

Theoretical Study of Liquid Hydrogen Fluoride. Application of the Averaged Solvent Electrostatic Potential/Molecular Dynamics Method

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We applied a Quantum Mechanics/Molecular Mechanics method (QM/MM) that makes use of the mean field approximation to study the polarization of hydrogen fluoride (HF) in its liquid phase. The method is based on the calculation of the Averaged Solvent Electrostatic Potential from Molecular Dynamics data (ASEP/MD). Our model considers the HF molecule to be nonrigid, the H–F bond length can vary, and includes the effect of the electron correlation calculated at the Møller–Plesset second-order (MP2) level and the effect of the solvent polarization. The H–F bond elongates and undergoes strong polarization when it passes from the gas to the liquid phase. The ASEP/MD method provides an adequate description of this polarization, and reproduces adequately both the thermodynamics and the structure of the liquid. A comparison between the performances of two-site and three-site models for the HF molecule is also presented.

Introduction

Due to the strong hydrogen bond network that characterizes its liquid phase, hydrogen fluoride (HF) constitutes a severe test for any theory of the liquid state. Liquid HF has been the subject of many theoretical^{1–10} and experimental^{11,12} studies. Theoretically, its thermodynamics and structural properties have been analyzed by Monte Carlo (MC) and Molecular Dynamics (MD) classical simulations using different potential models: rigid, nonrigid,⁹ polarizable,^{8,10} and nonpolarizable. An ab initio molecular dynamics simulation study of the liquid structure has also been reported.⁶ The different studies have failed in their attempts to simultaneously give an adequate description of both the thermodynamics (vaporization energy) and liquid structure (radial distribution functions).

To date, no quantum mechanics/molecular mechanics^{13–15} (QM/MM) study of this system has been performed, even though it has been shown that QM/MM methods are particularly suitable for the study of the polarization process in liquids and solutions. Indeed, given that QM/MM methods describe the solute molecule quantum mechanically, they incorporate the contribution of anisotropy and higher multipolar terms of the polarization, terms usually neglected in classical simulations.

Our aim in this paper is to see whether QM/MM methods can provide a satisfactory image of the HF liquid. We used a nontraditional QM/MM method that makes use of the mean field approximation. This approximation reduces drastically the number of quantum calculations (from several thousands to only a few), and introduces no significant inaccuracies in the interaction energies or dipole moments.¹⁶ As a consequence, the level of the quantum calculation can be increased. In most QM/MM methods the quantum mechanical system is described as semiempirical,¹³ Restricted-Hartree–Fock¹⁵ (RHF), or Density Functional Theory¹⁴ (DFT) level and, in general, reduced basis sets are used. In this paper the electron correlation is calculated at the MP2 level and the basis set use is of the quality aug-cc-pVDZ.¹⁷ The model referred to in previous papers¹⁸ as

Coupled ASEP/MD (averaged solvent electrostatic potentials from molecular dynamics calculations) permits one to simultaneously optimize the electronic structure and geometry of the solute molecule and the solvent structure around it. The ASEP/MD has been successfully applied to the study of the structure and thermodynamics of liquid water^{18e} and alcohols^{18f} and to the determination of solvent shifts in the VIS/UV spectra of carbonyl compounds^{18c} and pyrimidine.^{18d}

We also checked the influence that the number of charges representing the HF molecule during the simulation has on the thermodynamics and structural properties of the liquid. We compared two-site and three-site models, but, unlike previous studies^{4,5,7–10} where the charges on the hydrogen and fluorine atoms were equal, we permit these charges to be different.

The structure of the paper is as follows. In the next section the details of the ASEP/MD method are described. In Section III, we discuss the thermodynamic and structural properties of HF liquid. We compare our results with the available experimental data and with the results obtained by other workers. The comparison between the performances of two-site and three-site models is also discussed. Last, in Section IV, some conclusions are given.

Details of the Computational Scheme

The ASEP/MD method for the study of liquids and solutions has been described in detail in a number of publications.¹⁸ Here, we shall detail only those points pertinent to the current study.

The ASEP/MD method is an iterative procedure that alternates molecular dynamics with quantum mechanics calculations. During the MD simulation, the geometry and charge distribution of the solute and solvent molecules are considered as fixed. From the MD data we obtain the averaged solvent electrostatic potential that is introduced as a perturbation into the solute molecular Hamiltonian. By solving the associated Schrödinger equation we get a new solute charge distribution that serves as input for a new MD calculation. The process terminates when convergence in the solute charges and in the solute energy is reached. The procedure is described in Figure 1. If, as is the

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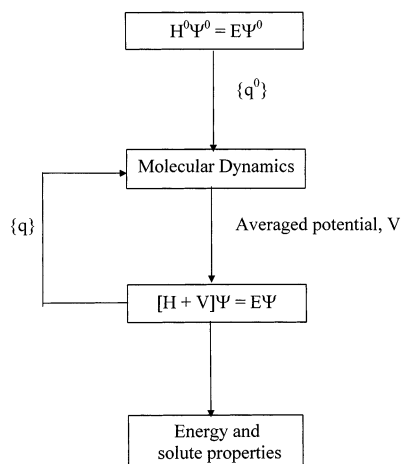


Figure 1. Flowchart of the coupled ASEP/MD model.

case for pure liquids, the solute and solvent molecule are the same then the solute charge distribution obtained from the quantum calculation also allows the charge distribution of the solvent molecules to be updated, i.e., all the molecules are simultaneously polarized. The same is true for the geometry of the molecules: at each step of the ASEP/MD process the optimized geometry obtained from the quantum calculation is used to describe all the molecules of the system. The ASEP/MD is thus halfway between a nonpolarizable simulation (the MD is performed at fixed values of the charges) and a polarizable simulation (the charge distribution is updated at each cycle of the procedure). The charges (two or three depending on the model selected) that represent the HF molecules are obtained from the wave function of the solute molecule in solution by using the CHELP method developed by Chirlian and Francl.¹⁹

All quantum calculations were performed with the program Gaussian 98.²⁰ We used the aug-cc-pVDZ basis set.¹⁷ Two procedures were used to include the electron correlation effect. In the first, named MP2E, the wave function was calculated at the restricted-Hartree-Fock (RHF) level and MP2 corrections to the energy were added at the end of the ASEP/MD cycle. In the second, MP2D, at each step of the ASEP/MD cycle both the energy and the wave function were obtained with the MP2 method.

When indicated, the geometry of the (solute and solvent) HF molecules were optimized. We used a technique described in a previous paper²¹ and based on the use of the free-energy gradient method.^{22–24} At each step of the ASEP/MD cycle the total gradient, F , and the Hessian, H , were calculated as the sum of the solute and solvent contributions and used to obtain a new geometry through the expression $r_{k+1} = r_k + H_k^{-1}F_k$. This expression was used iteratively until the gradient had converged. The new geometry was then used to represent both the solute and solvent molecules during the MD calculation.

The MD calculations were performed using the program MOLLY.²⁵ A total of 216 molecules were simulated at fixed intramolecular geometry by combining Lennard-Jones interatomic interactions with electrostatic interactions. The Lennard-Jones potential parameters were taken from Cournoyer and Jorgensen.⁵ Periodic boundary conditions were applied, and spherical cutoffs were used to truncate the molecular interactions at 9.0 Å. A time step of 0.5 fs was used. The electrostatic interaction was calculated with the Ewald method. The temperature was fixed at 273 K by using a Nosé-Hoover²⁶ thermostat. Each MD calculation simulation was run for 150 000 time steps (50 000 equilibration, 100 000 production).

TABLE 1: Comparison between the Vaporization Energies and Their Components (in kcal/mol) Obtained with the Two-Site and Three-Site Models

	two-site model MP2E	three-site model MP2E	three-site model MP2D	exptl
E_{vap}	-6.7	-6.8	-7.1	-6.9
E_{elect}	-24.4	-19.9	-24.4	
E_{dist}	3.7	2.5	4.2	
E_{LJ}	4.1	2.8	4.2	
E_{Stark}	-0.3	-0.8	-1.2	

In general, the ASEP/MD procedure converges in about 4–6 cycles.

Thermodynamic Results

Table 1 compares the thermodynamics results from the ASEP/MD calculations with the experimental data. Before discussing our results, it is necessary to clarify the way in which the vaporization energies were calculated. In our model the vaporization energies are obtained as

$$\langle E \rangle = \frac{1}{2}(E_{\text{elect}} + E_{\text{LJ}}) + E_{\text{dist}} + E_{\text{Stark}} \quad (1)$$

where E_{elect} is the QM/MM electrostatic solute solvent interaction energy calculated as $\langle \Psi | V_{\text{elect}} | \Psi \rangle$ where Ψ is the in-solution wave function and V_{elect} is the electrostatic potential generated by the charges that represent the solvent molecules. It is important to bear in mind that these charges vary at each cycle of the ASEP/MD procedure, i.e., they also include the contribution of the polarization component. E_{LJ} is the solute-solvent Lennard-Jones interaction energy, and E_{dist} is the distortion energy of the solute, i.e., the energy spent in polarizing the HF molecule. This energy is calculated as the difference:

$$E_{\text{dist}} = \langle \Psi | H^0 | \Psi \rangle - \langle \Psi^0 | H^0 | \Psi^0 \rangle \quad (2)$$

where Ψ and Ψ^0 are the in-solution and in-vacuo state functions, respectively. Due to the use of the mean field approximation our model neglects the Stark energy,^{27,28} i.e., the energy associated with the correlation that exists between the motion of the solvent nuclei and the response of the solute electron polarizability. In a previous paper,¹⁶ we proposed an approximate expression that provides an estimate of the Stark energy. The Stark energy, E_{Stark} , is proportional to the solute polarizability and to the fluctuations of the electric field generated by the solvent at the position occupied by the solute. The last row of Table 1 displays the estimated value for this component.

We present two types of results according to whether the solute is represented by a two-site or a three-site model during the MD calculation. In both cases the HF geometry was optimized in solution at the RHF level. In the MP2E model, corrections were applied only to the energy and not to the wave function. As a consequence, the dipole moments and rdfs calculated at RHF and MP2E levels are the same. Only the distortion energy and hence the final value of the vaporization energy are affected by the consideration of the correlation energy. The vaporization energy is reduced in value, a trend which confirms previous results obtained using both continuum models²⁹ and QM/MM methods.^{18f} The vaporization energies calculated at MP2E and MP2D levels are in very good agreement with the experimental data,³⁰ especially for the three-site model. The error is 7.2% at the RHF level and 2.8%, 1.4%, and 2.8% for the MP2E two-charge, MP2E three-charge, and MP2D three-charge models, respectively. Hence, the consider-

TABLE 2: In-Vacuo Dipole Moment, μ^0 , In-Solution Dipole Moment, μ , and Induced Dipole Moment in Debyes; In-Vacuo Quadrupole Moment, θ^0 , and In-Solution Quadrupole Moment, θ , in debyes-ångströms

	two-site model MP2E	three-site model MP2E	three-site model MP2D
μ^0	1.89	1.89	1.94
μ	2.49	2.36	2.20
$\Delta\mu$	0.59	0.46	0.46
θ_{xx}^0	-3.44	-3.44	-3.36
θ_{yy}^0	-5.70	-5.70	-5.73
θ_{zz}^0	-5.70	-5.70	-5.73
θ_{xx}	-3.20	-3.22	-2.92
θ_{yy}	-5.72	-5.72	-5.75
θ_{zz}	-5.72	-5.72	-5.75

ation of two or three charges has no appreciable effect on the thermodynamics of the system, but the electron correlation is a more important factor.

Table 1 also gives the contribution of the different components of the interaction energies to the vaporization energy. The main contribution is the electrostatic interaction as corresponds to a hydrogen-bonded system. The two-site model yields a larger value for this component that, as we will see later, has an effect on the solvent structure. However, the vaporization energy is almost the same in the two-site and three-site models because the large contribution of the electrostatic component in the two-site model is balanced out by a larger value of the Lennard-Jones and distortion energies, which are repulsive. It is also interesting to note the differences in the Stark component. These differences are associated with the smaller fluctuations in the electric field generated by the solvent in the two-site calculation. As we will show below, the two-site model yields a more rigid solvent structure. As a consequence, the contribution of the Stark component is less important than for the three-site models.

Polarization

In this section we consider the influence that the solvent has on the charge distribution of the HF molecule. Given that the in-solution multipole moment values are not experimentally accessible, we compare our results with those from the polarizable model of Jevlovszky and Vallauray⁸ (hereafter referred as JVp). We must remark that these authors assume rigid molecules; however, in our model the geometry varies at each step of the ASEP/MD procedure, so that a full comparison with our results is not possible. Table 2 lists the values of the total and induced dipole moments. The in-vacuo value obtained at the RHF level is 1.89 D, which compares well with the experimental value³¹ (1.83 D). The in-solution dipole moments calculated with the two-site and three-site models are 2.49 and 2.36 D, respectively. The induced dipole moments are 0.59 and 0.46 D, and they are oriented in the direction of the permanent dipole moment. These values compare well with the value of 0.51 ± 0.14 D obtained with the JVp model. Solution produces a notable increase in the dipole moment, about 25%–32%, similar to that found in a previous study on alcohols.^{18f} The two-site model yields a larger value of the dipole moments and also a larger value of the electrostatic solute–solvent interaction energy.

As has already been found for other systems (alcohols^{18f} and water,^{18e} for instance), the in-solution dipole moments are greater than the OPLS values proposed by Cournoyer and Jorgensen.⁵ The OPLS charges yield a dipole moment of 2.04 D. Nonpolarizable models neglect the distortion energy of the molecules and hence have to use underestimated dipole moments in order

TABLE 3: In-Vacuo, q^0 , and In-Solution, q , HF Charges (in au) Obtained by the CHELP Process

	two-site model MP2E	three-site model MP2E	three-site model MP3D
$q^0(\text{F})$	-0.429	0.743	0.736
$q^0(\text{H})$	0.429	0.693	0.690
$q^0(\text{bond})$		-1.436	-1.426
$q(\text{F})$	-0.553	0.394	0.343
$q(\text{H})$	0.553	0.734	0.741
$q(\text{bond})$		-1.128	-1.083

to reproduce the vaporization energies adequately. In our case, the distortion energies are considered explicitly.

Unlike the dipole moment, the quadrupole moment slightly decreases in solution. The basis set and quantum methods (RHF and MP2) used seem to underestimate the gas-phase value of this quantity. In any case, its contribution to the electrostatic energy, the solute–solvent interaction energy, is dominated by the dipole contribution, the quadrupole contribution being very small. The dipole contribution (-19.57 kcal/mol) accounts for 98% of the total value (-19.87 kcal/mol). The contribution of higher multipoles is only 0.3 kcal/mol.

Table 3 lists the final charges obtained by the CHELP procedure for the HF molecule in solution. It is evident that in all the cases the in-solution values are very different from the in-vacuo values. Clearly, it is a bad strategy to use in-vacuo charges in liquid simulations. In the three-site model, unlike the models previously proposed in the literature,^{4,5,7–10} we permit the hydrogen and fluorine atoms to bear different charges. In the gas phase, the charges on the H and F atoms are very similar. However, in the liquid phase the three-site model results in very different charges on each atom: +0.3940 au on the fluorine, +0.7341 au on the hydrogen, and -1.1281 au at a point on the H–F bond and at a distance from the F atom calculated as 0.181 times the H–F distance. In the JVp model, for instance, although the charge on the bond is very similar, -1.184 au, the positive charge is divided equally between the H and F atoms.

Structural Results

We begin this section by discussing the variation of the intramolecular H–F distance during the solution process. In the gas phase, the RHF and MP2 methods yield a distance of 0.89 and 0.92 Å, respectively. In solution, these values increase to 0.922 and 0.915 for the MP2E two-site, and MP2E three-site (in the MP2E method the optimization is performed at RHF level, the electron correlation correction only affects the final value of the energy), and to 0.946 Å in the MP2D three-site model. As we have shown previously, the two-charge model gives larger values for the in-solution dipole moment and electrostatic solute–solvent interaction energy than the three-charge models. It is thus expected to yield also a larger value of the H–F distance. The increases in the distances from the gas phase to solution are 0.032, 0.025, and 0.024 Å. The experimental increase has been estimated as 0.042 Å.^{11,32} Our model slightly underestimates the H–F distance in solution. In any case, our values are clearly better than the results obtained by Della Valle and Gazillo,⁹ 0.011 Å, using a flexible potential. Their small value of the increase in intramolecular distance is related to the small value of the vaporization energy that those authors obtained, only -3.7 kcal/mol.

We shall now discuss the solvent structure. For comparison with the experimental results^{11,12} we produce an intermolecular rdf by summing the FF, HF, and HH rdfs. We followed the procedure proposed by Pfliederer et al.,¹² calculating in the simulation the total $g(r)$ as a weighed average of the three partial

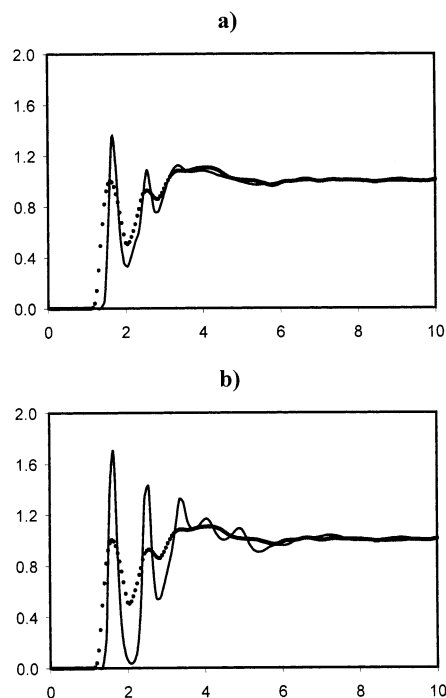


Figure 2. Comparison of the total pair function correlation of HF (a) as obtained from neutron diffraction experiments (black points) and from the three-site model (full line), (b) as obtained from neutron diffraction experiments (black points) and from the two-site model (full line).

pair correlation functions:

$$g(r) = 0.210g_{\text{FF}}(r) + 0.497g_{\text{HF}}(r) + 0.293g_{\text{HH}}(r) \quad (3)$$

The image of the HF liquid structure as obtained by nuclear diffraction experiments is characterized by two peaks situated at 1.62 Å, 2.53–2.56 Å, and a broad peak centered around 3.30–3.38 Å.

None of the models proposed to date adequately fits the experimental curve. The best results are probably obtained with the HF3 model of Klein and McDonald which reproduces the position of the different peaks but not their heights. The JVP model reproduces better the height of the peaks, but they are shifted toward too large distances. Our MP2E three-site model, Figure 2a shows the same behavior as the HF3 model: it yields a structure where the peaks are in general well placed, at 1.65, 2.55, and 3.35 Å, but their heights, especially the first, are overestimated. The broad third peak is well reproduced. The inclusion of the electron correlation effect on the wave function, MP2D method, does not modify this image. Only the height of the first peak is slightly increased (results not displayed). In a previous paper,³³ we compared the performance of our model with those of other models that do not make use of the mean field approximation, including a DFT/MM model developed by Ruiz López and co-workers.³⁴ The conclusion was that our model slightly overestimated the height of the peaks, so that we can expect traditional QM/MM methods to give even better agreement with the experimental curve.

The two-site model yields an over-structured solvent, see Figure 2b. As for the three-charge model, the position of the peaks is well described, but the height of the peaks and the depth of the minima are clearly overestimated. Furthermore, at large distances, there are peaks that do not appear in the experimental curve, and which show that this model overestimates the relative ordering of the most distant neighbors in the hydrogen-bonding chains, and yields a solidlike structure

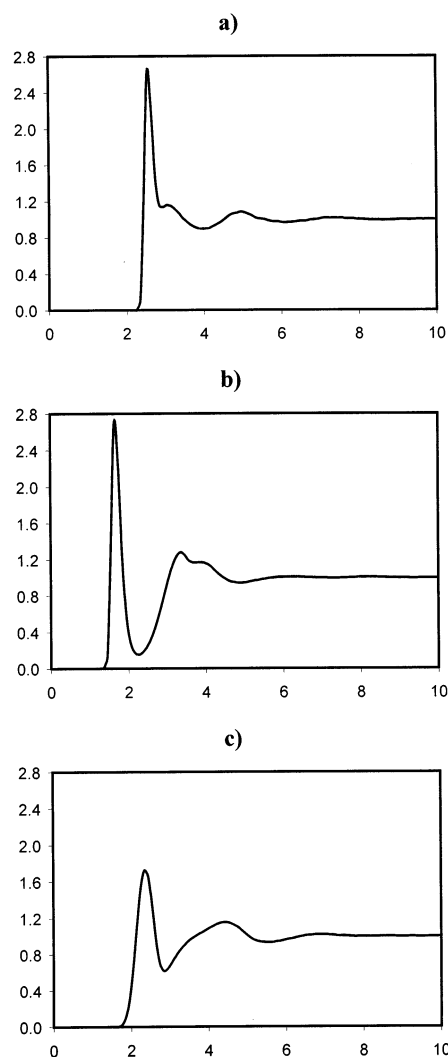


Figure 3. Three-site model. (a) FF radial distribution function. (b) HF radial distribution function. (c) HH radial distribution function.

characterized by long-distance order. Indeed the peaks in $g(r)$ only disappears at 6 Å or longer.

The individual rdf functions for the three-charge model are shown in Figure 3. The main characteristic of the FF radial distribution function is the presence of a shoulder at 3.2 Å. This shoulder has been related to the nearest-neighbor interchain distances and is completely analogous to the smallest interchain distances that appear in the solid at 3.2 Å. The position of the first peak agrees very well with the results of Röthlisberger and Parrinello⁶ using an ab initio molecular dynamics method. The height of the peak, however, is overestimated. The same is the case in the FH rdf. On the contrary the height and position of the first peak of the HH rdf agree very well with the RP results.

The integration of the first peaks of $g_{\text{FF}}(r)$, $g_{\text{FH}}(r)$, and $g_{\text{HH}}(r)$ up to the first minimum results in coordination numbers of 2.16, 1.00, and 2.24, respectively, for the two-site model and 2.16, 1.01, and 2.27 for the three-charge model. These results agree with the expectations on the basis of structural considerations (the vast majority of the molecules form two hydrogen bonds) and compares well with those obtained by other workers. Thus, for instance, the JVP model yields 2.25, 1.00, and 2.45, while the ab initio MD simulation yields 2.6, 1.00, and 2.2. It is important to note that the higher the peak, the narrower the peak and the deeper the following minimum. The result is that the two models studied, two-site and three-site, yield practically the same value for the coordination numbers.

Conclusions

We have applied a QM/MM method that makes use of the mean field approximation to study hydrogen fluoride in the liquid phase. The results permit us to conclude that this kind of method yields satisfactory results for the thermodynamics and structural properties of the liquid HF. We included in our model all the essential ingredients in the description of the system: flexible HF molecules, electron correlation, and solute and solvent polarization.

We compared the performance of two models: a two-site model and a three-site model. With the two-site model, the vaporization energy, the coordination numbers, and the position of the peaks of the rdf are well reproduced. However, the height of the peaks and the depth of the minima are clearly overestimated, with minima and maxima that extend out to large distances.

The best results were obtained with the three-site model. The picture provided by this model is a HF molecule whose bond distance increases as a consequence of its interaction with the rest of the molecules and which is strongly polarized (the dipole moment increases by about 25%). The final solute charge distribution is well represented by three charges, two positive charges on the hydrogen and fluorine atoms (+0.394 and +0.734) and an additional negative charge (-1.128) placed on the H-F bond. With this model we get a vaporization energy at the MP2 level between 6.8 and 7.1 kcal/mol that compares well with the experimental result. The structure of the solvent is also very well reproduced, especially the position of the peaks of the rdf and the coordination numbers. The height of the peaks, however, is slightly overestimated. This is probably an artifact of the method associated with the use of the mean field approximation. In a previous paper³⁵ we showed that the overestimation of the height of the peaks can be improved by fitting the van der Waals parameters.

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