

A practical approach to temperature effects in dissociative electron attachment cross sections using local complex potential theory

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ABSTRACT

We propose a practical computational scheme to obtain temperature dependence of dissociative electron attachment cross sections to polyatomic molecules within a local complex potential theory formalism. First we perform quantum path-integral molecular dynamics simulations on the potential energy surface for the neutral molecule in order to sample initial nuclear configurations as well as momenta. Classical trajectories are subsequently integrated on the potential energy surface for the anionic state and survival probabilities are simultaneously calculated along the obtained trajectories. We have applied this simple scheme to dissociative electron attachment processes to H_2O and CF_3Cl , for which several previous studies are available from both the experimental and theoretical sides.

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1. Introduction

Low-energy collisions of electrons with polyatomic molecules are among the most important elementary processes in various chemistry fields such as plasma chemistry, upper atmospheric chemistry, interstellar chemistry, and radiation chemistry [1,2]. In particular, bond breaking processes of polyatomic molecules induced by low-energy electrons are important chemical reactions, which are frequently called as dissociative electron attachment (DEA), and have been extensively investigated in the past. The importance of DEA to biomolecules has also been pointed out in the pioneering experimental work of Boudaïffa et al. [3], who showed that low-energy electrons can cause single and double strand breaks in DNA through DEA processes. Their work significantly stimulated further experimental studies on DEA to various biological molecules including DNA base molecules, amino acids and their related chemical compounds [4–6].

First-principles prediction of cross sections for DEA to polyatomic molecules is one of the important subjects in the theoretical chemistry field. This is especially true since it may be still difficult to measure absolute values of DEA cross sections within desired high energy resolution from the experimental side. In addition, theoretical approaches should be quite useful for understanding detailed DEA mechanisms at a molecular level. Low-energy DEA processes can be generally described via formation of temporary molecular anions with their lifetime τ or resonance decay width $\Gamma = h/2\pi\tau$, if only a single scattering resonance state of the

excess electron–molecule system is assumed to occur. In this case, nuclear dynamics of the DEA process may be governed by the complex-valued potential energy surface, $V(\mathbf{Q}) = E_R(\mathbf{Q}) - i\Gamma(\mathbf{Q})/2$, where E_R and \mathbf{Q} are the resonance energy of the temporal anion state and coordinates of the molecular configuration, respectively. This approach is called as a local complex potential approximation [7]. Once the functional forms of $E_R(\mathbf{Q})$ and $\Gamma(\mathbf{Q})$ are given, one can numerically solve nuclear dynamics equations quantum mechanically for small molecular systems including only a few atoms by either a time-independent [8–13] or time-dependent manner [14,15], where most of previous time-dependent studies have been performed with multi-configuration time-dependent hartree formalism [16]. In fact, full-dimensional quantum calculations have been previously applied to the dynamics of DEA to various small molecules including diatomic molecules, H_2O and H_2S [8–15], although it is well-known that the local complex approach is inaccurate in the near-threshold region. It should be emphasized that actual full-dimensional quantum dynamics calculations are limited only for very small chemical systems having fewer degrees of freedom since the computational difficulty significantly increases with an increase in molecular size. Therefore, the most commonly used approach is to freeze all modes other than one corresponding to the reaction coordinate. Recently, quantum dynamics calculations taking two and more active degrees of freedom into account have been carried out for CF_3Cl and C_2H_2 [17–22]. However, in order to understand the temperature dependence of DEA cross sections, one has to solve such complicated nuclear dynamics equations repeatedly with many different, but thermally accessible initial quantum states. Again, this computational scheme also becomes unfeasible as the size of the molecular system increases.

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In this work we propose a practical computational approach to obtain the temperature dependence of DEA cross sections to polyatomic molecules. In our approach, all degrees of freedom for the chemical system are taken into account in the dynamics, where the nuclear dynamics on the neutral molecular state for a given temperature is treated quantum mechanically with a path-integral approach, while the nuclear dynamics on the temporary anion state is treated classically. Here we investigate the feasibility and accuracy of our approach for the DEA processes to H_2O and CF_3Cl , for which many previous theoretical and experimental studies are available.

2. Computational procedure

As mentioned previously, we treat the nuclear dynamics of the DEA process within the local complex potential approximation. The classical DEA cross section can be formally written as [7,21,23]

$$\sigma = \frac{2\pi^2}{k_i^2} \int W(P, Q, T) \delta[H(P, Q) - E] \Gamma(Q) P_{\text{surv}}(P, Q) dP dQ, \quad (1)$$

where Q and P are the sets of initial nuclear coordinates and conjugated momenta. $k_i^2/2$ is the initial electron collision energy. $\Gamma(Q)$ is the resonance width function controlling the lifetime of the temporary anion. H is the classical Hamiltonian of the system and P_{surv} is the survival probability given by

$$P_{\text{surv}} = \exp \left[- \int_0^t \Gamma(Q(t)) dt \right] \quad (2)$$

accumulated along the classical trajectory on the anionic potential energy surface. W is the distribution function of the initial nuclear coordinates and conjugated momenta for a given temperature. The basic idea is very similar to previous theoretical work of Fiquet-Fayard and his co-workers [23], where a Wigner distribution function was used for W . We have alternatively calculated the distribution function W from the path-integral molecular dynamics (PIMD) approach with a constant temperature T on the potential energy surface of the neutral state. In the path-integral formalism, the quantum mechanical character of nuclei is described by cyclic bead chains, and one can then obtain the thermal equilibrium structure of the molecule including both the temperature and nuclear quantum effects [24,25]. The PIMD calculations were performed with 10–100 cyclic polymer beads depending on the simulation temperature as well as nuclear masses. The massive N ose-Hoover chain technique in the velocity Verlet algorithm was used to control the system temperature. Notice that thermal rotation is automatically included in PIMD simulations. The details of our PIMD computational code are described in Refs. [26–29]. Using the coordinates and conjugated momenta obtained from the PIMD simulations as an initial condition, we have solved classical equation motions with the standard Runge–Kutta numerical algorithm on the anionic potential energy surface. In addition, the survival probability was simultaneously calculated along the classical trajectory according to Eq. (2) until the potential energy of the anionic state becomes more stable than that of the neutral state. In this way, we can calculate the DEA cross sections as a function of temperature. In addition, since we treat the nuclear dynamics in full dimensions, we can also obtain the final energy distributions partitioned into the vibrational and rotational energies of the fragments formed in the DEA process. The DEA cross sections as well as the energy distribution functions can be easily extracted from the standard binning procedure.

3. Results and discussion

3.1. Application to $e^- + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^-$

First we have applied our practical approach to DEA to the H_2O molecule via the 2B_1 metastable anionic state since the global potential energy surfaces based on the local complex potential model have been already developed by Haxton et al. [8–13] and full quantum dynamics calculation results are also available. The PIMD simulations were performed with 50–100 polymer beads depending on temperature. A total of 50,000 classical trajectories were integrated on the anion potential energy surface.

Our computed cross sections obtained at $T = 100$ K for DEA to H_2O and D_2O are compared to the previous quantum results by Haxton et al. [9] in Fig. 1. Notice that the quantum cross sections were obtained from the $(v_1 v_2 v_3) = (000)$ initial vibrational state of H_2O or D_2O , where v_1 , v_2 and v_3 are vibrational quantum numbers of symmetric O–H stretch, bending, and antisymmetric O–H stretch, respectively. It should be mentioned that our computational results at $T = 100$ K are mostly dominated by the (000) lowest vibrational quantum state of H_2O or D_2O since we have confirmed that the calculations at $T = 50$ K yielded essentially the same result. The overall agreement between the present and previous quantum results is seen to be good. For example, the present calculations show that the DEA cross sections for D_2O are somewhat larger than those for H_2O while the energy width for H_2O is slightly wider than that for D_2O . These features are in qualitative agreement with the previous quantum results of Haxton et al. However, a clear deviation can be seen around threshold regions.

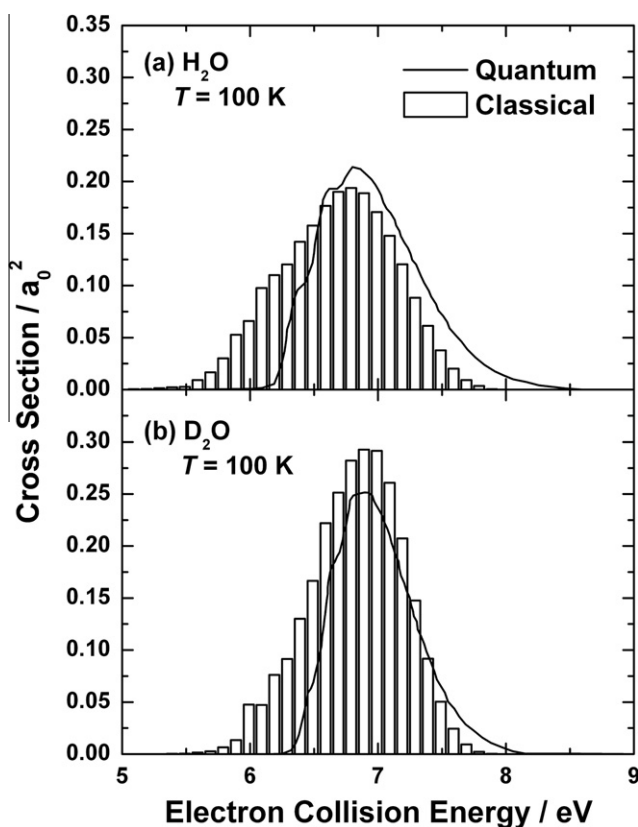


Fig. 1. DEA cross sections for (a) H_2O and (b) D_2O as a function of electron collision energy. The results obtained from the present model at $T = 100$ K are shown in bars. Solid lines correspond to the quantum dynamics results taken from Ref. [9]. The quantum results were obtained from the (000) initial vibrational state of H_2O and D_2O .

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