Dynamics of molecular ion $\text{(I}_2^-$) in condensed phases: hybrid quantum/classical method for a linear chain model

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Abstract

Photodissociation and recombination dynamics of I$_2^-$ in condensed phase environments is studied by a linear chain model consisting of a diatom in a chain of rare gas atoms. We use a hybrid quantum/classical method, in which the wavepacket dynamics of I$_2^-$ is treated quantum mechanically while the solvent atoms are described classically. Rapid recombination and subsequent solvent-induced coherent vibrations are observed when the mass of the solvent atom is comparable to that of the solute. The mechanism of charge switching and the possibility of nonadiabatic transitions are examined by introducing an effective electric field representing the change in solvent polarization.

1. Introduction

Dynamics of molecular ions in condensed phases such as in large molecular clusters or in liquids have been studied extensively to develop a microscopic picture of chemical reaction and solvation dynamics in such systems [1]. The study of solvent-mediated reactions in molecular clusters allows the examination of the stepwise effect of increasing solvation on electronic structure and reactivity. Photodissociation is one of the most widely studied chemical reactions both experimentally and theoretically [2]. In condensed environments, studies on a wide range of systems including diatomic molecules and complicated polyatomic systems have revealed sequential processes of photodissociation, geminate recombination, and vibrational relaxation. A pair of recoiling photofragments produced by initial photolysis can geminally recombine due to the caging effect of solvent molecules. The resulting vibrationally excited molecule loses its extra energy into the solvent bath and relaxes to the ground vibrational state.

Although the general features of photodissociation and recombination in condensed phases are well known, there are several unresolved issues concerning detailed microscopic pictures for the processes involved. Of particular interest is the role of electrostatic interactions on solution/cluster reaction dynamics and vibrational relaxation. To address such issues, time-resolved experiments on the photodissociation and recombination dynamics of I$_2^-$ in several solvents such as water or alcohols and in mass-selected clusters of the form I$_2$(CO$_2$)$_n$ have been done [3–7]. Molecular Dynamics and Monte Carlo simulations for the same systems have also been performed [8–10]. One of the main observations is very fast vibrational relaxation rate of the charged solute in polar solvents and clusters compared with the case of neutral molecule (I$_2$) in nonpolar solvents. It is partly attributed to the strong electrostatic
forces in these systems. Additionally, recurrences have been seen in absorption transients, which were interpreted as coherent vibrational motion of the caged fragments.

Theoretical treatments of the reaction dynamics occurring in condensed phases primarily rely on classical mechanics due to the large number of particles involved in these systems. Yet it is necessary to describe few relevant degrees of freedom quantum mechanically. A commonly used strategy is to partition the whole system into a subsystem (e.g. solute) which can be treated rigorously and the remaining bath degrees of freedom which are approximated by classical trajectories. It is based on the assumption that the motion of solute can be separated from that of the solvent (time-dependent Hartree approximation) [11]. The quantum and the classical dynamics are coupled self-consistently within the Ehrenfest framework. The hybrid quantum/classical (HQC) scheme has been applied to many different dynamical processes [12–18]. Recently Liu and Guo introduced a linear chain model to study \( \text{I}_2^- \) photodissociation dynamics in rare gas matrices by using a hybrid quantum/classical method [19–21].

In this Letter, we studied the photodissociation and recombination dynamics of \( \text{I}_2^- \) in a linear chain of Ar or Xe atoms. We first examined the HQC method by comparing it with exact quantum (EQ) description of the whole system in case of few number of solvent atoms. It is found that HQC results are consistent with EQ calculations especially for the dynamics of solute. Energy transfer and recombination dynamics are examined with the emphasis on the comparison between \( \text{I}_2^- \) and \( \text{I}_2 \) systems and the effects of different solvents. We have observed substantial energy transfer from the dissociating \( \text{I}_2^- \) to the solvent atoms and quite rapid recombination. In Ar solvent, the dynamics of \( \text{I}_2^- \) show different behavior than that of \( \text{I}_2 \) system. The oscillations in the average positions of the diatom after recombination, which is observed in \( \text{I}_2 \), are not found, reflecting the fact that the excited state is purely repulsive for \( \text{I}_2^- \) system. With the heavier solvent Xe, such oscillations are observed, which can be interpreted as solvent-induced coherent vibrations as suggested in the experiments.

For better understanding of the recombination dynamics, one needs to consider the dependence of the electronic structure on the solvent degrees of freedom at large internuclear distances. In other words, the gas phase potential energy surfaces for the solute molecule should be modified in this region. The full account of such effect on the electronic structure is rather complicated [22]. For a molecular ion such as \( \text{I}_2^- \), the primary role of the solvent molecules is to affect the charge separation process during photodissociation/recombination. In molecular clusters or solutions, the solvent molecules can take a configuration such that one part of the solute molecule is preferentially solvated compared to the others. Those solvent configurations give rise to an asymmetric electrostatic environment. In a simplified picture, one can model the solvent polarization by introducing an effective electric field [9]. We introduced an effective electric field due to the solvent polarization in our simple model and studied the role of the electrostatic interaction on the charge switching process during the photodissociation and the recombination dynamics of \( \text{I}_2^- \). The effective field provides an additional wall against dissociation and leads to faster recombination. The possibility of nonadiabatic transition, which can provide an efficient mechanism for the transition to the electronic ground state, is also discussed. These results are consistent with the experimental findings of the rapid relaxation rate of the charged solute.

2. Theory

2.1. Model

We use a one-dimensional model for the dynamics of photodissociation and recombination of a diatom. The model consists of a single diatom embedded in a symmetrically arranged linear array of rare gas atoms (Fig. 1). The same linear chain model was introduced by Liu and Guo to study the dynam-

![Fig. 1. Schematic diagram of linear chain model for \( \text{I}_2^- \) embedded in rare gas matrices. The number of solvents, \( N \), varies from 1 to 30.](image-url)
ics of I$_2$ [19]. Similar one-dimensional models have been used to obtain general features of the dynamics of photodissociation and the energy transfer processes [23–25]. The two atoms of the solute are coupled individually to the two adjacent rare gas atoms and all the solvent atoms are coupled to each adjacent atom. The Lennard-Jones potential is used for the nearest-neighbor interaction for the solvent atoms:

$$V_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right].$$

(1)

The same form of the potential is used for the solvent atom–solute atom interaction. The last solvent atom at each end of the chain are connected to static wall. The reflective boundary is not expected to affect short time dynamics, which is the main interest of the present study.

For the potential energy of the diatom, gas phase potentials for I$_2$ and I$_2^-$ are used [26,27]. Two electronic states are considered; the ground state and the excited state reached by photoabsorption. The electronic transitions responsible for photodissociation are taken to be X($^1\Sigma_g^+$) → A($^3\Pi_u$) for I$_2$ and $^2\Sigma_u^+ → ^2\pi_g$ for I$_2^-$, respectively. The potentials are modeled by Morse functions of the form:

$$V(x) = D \left[ \exp \left[ -2\beta(x-x_0) \right] - 2 \exp \left[ -\beta(x-x_0) \right] \right].$$

(2)

The potential parameters for the Morse functions are given in Table 1 along with those for the Lennard-Jones potentials. Fig. 2 shows the potential surfaces for I$_2^-$ and the corresponding potential surfaces for I$_2$ can be found in Fig. 2 of Ref. [21].

2.2. Hybrid quantum/classical (HQC) method

For simplicity, consider a system with only two solvent atoms. We assume that the motion of the center of mass for the diatom can be ignored (zero temperature) and the solvent atoms oscillate symmetrically relative to the center of the whole chain. In this case, one can describe the system by two coordinates (x, r). Here x represents the bond length of the diatom and r the relative distance of the two

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The parameters of potential functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse parameter</td>
<td>$D$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>I$_2$</td>
<td>A($^3\Pi_u$)</td>
</tr>
<tr>
<td></td>
<td>X($^1\Sigma_g^+$)</td>
</tr>
<tr>
<td>I$_2^-$</td>
<td>$^2\Sigma_u^+$</td>
</tr>
<tr>
<td></td>
<td>$^2\pi_g$</td>
</tr>
<tr>
<td>Lennard-Jones</td>
<td>$\epsilon$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>I–Ar</td>
<td>130.24</td>
</tr>
<tr>
<td>I$^-$/Ar</td>
<td>130.24</td>
</tr>
<tr>
<td>Ar–Ar</td>
<td>84</td>
</tr>
</tbody>
</table>

$^a$ Average value of I radius (1.96 Å) and I$^-$ radius (2.16 Å) + Ar radius (1.70 Å).

$^b$ Average value of I radius (1.96 Å) and I$^-$ radius (2.16 Å) + Xe radius (1.98 Å).
solvent atoms. The total Hamiltonian consists of three parts; the Hamiltonians for the system and the solvents (bath), and the interaction between them:

\[ H(x,r) = H_s + H_b + V_{sb}(x,r), \]

(3)

\[ H_s = \frac{p_s^2}{2\mu} + V_s(x), \]

(4a)

\[ H_b = \frac{p_b^2}{2m} + V_b(r), \]

(4b)

where \( V_s(x) \) is the potential energy surface for the diatom, and \( V_b(r) \) arise from the LJ potentials between solvent atoms. The coupling potential \( V_{sb}(x,r) \) represents the interaction of diatom with nearest neighbor solvent atoms.

The hybrid quantum/classical method is based on the time-dependent Hartree (TDH) approximation where the total wavefunction is assumed to be factorized as follows:

\[ \Psi(x,r,t) = \Phi_s(x,t) \Phi_b(r,t), \]

(5)

After such factorization, the dynamics for the system and the bath degrees of freedom can be treated separately. It is noted that the energy transfer between the system and the bath is possible in the TDH scheme. The dynamics of the two subsystems are now governed by the effective Hamiltonians of the form:

\[ \mathcal{H}_s = \frac{p_s^2}{2\mu} + V_s(x) + \left\langle V_{sb}(x,r) \right\rangle_s, \]

(6a)

\[ \mathcal{H}_b = \frac{p_b^2}{2m} + V_b(r) + \left\langle V_{sb}(x,r) \right\rangle_b. \]

(6b)

One can obtain the mean-field coupling potentials in several different ways. In hybrid quantum/classical method, the mean-field potential for the quantum system is determined by the instantaneous configuration of the classical particle comprising the solvent:

\[ \left\langle V_{sb}(x,r) \right\rangle_s = V_{sb}(x,r(t)). \]

(7)

The effective potential for the classical degrees of freedom is formally written using the wavefunction for the quantum part (Ehrenfest theorem):

\[ \left\langle V_{sb}(x,r) \right\rangle_s = \langle \Phi_s(x,t) | V_{sb}(x,r) | \Phi_s(x,t) \rangle. \]

(8)

A more simplified scheme can be used by first calculating the mean position for the quantum particles:

\[ \left\langle V_{sb}(x,r) \right\rangle_s = V_{sb}(x(t),r), \]

with

\[ \langle x(t) \rangle = \langle \Phi_s(x,t) | x | \Phi_s(x,t) \rangle. \]

The motion of the diatom is treated with time-dependent quantum mechanics. The initial wavefunction is assumed to be a Gaussian wavepacket representing the equilibrium position on the ground electronic state. After photoabsorption, the vertical transition places the wavepacket in the excited state and the subsequent evolution of the wavefunction is done using the excited state potential energy surface. The quantum wavepacket is propagated using a split operator method [28,29]. For the classical dynamics of the solvent atoms, the equations of motion are solved by using the velocity Verlet algorithm [30].

2.3. Solvent electric field model

The effects of the solvents on the electronic structure of a dihalide ion can be considered by a simple one-electron picture [9,10,22]. It is expected that the distribution of the excess charge in \( I^+_2 \) is mainly determined by the electrostatic potential difference between the iodine atoms (\( \Delta U \)), reflecting asymmetric electrostatic environment due to solvent atoms. A uniform electric field \( (\vec{E}) \) provides a reasonable model of solvation. The strength of the solvent electric field is determined to reproduce the potential energy difference, \( \varepsilon = \Delta U/R \) where \( R \) is the bond length of the diatom. We are concerned about evaluating potential energy surfaces of the ground and the excited states of \( I^+_2 \) under the influence of the solvent electric field. The solvent electric field can also be defined as the electrostatic field at the center of diatom exerted by the solvent charges. For the solute charge separated by \( R \), the potential energy difference should be given by \( \Delta U = \varepsilon R \). In the one-electron model, the extra electron feels the potential by the diatom core and the solvent electric field. The electronic structure of the system is determined by the Hamiltonian, \( \hat{H} = \hat{H}_0 + e\vec{E} \hat{\lambda} \), where \( \hat{H}_0 \) is the Hamiltonian for the isolated anion and the internuclear axis is along the \( x \) direction.
The calculations of the potential energy surfaces are done in the diabatic picture [8–10,22]. In the two electronic state model, the two adiabatic potential energy surfaces can be thought to be obtained by the following diabatic potential matrix:

\[
U_{\text{ab}} = \begin{pmatrix}
\alpha & -\beta \\
-\beta & \alpha
\end{pmatrix},
\]  

(10)

which is equivalent to writing

\[
E_{\text{gr}}^0 = E_{\text{ex}}^0 = \alpha(x) - \beta(x),
\]

\[
E_{\text{ex}}^0 = E_{\text{gr}}^0 = \alpha(x) + \beta(x),
\]

(11a, 11b)

for the ground and the excited states. The diabatic potential energy matrix elements \(\alpha(x)\) and \(\beta(x)\) can be obtained once the two adiabatic surfaces are known. In the presence of the effective electric field, the diabatic potential becomes

\[
U_{\text{ab}}(\vec{E}) = \begin{pmatrix}
\alpha - \frac{\epsilon \vec{E} \cdot \vec{x}}{2} & -\beta \\
-\beta & \alpha + \frac{\epsilon \vec{E} \cdot \vec{x}}{2}
\end{pmatrix},
\]

(12)

where \(\vec{E}\) is the magnitude of constant electric field. The resulting adiabatic potentials are given by

\[
E_{\pm}(\vec{E}) = \alpha \pm \frac{1}{2} \sqrt{(\epsilon \vec{E} \cdot \vec{x})^2 + 4\beta^2}.
\]

(13)

Note that the above results are independent of the sign of the effective electric field. We take the convention that positive electric field corresponds to the solvent configuration favoring the ground electronic state of the diatom. After photoabsorption the solvent configuration can change so as to solvate the excited state favorably, which is represented by the negative value for the effective field. For this model, the adiabatic potentials for the ground and the excited states in the presence of electric field take the following form:

\[
E_{\text{gr}}(\vec{E}) = E_{\text{gr}}^0 - \left[\text{sign}(\vec{E})\right] \Delta E,
\]

\[
E_{\text{ex}}(\vec{E}) = E_{\text{ex}}^0 + \left[\text{sign}(\vec{E})\right] \Delta E,
\]

(14a, 14b)

where

\[
\Delta E = \frac{1}{2} \sqrt{(\epsilon \vec{E} \cdot \vec{x})^2 + 4\beta^2} - \beta.
\]

(15)

We note that the solvent electric field is a dynamical variable determined by the solvent motions. In the early dynamics after photoexcitation, the solvent configuration can be considered as fixed until the solvent atoms start to respond to change in the charge distribution. The equilibrium bond length of \(1^-\) changes under the influence of electric field. The vibrational frequency of the ground state for \(1^-\) is changed accordingly when constructing initial wavepacket.

3. Results and discussion

First, we compared the EQ and HQC methods for the simplest case where only two solvent atoms are considered. In EQ, two dimensional initial wavepacket is constructed to represent the equilibrium structure of the total system. The spatial grid for interatomic distance for the diatom \((x)\) and that for solvent position \((r)\) in EQ are determined to guarantee converged results. The time step for the propagation of the wavepacket and the classical trajectory is set to 0.5 fs in most cases. We discuss the results for \(1^-\) system. With only two solvent atoms, which are in turn connected to an artificial wall, the model does not reflect any real physical situation. The main purpose of the calculation is to test the reliability of HQC method for the type of model we are considering. We compared the averaged 1–1 distance and the averaged relative position of the solvent atoms as a functions of time from the two calculations. The HQC method is found to give consistent results with those from the EQ treatment, especially for short time dynamics. The motion of the solute, which is treated quantum mechanically in both approaches, is well represented by HQC method for rather long times. This is expected because the primary role of the solvent is to provide a reservoir for the energy transfer from the solute, which can be described by HQC approach based on TDH scheme. As the coupling between the solute and the solvent gets more complex, the error resulting from the classical approximation of the solvent can become larger. The reliability of HQC scheme also depends on the type of quantity one wants to obtain from the calculations. We expect that the HQC method serves well for our purposes in this study.

The photodissociation/recombination dynamics of \(1^-\) in rare gas atoms was studied by Liu and Guo.
using the linear chain model [19–21]. In the present study, we compared the dynamics of $\text{I}_2$ and $\text{I}_2^-$ system in a linear chain of Ar or Xe solvent atoms. The motion of $\text{I}_2$ and the energy transfer show similar behavior as those discussed by Liu and Guo. Main difference is how the initial wavepacket is prepared. Fig. 3 shows the averaged I–I distance of the one-dimensional wavepacket in four cases we are considering. After rather fast (less than 500 fs) recombination by efficient energy transfer through the collisions with the solvent atoms, the $\text{I}_2$ motion shows oscillations in $\text{I}_2(\text{Ar})_{100}$ system. The oscillations are due to the bound potential resulting from the combination of a shallow well in the excited state potential of $\text{I}_2$ and the repulsive wall provided by the solvent. The heavier solvent Xe is found to induce faster recombination and larger amplitude oscillations. In contrast, the $\text{I}_2^-$ system shows different behavior. After being excited to the upper surface, the initial separation of the two I atoms is larger, which is due to the two factors: larger equilibrium bond distance (3.23 Å for $\text{I}_2^-$; 2.67 Å for $\text{I}_2$) and the larger extra energy after photoabsorption (0.558 eV for $\text{I}_2^-$; 0.312 eV for $\text{I}_2$). The iodide system also shows different behavior after recombination. In the lighter Ar solvent chains, the iodide system does not exhibit oscillations. It can be interpreted that the excited potential for $\text{I}_2^-$ is purely repulsive (see Fig. 2) and the large mass difference between Ar and I precludes the so-called ‘solvent-induced’ coherent vibrations for $\text{I}_2^-$. It is interesting to note that such coherent vibrations are observed when using the much heavier solvent Xe, which has comparable mass to I. Since there is no potential well for the gas phase excited state of $\text{I}_2^-$, the oscillations are entirely due to the coherent motions of the solute induced by collective motions of the solvent atoms, as suggested in the experiments. Faster energy transfer from the dissociating fragments to the solvent atoms and the difference between $\text{I}_2$ and $\text{I}_2^-$ system can also be seen in the time dependence of the energies of the diatom.

We studied the effect of solvent polarization on the dynamics of $\text{I}_2^-$ by introducing solvent electric field as described in the previous section. The initial solvent configuration favoring the ground state charge distribution is represented by a positive electric field ($E_0$). First, we assume that the electric field is constant for short times and follow the dynamics of the system under the influence of this field. Fig. 4 shows the time dependence of I–I distance in $\text{I}_2^-(\text{Ar})_{100}$ for various values of the solvent electric field. The presence of the solvent field makes the recombination faster and the resulting I–I distance shorter. It is also noted that the signature of more oscillations with higher frequency after recombination is found in the presence of the field. The charge separation in the excited state is not compatible with the initial solvent polarization after photoabsorption. Therefore the solvent electric field keeps the fragments from dissociating further, thus providing an extra repulsive

Fig. 3. The averaged I–I distance as a function of time for the four cases considered, as given in the picture.

Fig. 4. The time dependence of I–I distance in $\text{I}_2^-(\text{Ar})_{100}$ in the presence of solvent electric field. The positive electric field represents the solvent polarization favoring the ground state configuration.
wall. Eventually, the solvent configuration will change so as to solvate the charge separation in the excited state favorably. Such a situation corresponds to the change in the sign of the solvent field in our model. With negative electric field, the excited state becomes more stable while the ground state energy is raised at large internuclear distances. The resulting potential energy surfaces can have curve crossings. The curve crossing can provide an efficient mechanism for the nonadiabatic transition from the excited to the ground state electronic states.

For longer time dynamics, one needs to model the time-dependence of the solvent configuration. In our linear chain model, we can introduce a time-dependent solvent electric field. As discussed before, the solvent electric field will change from a positive value to a negative value as the solvent adjusts itself to the new charge distribution for the excited state. The time scale of the time-dependent electric field is governed by the response time of the solvent. One may write simple form for the electric field as \( \mathcal{E}(t) = \mathcal{E}_0 f(t; \tau) \), where the value of the function \( f \) varies from +1 at \( t = 0 \) to -1 at \( t = 2\tau \), for example, as \( \tau \) represents the time scale of how fast the solvent responds. Fig. 5 shows the potential energy surfaces of \( I_2^- \) as a function of time using such model for the time-dependent electric field. As the electric field becomes negative, curve crossing between the ground and the excited state occurs. In order to include the effects of such curve crossing in the dynamics of the system, we need to consider possible nonadiabatic transitions. Popular surface hopping methods [31–33] can provide an efficient algorithm which can be incorporated into our model.

The above results from our simple model provide a plausible explanation why the overall relaxation time for the photodissociation/recombination dynamics of the molecular ion is much faster than that of the neutral counterpart. The charge switching and the subsequent charge separation for the dissociating fragments is strongly coupled with the solvent polarization, which results in faster recombination and leads to more efficient transition to the ground state. The final process, which is the relaxation of the vibrationally excited diatom in the ground state, can also be accelerated by the strong coupling with the solvent through electrostatic interaction [8,9]. In other words, the interaction between the extra charge of the molecular ion and the polarizable solvent atoms is responsible for much faster processes in every stage of photodissociation/recombination dynamics.

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References