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Nonadiabatic dissociation dynamics of Cl···HD van der Waals complex initiated by electron detachment of Cl^-–HD

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Abstract

Nuclear dynamics following the electron detachment of the Cl^-–HD anion is investigated by a time-dependent wave packet propagation approach. Photodetachment of Cl^-–HD promotes it to the van der Waals well region of the reactive Cl···HD potential energy surface. The latter is a manifold of three electronic states coupled by the electronic and (relativistic) spin-orbit coupling. Among the three surfaces, the electronic ground one is of $^2\Sigma_{1/2}$ type and yields products in their electronic ground state. The remaining two, $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, on the other hand, yield products in their excited electronic states. However, these two can yield products in their electronic ground state via nonadiabatic transitions to the $^2\Sigma_{1/2}$ state. The channel specific, HCl + D or DCl + H or Cl + HD, dissociation probabilities on this latter state are calculated both in the uncoupled and coupled surface situations. Separate initial transitions (via, photodetachment) to the $^2\Sigma_{1/2}$, $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ adiabatic electronic states of Cl···HD are considered in order to elucidate the nonadiabatic coupling effects on this important class of chemical reactions initiated by an electron detachment.

Keywords: Nonadiabatic photodissociation dynamics; Van der Waals complex; Cl^-–HD; Cl···HD

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1. Introduction

Molecular dissociation following photodetachment of its anionic precursor represents a rarely explored class of chemical reactions, particularly, when the latter are guided by nonadiabatic interactions. Anion photoelectron spectroscopy [1–3] by and large has been utilized to probe the bound vibronic level structure of the corresponding neutral species, however, the dissociation of the latter can become an important event when its equilibrium geometry differs significantly from that of the anion precursor. More specifically, if the 'transition state' or the repulsive region of the potential energy surface (PES) of the neutral species is probed by photodetachment [1]. Experimental measurement of such a process is also tedious and it requires a careful combination of the photoelectron spectroscopy with the photofragment translational spectroscopy. Such a combination allows to record the kinetic energies and recoil angles of the photoelectron and the final photofragments are measured in co-incidence [3]. This technique has been applied to study the dissociative photodetachment dynamics of weekly bound cluster anions [4] and van der Waals complexes [5].

Over the past years the $Cl + H_2$ reactive system has been extensively studied both theoretically and experimentally [6]. Experimental photodetachment measurements have probed the van der Waals well of the reagent asymptote of the reactive $Cl + H_2$ (HD) PES [7]. This has been corroborated by the theoretical studies for the first time from our group [8,9]. Now, since the photodetachment of the anion precursor in this case samples the reagent channel of the reactive PES of the neutral, the repulsive energy in the latter may be sufficient to trigger chemical reactions.

The dissociation of Cl···HD followed by photodetachment of $C1^-$–HD is examined in this paper. The low-lying PESs of neutral Cl···HD are coupled by electronic and relativistic spin-orbit (SO) coupling [10,11]. The ground electronic state of Cl···HD is of $^2\Sigma_{1/2}$ type and the two immediate next excited electronic states are of $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ type in the collinear arrangements of the three nuclei ($1^2A'$, $1^2A''$ and $2^2A'$ symmetries, respectively, in non-collinear geometries). Of these only the lower state of A' symmetry ($^2\Sigma_{1/2}$) correlates with the electronic ground state of the products HCl/DCl ($X^1\Sigma^+$) + H (^2S), whereas, the other two excited states (the components

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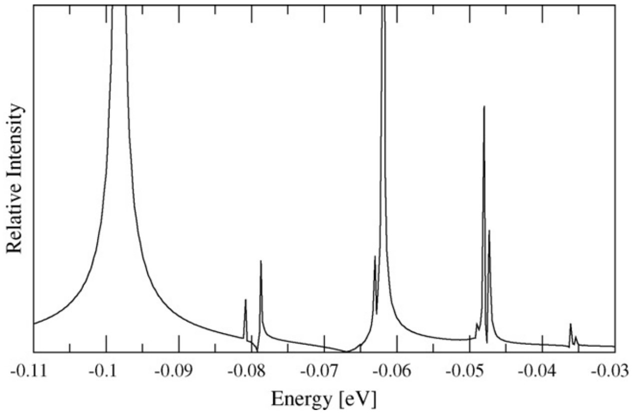

Fig. 1. The bound energy level spectrum of the electronic ground state of the Cl^-–HD anion obtained by spectral quantization method and locating a stationary GWP near the equlibrium geometry of Cl–HD (at $R \sim 6.01a_0$, $r \sim 1.402a_0$ and $\gamma \sim 0^\circ$ with width parameters 0.25, 0.25 and $0.2a_0$ along these coordinates, respectively). The intensity in arbitary units is plotted as a function of the energy measured relative to that of equilibrium geometry of the electronic ground state of Cl^-–HD.

of the $^2\Pi$ state) correlate with the products in their electronic excited state, HCl/DCl ($^3\Pi$) + H(^{2}S) (e.g. see Fig. 1 of Ref. [9]). The product excited state is considerably high in energy, thus the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states remain non-reactive in the adiabatic Born–Oppenheimer picture for low and moderate collision energies. However, they can form products via nonadiabatic transitions to the $^2\Sigma_{1/2}$ state. The two states of $^2A'$ symmetry are electronically coupled with each other and form a conical intersection [10]. Thus, two types of nonadiabatic coupling (i) Σ–Π electronic coupling and (ii) Σ–Π and Π–Π relativistic SO coupling, govern the nuclear dynamics following photodetachment. Recently, Capecchi and Werner have carried out multireference configuration interaction calculation and developed multiparameter global fits to calculate accurate potential energy surfaces for the above mentioned three electronic states and three nonadiabatic coupling surfaces between them [11]. We used these PESs in dynamical simulations presented here.

In the theoretical simulations the eigenfunctions of the energy levels of the electronic ground state of Cl^-–HD are vertically promoted to the coupled manifold of Cl···HD electronic states. These are then propagated on this final electronic manifold by numerically solving the time-dependent Schrödinger (TDSE) equation. The anionic wavefunctions are calculated by spectral quantization algorithm [12]. The channel specific dissociation probabilities of Cl···HD are calculated by recording the dissociative flux of the wave packet (WP) in time. We find that the nuclear dynamics is significantly affected by the nonadiabatic interactions. For instance, when the initial wavefunction is prepared on the $^2\Sigma_{1/2}$ electronic state, more WP flux moves to the reactive channels HCl + D or DCl + H in the coupled states situation than in the uncoupled one. The reactivity of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ electronic states via nonadiabatic transition to the $^2\Sigma_{1/2}$ state mostly populates the Cl + HD non-reactive channel of the latter. The dissociation to the reactive channels of the $^2\Sigma_{1/2}$ state in these cases are far less compared to the situation when dynamics is initiated on the $^2\Sigma_{1/2}$ electronic state. The formation of HCl + D is found to be more than DCl + H also for the excited eigenlevels of Cl^-–HD.

The theoretical computational details to treat the nuclear dynamics in the coupled manifold of electronic states are described in Section 2. In Section 3, we present the quantum dynamical results and discuss them. Finally, the paper is closed with a brief summary in Section 4.

2. Theoretical and computational details

The Cl^-–HD anion is promoted to the reactive PES of neutral Cl···HD upon photodetachment. A Franck–Condon (FC) transition is assumed for this step and the subsequent reactive dynamics of Cl···HD is simulated by means of quantum WP propagation. The final products (in their electronic ground state) may emerge in one of the following three channels, viz., (a) HCl + D (R1), (b) DCl + H (R2) and (c) Cl + HD (NR). Here R1 and R2 represents the two reactive channels and 'NR' stands for the non-reactive channel. The channel specific dissociation probabilities are calculated both for the uncoupled and coupled surface situations for the $^2\Sigma_{1/2}$ electronic state. Since, the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ electronic states yield products in their electronic ground state via nonadiabatic transitions to the $^2\Sigma_{1/2}$ state, the dynamics of these states are simulated in the coupled surface situation only. All dynamical calculations are carried out for the lowest value of the total angular momentum; $J = 0$ and 0.5 in the nonrelativistic and relativistic situations, respectively, and the effect of excited vibronic levels of Cl^-–HD on the nuclear dynamics is examined. The WP propagation in the coupled electronic manifold is carried out in a diabatic electronic representation [13]. This is to avoid the singular derivative coupling terms of the adiabatic electronic representation [14]. However, the latter representation is more realistic and therefore, the adiabatic initial WP pertinent to the Cl^-–HD anion transformed to a diabatic electronic basis prior to its propagation on the Cl···HD electronic states and the time-evolved WP at each time is transformed back to the adiabatic electronic basis again to calculate the dynamical quantities.

2.1. The Hamiltonian

The nuclear dynamics is simulated here on the three lowest electronic states of Cl···HD including both the electronic and SO couplings among them. We use Jacobi coordinates R (distance between Cl and the center of mass of HD diatom), r (HD internuclear distance) and γ (the angle between $\vec{R}$ and $\vec{r}$) in the body-fixed frame in the dynamical simulations. The body-fixed z axis is defined to be parallel to R and the diatom is in the (x, z) plane. The various angular momentum operators and their corresponding projection quantum numbers are defined following the work of Rebentrost and Lester [15], Schatz et al. [16] and Alexander et al. [17]. They are listed in Table 1. With this set of coordinates, the Hamiltonian of Cl···HD system for total angular momentum $J \neq 0$ in a diabatic electronic basis can be expressed as

$$\mathcal{H} = \mathcal{H}^{\mathrm{Nu}}\mathbf{1} + \mathcal{H}^{\mathrm{el}} + \mathcal{H}^{\mathrm{so}} \tag{1}$$