer to the above question, we first construct the ground and excited charge-transfer potential energy surfaces of the neutral $Cl \cdots NH_3$ cluster using state of the art *ab initio* quantum chemistry methods. We also evaluate surfaces of nonadiabatic couplings between these two electronic states. To model the dynamics following electron photodetachment, we vertically promote the vibrational wave packet corresponding to the anionic precursor to either neutral surfaces. Subsequently, the vibrational wave function is propagated by solving numerically the time-dependent Schrödinger equation on the two coupled electronic surfaces. The principal result is that for the initial wave packet prepared on the excited charge-transfer potential the main channel is nonadiabatic and reactive, leading to the formation of an HCl molecule and a NH_2 radical, both in their ground electronic state. To the best of our knowledge, this is the first described case of a nonadiabatic chemical reaction triggered by electron photodetachment, and the present complex thus serves as a benchmark system for investigating this new class of processes.

The excited $Cl^- \cdots NH_3^+$ complex, which has a $Cl^- \cdots H-NH_2^+$ hydrogen bonded structure (with dash and dots representing covalent bond and noncovalent interactions, respectively), possesses nine vibrational degrees of freedom. However, the investigated nonadiabatic reaction involving a proton transfer from the NH_3^+ to the Cl^- unit is essentially a one-dimensional process: a collinear H^+ motion between the Cl and N atoms. To a lesser extent, the relative motion of the two heavy atoms gets involved too. We assume that the remaining modes are practically decoupled from the reactive mode and act merely as spectators. Therefore, we construct the potentials and nonadiabatic couplings, as well as solve the quantum dynamical problem in a

reduced two-dimensional representation, involving the Cl-H and H-N collinear coordinates. For the purpose of simplifying the *ab initio* calculations, we further restrict our geometry to be planar with a C_{2v} symmetry. This is justified by the fact that the charge transfer equilibrium geometry is planar, and the reaction product Cl-H + NH₂ is also well described by this symmetry. Moreover, the initial (anionic) geometry is not very far from planarity [10,12]. On the other hand, the ground state equilibrium is far from being planar. However, the exact dynamics in this region are not the focus of our study and should be only of minor effect.

The quantum-chemical electronic structure calculations were carried out using a multireference complete active space self-consistent field (CASSCF) approach with an augmented correlation consistent polarization valence double zeta (aug-cc-pvdz) basis set [13] using the MOLPRO program package [14]. For the construction of the multireference wave function, all valence electrons were included in the active space. This wave function was also used for the evaluation of the nonadiabatic couplings between the ground and excited charge-transfer potentials of the neutral complex by the method of finite differences. Important parts of the potential surfaces were also recalculated using the multireference configuration interaction (MRCI) approach with single and double excitations, which accounts for both nondynamic and dynamic electron correlation effects. The result is that the inclusion of dynamic correlation practically does not change the shape of the surfaces but merely causes constant shifts in energy. Therefore, the simpler CASSCF approach is sufficient for the purpose of the present dynamical study. It also allows for the evaluation of the first-order nonadiabatic couplings. The active space included the full valence space plus one additional orbital in the B_2 representation of the C_{2v} point group.

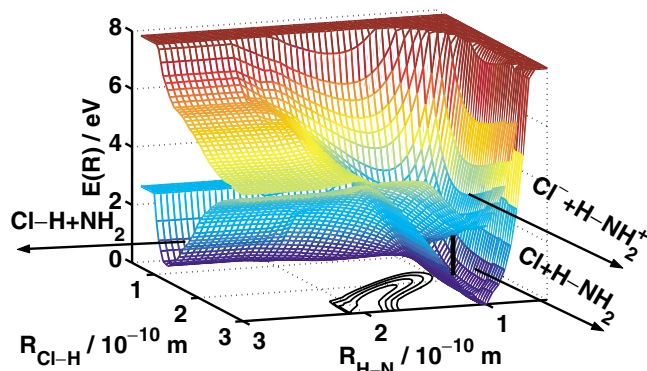


FIG. 1 (color online). Adiabatic potential energy surfaces for the ground (neutral) and the lowest charge transfer state of the Cl...NH₃ complex. The contours represent the energy gap in the avoided crossing region. The vertical bar indicates the center of the Franck-Condon region for vertical transition from the anionic precursor.

Figure 1 shows two-dimensional potential energy surfaces for the two lowest doublet B_2 states, i. e., the ground state and the lowest charge transfer state. Note that two other states, which are nearly degenerate with the electronic ground state, have been omitted. While the upper surface exhibits only one deep minimum corresponding to the charge transfer Cl⁻...H-NH₂⁺ arrangement, the situation on the lower surface is very different. Namely, two valleys exist there, reflecting the Cl...H-NH₂ and Cl-H...NH₂ channels. Note that the two surfaces come close to each other exhibiting an avoided crossing along a line where the two coordinates are approximately equal ($R_{\text{Cl-H}} - R_{\text{H-N}} = 60$ pm). This is also the region where the first-order nonadiabatic coupling becomes significant. As is demonstrated in Fig. 2, the two components of the derivative coupling along the Cl-H and H-N coordinates have, except for a sign change, a very similar shape with growing magnitude upon simultaneously increasing both coordinates.

The dynamics following electron photodetachment from the Cl⁻...NH₃ cluster is modeled by a vertical promotion of the vibrational wave packet of the anionic complex to one of the two potential surfaces of the neutral system, depending on the photon energy. The vertical bar in Fig. 1 denotes the center of this Franck-Condon region. The quantum dynamical simulation starts with the preparation of the initial wave function, which we took as the harmonic ground state vibrational function of the anionic Cl⁻...NH₃, projected on the Cl-H and H-N coordinates. This wave function is then placed on either of the two neutral surfaces. The subsequent time evolution of the two coupled states is governed by the following Hamiltonian:

$$\mathbf{H} = \mathbf{E} - \frac{\hbar^2}{2}(\nabla^T \mathbf{M}^{-1} \nabla \mathbf{1} + 2\mathbf{C}^T \mathbf{M}^{-1} \nabla + \mathbf{T}), \quad (1)$$

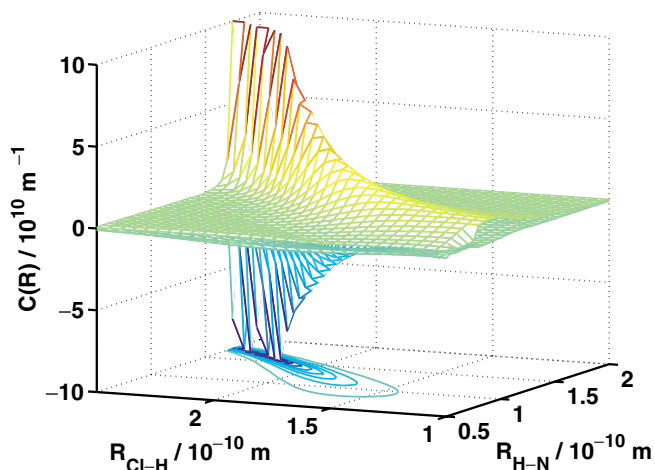


FIG. 2 (color online). First-order nonadiabatic coupling $C^{(\text{Cl-H})}(R)$ (positive surface) and $C^{(\text{H-N})}(R)$ (negative surface and contours) between ground and lowest charge transfer state of the Cl...NH₃ complex. Note that the orientation differs from that of Fig. 1.

where M^{-1} is the metric tensor for the collinear Cl-H and H-N coordinates. The first two terms on the right-hand side represent adiabatic quantum dynamics along the respective potential energy surfaces $E_i(R)$. The remaining two terms result from the action of the nuclear kinetic operator on the adiabatic electronic states

$$C_{ij}^{(k)}(R) = \left\langle \phi_i(R) \left| \frac{\partial}{\partial R_k} \right| \phi_j(R) \right\rangle, \quad k = \text{Cl-H, H-N},$$

$$T_{ij}(R) = \langle \phi_i(R) | \nabla_R^T M^{-1} \nabla_R | \phi_j(R) \rangle, \quad (2)$$

where $|\phi_i(R)\rangle$ stands for the adiabatic electronic state vector which parametrically depends on the nuclear coordinates R . In most studies of nonadiabatic effects on molecular quantum dynamics the second order term is neglected, thus rendering the truncated Hamiltonian to be non-Hermitian. In the simulations described below, this leads to an unphysical decrease of population by more than 30% during the time scale under consideration (14 fs). This problem can be circumvented by virtue of the following identity:

$$T_{ij} = \nabla^T M^{-1} C_{ij} - \langle \nabla^T \phi_i | M^{-1} | \nabla \phi_j \rangle, \quad (3)$$

which allows one to decompose the second order non-adiabaticity into an anti-Hermitian and a Hermitian contribution [15]. Including the former and neglecting only the latter term yields a first-order approximation to the full Hamiltonian operator of Eq. (1), which is Hermitian again and, hence, leads to unitary time evolution. The coupled time-dependent Schrödinger equations are solved numerically using a finite differencing scheme for the temporal problem. Wave functions are represented on an equidistant grid consisting of 256×256 points allowing for the use of fast Fourier transforms [16]. The

outgoing parts of the wave functions are smoothly absorbed near the edges of the grid.

Quantum dynamical simulations were carried out for two different photodetachment scenarios. First, the vibrational ground state wave function of the anionic complex is vertically promoted to the lower surface of the neutral system. The dominant part of the wave packet remains confined to the region of the bound $\text{Cl} \cdots \text{H-NH}_2$ complex without overcoming the barrier to the reactive $\text{Cl-H} \cdots \text{NH}_2$ channel. Also, practically no nonadiabatic transfer of population to the upper surface occurs. In a second set of simulations, the initial vibrational wave function is vertically placed on the excited potential surface of the neutral complex; see Fig. 3. The wave packet oscillates essentially along a line ($R_{\text{Cl-H}} + R_{\text{H-N}} = \text{const}$) thus passing the avoided crossing region. As can be seen in Fig. 4, only 25% of the population remain in the upper state after 14 fs. The emerging lower state population can be divided into the nonreactive and reactive channels. Only a small portion (21%) is found in the nonreactive $\text{Cl} \cdots \text{H-NH}_2$ region, while the remaining population (54%) is found in the reactive domain. This population partly remains bound in the $\text{Cl-H} \cdots \text{NH}_2$ potential well (11%), while the remainder dissociates into the $\text{Cl-H} + \text{NH}_2$ channel with a total quantum yield of 43%. The outgoing portion of the wave packet is absorbed near the edges of the grid, which causes the decrease of total population down to 57% during the first 14 fs; see Fig. 4. On a longer time scale the population dynamics remains qualitatively unchanged. After 50 fs successive nonadiabatic transitions deplete the upper state population down to 10%, while the population of the bound regions of the lower state decays down to 15%.

In conclusion, we have demonstrated two different scenarios for photodetachment of the $\text{Cl}^- \cdots \text{H-NH}_2$

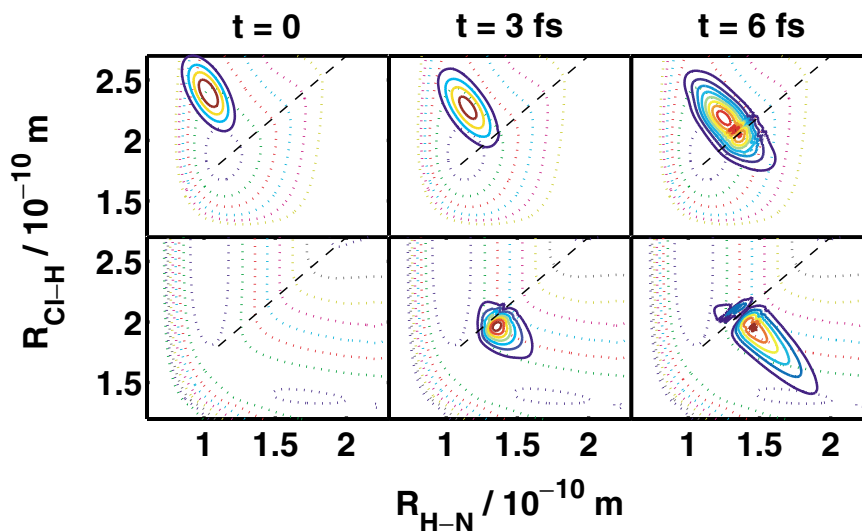


FIG. 3 (color online). Wave packet dynamics upon vertical excitation of the $\text{Cl}^- \cdots \text{NH}_3$ complex to the lowest charge transfer state of the neutral complex (upper panel). Upon reaching the avoided crossing region (dashed line), nonadiabatic transition to the ground state occurs (lower panel). Solid contours: density. Dotted contours: adiabatic potential energy surfaces (spacing 0.5 eV).

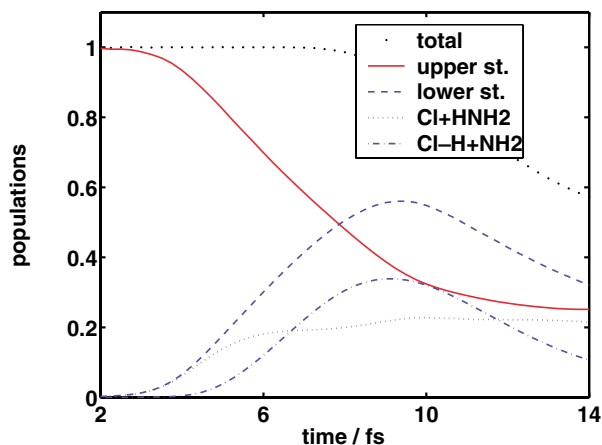


FIG. 4 (color online). Population dynamics upon vertical excitation of the $\text{Cl}^- \cdots \text{NH}_3$ complex to the excited state of the neutral complex. The lower state population emerging upon nonadiabatic population transfer is divided into nonreactive ($\text{Cl} \cdots \text{H-NH}_2$) and reactive ($\text{Cl-H} \cdots \text{NH}_2$) regions. Note that the effect of absorbing boundary conditions acting on the reactive $\text{Cl-H} + \text{NH}_2$ channel leads to a 43% loss of total population during the time interval considered (14 fs).

complex. Upon vertical excitation to the lower surface of the ground state, the dynamics can be viewed as nonreactive and electronically adiabatic. In contrast, the process initiated on the upper charge-transfer surface is dominated by an electronically nonadiabatic transition leading to the reactive $\text{Cl-H} + \text{NH}_2$ channel. Thus, the present system serves as a prototype of a new class of chemical reactions: nonadiabatic proton transfer triggered by electron photodetachment. Our prediction will hopefully motivate future ultrafast spectroscopic experiments. Currently, the only data available for the present system come from time-independent photoelectron spectroscopy [10,11]. Detachment of an electron from ammonia in the $\text{Cl}^- \cdots \text{NH}_3$ complex results in a detectable vibrational progression assigned to umbrella motion of NH_3^+ which is not included in our model. However, from the width of the experimental vibrational features, we can conclude that at least some of the population survives in the charge transfer state for tens of femtoseconds, which is consistent with our theoretical results. It is also possible that the inclusion of the umbrella mode into the model would slow down the decay of the charge transfer state population, since the reactive hydrogen would explore regions of the potential with a weaker nonadiabatic coupling.

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