Electronic properties of liquid hydrogen fluoride: A sequential quantum mechanical/Born–Oppenheimer molecular dynamics approach

Benedito J. Costa Cabral a,b,*, Kaline Coutinho c, Sylvio Canuto c

a Grupo de Física Matemática da Universidade de Lisboa, Av. Professor Gama Pinto 2, 1649-003 Lisboa, Portugal
b Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal
c Instituto de Física da Universidade de São Paulo, CP 66318, 05314-970 São Paulo, Brazil

Abstract

The electronic properties of liquid hydrogen fluoride (HF) were investigated by carrying out sequential quantum mechanics/Born–Oppenheimer molecular dynamics. The structure of the liquid is in good agreement with recent experimental information. Emphasis was placed on the analysis of polarisation effects, dynamic polarisability and electronic excitations in liquid HF. Our results indicate an increase in liquid phase of the dipole moment (∼0.5 D) and isotropic polarisability (5%) relative to their gas-phase values. Our best estimate for the first vertical excitation energy in liquid HF indicates a blue-shift of 0.4 ± 0.2 eV relative to that of the gas-phase monomer (10.4 eV).

1. Introduction

Chemical reactivity and kinetics in hydrogen bonding solvents is a subject of wide interest in chemistry and biochemistry. One archetypal hydrogen bonding solvent is hydrogen fluoride (HF). The mechanism and energetics of reactions involving proteins, carbohydrates, and related species in liquid HF were reviewed by Leonard [1]. It is generally accepted that reaction dynamics in hydrogen bond solvents are dependent on the electronic properties of the hydrogen bond network [2]. This picture is of particular relevance in the case of water, where chemical reactions are processes assisted by the solvent. Some specific features characterizing HF should be stressed. Hydrogen bonding in HF is the strongest in the series of hydrogen bonded halides; cooperative effects in small HF clusters are very important for understanding the energetics, electronic, and vibrational properties [3] of the aggregates.

Considering its importance as a solvent, several works were dedicated to the investigation of the electronic properties of water [4]. This is not the case of HF. However, although the well known difficulties involved in the study of this system, which requires highly secured experimental procedures, relevant investigations on the structure of HF were reported [5–10]. From the theoretical point of view, numerous investigations based on classical [11–16,10,17] and first principles [18–22] statistical mechanics simulations were reported and provided useful informations complementary to the experimental techniques. A recent QM/MM approach to liquid HF has been reported by Muñoz-Losa et al. [23].

In this Letter we are reporting theoretical results for the electronic properties of liquid HF. The theoretical approach is based on the sequential quantum mechanical calculation of electronic properties by using configurations generated by Born–Oppenheimer molecular dynamics (BOMD). Emphasis was placed on the analysis of the dipole moment, dynamic polarisability and excitation energies in liquid phase. After a brief discussion on the presently adopted theoretical approach we report a discussion on the structure of liquid HF by providing comparison of our results with experimental data and theoretical information from the literature. Then, we present results for the electronic properties of liquid hydrogen fluoride. We conclude by stressing the importance of a sequential quantum mechanical/BOMD approach to the electronic properties of liquid HF.

2. Computational details

Born–Oppenheimer molecular dynamics (BOMD) were carried out for a system with 64 HF molecules in a cubic cell with periodic boundary conditions. The hybrid Gaussian and plane-wave method GPW [24] as implemented in the QUICKSTEP program [25] was adopted. Goedecker, Teter, and Hutter (GTH) norm-conserving pseudopotentials [26] were used for representing the core electrons and only valence electrons were explicitly included in the quantum mechanical density functional theory (DFT) calculations of the forces to generate the dynamics. In this approach, Kohn–Sham orbitals are expanded into atom-centered double-zeta-valence-polarization (DZVP) Gaussian-type orbital functions, whereas the electron density is represented with an auxiliary plane-wave basis-set. A charge density cutoff of 280 Ry was used for the auxiliary basis-set and the self-consistent-field energy
threshold for calculating the electronic density was $10^{-8}$ Hartree. DFT calculations were performed with the Perdew–Burke–Erzenhof (PBE) exchange–correlation functional [27]. A timestep of 0.5 fs was used in all the MD runs. The simulations were performed in the (NVE) microcanonical ensemble at a density of 1.015 g cm$^{-3}$ and a target temperature of 273 K. The total time of the simulation was 20 ps (40000 steps). Averages were calculated over the last 10 ps of the MD run. The final average temperature of the BOMD was 278.7 ± 5 K, which is practically the same (within error bars) as the average temperatures for the classical molecular dynamics.

Results for the liquid HF structure based on classical molecular dynamics are also reported. Two effective non-polarisable interaction models (A and B) were used in the classical simulations. Model A was proposed by Jedlovsky and Vallaui [13], whereas model B was used in simulations of dense hydrogen fluoride at higher temperatures [10]. In both models the fluorine atoms interact through a Lennard–Jones potential $V_{LJ}(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^{6}]$ with $\sigma = 2.83$ Å and $\epsilon/\hbar = 60$ K. In addition, the following charge distribution is assigned to each HF monomer: two positive charges ($+q = 0.592$ a.u.) on the F and H atoms, and a third charge of $-2q$, placed at a site X along the HF bond at a distance $r_{HF} = \beta \times r_{HF}$ from the fluorine atom with the parameter $\beta = 0.16927$. In model A, the charge distribution reproduces the experimental values for the dipole ($\mu = 1.83$ D) [28] and quadrupole ($Q_0 = 2.36$ B) [29] of the gas-phase HF monomer. The only difference between the two classical models concerns the F–H bond distance, which is 0.973 and 0.950 Å for the A and B models, respectively. The classical molecular dynamics simulations were carried out with the MOL-DY program [30].

For performing sequential calculations of the electronic properties of liquid HF, 100 (one hundred) configurations separated by 0.1 ps from the last 10 ps of the BOMD were selected. The sequential calculations rely on the definition, for a given liquid state configuration, of a quantum system including explicitly a few HF molecules, which are embedded in a charge distribution of the surrounding molecules. Each configuration includes a quantum system with one to six HF molecules $N = 1$–6, which are embedded in the charge distribution of the closest 54 surrounding HF molecules. The embedding charges representing the electrostatic background due to 54 HF molecules were chosen as those corresponding to the classical model A. We have recently analysed the dependence of the electronic properties on the choice of the electrostatic embedding. One main conclusion was that by using different charge distributions from different intermolecular interaction potentials for liquid water, including polarisable models, very similar results for the dipole moment, polarisabilities and absorption spectrum are obtained. This conclusion was also supported by the weak dependence of the results on the number of molecules of the quantum system [31]. No periodic boundary conditions are applied in the sequential QM calculations.

The average dipole moment as well as the isotropic polarisability in liquid HF were investigated by carrying out DFT calculations with the BHandHLYP functional. The dipole moment on each HF molecule was estimated by fitting three point charges to the electrostatic potential accordingly to the Breneman and Wiberg CHELPG scheme [32]. The localization of these charges is the same of the charge distribution for the classical models previously discussed [13,10].

The average isotropic polarisability in liquid HF was calculated by using a full sum-over-states procedure [31]. Excitation energies were determined by time dependent density functional theory (TDDFT) [33] and the equation-of-motion coupled-cluster with single and double excitations (EOM-CCSD) [34] method. Dunning’s double zeta correlation consistent basis-set augmented with a single [aug-cc-pVQZ (apvQZ)] and double [d-aug-cc-pVQZ (dapvQZ)] sets of diffuse functions [35] were used in the sequential quantum mechanical calculations. TDDFT calculations were carried out with the Gaussian-03 program [36], EOM-CCSD excitation energies were calculated with the Molpro program [37].

The reliability of the TDDFT approach for predicting the excitation energies of HF can be assessed by comparing TDDFT and EOM-CCSD calculations, which can be taken as reference. By using the dapvQZ basis-set, the TDDFT/BHandHLYP prediction for the first excitation energy of the gas-phase HF molecule at its experimental geometry ($r_{HF} = 0.917$ Å) [38] is 10.41 eV, which is in good agreement with the EOM-CCSD result (10.28 eV). The good agreement between TDDFT and EOM-CCSD calculations is also illustrated in Fig. 1, where the potential energy curves for the ground ($^1\Sigma$) and first excited ($^1\Pi$) singlet states are shown as a function of the interatomic $r_{HF}$ distance.

### 3. Results and discussion

#### 3.1. Structure of liquid hydrogen fluoride

The partial radial distribution functions (RDFs) of liquid HF predicted by the BOMD are reported in Fig. 2. For comparison, results from classical molecular dynamics (CLMD) by using models A (CLMD-A) and B (CLMD-B) are also reported.

The present BOMD results for the structure of liquid HF indicate that the F–F RDF (bottom panel of Fig. 2) has a first maximum (3.6) at 2.48 Å. The position of this maximum is in good agreement with data for solid HF (2.49 Å) as well as with Car–Parrinello results for liquid HF at a slightly different thermodynamic condition (290 K and 0.960 g cm$^{-3}$) [18]. Integration of the F–F RDF up to the first minimum (2.78 Å) leads to an average number of 2.2 molecules in the first coordination shell of liquid HF. The present BOMD predictions are in very good agreement with recent neutron and X-ray diffraction data for HF at 296 ± 2 K [9]. These experiments predict that the first F–F RDF maximum position is 2.51 ± 0.03 Å and the F–F coordination number is 2.1 ± 0.1 [9].

The inset of Fig. 2 shows the F–H intramolecular distance distribution in liquid HF, which exhibits a maximum close to 1.0 Å. This result indicates that the F–H bond distance in liquid HF is significantly stretched in comparison with the gas-phase value (0.937 Å) predicted at the same theoretical level of the BOMD (PBE/GTH/DZVP), whereas the experimental gas-phase value for the HF monomer is 0.917 Å [38]. Previous first principles molecular dynamics results for liquid HF at $T = 373$ K lead to an average F–H bondlength close to 0.95 Å [20]. A more recent result using an

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**Fig. 1.** Potential energy (eV) dependence on $r_{HF}$ for the ground ($^1\Sigma$) and first singlet excited state ($^1\Pi$).
intermolecular potential parametrized from ab initio calculations for the HF dimer predicts that F–H is 0.969 Å [21]. Experimental values are in the 0.93–0.97 Å range [7] depending on the thermodynamic state. Theoretical calculations for (HF)\(_{N=10}\) optimized gas-phase aggregates indicate that the average value is close to 0.96 Å for \(N > 5\) [3].

Hydrogen bonding in liquid HF can be assessed by the analysis of the F–H RDF, which exhibits a first maximum at 1.50 Å and a well defined first minimum at 2.10 Å. Integration of the intermolecular F–H RDF up to this minimum leads to a coordination number of 1.0. Comparison between these results and the experimental information reported by McLain et al. [9] shows a good agreement. These authors predict that the first maximum is at 1.60 ± 0.04 Å and that the coordination number (calculated from 1 to 2 Å) is 0.86 ± 0.10 [9].

The H–H RDF shows a first maximum at 2.15 Å and a minimum at 2.7 Å. Integration of the H–H RDF up to this value leads to 2.1. These results are in good agreement with those reported by Röhlisberger and Parrinello [18]. These authors predict a first maximum at 2.2 Å and a coordination number of about two [18]. They are also in good agreement with the recent experimental data from McLain et al. [9]. From these data the H–H RDF exhibits a maximum at 2.1 ± 0.1 Å with a coordination number of 1.69 ± 0.10.

Comparison between the structure predicted by the classical models (A and B) and BOMD shows some differences that mainly concern the RDFs peak positions, which are shifted to lower distances by the classical models. This trends cannot be only related to the large average intramolecular H–F distance (~ 1.0 Å) of the BOMD approach. Actually, the \(r_{HF}\) distance of model A (0.973 Å) is larger than that of model B (0.950 Å), although the RDFs from model A are slightly shifted to lower distances relative to model B. This trend was also observed in a classical MD simulation of dense hydrogen fluoride [10].

Our results seem to provide a correct description of the liquid HF structure, which is in keeping with recent experimental information [9]. Moreover, with the exception of the H–H RDF, the A and B models also lead to an acceptable picture for the liquid structure. Therefore, although sequential quantum mechanical calculations will rely on the BOMD structure of liquid HF, we will assume that an adequate representation of the electrostatic background of a quantum system including a few HF molecules can be provided by the embedding charges of the effective interaction models. The parameter \(\beta = 0.16927\) [13] will be also used for locating the third (–2q) charge along each one of the H–F bonds of the BOMD configurations. A snapshot from BOMD illustrating the presence of chains in liquid HF is shown in Fig. 3.

### 3.2. Dipole moment and dynamic polarisability of liquid HF

We report in Table 1 the results for the average values of the intramolecular distance (\(r_{HF}\)), monomeric dipole moment (\(\mu\)), and isotropic polarisability per monomer (\(\alpha\)) of HF in the liquid phase. These results are for quantum systems including up to 6 explicit HF molecules. The average values for the intramolecular distances and monomeric dipoles correspond to two averaging procedures. The first involves the calculation for a given configuration of the average over the different monomers of the quantum system. The second one relies on the calculation of the average values by using the selected set of 100 configurations from the BOMD run. The results for the average intramolecular distance in the liquid phase are not dependent on the number of HF molecules in the quantum system. In agreement with our previous analysis for the structure, \(r_{HF}\) for liquid HF is close to 1.0 Å. This means that the average \(r_{HF}\) is increased by ~ 0.08 Å relative to gas-phase value for the monomeric species (0.917 Å).

Hydrogen bond cooperativity has been the subject of numerous works [3,39]. One of the central aspects related to this concept concerns polarisation effects induced by hydrogen bond formation. Polarization effects in water lead to an increase of the monomeric dipole moment of ~0.8–1.2 D from the gas to liquid water [40–43]. As shown in Table 1, at the BHandHLYP/dapvdz level, the theoretical gas-phase value for the HF dipole moment is 1.85 D, which is in excellent agreement with the experimental values (1.85 [28]; 1.83 [29]). The present theoretical estimates for the average monomeric HF dipole in liquid HF show a weak dependence on the number of molecules in the quantum systems. The average dipole ranges from 2.48 ± 0.12 (\(N = 1\)) to 3.23 ± 0.14 D (\(N = 6\)). Weak dependence on the size of the quantum system was also observed for liquid water [43] and suggests that by including embedding the average monomeric dipole moment in liquid phase can be estimated as a “local” property. Our results indicate that the dipole moment of HF increases by ~ 0.5 D from the gas to the liquid phase. A polarisable model for liquid HF allows to estimate the monomeric dipole increase as ~ 0.4 – 0.5 depending on the thermodynamic state.
The real part of the dynamic polarisability $\alpha(\omega)$ of liquid HF is shown in Fig. 4, where we compare results for the gas-phase monomer (black circles) with those based on sequential TDDFT/BOMD calculations. The quantum mechanical calculations were performed for embedded systems with one, two and three explicit HF molecules. These calculations rely on a full sum-over-sates (SOS) procedure using the following expression

$$\alpha(\omega) = \sum_{k=0}^{\infty} f_k \left( \frac{1}{\Delta E_k - \omega^2} \right)$$

where $\Delta E_k$ and $f_k$ are transition energies and oscillator strengths, respectively. A discussion on the convergence of the above expression for the calculation of the dynamic polarisability of water with Dunning’s correlation consistent basis-sets can be found in Ref. [31]. For HF and by using the dpvdz basis-set for quantum systems with 1, 2, and 3 molecules, the number of states included in the full SOS calculations are, 200, 800, and 1800, respectively.

The dynamic polarisability for the HF gas-phase monomer is represented in the top panel of Fig. 4. The divergences near 10.3, 12.7, and 14.3 eV are related to resonances at these electronic excitation energies. The dynamic polarisability per monomer in liquid HF for an embedded quantum system with $N=3$ is shown in the bottom panel of Fig. 4, whereas the inset panel shows the low-energy behaviour of $\alpha(\omega)$. Comparison between gas and liquid phases dynamic polarisabilities suggest that the first electronic excitation in the liquid is blue-shifted relative to that of the gas. The magnitude of this shift is discussed below.

3.3. Electronic excitations in liquid HF

A comprehensive discussion on the vertical excitation spectrum of HF has been recently reported by Pitarch-Ruiz et al. [45]. The two lowest singlet–singlet vertical excitation energies for the gas and liquid phases of HF are presented in Table 2. For the gas-phase, these excitations correspond to the $A^1\Pi \rightarrow \Sigma$ and $B^1\Pi \rightarrow \Sigma$ transitions [45]. The experimental values for the two first vertical excitation energies of HF are 10.35 and 13.03 eV, respectively [46]. As illustrated in Table 2, excitation energies calculated with the apvdz and dpvdz basis-sets are quite similar. Comparison between TDDFT (10.41 eV) and EOM-CCSD (10.28 eV) predictions for the first excitation shows a good agreement. Comparison with experimental data [46] indicates that TDDFT underestimates the second excitation energy by 0.25 eV, whereas the EOM-CCSD result (12.94 eV) is in good agreement with experiment. For the gas-phase HF monomer our TDDFT/BHandHLYP and EOM-CCSD results

![Fig. 4. Dynamic polarisability $|\alpha(\omega)|$ in a.u. for the gas-phase HF monomer (top) and liquid HF (bottom). The inset panel shows the low-energy behavior of $\alpha(\omega)$.](image-url)
The average values for the first excitation energy of non-embedded quantum systems are also reported in Table 2 (bracketed values). For $N = 1$ the result ($9.71 \pm 0.3$ eV) corresponds to the excitation energy of a HF monomer with an average $r_{HF}$ distance of $0.990 \pm 0.039$ Å. In this case and in agreement with the dependence of the excitation energy on the intramolecular distance illustrated in Fig. 1, a $\sim 0.7 \pm 0.3$ eV red-shift relative to the gas-phase monomer at the equilibrium distance is observed. The results for non-embedded quantum systems including up to six HF molecules show that the first excitation energies of these aggregates are red-shifted by $\sim 0.5$ eV from $N = 1$ to $N = 6$. However, the first average excitation energies for $N = 5$ and $N = 6$ are quite similar. Non-embedded clusters are not equivalent to gas-phase optimized clusters. The structures of these aggregates are determined by thermal effects and by the interactions with the other HF molecules of the liquid state configurations. Our results for non-embedded clusters indicate that the increase of the intramolecular $r_{HF}$ distance induced by hydrogen bonding leads to a red-shift of the first excitation energy.

By including electrostatic embedding our TDDFT results show that when $N = 1$ the average value of the first excitation energy ($11.08 \pm 0.29$ eV) is blue-shifted by $\sim 0.7$ eV relative to that for the gas-phase monomer at the experimental equilibrium distance ($10.41$ eV). Moreover, when $N = 1$ embedding leads to a blue-shift of $\sim 1.4$ eV of the first average excitation energy relative to the non-embedded aggregates. The results of Table 2 for liquid HF suggest some dependence of vertical excitation energies on the size of the embedded quantum system. At the TDDFT/dapvdz level, they change from $11.07 \pm 0.29$ eV ($N = 1$) to $10.72 \pm 0.22$ eV ($N = 6$). Considering that the results for $N = 5$ and $N = 6$ are quite similar, indicating that the energies are close to convergence, we will take the $N = 6$ as our best TDDFT estimate for the first excitation energy in liquid HF. Comparison between TDDFT and EOM-CCSD calculations shows a very good agreement for all the $N$ values. This agreement can be seen as an indication on the reliability of TDDFT/BHandHLYP to predict the first excitation energy of large HF aggregates for which EOM-CCSD calculations may become not affordable.

In contrast with the results for the gas-phase monomer, where two well defined transitions are observed, the two first excitation energies for embedded clusters are almost degenerate. Moreover the differences between them slightly decreases with the number of monomers in the quantum system. Thus, this difference is $0.31$ eV ($N = 1$) and decreases to $0.15$ eV ($N = 5, 6$). This behavior reflects electronic and thermal broadening. Electronic broadening is related to hydrogen bonding formation, which leads to similar excitation energies that may involve different monomers in the aggregates. Thermal broadening is related to the presence, for a given number of monomers, of different configurations from the BOMD sampling. We are also reporting in Table 2, the average values of oscillator strengths for the two first excitation energies. Most of the results rely on TDDFT although some values from EOM-CCSD calculations are presented. For the HF monomer ($N = 1$) the average oscillator strength increases from $0.027 \pm 0.003$ a.u. (non-embedded) to $0.040 \pm 0.005$ (embedded quantum system). A similar trend can be observed for the larger quantum systems. In keeping with the behavior of the difference between the two first excitation energies with $N$, oscillator strengths are quite similar for larger values of $N$.

It should be observed that by increasing the size of the quantum system, an improved description of dispersion interactions is provided since these interactions are related to the correlations between electronic density fluctuations of the aggregates. Therefore, the decrease of the excitation energies with increasing

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**Table 2**

Average values for the two lowest singlet–singlet vertical excitation energies ($\omega$ in eV) and corresponding oscillator strengths ($f$ in a.u.) of HF in liquid phase (values for the gas-phase monomer in parenthesis). Averages for the first excitation energies and oscillator strengths of non-embedded systems are shown in brackets. $N$ is the number of explicit HF molecules in the quantum system.

<table>
<thead>
<tr>
<th>$N$</th>
<th>TDFFT</th>
<th>EOM-CCSD</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$1^*$</td>
<td>$2^*$</td>
</tr>
<tr>
<td>1</td>
<td>$10.08 \pm 0.29 (9.71 \pm 0.30)$</td>
<td>$11.39 \pm 0.32$</td>
</tr>
<tr>
<td></td>
<td>$0.040 \pm 0.005 {0.027 \pm 0.003}$</td>
<td>$0.046 \pm 0.005$</td>
</tr>
<tr>
<td>2</td>
<td>$10.17 \pm 0.29$</td>
<td>$11.39 \pm 0.32$</td>
</tr>
<tr>
<td></td>
<td>$(10.41)$</td>
<td>$(12.78)$</td>
</tr>
<tr>
<td></td>
<td>$0.037 \pm 0.005$</td>
<td>$0.044 \pm 0.006$</td>
</tr>
<tr>
<td>3</td>
<td>$10.94 \pm 2.29 (9.44 \pm 0.37)$</td>
<td>$11.15 \pm 0.25$</td>
</tr>
<tr>
<td></td>
<td>$0.019 \pm 0.009 {0.009 \pm 0.004}$</td>
<td>$0.029 \pm 0.018$</td>
</tr>
<tr>
<td>4</td>
<td>$10.94 \pm 2.29 (9.40 \pm 0.35)$</td>
<td>$11.10 \pm 0.22$</td>
</tr>
<tr>
<td></td>
<td>$0.017 \pm 0.011$</td>
<td>$0.023 \pm 0.015$</td>
</tr>
<tr>
<td>5</td>
<td>$10.84 \pm 0.25 (9.29 \pm 0.32)$</td>
<td>$11.02 \pm 0.21$</td>
</tr>
<tr>
<td></td>
<td>$0.027 \pm 0.017 {0.012 \pm 0.011}$</td>
<td>$0.031 \pm 0.019$</td>
</tr>
<tr>
<td>6</td>
<td>$10.76 \pm 0.24$</td>
<td>$10.91 \pm 0.19$</td>
</tr>
<tr>
<td></td>
<td>$0.026 \pm 0.015$</td>
<td>$0.026 \pm 0.015$</td>
</tr>
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$^a$ For the gas-phase HF monomer the two lowest excitations correspond to the $\Pi^\pi \to \Sigma^\pi$ and $\Pi^\pi \to \Sigma^\pi$ transitions.

$^b$ Present gas-phase result with $r_{HF} = 0.917$ Å.

$^c$ Full-CI result from Nakatsuji [47].

$^d$ Experimental value from Hitchcock and Brion [46].

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for the first excitation energy are also in good agreement with the full-CI value (10.38 eV) reported by Nakatsuji [47].
N is apparently in agreement with a better description of the dispersion interactions. In keeping with the previous discussion on the dynamic polarisability, our results indicate that the first excitation energy of liquid HF is blue-shifted relative to the gas-phase. From both TD-DFT and EOM-CCSD calculations this shift is ~0.4 ± 0.2 eV. In comparison with liquid water, for which the blue-shift of the first excitation energy relative to the gas-phase monomer is ~0.96 eV [48,31], this seems to be a less pronounced condensed phase effect. The magnitude of the effect in liquid HF seems to reflect some particular features of hydrogen bonding in this system, specifically a stretched intramolecular $r_\text{HF}$ distance relative to the gas-phase and the topology of HB network characterized by the presence of short and strongly hydrogen-bonded chains. However, our results also suggest that this effect (blue-shift of the first excitation energy of the liquid relative to the monomeric gas-phase value) cannot be assessed by carrying out calculations for a single HF monomer in a charge background representing the liquid environment and the dependence of the results for the first vertical excitation energy on the size of the quantum system provides a clear illustration on this issue.

4. Conclusions

The electronic properties of liquid HF were investigated by carrying out quantum mechanical calculations over configurations generated by Born–Oppenheimer molecular dynamics. The average dipole moment of liquid HF increases by ~0.5 D from the gas to the liquid phase. Comparison between the gas and liquid phases isotropic polarisabilities indicates a small increase (less than 5%) of the polarisability for the liquid, a tendency opposite to that one observed for liquid water, where recent results stress the importance of a sequential quantum mechanical/BOMD approach to the electronic properties of liquid HF. Moreover, a sequential approach makes possible calculations of the HF intramolecular flexibility and many-body polarisation interactions, it was also found that the first excitation energy of liquid HF is blue-shifted relative to the gas-phase. From EOM-CCSD calculations, it was also found that the first excitation energy of liquid hydrogen fluoride is blue-shifted by ~0.4 ± 0.2 eV relative to the gas-phase value. This is smaller than the value for liquid water, where recent calculations predicted a small decrease of the isotropic polarisability of the liquid relative to the gas-phase [31]. From EOM-CCSD calculations, it was found that the first excitation energy of liquid hydrogen fluoride is blue-shifted by ~0.4 ± 0.2 eV relative to the gas-phase value. This is smaller than the value for liquid water, where a blue-shift of ~0.96 eV is observed [48]. The present results stress the importance of a sequential quantum mechanical/BOMD approach to the electronic properties of liquid HF. Firstly, the structure predicted by BOMD is in better agreement with experimental information than those relying on effective intermolecular potentials for liquid phase. The implicit treatment of the HF intramolecular flexibility and many-body polarisation effects are certainly relevant for improving the description of liquid HF. Moreover, a sequential approach makes possible calculations of the electronic properties through high level ab initio methods. By adopting an adequate representation for the electrostatic embedding, sequential ab initio/BOMD calculations open the way for an accurate prediction of the electronic properties in condensed phases.

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