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Ab initio calculations of anharmonic vibrational spectroscopy for hydrogen fluoride $(HF)_n$ (n=3,4) and mixed hydrogen fluoride/water $(HF)_n(H_2O)_n$ (n=1,2,4) Clusters

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Abstract

Anharmonic vibrational frequencies and intensities are computed for hydrogen fluoride clusters $(HF)_n$ with n=3,4 and mixed clusters of hydrogen fluoride with water $(HF)_n(H_2O)_n$ where n=1,2. For the $(HF)_4(H_2O)_4$ complex, the vibrational spectra are calculated at the harmonic level, and anharmonic effects are estimated. Potential energy surfaces for these systems are obtained at the MP2/TZP level of electronic structure theory. Vibrational states are calculated from the potential surface points using the correlation-corrected vibrational self-consistent field (CC-VSCF) method. The method accounts for the anharmonicities and couplings between all vibrational modes and provides fairly accurate anharmonic vibrational spectra that can be directly compared with experimental results without a need for empirical scaling.

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For $(HF)_n$, good agreement is found with experimental data. This agreement shows that the MP2 potential surfaces for these systems are reasonably reliable. The accuracy is best for the stiff intramolecular modes, which indicates the validity of MP2 in describing coupling between intramolecular and intermolecular degrees of freedom. For $(HF)_n(H_2O)_n$ experimental results are unavailable. The computed intramolecular frequencies show a strong dependence on cluster size. Intensity features are predicted for future experiments.

I. Introduction

Theoretical computations of molecular vibrations have become very common practice for interpretation of experimental infrared spectra. Moreover, theoretical calculations are often used to predict vibrational spectra in guidance of future experiments. Many electronic structure algorithms obtain vibrational frequencies in the harmonic approximation. However, this level is often inadequate for direct comparison with experimental data. Indeed, not only can the magnitude of anharmonic effects be such as to make them essential in the interpretation of spectroscopic experiments, but also the anharmonic contributions to the spectra include information on the anharmonic part of the potential energy surface, which is of great interest. Comparison of theoretical calculations with experimental data can be used to test the computed anharmonic part of the potential energy surface, provided that the vibrational states are obtained by a method that incorporates anharmonic effects. Such calculations of vibrational spectroscopy beyond the harmonic approximation for systems where the anharmonic effects are large is our goal here. Very often, in order to bring theoretical calculations of force fields into better agreement with experimental frequencies, a variety of empirical scaling techniques is used, including scaling of harmonic vibrational frequencies (see reference 1 for a review), and the scaled quantum mechanical (SQM) technique, where different scaling factors are assigned to different force constants before normal mode analysis is performed[2]. Regardless of the merits of scaling methods in predicting frequency values in better agreement with experiment[1,2], it is important to note that these methods do not address the problem treated here, which is to compute vibrational states using the anharmonic potential energy surface, and in this way make possible the testing of the anharmonic interactions by experimental spectroscopy. One of the theoretically based methods used for computing polyatomic spectroscopy beyond the harmonic approximation is the vibrational self-consistent field (VSCF) method and its correlation-corrected extensions[3-10]. Though based on the separability approximation, VSCF method accounts for anharmonicities and couplings between vibrational modes and provides a substantial improvement over the harmonic level, bringing the calculated frequencies into much closer agreement with experiment. With the use of empirical potentials, this method has been successfully applied to highly anharmonic systems including water clusters[10] and biological systems: peptide-water complexes[11] and the protein BPTI with hydration water molecules[12,13]. Recently, our group has developed an algorithm that combines this anharmonic vibrational spectroscopy method with direct calculation of accurate potentials from electronic structure codes[14,15]. The main advantage of this approach that uses *ab initio* potential points calculated on grids is its generality and applicability to any chemical system of the moderate size of up to 12-15 atoms, including highly anharmonic hydrogen-bonded systems. There is no need to fit an analytic form of the potential function, and there is no need to calculate very expensive higher (third and fourth) order derivatives. The CC-VSCF program is built into the electronic structure package (GAMESS[16]) which makes calculations of anharmonic frequencies user friendly and straightforward. In addition, transitions other than fundamental (overtone and combination excitations) can be also obtained, as well as the corresponding IR intensities.

In our previous work[17], this method has been applied to a number of weakly bound hydrogen-bonded complexes including water clusters, complexes of negatively (Cl^-) and positively (H^+) charged ions with water and complexes of methanol with water. The second-order Møller-Plesset (MP2)[18] level of electronic structure theory, together with a reasonably large Dunning's triple-ζ + polarization (TZP) basis set[19] was found to provide accurate enough potential energy surfaces. For the above hydrogen-bonded systems, where experimental infrared spectra are available, the results showed good agreement between the calculated and experimental frequencies, with the typical deviations of the order of 30–50 cm^{-1}. Though this accuracy is still far from the spectroscopic accuracy, it is a substantial improvement over the harmonic level theoretical predictions. The errors of this approach are much more consistent and transferable than those obtained with scaling techniques. The direct CC-VSCF method in conjunction with the MP2/TZP ab initio potentials was also applied to hydrogen-bonded and ionic clusters of $(HCl)_n(NH_3)_n$ and $(HCl)_n(H_2O)_n$[20] where the anharmonic effects for the proton stretching motions involved in hydrogen or ionic bonding were found to be very large (from 120 to 400 cm^{-1}). To correct for these anharmonicities by scaling techniques, scaling factors would have to range from 0.96 to 0.76.

In this paper, we examine clusters of hydrogen fluoride $(HF)_n$ with n=3,4 and mixed clusters of hydrogen fluoride with water $(HF)_n(H_2O)_n$ where n=1,2, and 4. A study of these systems by the method employed here is particularly useful for two reasons. First, these systems are strongly anharmonic. The stiff modes such as OH stretches that are experimentally very accessible, and for which the present version of the method is best geared, are strongly anharmonic. Second, empirical force fields of suitable quality are unavailable. Thus, the use of a method that computes spectroscopy from ab initio potential surface points is essential. Vibrational spectra of $(HF)_n$ clusters have been previously studied by experimental and theoretical techniques, while practically no data is available for the mixed HF/ H_2O clusters. The main objective of our present study is to compute *anharmonic* vibrational spectra for these clusters using ab initio potential energy surfaces and the direct correlation corrected vibrational self-consistent field (CC-VSCF) approach in order to assist in interpretation of experimental data on $(HF)_n$ clusters and predict vibrational spectra of mixed $(HF)_n(H_2O)_n$ clusters. In addition, geometrical and vibrational properties of the later clusters will be compared with those of the $(HCl)_n(H_2O)_n$ clusters obtained previously[20]. The structure of the article is as follows: In Section II, the methodology is briefly presented. The results and the analysis are the topics of Section III. Concluding comments are given in Section IV.

II. Methodology

All ab initio calculations in this study are performed using the second-order Møller-Plesset (MP2) level of electronic structure theory[18] with Dunning's triple-ζ + polarization (TZP)[19] basis set. The electronic structure package GAMESS[16] is used for these calculations. The equilibrium geometries of the complexes are optimized using analytic gradients. Second derivative (Hessian) matrices are calculated numerically using double differencing of analytic gradients. Previous studies showed that this level of theory gives satisfactory results compared with larger basis sets[17,20]. Anharmonic vibrational frequencies are obtained using vibrational self-consistent field (VSCF) method[3,4] and its correlation corrected (CC-VSCF) extension via second-order perturbation theory[10]. The calculations are performed using the combined ab initio / VSCF approach described in detail previously[14]. This method employs a grid over a region of the space of normal coordinates, which covers the domain of nuclear configurations relevant to the vibrational states computed. The potential energy values are computed for these grid points directly from the ab initio program. For the smaller clusters considered in this study, HF-H_2O and $(HF)_3$, the potential values are calculated on more dense grids, with the total number of points being 9360 and 17088, respectively. The number of potential energy points computed for the larger systems, $(HF)_4$ and $(HF)_2(H_2O)_2$, is 9936 and 17856, respectively. The same MP2/TZP ab initio level used to obtain equilibrium structures and harmonic normal modes, is also used to obtain potential energies on grids. The question of whether the MP2 level of ab initio theory is sufficient is an important issue, and comparison with spectroscopic experiments provides a test of this. It should be noted that vibrational spectroscopy is sensitive to the shape of the multidimensional potential energy surface. The accuracy needed here is of the potential energy landscape, rather than, e.g. the absolute energy at one point such as the minimum configuration. For this purpose, it is essential to have a method that can effectively compute many potential surface points, and do so with consistent accuracy. Any conclusions on the spectroscopic accuracy of the potential may differ considerably from these of the minimum energy point tests.

The VSCF method is based on a separability approximation[3,4], that reduces the problem of solving the N-dimensional vibrational Schrödinger equation for the N-mode system to solving N single-mode VSCF equations of the form:

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial Q_j^2}+\bar{V}_j^{(n_j)}(Q_j)\right]\psi_j^{(n_j)}=\varepsilon_n\psi_j^{(n_j)} \qquad (1)$$

where $\bar{V}_j^{(n_j)}(Q_j)$ is the effective VSCF potential for mode Q_j :

$$\bar{V}_j^{(n_j)}(Q_j)=\left\langle\prod_{l\neq j}^{N}\psi_l^{(n_l)}(Q_l)\middle|V(Q_1,\dots,Q_N)\middle|\prod_{l\neq j}^{N}\psi_l^{(n_l)}(Q_l)\right\rangle \qquad (2)$$

$V(Q_1,\dots,Q_N)$ is the full potential of the system. The total vibrational state of the system in this approximation is given by $\Psi=\prod_j^N\psi_j^{(n_j)}(Q_j)$.

The above (1)-(2) equations are solved self-consistently. The resulting solutions are further corrected for correlation effects between the vibrational modes using second order perturbation theory (CC-VSCF)[10].

The following approximation for the potential is used[10]: the potential of the system is represented by the sum of separable (single mode) terms and pair coupling terms, neglecting interactions of triples of normal modes and higher-order interactions

$$V(Q_1,\dots,Q_N)=\sum_j^N V_j^{diag}(Q_j)+\sum_i^{N-1}\sum_{j>i}^{N}V_{ij}^{coup}(Q_i,Q_j) \qquad (3)$$

Experience from previous applications to other hydrogen-bonded systems[17,20] supports the validity of this approximation, though in principle it must be tested carefully for each new system. "Diagonal" (single-mode) terms $V_j^{diag}(Q_j)=V(0,\dots,Q_j,\dots,0)$ and the pairwise mode-mode coupling terms $V_{ij}^{coup}(Q_i,Q_j)=V(0,\dots,Q_i,\dots,Q_j,\dots,0)-V^{diag}(Q_i)-V^{diag}(Q_j)$ were calculated directly from the ab initio program on 16 point grids along each normal coordinate, and on 16x16 square grids for each pair of normal coordinates. For larger clusters (with N≥18) 8x8 point grids were calculated and subsequently interpolated into 16x16 point grids using polynomial interpolation. The one-dimensional VSCF equations were solved numerically employing the collocation method of Yang and Peet[21]. This technique was shown to work reasonably well for water clusters and other hydrogen-bonded systems studied previously, and to predict anharmonic frequencies for the highest frequency stretching vibrations with the accuracy of 30-50 cm^{-1} compared with experiment[17]. The VSCF method in its present version can however be seriously in error for very soft modes in extremely floppy systems. We refer for instance to the strongly coupled, highly anharmonic soft modes of $(HF)_2$. For these, the near-separability assumed in VSCF breaks down. Extensive experience has shown that even in such systems the stiff mode excitations are correctly predicted. Furthermore, the larger clusters such as $(HF)_n$, $(H_2O)_n$, where $n > 2$, are considerably stiffer than the dimers, and in these cases CC-VSCF is expected to work better even for the soft modes.

In addition to anharmonic vibrational frequencies, the anharmonic IR intensities are calculated in this study using the ab initio dipole moments computed along the normal coordinates Q_i:

$$I_i = \frac{8\pi^3 N_A}{3hc}\omega_i \left|\left\langle \psi_i^{(0)}(Q_i)\middle|\vec{\mu}(Q_i)\middle|\psi_i^{(m)}(Q_i)\right\rangle\right|^2 \qquad (4)$$

where ω_i is the CC-VSCF vibrational frequency for the normal mode i; $\psi_i^{(0)}$ and $\psi_i^{(m)}$ are the VSCF wave functions for the ground and the m-th excited vibrational states.

III. Results and discussion

$(HF)_n$ complexes

While there is extensive experimental and theoretical data on infrared spectra of hydrogen fluoride dimer (see for example references 22,23 that provide very accurate six-dimensional ab initio HF dimer potential energy surface, as well as comprehensive overview of theoretical and experimental results available for this system), the spectroscopy of larger HF clusters is far from being complete. Experimental vibrational spectra have not been definitely assigned yet[24,25]. In ref. 25, experimental rotationally-resolved spectrum for HF tetramer was obtained, and harmonic frequencies computed at high (MP2 and CCSD(T)) levels of ab initio theory were used to assist in interpretation of experimental results. It was concluded that anharmonic corrections are necessary for direct comparison of calculated and experimental vibrational frequencies, and for correct interpretation of the experimental data. Especially troublesome are H-F stretching vibrations that are shifted to the red due to hydrogen bonding effects and are highly anharmonic. Unfortunately, anharmonic vibrational spectroscopy calculations employing CCSD(T) potential energy surfaces are not feasible at the present time. Here, we attempt to clarify the experimental assignments made in references 24 and 25 using lower level ab initio level (MP2/TZP), but providing anharmonic results for vibrational frequencies and infrared intensities.

The MP2/TZP geometrical structures of the lowest cyclic isomers of hydrogen-bonded HF trimer and tetramer are shown in Figure 1. They have C_{3h} and C_{4h} symmetry, respectively. Our calculated H-F distances are somewhat (0.05-0.07 Å) shorter than those obtained at higher levels of ab initio theory (e.g., CCSD(T) with larger basis sets[25]). This results in higher harmonic frequencies for H-F stretching vibrations. However, we expect anharmonic corrections also to be somewhat higher at our level, which should compensate the overestimated harmonic frequencies in the present calculations. Harmonic and anharmonic (CC-VSCF) vibrational frequencies estimated using the MP2/TZP potential energy surfaces are given in Tables 1 (HF trimer) and 2 (HF tetramer). It should be noted that these highly symmetric systems have several sets of doubly degenerate vibrational frequencies. However, the VSCF procedure we use does not preserve symmetry, and therefore the degenerate vibrational frequencies are often split at the CC-VSCF level due to numerical errors. The magnitude of splittings is within the errors of the CC-VSCF method, which is of the order of 30-50 cm^{-1}. Work is in progress to correct for this flaw by constructing symmetry-adapted VSCF wave functions. Despite the missing treatment of symmetry, CC-VSCF frequencies are significantly improved compared with the harmonic level and are much closer to experimental values. Table 1 shows that the HF trimer has two degenerate H-F stretching frequencies with high intensities (about 600 km/mol), that are predicted to be located at about 3655-3660 cm^{-1} by the CC-VSCF calculation. This is about 350 cm^{-1} below the H-F stretch of the isolated HF molecule (CC-VSCF value of which is 4008 cm^{-1}). The calculated result is somewhat lower, but is still in a good agreement with experimental value 3702 cm^{-1} obtained for $(HF)_3$ in solid Ar matrix[26]. The doubly degenerate in-plane modes are calculated at 460-480 cm^{-1} vs. experimental value in Ar of 446 cm^{-1}. There are two more IR active vibrations in this system: out-of-plane vibration predicted at about 640 cm^{-1} and doubly degenerate intermolecular stretch at about 160-170 cm^{-1}. Unfortunately, experimental data for these vibrations is not available. The HF tetramer also has very intense degenerate H-F stretching transitions (Table 2). They have much higher intensities (about 1500 km/mol) and lower frequencies (by about 200 cm^{-1}) than the HF trimer. These frequencies are predicted to appear at 3426 cm^{-1} by our calculations and are very close to experimental values of 3445 cm^{-1} measured by Blake et al.[25] and 3453 cm^{-1} obtained by Huisken et al. and assigned to $(HF)_5$[24]. Our calculations confirm that this transition should be assigned to the doubly degenerate H-F stretch of the HF tetramer, rather than to higher order HF clusters. Two other doubly degenerate IR active vibrations that are calculated at 773 cm^{-1} (in-plane torsion) and 241 cm^{-1} (intermolecular F-F stretch) are also in a good agreement with the observed values of Blake et al.[25]: 753 cm^{-1} and 195 cm^{-1}, respectively. The out-of-plane frequency is however overestimated in our calculation (824 cm^{-1} vs. measured 715 cm^{-1}). Our previous experience shows that the level of calculation used here (CC-VSCF combined with the MP2/TZP level of ab initio theory) gives very good results for high frequency stretching modes, but may be somewhat less accurate for low frequency torsional vibrations. We are quite confident that the method used here predicts the H-F stretching vibrations within about 30 cm^{-1} accuracy and they can be directly compared with experimental measurements and assist in its interpretation. The anharmonic corrections are found to be very high (over 300 cm^{-1}) for H-F stretches of the HF trimer and tetramer, much higher than those of the isolated

HF molecule or the HF dimer (which are of the order of 200 cm^{-1}). The anharmonicity for the degenerate IR active H-F stretching vibration in the HF tetramer is found to be almost 350 cm^{-1}, which explains the previous difficulties of harmonic level ab initio calculations to assign these frequencies correctly. The general conclusion from this part is that the MP2 potential surfaces for $(HF)_n$ seem quite reliable. The good results, especially for the stiff modes, suggest that the potentials account for the interactions between the intramolecular and intermolecular modes reasonably well. As we noted, vibrational spectroscopy tests mostly the shape of the potential energy surface, and it seems that the shapes are correctly described at the MP2 level.

$(HF)_n(H_2O)_n$ *complexes*

The geometries of 1:1 and 2:2 complexes of hydrogen fluoride with water are shown in Figure 2. Also shown are partial charges, obtained using the Löwdin population analysis[27]. These complexes have hydrogen-bonded structures similar to those of the small hydrogen chloride/water complexes[20]. The geometrical parameters and the dissociation energy of the $H_2O\cdots HF$ complex calculated in this study (MP2/TZP level of theory) are in good agreement with those obtained at the MP2 level of theory with larger, augmented correlation-consistent basis sets[28]. The length of the O···H hydrogen bond in the $H_2O\cdots HF$ complex is 1.70 Å. This is much shorter than the O···H hydrogen bond in the $H_2O\cdots HCl$ complex (1.86 Å)[20] and in the H_2O dimer (1.92 Å)[17]. It is also shorter than the F···H hydrogen bond in the HF dimer (1.84 Å) at the same level of ab initio theory. The dissociation energy (D_e) of the $H_2O\cdots HF$ complex is about 8.4 kcal/mol (when basis set superposition error (BSSE) correction is included), which is also much higher than the dissociation energies of the $H_2O\cdots HCl$ complex[20] and of the H_2O dimer. The exceptional strength of the $H_2O\cdots HF$ hydrogen bond leads to significant elongation of the H-F bond, by 0.016 Å compared with the isolated HF molecule. This in turn leads to a significant (about 400 cm^{-1}) red shift for the H-F stretching frequency in the $H_2O\cdots HF$ complex: from 4008 in the isolated HF down to 3632 cm^{-1} in the complex. The intensity of this stretching vibration is enhanced by about a factor of 8. All calculated fundamental vibrational frequencies for the $H_2O\cdots HF$ are given in Table 3.

$(HF)_2(H_2O)_2$ complex also has a hydrogen-bonded structure (Fig.2), but it is much more strongly bound than the 1:1 complex. This structure has two very strong $H_2O\cdots H\text{-}F$ hydrogen bonds, with the length of only 1.564 Å. The H-F bonds participating in this hydrogen bonding are elongated by 0.04 Å, as compared with the free HF distance. This elongation is much larger than in the 1:1 complex and the hydrogen bonds are much stronger. The $H_2O\cdots HF$ hydrogen bonds in the $(HF)_2(H_2O)_2$ complex are also much stronger than the $HF\cdots HF$ hydrogen bonds in the $(HF)_4$ cyclic complex (see Fig.1), and the $H_2O\cdots HCl$ hydrogen bonds in the $(HCl)_2(H_2O)_2$ complex[20]. In addition to these two very strong $H_2O\cdots HF$ hydrogen bonds, $(HF)_2(H_2O)_2$ complex also has two weaker $HOH\cdots FH$ hydrogen bonds, with the lengths of 1.816 Å. The binding energy of the $(HF)_2(H_2O)_2$ complex is about 30 kcal/mol, almost 4 times that of the 1:1 complex. It is also higher than the binding energy of the $(HCl)_2(H_2O)_2$ complex (which is about 20 kcal/mol)[20]. The calculated harmonic and CC-VSCF corrected vibrational frequencies of the $(HF)_2(H_2O)_2$ complex are listed in Table 4. It can be seen from the table that one of the H-F stretches has a very high intensity. Its anharmonic frequency is calculated to be 3013 cm^{-1}, more than 600 cm^{-1} lower than the H-F stretching frequency of the 1:1 $H_2O\cdots HF$ complex and almost 1000 cm^{-1} lower than the H-F stretching frequency of the isolated HF molecule. The intensity of this H-F stretch is calculated to be 25 times that of free HF. This vibration is a good candidate for experimental observation. In addition, there are two O-H stretches that have high intensities and thus should be also observable. Their calculated anharmonic frequencies are 3426 and 3689 cm^{-1}.

While smaller (1:1 and 2:2) complexes of HF and H_2O have only hydrogen-bonded structures, larger (4:4) complex already has two minima on the potential energy surface: one is hydrogen-bonded and another one is ionic. Their structures (as well as the partial charges) are shown in Fig. 3. For the analogous cubic 4:4 complex of HCl with H_2O, the ionic isomer corresponds to the global minimum[20]. In the case of HF, the ionic isomer is about 16 kcal/mol higher than the hydrogen-bonded one. The binding energy of the ionic structure is 67 kcal/mole at the MP2/TZP level, similar to that of the ionic isomer of $(HCl)_4(H_2O)_4$. However, the hydrogen-bonded isomer of the $(HF)_4(H_2O)_4$ is much more strongly bound than the corresponding isomer of the $(HCl)_4(H_2O)_4$ (83 vs. 55 kcal/mol). The reason is that although this isomer still has HF and H_2O fragments and can be viewed as hydrogen-bonded, it has a very significant ionic character. Its H-F fragments are much more ionic than the H-Cl fragments in the corresponding $(HCl)_4(H_2O)_4$ hydrogen-bonded complex[20]: e.g, the charges on the F atoms are –0.30, while the corresponding charges of the Cl atoms are only –0.18. Smaller (1:1 and 2:2) hydrogen-bonded complexes of HF with H_2O are also very ionic, but the ionic character increases as the size of the cluster grows. As a consequence, the 4:4 hydrogen-bonded isomer is considerably stabilized relative to the 1:1 and 2:2 complexes. The length of the H-F bonds increases with the size of the complex: from 0.933 Å in the 1:1 complex to 0.957 Å in the 2:2 complex to 0.974 Å in the 4:4 complex (for comparison, its value is 0.917 Å in the isolated HF molecule). At the same time, the length of the $FH \cdots OH_2$ hydrogen bond decreases to 1.497 Å, compared with 1.564 Å in the 2:2 complex and 1.705 Å in the 1:1 complex.

Although the $(HF)_4(H_2O)_4$ ionic structure is higher in energy than the hydrogen-bonded one, it also corresponds to a stable minimum on the potential energy surface. This structure has four equivalent H_3O fragments with all three O-H bonds pointing towards F atoms that have much larger negative charge on them (-0.54). This structure can be viewed as $[(H_3O)^+]_4\ [F^-]_4$, though the partial charges are far from ±1 and are closer to ±0.5.

The calculated harmonic vibrational frequencies for both isomers are given in Table 5. Only frequencies above 1000 cm^{-1}, as well as the corresponding intensities, are presented. Vibrational frequencies of these complexes (especially the ones that correspond to stretching vibrations) can be expected to be very anharmonic, even to a higher extent than the stretches of the smaller (1:1 and 2:2) complexes. However, CC-VSCF calculations for such large (20 atom) systems are not feasible at the present time (due to the large number of required potential surface points). Therefore, here we present only estimates for anharmonic corrections, that are based on the CC-VSCF results for smaller complexes. The harmonic data in Table 5 already shows very interesting features of vibrational spectra of both hydrogen-bonded and ionic isomers. The hydrogen-bonded structure has two very intense H-F stretches at about 3000 and 3100 cm^{-1} (harmonic values). Anharmonic effects (that should be about 300 cm^{-1} for the H-F and O-H stretches), lead to estimated H-F stretching frequencies of approximately 2700 and 2800 cm^{-1}. Similar estimates suggest that the four asymmetric O-H stretches of the hydrogen-bonded structure should be located around 3600 cm^{-1}, while the four symmetric O-H stretches should appear 100 cm^{-1} below, around 3500 cm^{-1}. The O-H stretches of the ionic structure (that are IR active) are located in the region of 3060 and 2975 cm^{-1} in the harmonic approximation, and probably shift to about 2750 cm^{-1} and 2650 cm^{-1} when anharmonicity is included. These frequencies in the region of about 2650-2750 cm^{-1} are much lower than those of free O-H stretches (~3700 cm^{-1}) or hydrogen-bonded O-H stretches (~3400-3600 cm^{-1}) and can serve as fingerprints of the $(HF)_4(H_2O)_4$ ionic structure for experimental identification. Finally, the lessons of the previous study on $(HCl)_n(H_2O)_n$, and the trend found here also for $(HF)_n(H_2O)_n$ suggest an interesting conjecture: that the 1:1 solid of H_2O and HF should be ionic, since the stability of the ionic structure grows with cluster size. For HCl-H_2O, the hydronium chloride solid is indeed known to be ionic.

IV. Conclusions

In this study, ab initio MP2/TZP potential energy surfaces are employed to compute anharmonic vibrational spectra for the hydrogen-bonded $(HF)_n$ (n=3,4) and $(HF)_n(H_2O)_n$ (n=1,2) complexes. The correlation-corrected vibrational SCF (CC-VSCF) method is used which explicitly includes anharmonicity and coupling between different normal modes in the calculated vibrational frequencies. Anharmonic effects in these systems are found to be very large, and their incorporation to be crucial for prediction of reliable vibrational spectra. For larger $(HF)_4(H_2O)_4$ complexes harmonic vibrational frequencies are calculated, and anharmonic corrections are estimated based on the results for the smaller complexes.

For HF complexes the highest IR active H-F stretching vibrations are calculated at 3659 cm^{-1} and 3426 cm^{-1} for HF trimer and tetramer, respectively. These are in good agreement with experimental results and help to assign experimental data in questionable cases. Our calculations show very high anharmonicities for these F-H stretching vibrations, which are of the order of 300-350 cm^{-1}. These anharmonicities are even slightly higher than those of O-H stretches in the corresponding water clusters. The agreement between theory and experiment for $(HF)_n$ shows the ability of the MP2 ab initio level to describe the shape of potential energy surfaces for these systems with acceptable accuracy. The quality of the agreement for the stiff intramolecular frequencies suggests that coupling of intramolecular and intermolecular modes is quite accurately represented at this level.

Small (1:1 and 2:2) complexes of HF with H_2O are found to have hydrogen-bonded structures. The H-F fragments of these complexes have much longer bond distances and higher ionic character than the isolated HF molecule and the H-F fragments of the $(HF)_n$ clusters. This results in a very large red shift of the H-F stretching frequency in these complexes accompanied by a significant increase of its infrared intensity. The red shift is about 400 cm^{-1} in the 1:1 complex and almost 1000 cm^{-1} in the 2:2 complex. For the 4:4 complex, besides the strongly bound hydrogen-bonded isomer, ionic isomer is found to correspond to a local minimum. The ionic structure is higher in energy than the hydrogen-bonded one for the gas phase complexes, but may become more stable in matrix environments with high polarization effects. For the ionic isomer, extremely intense transitions are predicted in regions very different from those of free HF and H_2O molecules and from those of the hydrogen-bonded complexes. Both hydrogen-bonded and ionic complexes have very unique spectroscopic features and are promising candidates for experimental identification.

Finally, the results for both $(HF)_n$ and $(HF)_m(H_2O)_m$ show that spectroscopy and coupling of vibrational modes in such systems would be extremely challenging to obtain by empirical potentials. It seems obvious that only very sophisticated empirical potentials, including strong polarization effects could possibly be successful. Perhaps the multiple ab initio potential surface points generated in the course of this study could be used in the future to fit and develop such polarizable potential functions.

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References

1. Scott, A. P. ; Radom, L. *J. Phys. Chem.*, **1996**, *100*, 16502.

2. (a) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037. (b) Allen, W. D.; Császár, A. G.; Horner, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 6834.

3. J. M. Bowman. *J. Chem. Phys.* **1978**, 68, 608.

4. R. B. Gerber and M. A. Ratner. *Chem. Phys. Lett.* **1979**, 68, 195.

5. J. M. Bowman, *Acc. Chem. Res.* **1986**, 19, 202.

6. R. B. Gerber and M. A. Ratner, *Adv. Chem. Phys.* **1998**, 70, 97.

7. L. S. Norris, M. A. Ratner, A. E. Roitberg, and R. B. Gerber, *J. Chem. Phys.* **1996**, 106, 11261.

8. S. Carter, S. J. Culik, and J. M. Bowman, *J. Chem. Phys.* **1997**, 107, 10459.

9. J.-O. Jung and R. B. Gerber, *J. Chem. Phys.* **1996**, 105, 10682.

10. J.-O. Jung and R. B Gerber, *J. Chem. Phys.* **1996**, 105, 10332.

11. S. K. Gregurick, E. Fredj, R. Elber, and R. B. Gerber, *J. Phys. Chem. B* **1997**, 101, 8595.

12. A. Roitberg, R. B. Gerber, R. Elber, and M. A. Ratner, *Science* **1995**, 268, 1319.

13. A. E. Roitberg, R. B. Gerber, and M. A. Ratner, *J. Phys. Chem.* **1997**, 101, 1700.

14. Chaban, G. M.; Jung, J.-O.; Gerber, R. B. *J. Chem. Phys.* **1999**, *111*, 1823.

15. Wright, N. J., Gerber, R. B. *J. Chem. Phys.* **2000**, *112*, 2598.

16. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comp. Chem.* **1993**, *14*, 1347.

17. Chaban, G. M.; Jung, J.-O.; Gerber, R. B. *J. Phys. Chem. A* **2000**, *104*, 2772.

18. J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem.* **1976**, *10*, 1.

19. T. H. Dunning, *J. Chem. Phys.* **1971**, *55*, 716.

20. Chaban, G. M.; Gerber, R. B.; Janda, K. C. *J. Phys. Chem. A* **2001**, *105*, in press.

21. W. Yang and A. C. Peet, *J. Chem. Phys.* **1990**, 92, 522.

22. Klopper, W.; Quack, M.; Suhm, M. A. *Chem. Phys. Lett.* **1996**, *261*, 35.

23. Quack, M.; Suhm, M. A. *Theor. Chim. Acta.* **1996**, *93*, 61.

24. Huisken, F.; Kaloudis, M.; Kulcke, A.; Laush, C.; Lisy, J. M. *J. Chem. Phys.* **1995**, 103, 5366.

25. Blake, T. A.; Sharpe, S. W.; Xantheas, S. S. *J. Chem. Phys.* **2000**, 113, 707.

26. Andrews L; Souter, P. F. *J. Chem. Phys.* **1999**, 111, 5995.

27. Löwdin, P.-O. *Adv. Quantum. Chem.* **1970**, *5*, 185.

28. Paizs, B.; Salvador, P.; Császár, A. G.; Duran, M.; Suhai, S. *J. Comp. Chem.* **2001**, 22, 196.

Table 1. Vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of fundamental excitations for HF trimer (MP2/TZP level of theory).

mode	frequencies			intensities	interpretation
	harmonic	CC-VSCF	experiment[a]		
1	3981	3659	3702	611	HF stretch
2	3981	3655	3702	604	HF stretch
3	3900	3575		0	HF stretch
4	886	835		0	
5	677	643		620	out-of-plane bending
6	511	485	446	391	in-plane bending
7	511	458	446	379	in-plane bending
8	456	445		0	
9	456	417		0	
10	201	187		0	
11	172	170		24	intermolec. stretch
12	172	162		24	intermolec. stretch

[a] experimental data in Ar matrix, reference 26.

Table 2. Vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of fundamental excitations for HF tetramer (MP2/TZP level of theory).

mode	frequencies			intensities	interpretation
	harmonic	CC-VSCF	experiment[a]		
1	3836	3562		0	HF stretch
2	3774	3426	3445	1520	HF stretch
3	3774	3426	3445	1520	HF stretch
4	3628	3338		0	HF stretch
5	1065	1023		0	
6	806	773	753	507	in-plane
7	806	773	753	507	in-plane
8	784	824	715	856	out-of-plane
9	651	693		0	
10	651	693		0	
11	616	635		0	
12	586	631		0	
13	267	254		0	
14	250	241	195	42	intermolec. stretch
15	250	241	195	42	intermolec. stretch
16	195	183		0	
17	83	81		0	
18	47	76		0	

[a] reference 25.

Table 3. Vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of fundamental excitations for HF···H_2O complex and H_2O and HF molecules (MP2/TZP level of theory).

	HF···H_2O complex			H_2O + HF			
mode	frequencies		intensities	frequencies		intensities	interpretation
	harm	CC-VSCF		harm	CC-VSCF		
1	4008	3736	99	4015	3797	49	OH stretch
2	3882	3650	24	3877	3691	5	OH stretch
3	3837	3632	881	4185	4008	111	HF stretch
4	1628	1559	83	1603	1547	77	H_2O bend
5	870	949	204				
6	706	858	242				
7	258	337	87				
8	245	522	4				
9	222	437	146				

Table 4. Vibrational frequencies (cm^{-1}) and IR intensities (km/mol) for the $(HF)_2$-$(H_2O)_2$ complex (MP2/TZP level of ab initio theory)

mode	frequencies		intensities	interpretation
	harm	CC-VSCF		
1	3975	3689	229	free OH str
2	3975	3724	48	free OH str
3	3734	3426	673	bonded OH str
4	3733	3480	3	bonded OH str
5	3403	3013	2834	HF stretch
6	3321	2916	0	HF stretch
7	1662	1616	43	H_2O bend
8	1655	1612	165	H_2O bend
9	1181	1166	4	
10	1081	1078	461	
11	941	971	609	
12	875	911	55	
13	655	745	182	
14	601	720	81	
15	459	599	60	
16	415	573	45	
17	326	328	35	F-O str
18	317	350	3	F-O str
19	262	500	55	
20	240	492	207	
21	210	284	18	F-O str
22	191	180	0	F-O str
23	84	118	3	F-F, O-O str
24	49	134	15	out of plane

Table 5. The highest (>1000 cm^{-1}) harmonic vibrational frequencies (cm^{-1}) and IR intensities (km/mol) for hydrogen-bonded and ionic $(HF)_4$-$(H_2O)_4$ complexes (MP2/TZP level of ab initio theory)

	H-bonded			ionic		
mode	harm. freq.	intens.	intrepretation	harm. freq.	intens.	interpretation
1	3890	539	asym OH str	3085	0	OH stretch
2	3881	319	asym OH str	3059	864	OH stretch
3	3881	319	asym OH str	3058	917	OH stretch
4	3869	0	asym OH str	3058	925	OH stretch
5	3790	0	sym OH str	2976	3618	OH stretch
6	3787	64	sym OH str	2976	3624	OH stretch
7	3787	64	sym OH str	2974	3695	OH stretch
8	3784	276	sym OH str	2670	0	OH stretch
9	3072	3227	HF stretch	2668	0	OH stretch
10	3072	3227	HF stretch	2667	0	OH stretch
11	3016	13	HF stretch	2667	0	OH stretch
12	2961	0	HF stretch	2664	0	OH stretch
13	1714	86	H_2O bend	1871	0	HOH bend
14	1694	87	H_2O bend	1871	0	HOH bend
15	1694	87	H_2O bend	1852	113	HOH bend
16	1687	0	H_2O bend	1852	113	HOH bend
17	1290	266		1852	113	HOH bend
18	1262	0		1749	0	HOH bend
19	1209	74		1749	0	HOH bend
20	1209	74		1749	0	HOH bend
21	1131	0		1612	0	H_3O^+ umbrella
22	1028	639		1460	1076	H_3O^+ umbrella
23	1010	400		1460	1076	H_3O^+ umbrella
24	1010	400		1460	1076	H_3O^+ umbrella

Figure captions

Figure 1. Equilibrium structures (angs.) of $(HF)_n$ complexes, n=3,4 (MP2/TZP level of ab initio theory).

Figure 2. Equilibrium structures (angs.) and partial charges of 1:1 and 2:2 hydrogen-bonded complexes of HF with H_2O obtained at the MP2/TZP level of ab initio theory.

Figure 3. Equilibrium bond lengths (angs.) and partial charges of the hydrogen-bonded and ionic compexes of 4 HF with 4 H_2O obtained at the MP2/TZP level of theory.

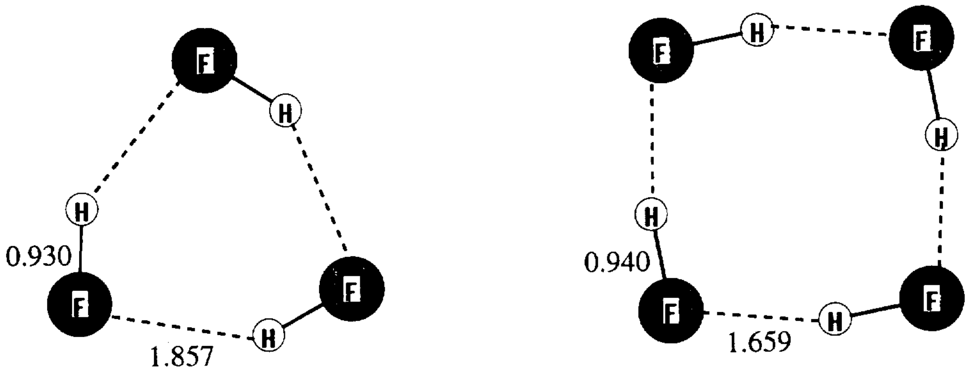


Figure 1. Equilibrium structures (angs.) of (HF)n complexes, n=3,4 (MP2/TZP level of ab initio theory).

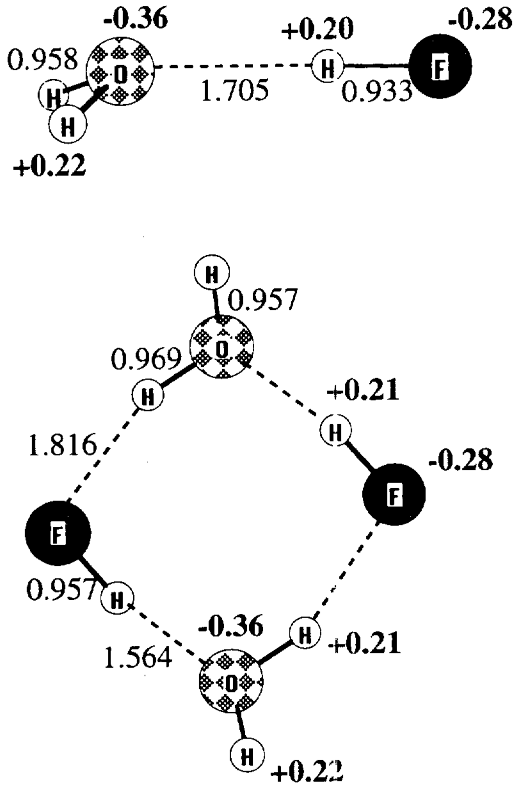
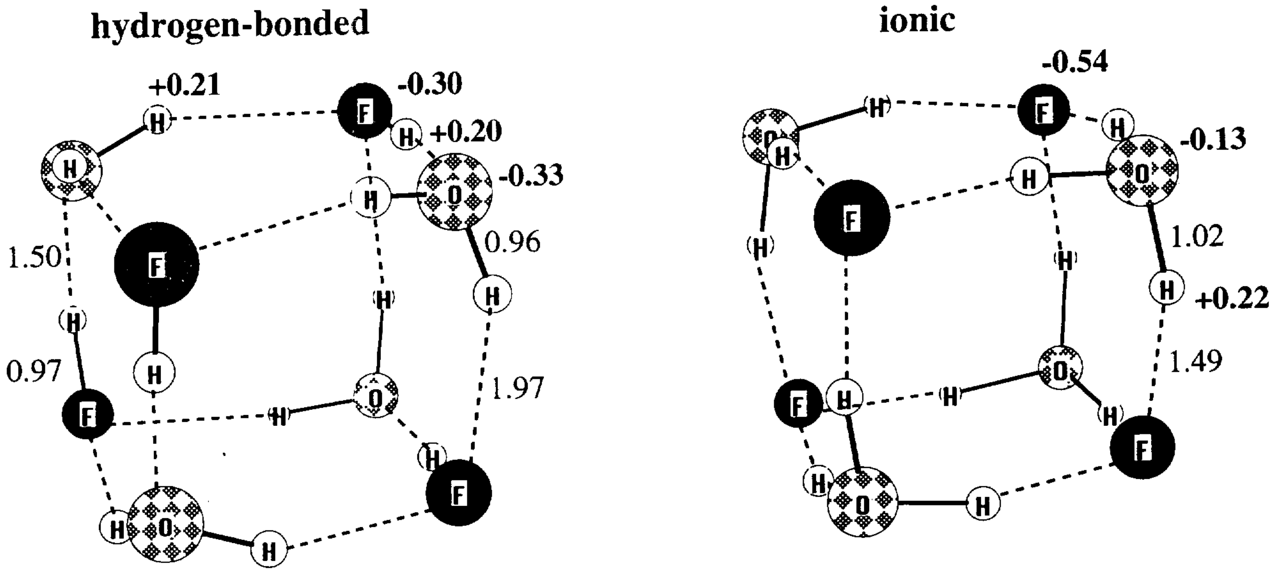


Figure 2. Equilibrium structures (angs.) and partial charges of 1:1 and 2:2 hydrogen-bonded complexes of HF with H_2O obtained at the MP2/TZP level of ab initio theory.


hydrogen-bonded

ionic

Figure 3. Equilibrium bond lengths (angs.) and partial charges of the hydrogen-bonded and ionic compexes of 4HF with $4H_2O$ obtained at the MP2/TZP level of theory.