Structure and dynamics of $I_2^- (N_2O)_n$: Monte Carlo and molecular dynamics simulations

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The structures and relaxation dynamics of $I_2^-$ embedded in clusters of $N_2O$ molecules are studied by Monte Carlo and molecular dynamics simulations. The equilibrium structures of $I_2^- (N_2O)_n$ clusters are obtained as a function of cluster size and the closing of the first solvation shell is found to occur at $n = 13$, consistent with experimental observation. By comparing with the previous studies with different types of solvent molecules, it is found that differences in solvent polarity lead to noticeable changes in equilibrium structures and caging dynamics of clusters. $N_2O$ clusters tend to form more symmetric, spread-out solvent configurations, resulting in a weaker solvent electric field being exerted on the solute. The localization of the charge distribution for large internuclear separations happens for longer bond length and much more rapidly in $I_2^- (N_2O)_{16}$ than in $I_2^- (CO_2)_{16}$ clusters. Molecular dynamics simulations showed that $I_2^-$ vibrational relaxation is very rapid, losing almost 90% of its internal energy within 1 ps of recombination. It is suggested that the change of $I_2^-$ charge distribution provides an efficient mechanism for energy transfer from the anion to the surrounding solvents. The $N_2O$ solvent with permanent dipole moment exhibits a slightly shorter relaxation time than the nonpolar $CO_2$ solvent. The electrostatic interactions are found to be major driving forces for the compression of the solute throughout the relaxation processes. The effects of solvent flexibility on the relaxation dynamics are investigated for $I_2^-$ embedded in clusters of flexible $N_2O$ solvents. It is found that including the flexibility of the $N_2O$ molecules has minimal effect on the vibrational relaxation dynamics of $I_2^- (N_2O)_{16}$ clusters. © 2001 American Institute of Physics.

I. INTRODUCTION

The presence of solvents can profoundly influence the course of a chemical reaction. One of the most widely studied examples is the solvent-induced recombination of photo-dissociated fragments such as the caging dynamics of $I_2$ in various solutions. The sequential procedures of photodissociation, geminate recombination, and vibrational relaxation can usually be understood in terms of the kinematics between solvent and solute. The effects of solvents become much more important when charged species are involved in the reaction. Electrostatic interactions between the solute and polar or polarizable solvents lead to changes in the potential energy surfaces by modifying the solute electronic structure. The detailed reaction dynamics under the influence of such strong solvent-solute interaction has not been fully appreciated.

The study of photochemical or other reactions of molecular species in a cluster can give new insights for important issues of chemical dynamics. The simplest type of photochemical reactions in clusters is the photolysis of a diatomic molecule weakly bound to a chemically inert atom or molecular clusters. Molecular clusters offer a unique environment where the size of the solvent cage can be controlled, allowing one to examine the structural properties and the effects of solvation on reaction dynamics. Reactions in clusters also can provide a better understanding of the relation between gas-phase and condensed matter dynamical processes.

Diatomic anions such as $I_2^-$ or $ICl^-$ have provided typical systems through which one can address the issues concerning the role of electrostatic interactions in solution/cluster reaction dynamics and vibrational relaxation. Early studies include 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 $I_2^- (CO_2)_n$. One of the main observations is a very fast vibrational relaxation rate of the charged solute in polar solvents and clusters compared with the case of neutral molecules ($I_2$) in nonpolar solvents. This is partly attributed to the strong electrostatic forces in these systems.

Several experiments have also been done on $I_2^-$ clustered with different solvents such as $Ar$, $N_2O$, and OCS. These studies allow for a comparison of the effects of isovalent solvents with differing electrostatic properties on the dissociation and recombination dynamics. In these experiments, a near IR ($700$–$800$ nm) laser pulse excites the diatomic anion to the repulsive $A'$ state of $I_2^-$. The branching ratio for dissociation versus recombination is determined from the mass spectra of the ionic fragments. The onset of caging as a function of cluster size was found to be very rapid, reaching 100% by the completion of the first solvation structure, a fact

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which was attributed to the presence of long-range electrostatic interactions. The detailed features in the fraction of recombined photoproducts show subtle differences for different solvent molecules. More recently, Lineberger and co-workers have performed analogous experiments using UV excitation.\textsuperscript{16,17} The initially excited B state in the isolated molecule correlates in the isolated molecule to a spin–orbit excited iodine atom and I\textsuperscript{−} ion. It was found that a relatively small number of solvent molecules were able to cage the highly excited state and induce electronic relaxation. Neuhaus and co-workers have also studied the photodissociation of I\textsubscript{2}(Ar)\textsubscript{n} and I\textsubscript{2}(CO\textsubscript{2})\textsubscript{n} clusters using anion femtosecond photodetachment spectroscopy.\textsuperscript{18–21} These experiments provide insights into the reaction dynamics of the ionic clusters that complement those obtained by the time-resolved absorption recovery experiments.

The simulations of dihalide anion photodissociation dynamics were first performed by Perera and Amar on Br\textsubscript{2}(Ar)\textsubscript{n}, Br\textsubscript{2}(CO\textsubscript{2})\textsubscript{n}, and I\textsubscript{2}(CO\textsubscript{2})\textsubscript{n} clusters.\textsuperscript{22,23} Parson and co-workers have extended these earlier works by incorporating, in a self-consistent manner, a description of the electronic structure that depends on both the solute bond length and the solvent degrees of freedom.\textsuperscript{24–26} The influence of the solvent is treated by a collective solvent coordinate representing the electric field that the solvent exerts on the solute charge distribution. They found very rapid (<3 ps) vibrational relaxation times after recombination from the simulations of I\textsuperscript{2}(CO\textsubscript{2})\textsubscript{16}. The simulations and dynamics of I\textsuperscript{−} embedded in clusters of flexible CO\textsubscript{2} molecules were also studied using molecular dynamics simulations.\textsuperscript{27} The recombination and vibrational relaxation of I\textsuperscript{−} in solution were investigated by Hynes and co-workers.\textsuperscript{28,29} The nonequilibrium free energy surface describing the change in the solute electronic structure during the reaction is obtained from the microscopic valence bond Hamiltonian. It was found that the additional force along the vibrational coordinate due to the shifting charge distribution accelerates the vibrational relaxation rate.

The theoretical studies described above were mainly concerned with ground-state relaxation dynamics. Recently, theoretical models that treat solvent effects in ground and excited states in a self-consistent fashion have been developed.\textsuperscript{30–38} These studies are based on a quantum-classical molecular dynamics method where the nonadiabatic transitions between coupled electronic states (surfaces) are treated by the surface-hopping method. Different methods by which the model Hamiltonian for the solute electronic structure is constructed have been proposed. Coker and co-workers used a semiempirical diatomics-in-ionic-system Hamiltonian as a natural extension of diatomics-in-molecules (DIM) Hamiltonian to ionic systems, while Faeder et al. constructed an effective Hamiltonian by evaluating the solvent-solute interaction in the representation defined by \textit{ab initio} electronic states of the isolated solute. Despite the differences in the model Hamiltonian, the overall trends and main conclusions are in agreement in those studies. The calculated photofragmentation yields of various charged product clusters showed very good agreement with experiments.\textsuperscript{13} In order to explain the peculiar dissociation mechanism by the ejection of an I\textsuperscript{−} ion from the cluster, the concept of “anomalous charge switching” in the excited state has been introduced. The parallel polarizability of I\textsuperscript{−} in this state is negative, resulting in the charge flow toward the less solvated atom. The same nonadiabatic molecular dynamics simulations have successfully reproduced the time-resolved photodetachment spectra and the transient absorption recovery.\textsuperscript{39} More recently, such simulations have made successful predictions for the rapid electronic quenching following UV excitation of large I\textsubscript{2}(CO\textsubscript{2})\textsubscript{n} clusters.\textsuperscript{33,38}

In this paper, we report theoretical studies on the photodissociation and relaxation dynamics of I\textsubscript{2} in N\textsubscript{2}O clusters. Our main purpose is to investigate the effect of solvent polarity on the reaction dynamics of such clusters. In particular, we will compare the structural properties and relaxation dynamics in such clusters with nonpolar (CO\textsubscript{2}) and polar (N\textsubscript{2}O) solvent molecules. In a recent study, Kuchta and Ladanyi compared minimum energy structures and solvation energies for I\textsubscript{2}(CO\textsubscript{2})\textsubscript{16} and I\textsubscript{2}(N\textsubscript{2}O)\textsubscript{16} clusters.\textsuperscript{40} In the present study, we will use a different potential model for the N\textsubscript{2}O molecule and examine the vibration relaxation dynamics in more detail. The effect of the flexibility of N\textsubscript{2}O molecules on the dynamics is also investigated.

The paper is organized as follows. The definition of the theoretical model and a brief description of the simulation methods are given in Sec. II. Equilibrium cluster structures and the energetic properties of clusters are presented in Sec. III. Section IV analyzes the vibrational relaxation process and compares relaxation dynamics in rigid and flexible solvent models. Section V summarizes the conclusions along with some discussion.

II. THEORETICAL MODEL AND SIMULATION TECHNIQUES

A. I\textsubscript{2}(N\textsubscript{2}O)\textsubscript{n} potential model

The potential model adopted in this paper is similar to that used by Papanikolas et al.\textsuperscript{24,26} The potential function consists of three terms:

\[ U_{\text{total}} = U_S + U_{XX} + U_{SX}, \]

where the subscripts “S” and “X” denote the I\textsubscript{2} solute and N\textsubscript{2}O solvent, respectively.

The solvent–solvent intermolecular potential consists of site–site Lennard-Jones (LJ) energy and Coulomb interaction energy. We chose the intermolecular N\textsubscript{2}O–N\textsubscript{2}O interaction model developed by Cardini et al.\textsuperscript{41} In this model, each N\textsubscript{2}O solvent has three point charges placed on the nuclei so as to reproduce a dipole moment of N\textsubscript{2}O. Therefore, the N\textsubscript{2}O–N\textsubscript{2}O pair interaction potential (\(u_{XX}\)) is given by:

\[ u_{XX} = \sum_{i=1}^{3} \sum_{j=1}^{3} u_{13}(r_{ij}) + \sum_{k=1}^{3} \sum_{l=1}^{3} \frac{1}{4\pi\varepsilon_o} \frac{q_k q_l}{r_{kl}}, \]

where \(u_{13}\) has a Lennard-Jones (6-12) form.

The ion-solvent interaction potential (\(U_{SX}\)) is similar in form to the solvent–solvent interaction potential. The I\textsuperscript{−} repulsive core and charge distribution are represented by two
LJ sites with two partial charges \((q_A\) and \(q_B\)) placed at the center of each I atom. Thus the ion-solvent potential energy \((U_{\text{ion}})\) is expressed as

\[
U_{\text{ion}} = \sum_{\text{LJ}} \left[ U_{\text{LJ}}(r_{ij}) + u_{\text{LJ}}(r_{ij}) \right] + \sum_{j=1}^{3N} \frac{1}{4\pi\varepsilon_0} \left[ \frac{q_j q_A}{r_{ij}} + \frac{q_j q_B}{r_{ij}} \right],
\]

where \(r_{ij}\), for example, represents the distance between the \(j\)th N\(_2\)O partial charge (also the LJ site) and the iodine atom \(A\). The values used for the LJ parameters, and the magnitudes of the N\(_2\)O partial charges are given in Table I.

The I\(_2\) charge distribution and intramolecular potential are both determined by the electronic Hamiltonian. The electronic structure of the solute is linked to the solvent environment of the cluster through the uniform electric field exerted on the I\(_2\) by the solvent at the I\(_2\) center of mass.\(^{25,26,42,43}\) The charge of the I\(_2\) solute is not fixed but determined by this solvent electric field and the iodine internuclear separation. The magnitude of the charge separation is calculated by the relation:

\[
\delta q(R_{AB}, \mathbf{E}_{AB}) = \tanh[\eta R_{AB}^\rho \mathbf{E}_{AB}],
\]

where the parameters \(\eta\) and \(\rho\) are the same as those used in the previous work by Papanikolas and co-workers.\(^{24,26}\) The solvent electric field is determined by \(\mathbf{E}_{AB} = F_{\text{CM}}(\mathbf{R}_{AB}/R_{AB})\) with \(R_{AB} = r_A - r_B\). The partial charges of the I\(_2\) solute, \(q_A\) and \(q_B\), are given by

\[
q_A = -\frac{e}{2} (1 - \delta q); \quad q_B = -\frac{e}{2} (1 + \delta q).
\]

The I\(_2\) intramolecular potential energy consists of the potential for the isolated I\(_2\) ion and the self-energy term, which represents the amount of work required to polarize the I\(_2\) charge distribution. The gas phase potential for I\(_2\) is taken to be the semiempirical Chen–Wentworth potential,\(^{44}\) which has a Morse functional form for the ground state. The self-energy calculated from the effective one-electron Hamiltonian was fitted to an analytical function of the solvent electric field and the internuclear separation. The functional form of the self-energy term is the same as that used by Papanikolas.\(^{24}\)

### B. Simulation methods

Monte Carlo simulations using the Metropolis algorithm in the canonical ensemble are used to search for the I\(_2\) (N\(_2\)O)\(_n\) minimum energy structures. The MC runs were performed with the distance between iodine atoms kept constant within each run. The lowest energy structures of the clusters are determined using the procedure based on the simulated annealing technique.\(^{27}\) It required a number of heating/cooling MC cycles. In each cycle, the MC run is initiated by heating the initial configuration to a temperature above its melting point, typically 130–180 K in the present system. After 25 000 iterations are performed, the cluster is cooled down to 5 K and another 25 000 iterations were carried out to search for the lowest energy structures. If the
energy of the lowest structure found during the cooling cycle is less than that of the initial structure, the lowest energy structure is saved and used as input for the next cycle. In searching for the global minimum energy structures, we repeated these cycles 20–40 times.

In molecular dynamics simulations, the equations of motion were integrated using the leap-frog algorithm with a time step of 0.2 fs. The solvent N$_2$O molecules were forced to remain rigid by implementing the SHAKE algorithm. The vibrational relaxation dynamics of I$_2$(N$_2$O)$_n$ clusters are investigated through the molecular dynamics trajectories which are divided into several stages.\textsuperscript{26} Starting from the minimum energy cluster structures at an I$_2$ equilibrium bond length of 6.1 a.u., MD simulations are performed for 1.0–1.6 ps on the I$_2$ ground electronic state. The I$_2$ solute is then promoted from the ground state to the dissociative $A'$($^2\Pi_{g,1/2}$) excited state. After photoexcitation of the I$_2$ solute, MD trajectories are followed on the repulsive I$_2$ excited state potential. At very large internuclear separation, the isolated ion ground and excited potentials are essentially equal. If the bond length of I$_2$ becomes 12 a.u., I$_2$ is instantaneously switched back to the ground state. After the solute recombines on the ground state surface, subsequent relaxation dynamics is monitored by MD simulations. The relaxation dynamics is assumed to start from the moment when the bond length of I$_2$ has decreased to 11 a.u. It is noted that the electronic transitions from the excited to the ground state involved in the recombination dynamics are treated in a rather ad hoc fashion. The main focus of the present study is to examine the vibrational relaxation after the recombination for I$_2$(N$_2$O)$_n$ clusters.

### III. STRUCTURE AND ENERGETICS

The lowest energy structures for I$_2$(N$_2$O)$_n$ clusters as a function of cluster size are shown in Fig. 1. In these structures, the bond length of iodine is constrained to the equilibrium value of 6.1 a.u. The N$_2$O molecules in clusters with $n = 3$ spread out around the waist of I$_2$ molecules. This structure is similar to that of I$_2$(CO$_2$)$_n$ clusters with ion-induced dipole interaction incorporated into the potential in CO$_2$ solvents.\textsuperscript{26} As N$_2$O molecules are added to the cluster, the solvent cage changes from a structure where both iodine atoms are equally solvated ($n \leq 6$), to a structure in which one side of the solute is preferentially solvated over the other. The asymmetry of the solvent configuration is most pronounced for the cluster with $n = 9$. As the cluster size is increased further, the solvent structure shifts again to a symmetric configuration until the formation of the first solvation shell. Experimentally, 100% caging was found to occur at $n = 13$ for I$_2$(N$_2$O)$_n$ clusters (Fig. 2). Figure 3 shows the minimum energy structures for $n = 12–14$ as viewed along the axes parallel to the I$_2$ bond. As we add one more N$_2$O molecule to the cluster with $n = 12$, it occupies the site at the less-solvated side of the solvent configuration, closing the

![FIG. 1. Minimum energy structures obtained from the MC simulations for I$_2$(N$_2$O)$_n$ clusters as a function of cluster size.](image1)

![FIG. 2. Probabilities of I$_2$ recombination (caging), plotted as functions of the parent cluster size, in the I$_2$(Ar)$_n$, I$_2$(CO$_2$)$_n$, I$_2$(N$_2$O)$_n$, and I$_2$(OCS)$_n$ clusters following 790 nm photoexcitation. (Reproduced from the experimental results given in Refs. 12–16.)](image2)

![FIG. 3. Minimum energy structures of the I$_2$(N$_2$O)$_n$ clusters with $n = 12$, 13, and 14 as viewed along the axes parallel to the I$_2$ bond.](image3)
last collision-free escape route for dissociation fragments. This finding is consistent with the experimental observation.

Differences in solvent polarity can lead to noticeable albeit subtle changes in equilibrium structures and caging dynamics of clusters. Figure 2 shows the experimentally determined caging fraction for I₂(X)ₙ clusters with four different types of solvent molecules. The equilibrium structures of I₂(CO₂)ₙ, I₂(OCS)ₙ, and I₂(Ar)ₙ clusters as a function of cluster size have been determined theoretically. It is noted that the four solvents have different electrostatic properties: CO₂ is nonpolar with large quadrupole moment (4.30 D Å); N₂O has a relatively small dipole moment (0.17 D) with a large quadrupole moment (4.43 D Å); OCS has a large dipole moment (0.72 D) but a small quadrupole moment (0.79 D Å); and the atomic solvent Ar has neither a dipole nor a quadrupole moment. The detailed cluster structures showed interesting differences for these solvent molecules. For I₂(N₂O)₅ clusters, three of five solvent molecules spread around the waist of I₂ and the remaining two were located near the I atoms on each side. In contrast, CO₂ molecules tend to pack together on one side of I₂ core for small clusters of I₂(CO₂)ₙ, while OCS molecules in I₂(OCS)₃ form a ring structure about the waist of I₂ with the sulfur atoms closer to the solute (see Figs. 3 and 4 of Ref. 16).

The electric field exerted by the solvent along the I₂ internuclear axis (E_{AB}) represents the degree of asymmetry in the solvent environment. The solvent electric field generated in the minimum energy structures of I₂(N₂O)ₙ as a function of cluster size is shown in Fig. 4. The magnitude of the electric field increases with cluster size, reaches a maximum value of 0.0044 a.u. at n = 9, and then gradually decreases to essentially zero at n = 16. The solvent field of I₂(N₂O)ₙ is smaller than that of I₂(CO₂)ₙ for the cluster sizes 9 ≤ n ≤ 15 (Fig. 4). This result shows that I₂(N₂O)ₙ has much more symmetric structure than I₂(CO₂)ₙ for larger sizes of clusters. The very small values of the solvent fields for the cluster sizes of n = 12–14 are consistent with the fact the first solvation shell of I₂(N₂O)ₙ is almost closed for n ≈ 13 as discussed above.

The solvation energy of the lowest energy structures is defined as

\[ U_{\text{solvation}} = U_{\text{SX}} + U_{XX} + \Delta E_{\text{self}}. \]  

(3.1)

For a cluster size with n ≥ 9, the total solvation energy per N₂O is approximately 180 meV, which is somewhat smaller than the corresponding value (~200 meV) for CO₂ clusters. The solvation energy can be decomposed into five different terms and the overall trends in solvation energies are similar to those in I₂(CO₂)ₙ clusters. The electrostatic interaction term between I₂ and N₂O provides the largest contribution to the total solvation energy. For small clusters (n ≤ 5), the Coulomb interaction energy between I₂ and solvent molecules has a value more negative than the energy for clusters with CO₂ solvents. This difference can be attributed to the interaction between the N₂O dipole and the solute charge distribution. As more solvent molecules are added, the electrostatic solute-N₂O interaction becomes less effective for large clusters.

We examined a potential energy surface for I₂(N₂O)₁₆ clusters by determining the minimum energy structures at different bond lengths using MC simulations. Figure 5 shows the charge shift in the solute as a function of bond length for I₂(N₂O)₁₆ clusters. As the bond length increases, the charge distribution shifts from delocalized to the localized form. The shift in the charge distribution is closely related to the changes in the solvent configurations. The minimum energy structures showed that the solvent cage equally solvates both iodine atoms with the charge separation being nearly zero for I₂ bond lengths less than 7.0 a.u. As the bond length increases, the solvent molecules start solvating the I⁻ side of the solute exclusively. The localization of the charge distribution in the I₂(N₂O)₁₆ cluster happens for a longer bond length and much more rapidly than in the I₂(CO₂)₁₆ cluster (Fig. 5).
IV. CAGING AND RELAXATION DYNAMICS

A. Vibrational relaxation in rigid N2O clusters

We have investigated vibrational relaxation dynamics of $I_2(N_2O)_{16}$ clusters by using the MD simulation methods described in Sec. II. The excited state dynamics are mainly used to generate the cluster configurations that will undergo relaxation dynamics following the recombination onto the ground state. As mentioned above, the nonadiabatic electronic transitions involved in the recombination are not treated explicitly and the main focus of the present study is on the vibrational relaxation on the adiabatic ground state surface. We have examined the trajectories that have undergone recombination back to the ground electronic states. An ensemble of 100 such configurations has been generated by the procedure described in Sec. II. We assume (somewhat arbitrarily) that relaxation dynamics start at the moment when the separation of $I_2$ reaches 11 a.u. Each initial structure for vibrational relaxation is characterized by a molecular dynamics temperature, prior to photoexcitation, of approximately 40 K. In the previous study, the configuration of $I_2(CO_2)_{16}$ after the completion of vibrational relaxation was found to show substantial disintegration of the solvent cage. In contrast, the solvent configuration of $I_2(N_2O)_{16}$ is found to maintain well-defined structures after the relaxation.

The primary quantity of interest is the average $I_2$ internal energy $\langle E_{AB}(t) \rangle_{av}$ after recombination, which is given by the expression:

$$\langle E_{AB}(t) \rangle_{av} = \langle U_{AB}(t) \rangle_{av} + \langle KE_{AB}(t) \rangle_{av},$$

(4.1)

where $U_{AB}$ is the $I_2$ total potential energy, which is the sum of the potential for the isolated $I_2$ ion and the self-energy term, and $KE_{AB}$ is its kinetic energy. $\langle \ldots \rangle_{av}$ indicates an ensemble average over trajectories. The change in the $I_2$ internal energy is described by the normalized response function:

$$C(t) = \frac{\langle E_{AB}(t) \rangle_{av} - \langle E_{AB}(\infty) \rangle_{av}}{\langle E_{AB}(0) \rangle_{av} - \langle E_{AB}(\infty) \rangle_{av}},$$

(4.2)

where $E_{AB}(\infty)$ represents the limiting value of the $I_2$ internal energy when equilibrium has been reached with respect to the $I_2$ vibrational energy. We obtain $\langle E_{AB}(\infty) \rangle_{av}$, which differs from the well depth of the ground state potential energy of $I_2$ molecule because of solute kinetic and self-energy, from the fit to an exponential curve of the form, $\langle E_{AB}(\infty) \rangle_{av} + B \exp(-t/\tau)$, in the time interval 1.2 ps $< t < 7.0$ ps.

The behavior of the anion charge separation, $\langle \delta q(t) / \delta q(0) \rangle_{av}$, is found to be similar to the decay of the normalized response function. The results showed that $I_2$ vibrational relaxation is very rapid, as was observed in earlier studies. In this simulation, $I_2$ loses almost 90% of its internal energy within 1 ps of recombination. This fast relaxation can be attributed to the long-range electrostatic interaction between the solute and the solvent. Since the decay of the internal energy cannot be fitted with a simple exponential, we define the relaxation time as $\tau = \int_0^t C(t) dt$. The N2O solvent with permanent dipole moment has a shorter relaxation time ($\tau = 0.78$ ps) than the nonpolar CO2 solvent ($\tau = 1.05$ ps).

We also calculated the forces exerted by the solvent on the $I_2$ bond,

$$\langle F_{AB}(t) \rangle_{av} = \langle (F_A(t) - F_B(t)) \cdot \hat{r}_{AB} \rangle_{av},$$

(4.3)

where $F_A, F_B$ are the forces exerted on $I_A$ and $I_B$, respectively; $\hat{r}_{AB} = (r_A - r_B)/R_{AB}$ is the unit vector directed along the $I_2$ bond. If the solvent molecules push two iodine atoms apart, then the value of the force is defined as positive; if, on the other hand, the solvent molecules compress two iodine atoms, then $\langle F_{AB}(t) \rangle$ is negative. As the solute bond length is decreased from 11 a.u. to 6 a.u. along the minimum energy path, the long-range electrostatic energy of $I_2$ and N2O is found to increase to $\approx 280$ meV. This increase in electrostatic energy reflects the fact that a large internuclear separation is favored for the localized charge distribution with asymmetric solvent configurations. The initial peak point of the solute-solvent electrostatic force corresponds to the moment of transition from a localized anion charge distribution to a delocalized one. The efficiency of the electrostatic force in removing energy from the solute can be illustrated by the instantaneous relaxation rate. Figure 6 shows the instantaneous kinetic energy change, $d\langle KE_{AB}(t) \rangle_{av}/dt$, and the electrostatic force exerted by the solvent on the $I_2$ bond for comparison. The figure shows that the peak of $d\langle KE_{AB}(t) \rangle_{av}/dt$ coincides with that of the solute-solvent electrostatic force. It can be concluded that the change of anion charge distribution provides an efficient mechanism for energy transfer from the anion to the surrounding solvent molecules. The Lennard-Jones force was also found to increase initially in the relaxation dynamics. This can be attributed to the N2O solvent configurations after recombination where several N2O solvents intervene between two iodine atoms and exert a force against the recombination of the solute. The time scale for the LJ force to change from expansion to compression is longer than that for the electrostatic force, which reflects the slow response time of the nuclear motions of N2O solvents. In the $I_2(CO_2)_{16}$ clusters, the ion-quadrupole interaction does not contribute significantly to the compression of the
This means that LJ interactions are dominant in the later stages of relaxation dynamics. On the contrary, the electrostatic interactions in the \( \text{I}_2(\text{N}_2\text{O})_{16} \) clusters, which include contributions from both the permanent dipole and the quadrupole of \( \text{N}_2\text{O} \), provide a major driving force for the compression of the solute throughout the relaxation processes.

In Fig. 7, we present the change of \( \text{I}_2 \) bond length and solvent field during the \( \text{I}_2 \) vibrational relaxation. After recombination, the iodine bond length decreases rapidly, reaching a value of about 8 a.u. after only 0.5 ps, which coincides with the peak time of electrostatic force. On the other hand, the solvent field changes by only 20% of its initial value during this time. The results suggest that solvent configurations change slowly compared with the solute configuration. The finite response time of the solvent molecules can be clearly illustrated by the relaxation paths of \( \text{I}_2(\text{N}_2\text{O})_{16} \) along the \( \text{I}_2 \) bond length and the solvent field. We have chosen 40 representative trajectories in the time interval \( 0 < t < 2.0 \) ps. The relaxation paths of the trajectories are compared with the minimum energy path (MEP) obtained from the MC simulations. The trajectories were found to roughly follow the MEP until the internuclear separation reaches 8.0 a.u., at which point the anion charge of the \( \text{I}_2 \) becomes delocalized. After the delocalization of the excess electron, the deviations of the trajectories from the MEP become more noticeable. The path to the equilibrium bond length initially involves a rapid change in the internuclear separation. After the equilibrium bond length is reached, further equilibration occurs mainly through oscillations about the internuclear separation with a gradual decrease in the solvent field.

B. Relaxation dynamics in flexible \( \text{N}_2\text{O} \) clusters

The effects of solvent flexibility on the relaxation dynamics have been investigated by MD simulations of \( \text{I}_2 \) embedded in clusters of flexible \( \text{N}_2\text{O} \) solvents. The potential model is extended by taking account of the low-frequency bending vibrations of the solvent molecules. In \( \text{N}_2\text{O} \), the ONN bond angle \( \phi \) is described by the harmonic potential

\[
u_{\text{bend}} = \frac{1}{2} k_b (\phi - \pi)^2.
\]

The stretching force constants in the N–N bond \( (k_1) \) and the N–O bond \( (k_2) \), which are described by harmonic potentials, are also incorporated to represent real solvents. It is noted that the stretching frequencies of \( \text{N}_2\text{O} \) are even higher than the bending frequency. The values of force constants are given in Table I.

Figure 8 shows the \( \text{I}_2 \) internal energy and its normalized response function as a function of time after recombination. In flexible solvents, \( \langle E_{\text{AB}}(t) \rangle_{\text{av}} \) begins at a slightly higher value and relaxes a little faster up to \( t = 0.75 \) ps, compared with rigid solvents. The relaxation time, \( \tau \), obtained from \( C(t) \) and the asymptotic value of the internal energy, \( \langle E_{\text{AB}}(\infty) \rangle_{\text{av}} \), for two solvent models are given in Table II. The results show that the relaxation rate is approximately the same in the two solvent models. In contrast, the difference in the relaxation time between the rigid and the flexible solvent models is about 0.1 ps for \( \text{CO}_2 \) clusters.

\[
\begin{array}{cccc}
\text{Solvent model} & \langle E_{\text{AB}}(\infty) \rangle_{\text{av}} & \tau (\text{ps}) \\
\text{N}_2\text{O rigid} & -1.0754 & 0.78 \\
\text{N}_2\text{O flexible} & -1.0649 & 0.76 \\
\text{CO}_2 \text{ rigid} & -1.0571 & 1.05 \\
\text{CO}_2 \text{ flexible} & -1.0598 & 0.94 \\
\end{array}
\]

\( ^{a}\text{Reference 27.} \)
structures of $I_2^-(N_2O)_n$ clusters as a function of cluster size are obtained by the simulated-annealing MC method. As $N_2O$ molecules are added to the cluster, the solvent cage changes from a structure where both iodine atoms are equally solvated ($n\leq6$), to a structure in which one side of the solute is preferentially solvated over the other. As the cluster size is increased further, the solvent structure shifts again to a symmetric configuration. The closing of the first solvation shell is found to occur at $n=13$ for $I_2^-(N_2O)_n$ clusters, which is consistent with experimental observation.

By comparing with the previous studies with different types of solvent molecules, it is found that differences in solvent polarity lead to noticeable changes in equilibrium structures and the caging dynamics of clusters. The packing of CO$_2$ molecules tends to increase the number of pairwise interactions within the solvent shell because of the strong solvent–solvent interactions arising from the large quadrupole moment. On the other hand, the strong interactions between solute charge and solvent dipoles in $I_2^-(OCs)_n$ clusters result in the formation of ring structures. With a comparable quadrupole moment, the strength of the solvent–solvent interaction in $N_2O$ clusters is similar to that of CO$_2$ solvent. The presence of a small dipole moment makes $I_2^- (N_2O)_n$ clusters adopt spread-out configurations where the $N_2O$ molecules arrange themselves for favorable dipole–dipole interactions. The solvent electric field of $I_2^- (N_2O)_n$ is found to be smaller than that of $I_2^- (CO_2)_n$, indicating that $I_2^- (N_2O)_n$ has much more symmetric structure than $I_2^- (CO_2)_n$ for larger sizes of clusters. $N_2O$ molecules can form a first solvation shell with fewer molecules than CO$_2$ molecules. The polar $N_2O$ molecules have stronger interaction with solute and induce caging more efficiently than nonpolar CO$_2$ molecules.

In $I_2^- (N_2O)_n$, as the $I_2^-$ bond length increases, the anion charge shifts from a delocalized to a localized form. The localization of the charge distribution in the $I_2^- (N_2O)_6$ cluster happens for a longer bond length and much more rapidly than in the $I_2^- (CO_2)_6$ cluster. This “slower but steeper” charge shift can be attributed to the presence of a dipole moment of $N_2O$. As discussed above, $N_2O$ clusters tend to form more symmetric, spread-out solvent configurations, resulting in a weaker electric field being exerted on the solute. Therefore, the onset of the charge shift occurs for the longer bond length. Once the localization of charge is started, the interaction between the solute charge and the $N_2O$ dipole facilitates the charge shift.

We have investigated the vibrational relaxation dynamics of $I_2^- (N_2O)_n$ using the MD simulation methods. The ability of the solute to reach a rather large internuclear separation ($\geq10$ a.u.) demonstrates the elasticity of the solvent cage. The time period to reach $R=12$ a.u. after the photoexcitation is somewhat longer for the $N_2O$ solvents than for the $CO_2$ solvents. This result suggests that the strong interaction between the solute and the dipoles of $N_2O$ solvents is more efficient in retarding the dissociation of $I_2^-$. It is found that the $I_2^-$ vibrational relaxation is very rapid, losing almost 90% of its internal energy within 1 ps of recombination. This fast relaxation can be attributed to the long-range electrostatic interaction between the solute and the solvent. It is suggested that the change in the anion charge distribution provides an

The solvent dependence of $\langle\Delta E_{\text{sol}}(t)\rangle_{av}$ and $\langle KE_{AB}(t)\rangle_{av}$ along the time evolution is compared. Both $\langle\Delta E_{\text{sol}}(t)\rangle_{av}$ and $\langle KE_{AB}(t)\rangle_{av}$ increase to a maximum value within 1 ps and then decay to equilibrium as the $I_2^-$ undergoes vibrational relaxation. The heights of the maximum peaks in the two energies exhibit opposite trends: the peak in $\langle\Delta E_{\text{sol}}(t)\rangle_{av}$ is slightly higher for the rigid solvents, while the peak in $\langle KE_{AB}(t)\rangle_{av}$ is higher for the flexible solvents. The self-energy equilibrates to roughly the same value, almost zero, for the two solvent models, while the kinetic energy has a finite asymptotic value, somewhat larger for flexible solvents. Figure 9 displays the ensemble averages of the electrostatic and LJ forces, $\langle F_{AB}(t)\rangle_{av}$, exerted by the solvent on the $I_2^-$ bond along $R_{AB}$. The overall behavior of the electrostatic part of $\langle F_{AB}(t)\rangle_{av}$ is similar in the two solvent models except in that the maximum value of the force occurs slightly faster for the flexible $N_2O$ solvent. The Lennard-Jones part of $\langle F_{AB}(t)\rangle_{av}$ shows some noticeable differences in the two solvent models. The changes in the LJ force can be related to the fact that the flexible solvent molecules have additional degrees of freedom for energy transfer, although the contributions from these high frequency modes can be quite small.

V. CONCLUDING REMARKS

We have studied structures and dynamics of $I_2^-(N_2O)_n$ clusters by using MC and MD simulations. The equilibrium
efficient mechanism for energy transfer from the anion to the
surrounding solvent molecules. The N$_2$O solvent with
permanent dipole moment has a slightly shorter relaxation time
than the CO$_2$ solvent.

The effects of solvent flexibility on the relaxation dy-
namics have been investigated for I$_2$ embedded in clusters of
flexible N$_2$O solvents. It is found that including the flexibility
of the N$_2$O molecules has minimal effect on the vibrational
relaxation dynamics of the I$_2$(N$_2$O)$_{16}$ clusters. The energy
transfer from the solute into solvent vibrational modes oc-
curs mainly through solute-solvent electrostatic interactions.
Since the permanent dipole moment of N$_2$O does not change
appreciably due to the high frequency bending mode, the
solute-solvent electrostatic interactions are not affected much
by including the flexibility of N$_2$O. Therefore, the vibrational
relaxation dynamics should be similar in the two solvent
models. Theses results are in contrast with those for CO$_2$
Solvents. It was shown that the electrostatic force shows ap-
preciable dependence on the flexibility of the solvent for
I$_2$(CO$_2$)$_{16}$~$^\ddagger$~$^\ddagger$. The nonpolar CO$_2$ molecules can be vibration-
ally “polarized” by the bending motions. As a conse-
quence, the vibrational dynamics in the flexible solvent can
show a different behavior than in rigid solvent for I$_2$(CO$_2$)$_{16}$

In the present study, we have been concerned mainly
with the dynamics on a single electronic potential energy
surface. The nonadiabatic transitions between several elec-
tronic states involved in the recombination dynamics are not
considered rigorously. A complete description of the cluster
dynamics needs to treat solvent effects in ground and excited
states in a self-consistent fashion. It was shown that the
charge switching and the subsequent charge separation for the
dissociating fragments are strongly coupled with the fluctu-
tating solvent polarization for photodissociation dynamics of
diatomic anions.~$^\ddagger$~$^\ddagger$ The structural differences between
clusters with N$_2$O and CO$_2$ can play significant role in the
nonadiabatic transitions for I$_2$(CO$_2$)$_{16}$.~$^\ddagger$~$^\ddagger$

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