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Interactions of triiodide cluster ion with solvents

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Abstract. An equilibrium molecular dynamics model is developed to investigate the interactions of triiodide cluster ion with solvents. The internal dynamics of the triiodide ion is described by a valence bond model which responds to the field of the classical solvent molecules. The solvent molecules were described by standard classical models with rigid molecules, fixed partial charges on atomic sites and site-site Lennard-Jones interactions. One finds the solvent effects on the I_3^- are unusually strong as it is a very polarizable species. Protic solvents such as water, ethanol, and methanol that can form hydrogen bonds to lead to the I_3^- geometry with two unequal bonds and an asymmetric distribution of charges. But for the solvents such as xenon, tetrahydrofuran, methyltetrahydrofuran, and acetonitrile, the I_3^- only illustrates a geometry with two equal bonds. We find that structure changing is induced by local electrostatic attraction between solvent molecules.

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1 Introduction

The excitation, dissociation and recombination of the I_3^- has been extensively studied using femtosecond laser spectroscopy. Such studies also give information about the ground state of the cluster I_3^-. It is now known that, in the ground, the triiodide ion is linear and symmetric with two equal bond lengths and no dipole moment state in the gas phase [1–3]. It has three distinct normal modes which are determined by symmetry to be the symmetric stretch, the antisymmetric stretch and the bend; the last of these is doubly degenerate. What happens if we put the I_3^- in solvent? The experiments suggested that the bonds of this ion are unequal in alcohols, but equal in acetonitrile [1]. Thus the triiodide ion shows solvent-induced structure changing resulted from the I_3^--solvent interactions. Some earlier works [4–7] have demonstrated symmetry breaking of I_3^- in aqueous solution using atomistic simulation. The present report will address the interactions resulting in the structure changes of the I_3^- cluster.

We perform extensive atomistic molecular dynamics calculations of a model of triiodide in a range of solvents such as xenon, tetrahydrofuran (THF), methyltetrahydrofuran (MTHF), acetonitrile (MeCN), methanol (EtOH), ethanol (MeOH) and water. One finds the solvent effects on the I_3^- are unusually strong as it is a very polarizable species. Protic solvents such as water, EtOH, and MeOH that can form hydrogen bonds to lead to the I_3^- geometry with two unequal bonds and an asymmetric distribution of charges. While for the solvents such as xenon, THF, MTHF, and MeCN, the I_3^- only illustrates a geometry with two equal bonds. It is found that structure changing is induced by local electrostatic attraction between solvent molecules.

2 Method

The Hamiltonian of solute I_3^- in solvent can then be represented as following,

$$\begin{aligned}
\hat{H} &= \hat{H}_{solute} + \hat{H}_{solvent} + \hat{H}_{coupling}, \\
\hat{H}_{solute} &= \hat{H}_{spec} + \hat{H}_{solute(pol)}, \\
\hat{H}_{solvent} &= \hat{H}_{LJ} + \hat{H}_{ES(q-q)}, \\
\hat{H}_{coupling} &= +\hat{H}_{solute-solvent(LJ)} \\
&\quad +\hat{H}_{solute-solvent(ES(q-q+q-\mu))}, \qquad (1)
\end{aligned}$$

where $\hat{H}$, $\hat{H}_{solute}$, $\hat{H}_{solvent}$, and $\hat{H}_{coupling}$ are the Hamiltonian of the system, the solute, the solvent, and their coupling, respectively.

The $\hat{H}_{solute}$ of the ion is described using the diatomics in molecules method with additional terms due to the fact that the species is charged [8], the same as used in our previous work [5,9–12]. Provided the ion is constrained to be

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Table 1. Potential parameters of Xe.

atom	q_i/e	ϵ_{ij}/kJ mol^{-1}	σ_{ij}/Å
Xe		1.90402	4.055
I	varies	0.4184	5.167

linear, its ground state is described by a 3×3 Hamiltonian matrix, whose matrix elements depend on the instantaneous values of the bond lengths and the external potential due to the solvent. Allowing I_3^- to bend in this diatomics in molecules method requires a considerable expansion of the basis set. The influence of bending vibrations are thus ignored since including them significantly increase the computation cost. The most important is, the recent experiments [1–3] support the I_3^- is linear in solvents. Thus one can suppose the electronic properties of this cluster ion which influence the response of the surrounding molecules of solvent vary little with bending and that the linear structure offers a typical representation of this polarization response.

There are three types of contributions to the matrix elements. The first type $\hat{H}_{spec}$ are diatomic contributions which are obtained from spectroscopic data on I_2 and I_2^-. These depend only on the bond lengths and are independent of the solvent configuration. The second type of term $\hat{H}_{solute-solvent(LJ)} + \hat{H}_{solute-solvent(ES)}$ depends on the instantaneous value of the electrostatic potential and the Lennard-Jones potential at each site, and depends on both the bond lengths and the solvent configuration. The third type of term $\hat{H}_{solute(pol)}$ is polarization term which is calculated self consistently from the instantaneous electric field at each site. Actually, as indicated before, the polarization of I_2 is not only affected by the I^-, but also by the external electrostatic fields from solvent molecules. These terms also depend on the instantaneous values of the triodide bond lengths and the solvent configuration. The $\hat{H}_{solvent}$ of the solvent molecules are modelled by classical models of a standard type with partial charges on atomic sites and Lennard-Jones interactions $\hat{H}_{LJ} + \hat{H}_{ES(q-q)}$, and also the partial charges on atomic site with dipole of triiodide interactions of $\hat{H}_{solute-solvent(q-\mu)}$.

The solvent considered were xenon, THF, MTHF, MeCN, MeOH, EtOH, and water. All these were modelled using the parameters have used in literatures [13,14]. A OPLS type of model for MTHF was constructed for this work by taking the Lennard-Jones parameters from Jorgenson [15,16] and calculating the geometry and partial charges using Gaussian 98 ([17]) with a 6-31G(d,p) basis set. The partial charges were calculated using the CHELP protocol which fits charges to the electrostatic filed surrounding the molecule. The Lennard-Jones potential between the iodine and oxygen sites was the same as used in our previous work with water and ethanol [4,10]. The Lennard-Jones parameters and the partial charges for sites of Xe and water are given in Tables 1 and 2. The structure of water is shown in Table 3. These for solvents of THF, MTHF, MeCN, MeOH, and EtOH will be published elsewhere.

Table 2. Potential parameters of H_2O.

atom	q_i/e	ϵ_{ii}/kJ mol^{-1}	σ_{ii}/Å
H	0.4238	0	0
O	–0.8476	0.6502	3.169
I	varies	0.4184	5.167

Table 3. Bonds and angles of H_2O (bent).

bond	length/Å	angle/deg
H-O	1	
H-O-H		109.47

Quantum mechanical forces on both iodine and solvent sites were calculated using the Hellman-Feynman theorem

$$\mathbf{F}_i = -\sum_{\alpha\beta} c_{0\alpha} c_{0\beta} \frac{\partial H_{\alpha\beta}}{\partial \mathbf{r}_i}, \tag{2}$$

while the forces arising from the three classical terms in equation (1) were calculated in the usual way within the molecular dynamics program. The forces to solute and solvent molecules can be easily given as following,

$$\begin{aligned} \mathbf{F}_{solute} &= \mathbf{F}_{spec} + \mathbf{F}_{solute(pol)} + \mathbf{F}_{solvent(pol)} \\ &+\mathbf{F}_{solute-solvent(LJ)} \\ &+\mathbf{F}_{solute-solvent(q_I-q_i)} \\ &+\mathbf{F}_{solute-solvent(\mu_I-q_i)}, \end{aligned} \tag{3}$$

$$\begin{aligned} \mathbf{F}_{solvent} &= \mathbf{F}_{solvents(ES)} + \mathbf{F}_{solvents(LJ)} \\ &+\mathbf{F}_{solvent-solute(LJ)} \\ &+\mathbf{F}_{solvent-solute(q_i-q_I)} \\ &+\mathbf{F}_{solvets-solute(q_i-\mu_I)}. \end{aligned} \tag{4}$$

One may make split the force to the ith solute atom as following,

$$\begin{aligned} \mathbf{f}_i &= \mathbf{f}_i^{intra} + \mathbf{f}_i^{inter} \\ \mathbf{f}_i^{intra} &= \mathbf{f}_i^{spec} + \mathbf{f}_i^{pol} + \mathbf{f}_i^{constr} \\ \mathbf{f}_i^{inter} &= \mathbf{f}_i^{LJ} + \mathbf{f}_i^{ES} + \mathbf{f}_i^{\mu-q} \end{aligned} \tag{5}$$

and one can also project the force to the normal modes of the cluster I_3^-.

Molecular dynamics simulations were carried out using a version of the dlpoly program [18] which was modified to include the construction and diagonalisation of the Hamiltonian and the calculation of the Hellman-Feynman forces. The simulation box contained one triiodide ion and 340 solvent molecules with a temperature 300 K. Each system was equilibrated at the desired temperature and zero pressure with a time step of 1 fs. These simulations with a flexible triiodide ion were analyzed to determine the average geometry of the ion, the vibrational frequencies of the symmetric and antisymmetric stretching modes.

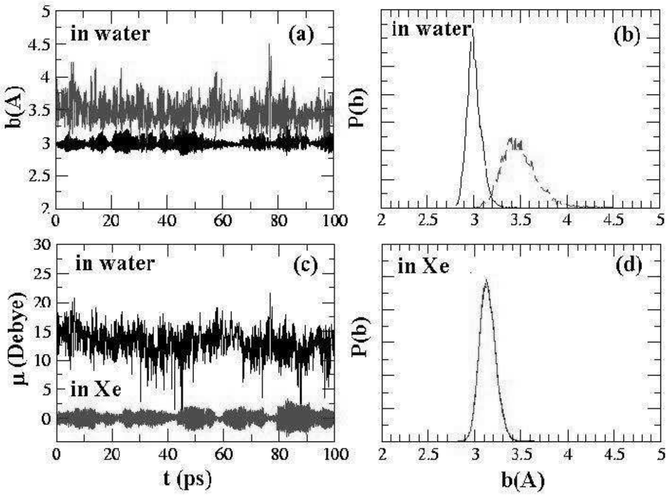

Fig. 1. Time evolutions of the bond lengths in Å (a) and the dipole moments in Debye (c) for the I_3^- in water and in Xe and the distributions of intermolecular distance for the I_3^- in water (b) and in Xe (d) at 300 K.

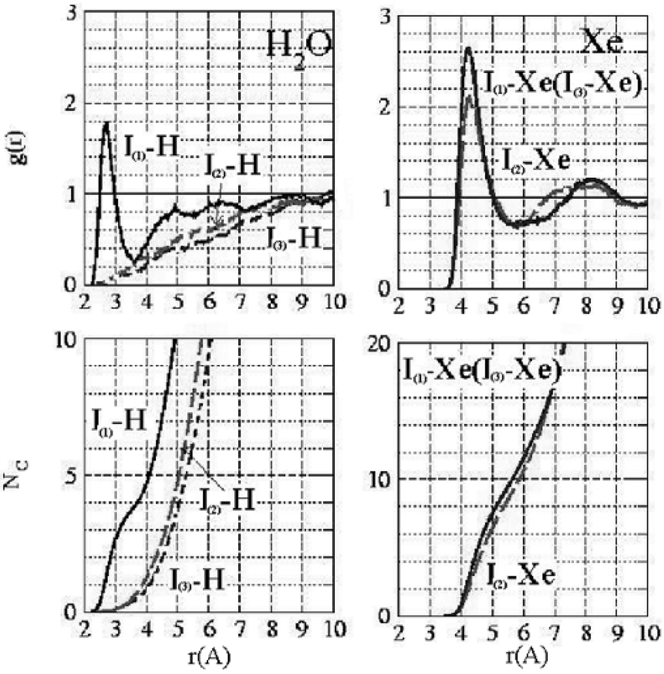

Fig. 2. Radial distributions of the three atoms with H in water (top-left) and Xe in the solvent of Xe (top-right) at 300 K. The two panels bottom are the coordinate numbers corresponding to the top ones. The illustrations here are only for 100 ps simulations in which the bond length between $I_{(1)}$ and $I_{(2)}$ is longer than that between $I_{(2)}$ and $I_{(3)}$ in water but this is not necessary in Xe since the interconvertion time in water is as large as 210 ps and that is identical to the period of the antisymmetric mode, 0.24 ps in Xe.

3 Results and discussion

Figure 1 shows the time evolutions of the bond lengths (a) and the dipole moments in Debye (c) for the I_3^- in water and in Xe for 100 ps. Figures 1b and 1d show the distributions of intermolecular distance in the I_3^- with the solid curve the distribution of distance between atoms 1 and 2, and the dashed curve distance distribution for atoms 2 and 3. Figures 1a, 1b, and 1d show two maximum in the distribution at 3.001 Å and 3.488 Å (corresponding to an antisymmetrical coordinate 0.199 Å) showing that there is a spontaneous symmetry breaking of the I_3^- in water, while Figure 1c shows only one maximum at 3.106 Å indicating that the symmetry still keeping for the I_3^- in the solvent of Xe. Figure 1d shows that the dipole moment for the I_3^- is as large as 13.544 Debye in water and that is only fluctuating around zero in Xe. Evidently, the I_3^- shows different behavior as putting in different solvents such as in hydrogen-bond one, water, the structure has changed; while in Xe, the symmetry still keeping with a small distortion. For the cases of other hydrogen bonding solvents such as MeOH and EtOH, one finds symmetry breaking with the antisymmetrical coordinate and the dipole moment are 0.123 Å, 9.348 Debye for MeOH and 0.105 Å, 8.400 Debye for EtOH, respectively, depending on the strength of interactions. While for the cases of MTHF, THF, and MeCN, one just finds symmetry keeping but with various distortions depending on the strength of interactions.

Whether hydrogen-bond interaction make so difference needs further investigation. We try to understand this by showing the radial distributions of each triiodide atom $I_{(1)}$ and $I_{(3)}$ (two ends atom), and $I_{(2)}$ (middle atom) with hydrogen in water (top-left) and Xe in the solvent of Xe (top-right) of Figure 2. The coordinate numbers are also shown in the bottom panels of Figures 2. Surprisingly, one finds the most probable interaction distance between H and one end iodide is only 2.7 Å, the coordinate number of H is as large as 7.7, a typical hydrogen-bond interaction with one end iodide. For hydrogen-bond solvents such as MeOH and EtOH, one finds the same conclusion but with different values of coordinate number and the positions of the most probable interaction distance. For Lennard-Jones solvents, the most probable interaction distance between Xe atom and one end iodide is 4.2 Å with coordinate number of the Xe atom as large as 10. For the cases of I_3^- in non-hydrogen binding polar solvents such as MTHF, THF, and MeCN, the conclusions are basically the same as in Xe, but with different magnitude of coordinate numbers and positions of the most probable interaction distance since electrostatic interactions included. The solvents which induce symmetry breaking at have hydroxyl groups which can form hydrogen bonds to the atom which carries the charge in the distorted triiodide ion. In this model hydrogen bonds are purely electrostatic and occur because of the small size of the hydrogen atom combined with a positive partial charge. This allows a strong electrostatic attraction. We can draw a conclusion that the structure changing is induced by local electrostatic attraction between solvent molecules.

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