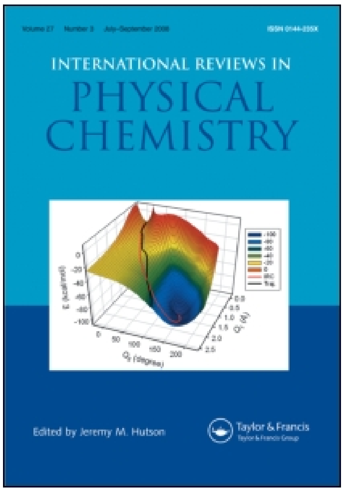

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Anharmonic vibrational spectra of hydrogen bonded clusters: comparison between higher energy derivative and mean-field grid based methods

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We present a comparison between two different approaches for calculating anharmonic frequencies, namely mean-field grid-based methods (VSCF, CC-VSCF, VCI) and those obtained by second-order perturbation theory from the third and fourth energy derivatives. For a meaningful comparison between the two approaches we report the results for the anharmonic frequencies with the two approaches for the $F^-(H_2O)$, $Cl^-(H_2O)$, HNO_3 and $HNO_3(H_2O)$ molecular systems at the same level of electronic structure theory and basis set. The two methods were found to produce results of similar accuracy for the origin of the fundamental band and selected overtone and combination bands. The optimal equilibrium and vibrationally averaged geometries, spectroscopic constants and anharmonic frequencies of the $(HF)_n$, $n = 2$–4 clusters are reported at the MP2/aug-cc-pVDZ level of theory based on calculations of higher energy derivatives and compared to previous results obtained from CC-VSCF calculations at the MP2/TZP level of theory.

Contents

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1. Introduction

It has long been established that the infrared (IR) spectra of hydrogen bonded clusters represent a fingerprint of the underlying hydrogen bonding network [1–3]. This is a direct consequence of the elongation of the hydrogen bonded stretch and the resulting red shift in the corresponding vibrational frequency in accordance with Badger's rule [4] but also of the fact that different cluster isomers (and in turn different hydrogen bonding networks) have dissimilar spectral signatures [2, 5]. This so-called 'structural–spectral' correspondence (i.e. the correlation between structures and spectra) has been previously successfully used for the assignment of cluster structures from the experimentally measured spectra [6]. The pioneering work of Roger E. Miller and coworkers [7] among others, has clearly played a major role in obtaining the experimental information needed for the assignment of cluster structures for many archetypal hydrogen bonded systems.

To a first approximation, which is associated with the least computational cost, the experimentally measured band origins (ν) are typically compared to the calculated harmonic (ω) vibrational frequencies obtained from first principles electronic structure calculations. This provides for a qualitative comparison between theory and experiment as the typical anharmonicities of the intramolecular stretching frequencies are in the range of $\sim$100–200 cm^{-1}. Oftentimes, the fact that the anharmonicities of the 'free' and 'hydrogen bonded' C–H, N–H, O–H or F–H stretches can be comparable in magnitude has been used as a guide in order to assign the spectra. This is achieved by comparing the calculated (harmonic, $\Delta\omega$) with the measured (anharmonic, $\Delta\nu$) *relative* shifts between the 'hydrogen bonded' and 'free' (non-hydrogen bonded) vibrations and making use of the approximate relation $\Delta\omega \approx \Delta\nu$. This approach is schematically shown in figure 1 for typical red shifts of the OH stretching vibrations in aqueous clusters and provides a crude (but oftentimes useful) approximation in the comparison between experiment and theory. Several scaling factors, depending on the level of electronic structure theory used, have been proposed [8] in order to be able to compare the (scaled) calculated harmonic frequencies to the measured anharmonic band origins in the region

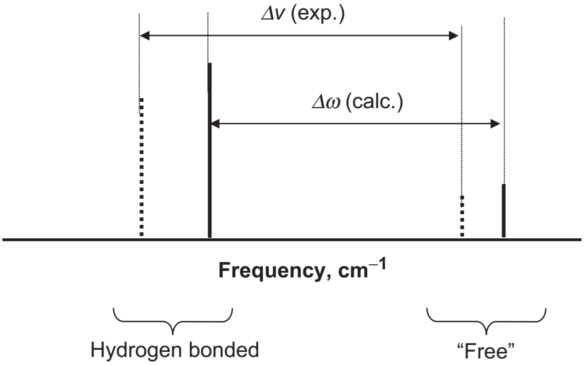

Figure 1. Harmonic ($\Delta\omega$) and experimental ($\Delta\nu$) frequency shifts due to hydrogen bonding.

of the IR spectra that probes the hydrogen bonding network (typically 3000–4000 cm^{-1}).

A more computationally demanding approach for the comparison between theory and experiment requires the calculation of the anharmonic frequencies. Given the complexity of the problem arising from the calculation of the full anharmonicities on a multidimensional potential energy surface (PES), a fact that can result in a computationally intractable problem as the size of the system increases, several approaches have been proposed for the efficient calculation of the anharmonic frequencies.

In recent years the Bowman and Gerber groups have developed computer codes that can calculate the ahnarmonic vibrational frequencies of polyatomic systems and clusters. Both approaches are based on the use of the Watson Hamiltonian [9] and the subtle differences in the two implementations are outlined in a recent review [10]. Following Gerber and coworkers [11] and Bowman and coworkers [12], the solution of the vibrational Schrödinger equation in mass-weighted normal mode coordinates Q_k:

$$\left[-\frac{1}{2}\sum_{k}^{N}\frac{\partial^2}{\partial Q_k^2}+V(Q_1,\ldots,Q_N)\right]\psi_n(Q_1,\ldots,Q_N)=E_n\psi_n(Q_1,\ldots,Q_N) \tag{1}$$

via a self-consistent procedure [13, 14] (VSCF) is the starting point in obtaining anharmonic frequencies at the equilibrium geometry. It should be noted that the above Hamiltonian, which is used by the Gerber group, does not include vibrational angular momentum terms and it is also limited to zero total angular momentum. These effects, which are usually either small or constant at the second order perturbation theory, are included in the implementation by the Bowman group. In the above expression $V=V(Q_1,\ldots,Q_N)$ is the potential and N is the number of vibrational degrees of freedom. The VSCF approximation is based on the approximation that the modes are separable, viz.

$$\psi_n(Q_1,\ldots,Q_N)=\prod_{k=1}^{N}\psi_k^{(n)}(Q_k), \tag{2}$$

which reduces the problem to solving the equations for each mode Q_k:

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial Q_k^2}+V_k^{eff}(Q_k)\right]\psi_k^{(n)}(Q_k)=\varepsilon_n\psi_k^{(n)}(Q_k) \tag{3}$$

with the effective potential

$$V_k^{eff}(Q_k)=\left\langle\prod_{\ell\neq k}^{N}\psi_\ell^{(n)}(Q_\ell)\middle|V(Q_1,\ldots,Q_N)\middle|\prod_{\ell\neq k}^{N}\psi_\ell^{(n)}(Q_\ell)\right\rangle, \tag{4}$$

which effectively couples in an average manner each mode Q_k with all the others. The self-consistent solution of equation (3) for each mode yields the mode energies, $\varepsilon_k^{(n)}$, and wavefunctions, $\psi_k^{(n)}$, from which the VSCF energy

$$E_n^{VSCF} = \sum_{k=1}^{N} \varepsilon_k^{(n)} - (N-1)\left\langle \prod_{k=1}^{N} \psi_k^{(n)}(Q_k) \middle| V(Q_1, \ldots, Q_N) \middle| \prod_{k=1}^{N} \psi_k^{(n)}(Q_k) \right\rangle \tag{5}$$

is obtained.

In parallel to the correlation problem in electronic structure theory, VSCF can be thought of as only the starting point in describing the mode correlations. To this end, higher inter-mode correlations that are based on second order perturbation theory [15] (VMP2) as well as on configuration interaction [16] (CI) expansions have been proposed. Those are based on either mixing a group of VSCF states, leading to a generalized eigenvalue problem (VSCF+CI) or on using the orthonormal basis of eigenfunctions of a single VSCF Hamiltonian, usually the one for the ground state (VCI).

Bowman and coworkers [17] have relied on a representation of the potential energy surface in terms of a hierarchical expansion of the normal coordinates Q_N according to

$$\begin{aligned} V(Q_1, Q_2, \ldots, Q_N) = {} & \sum_{i=1}^{N} V_i^{(1)}(Q_i) + \sum_{i,j=1}^{N} V_{ij}^{(2)}(Q_i, Q_j) + \sum_{i,j,k=1}^{N} V_{ijk}^{(3)}(Q_i, Q_j, Q_k) \\ & + \sum_{i,j,k,\ell=1}^{N} V_{ijk\ell}^{(4)}(Q_i, Q_j, Q_k, Q_\ell) + \cdots \end{aligned} \tag{6}$$

The potential is therefore expressed in terms of one-, two-, three-, $\ldots$, m-mode representations $V_{12\ldots m}^{(m)}(Q_1, Q_2, \ldots, Q_m)$, which are cuts along the normal mode coordinates $Q_1, Q_2, \ldots, Q_m$ with all remaining normal mode coordinates set to zero. In this scheme, the three-mode representation is exact for three-atom systems, the six-mode coupling is exact for four-atom systems, and so on.

The computational cost is associated with the evaluation of a grid of points on the multidimensional PES, using either *ab initio* electronic structure methods or classical potentials [18]. Typical grids of eight (for the diagonal) and 8×8 (for the two-mode correlations) are employed and the number of points, N_{points}, needed when casting equation (6) in just the diagonal and pair-coupling potentials on a grid is equal to [11]:

$$N_{points} = N_{mode} \bullet N_{grid} + \frac{1}{2} N_{mode} \bullet (N_{mode} - 1) \bullet N_{grid}^2. \tag{7}$$

An approach that is different than the one introduced by the Bowman and Gerber groups is the one that is based on second-order perturbation theory [19, 20] which provides closed expressions for most of the spectroscopic constants needed for obtaining anharmonic frequencies. Starting from the analytical second derivatives of the electronic energy with respect to the nuclear displacements at a particular level of *ab initio* theory, the third and semidiagonal fourth derivatives can be obtained by a finite difference approach. This procedure, which requires the evaluation of $(2n+1)$

second derivatives for a system with n normal modes can be very competitive when compared to the mean-field grid-based methods, especially with the recent advances in the efficient calculation of analytic energy derivatives and their efficient implementation on parallel computer architectures.

Following the formulation by Barone and coworkers [21, 22], the third energy derivatives with respect to normal coordinates, Φ_{ijk}, can be evaluated by numerical differentiation of the analytical second derivatives, Φ_{ij}, at small displacements δq according to:

$$\Phi_{ijk} = \frac{1}{3}\left[\frac{\Phi_{jk}(\delta q_i) - \Phi_{jk}(-\delta q_i)}{2\delta q_i} + \frac{\Phi_{ki}(\delta q_j) - \Phi_{ki}(-\delta q_{ji})}{2\delta q_j} + \frac{\Phi_{ij}(\delta q_k) - \Phi_{ij}(-\delta q_k)}{2\delta q_k}\right]. \tag{8}$$

The numerical calculation of the full fourth derivatives requires simultaneous displacements along two normal coordinates. For the evaluation of the ro-vibrational energies by second order perturbation theory the required even derivatives are obtained by performing displacements along a single normal coordinate to evaluate terms with at most three distinct indices [19, 22]

$$\Phi_{ijkk} = \frac{\Phi_{ij}(\delta q_k) + \Phi_{ij}(-\delta q_k) - 2\Phi_{ij}(0)}{\delta q_k^2} \tag{9}$$

and

$$\Phi_{iikk} = \frac{1}{2}\left[\frac{\Phi_{ii}(\delta q_k) + \Phi_{ii}(-\delta q_k) - 2\Phi_{ii}(0)}{\delta q_k^2} + \frac{\Phi_{kk}(\delta q_i) + \Phi_{kk}(-\delta q_i) - 2\Phi_{kk}(0)}{\delta q_i^2}\right]. \tag{10}$$

The vibrational Hamiltonian consists of the zero-order harmonic term (including a kinetic contribution from the vibrational angular momentum) and additional terms containing the contribution of cubic, quartic and higher components of the potential. A complete description of the rovibrational Hamiltonian and the subsequent evaluation of the spectroscopic constants and anharmonic frequencies is available in [22]. Barone and coworkers have implemented this procedure in the 'Prova' program, which interfaces with major electronic structure codes for the calculation of the anharmonic frequencies and rovibrational energies.

In this study we use this second approach (numerical evaluation of third derivatives and semidiagonal fourth derivatives) for the calculation of anharmonic vibrations for $(HF)_n$ clusters, $n = 2$–4. In section 2 we outline the details of the electronic structure calculations. In section 3 we first perform a comparison between the two approaches, viz. the use of a grid and the numerical evaluation of higher derivatives for various model systems and subsequently present the results for the $(HF)_n$ clusters, $n = 2$–4, and compare them with the experimentally available data. Final conclusions are presented in section 4.

2. Details of the electronic structure calculations

We used the numerical evaluation of higher derivatives as implemented in the Gaussian 03 [23] electronic software program. Since analytical evaluation of second derivatives is a prerequisite, we performed all calculations at the MP2 level of theory. The aug-cc-pVDZ basis set of Dunning and coworkers [24] was used to optimize the geometries of the monomer through tetramer clusters at the MP2 level of theory and obtain the harmonic vibrational frequencies analytically. For all geometry optimizations the 'verytight' criterion was used to ensure that the RMS force convergence criterion is $\leq 1 \times 10^{-6}$. Anharmonic frequencies and anharmonic vibrational–rotational couplings were computed by a perturbative evaluation including cubic force constants to second order and semidiagonal quartic constants to first order at the MP2 level of theory with the aug-cc-pVDZ basis set for the monomer through tetramer clusters. All electronic structure calculations were performed at the National Energy Research Scientific Computing Center (NERSC) at Lawrence Berkeley National Laboratory.

The comparison between mean-field grid-based methods (VSCF, CC-VSCF, VCI, etc.) and the approach based on higher energy derivatives, was performed for systems for which published data exist with the first approach. For a meaningful comparison we used the same level of theory and basis set that was employed in the mean-field grid-based methods from the Gerber and Bowman groups. We performed MP2 anharmonic calculations the $F^-(H_2O)$ [25], $Cl^-(H_2O)$ [26] and HNO_3, $HNO_3(H_2O)$ [27] clusters. For the first two we used the aug-cc-pVTZ basis set whereas for the last two the TZP basis set [28] was employed.

3. Results and discussion

3.1. *Comparison between higher energy derivative and mean-field grid-based methods for model systems*

The MP2/aug-cc-pVTZ anharmonic frequencies for the $F^-(H_2O)$ cluster obtained via the perturbative approach are compared with the corresponding ones previously reported [25] with the correlation-corrected VSCF (CC-VSCF) method in table 1 using a grid of points on the PES obtained at the same level of electronic structure theory with the same basis set. The experimental results [29] obtained from the Johnson group are also listed for comparison. In general there is very good agreement between the results of the two methods with typical differences ranging from 3 to 40 cm^{-1} with the exception of the very anharmonic ν_5 mode [30] for which the zero-order picture of a fluoride ion interacting with a water molecule breaks down due to the significant amplitude of the wave function corresponding to the $FH\cdot\cdot OH^-$ complex [29(b), 30].

The comparison between the perturbative approach and vibrational CI (VCI) is shown in table 2 for the $Cl^-(H_2O)$ cluster at the MP2/aug-cc-pVTZ level of theory. The VCI results [26] are obtained using the five mode-coupling approximation (equation (6)). It should be noted that VCI anharmonic results using a PES at a higher correlation level of theory [CCSD(T)] are available and those VCI//CCSD(T)/aug-cc-pVTZ results are in much better agreement with experiment than those at the MP2 level. However, as mentioned earlier, due to the current availability of analytical second energy derivatives at the MP2 level only, we have chosen to compare our results with the ones obtained at the VCI//MP2/aug-cc-pVTZ level for a meaningful comparison between the two approaches which is based on the same level of electronic structure theory for the PES. Again the typical differences between the two methods are very

Table 1. Comparison of anharmonic frequencies with the CC-VSCF and perturbative (including third derivative) approaches for $F^-(H_2O)$ at the MP2/aug-cc-pVTZ level of theory. Experimental results are also indicated.

Mode	Harmonic	CC-VSCF[a]	This work	Exp.[b]
ν_1	392.2	443	420.6	
ν_2	581.0	575	572.4	
ν_3	1176.8	1170	1208.6	1083–1250
ν_4	1698.5	1618	1609.5	1650
ν_5	2089.7	1450	917.3	
ν_6	3891.6	3691	3720.7	3687
$2\nu_5$	4179.4	2844		2905 ± 20

[a] Reference [25].
[b] References [29(a), 29(b)].

Table 2. Comparison of anharmonic frequencies with the VCI (five-mode coupling) and perturbative (including third derivative) approaches for $Cl^-(H_2O)$ at the MP2/aug-cc-pVTZ level of theory. Experimental results are also indicated.

Mode	Harmonic	VCI (5 mode-coupling)[a]	This work	Exp.[b]
ν_1	202.9	202.3	198.2	210[c]
ν_2	365.7	369.5	342.7	
ν_3	752.7	724.7	746.4	745
ν_4	1669.5	1630.3	1633.6	1650
ν_5	3338.0	3040.6	3062.7	3130 ± 10
ν_6	3893.5	3713.8	3711.7	3699
$2\nu_3$	1505.4	1420.2	1446.6	
$2\nu_4$	3338.9	3237.8	3256.6	3283
$\nu_1 + \nu_5$	3540.9	3269.2	3286.0	

[a] Reference [26].
[b] References [29(b), 31].
[c] Observed as a combination band with the ionic hydrogen bond.

small and they both yield results which are in good agreement with the experimentally observed band origins [29(b), 31]. For this system the intramolecular HOH bend and OH stretches, which are usually probed during IR experiments, are also in close agreement between the two methods. This is also the case for the computed combination band ($\nu_1 + \nu_5$) and overtones ($2\nu_3, 2\nu_4$), the latter being in excellent agreement with the experimental observation.

The final comparison between the results of the two methods is for the HNO_3 and $HNO_3(H_2O)$ systems. Due to the availability of anharmonic CC-VSCF results at the MP2/TZP level of theory we performed our anharmonic calculations with this basis set. Our results for HNO_3 are shown in table 3 together with the previous ones [27] at the CC-VSCF level as well as the experimentally measured fundamental [32] and overtone [33] frequencies. Again the calculated anharmonic frequencies with both methods are very close to experiment except for the NO_2 asymmetric stretch frequency (ν_2) for which deviations of over 100 cm^{-1} are observed for both methods with respect to experiment. CC-VSCF also seems to predict a very accurate OH stretch overtone when compared to experiment whereas our result overestimates it by about 80 cm^{-1}. It should again be

Table 3. Comparison of anharmonic frequencies and selected overtones and combination bands with the CC-VSCF and perturbative (including third derivative) approaches for HNO_3 at the MP2/TZP level of theory. Experimental results are also indicated.

Mode	Harmonic	CC-VSCF[a]	This work	Exp.[b]
ν_9	468		437	458
ν_7	591	573	579	580
ν_6	660	642	641	647
ν_8	762	750	751	763
ν_5	894	873	867	879
ν_4	1314	1296	1296	1304
ν_3	1351	1261	1323	1326
ν_2	1864	1840	1841	1710
ν_1	3784	3547	3597	3550
$2\nu_1$	7568	6940	7025	6944[c]

[a] Reference [27].
[b] Reference [32].
[c] Reference [33].

noted that recently the fundamentals of HNO_3 were reported [34] to second order perturbation theory using a PES obtained at the CCSD(T)/ANO level of theory. However, for the same reasons that were previously outlined for the Cl^-H_2O complex having to do with the current availability of analytic second energy derivatives at the MP2 level only, we have chosen to compare our MP2/TZP results with the ones obtained at the CC-VSCF//MP2/TZP level for a meaningful comparison between the two approaches which is based on the same level of electronic structure theory for the underlying PES. The corresponding theoretical [27] and experimental [35, 36] results for $HNO_3(H_2O)$, listed in table 4, also show a close resemblance between the computed frequencies with the two methods except for the OH symmetric stretch of H_2O (ν_1) and the OH stretch of HNO_3 (ν_3) for which the differences are $>100\,\text{cm}^{-1}$ with the CC-VSCF result for ν_3 being closer to experiment, albeit still too large by $120\,\text{cm}^{-1}$. Both methods also seem to overestimate the NO_2 asymmetric stretch (ν_4) by $>100\,\text{cm}^{-1}$ with respect to experiment. Results of mixed accuracy are also obtained for the combination and overtone bands for which experimental measurements are available. The position of the combination band $\nu_4+\nu_7$ is very accurately described by both methods but the one for $\nu_4+\nu_6$ and the overtone of the NO_2 symmetric stretch ($2\nu_7$) is $>200\,\text{cm}^{-1}$ away from experiment.

3.2. *Minimum energy and vibrationally averaged geometries of $(HF)_n$, $n = 2$–4 clusters*

The minimum energy structures for the hydrogen fluoride monomer through tetramer clusters are shown in figure 2. They correspond to the homodromic structures [37] where every molecule is simultaneously a proton donor and a proton acceptor. The total energies (E_e in a.u.) at the optimized structures are listed in table 5. The equilibrium and vibrationally averaged structural parameters of the global cluster minima are listed in table 6. In this table, R_{FF} denotes the intermolecular F–F separation whereas r indicates the intramolecular H–F bond. Due to the symmetry of

Table 4. Comparison of anharmonic frequencies and selected overtones and combination bands with the CC-VSCF and perturbative (including third derivative) approaches for $HNO_3(H_2O)$ at the MP2/TZP level of theory. Experimental results are also indicated.

Mode	Harmonic	CC-VSCF[a]	This work	Exp.[b]
ν_{18}	67		63	
ν_{17}	103		79	
ν_{16}	179		104	
ν_{15}	226		205	
ν_{14}	303		163	
ν_{13}	408		353	
ν_{12}	648	642	633	
ν_{11}	698	688	685	
ν_{10}	771	763	759	770
ν_9	842	863	771	
ν_8	948	927	924	931
ν_7	1330	1310	1305	1308
ν_6	1519	1466	1443	1412
ν_5	1617	1569	1585	
ν_4	1837	1809	1811	1694
ν_3	3405	3146	3270	3025
ν_2	3866	3682	3695	
ν_1	3999	3601	3813	
$\nu_4+\nu_7$	3167	3118	3116	3126
$\nu_4+\nu_6$	3355	3276	3206	2980
$2\nu_7$	2661		2604	2784

[a] Reference [27].
[b] Reference [35, 36].

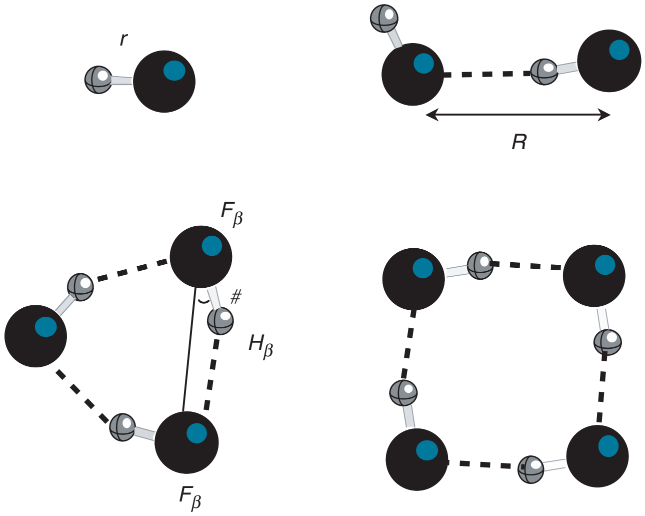

Figure 2. [Colour online] Optimal geometries of the $(HF)_n$, $n=1$–4 clusters and definition of geometrical parameters (see table 6).

Table 5. Energies (in a.u.) at the optimal geometries of the $(HF)_n$, $n = 1–4$ clusters at the MP2/aug-cc-pVDZ level of theory.

Cluster	Energy (a.u.)
HF	−100.25580447
$(HF)_2$	−200.51907518
$(HF)_3$	−300.79204677
$(HF)_4$	−401.06861284

Table 6. Equilibrium and vibrationally averaged geometries of the $(HF)_n$, $n = 1–4$ clusters at the MP2/aug-cc-pVDZ level of theory. R_{FF} denotes the intermolecular F–F separation, r the intramolecular H–F separation and θ the H_α–F_α–F_β angle where α and β denote adjacent molecules.

Cluster	Symmetry	Coordinate	Equilibrium	Vibrationally averaged
HF	$C_{\infty v}$	r (Å)	0.9248	
$(HF)_2$	C_1	R_{FF} (Å)	2.7532	2.8132
		r_1 (Å)	0.9311	0.9080
		r_2 (Å)	0.9277	0.9047
		θ_1 (Å)	6.54	3.34
		θ_2 (Å)	110.18	116.07
$(HF)_3$	C_{3h}	R_{FF} (Å)	2.6190	2.6719
		r (Å)	0.9419	0.9277
		θ (Å)	21.49	23.02
$(HF)_4$	C_{4h}	R_{FF} (Å)	2.5362	2.5584
		r (Å)	0.9535	0.9465
		θ (Å)	9.41	10.25

the clusters, the optimal geometries can be described with the previous two distances and the angle $\theta = (H_\alpha–F_\alpha–F_\beta)$, where α and β denote adjacent molecules (cf. figure 2). We note a systematic contraction of the intermolecular F–F separation by almost 0.22 Å from the dimer to the tetramer. This is larger than the corresponding elongation in water clusters [37] (0.177 Å) and it is consistent with the fact that the cooperative three-body term at the minimum energy configurations is stronger for $(HF)_3$ (22%, [38]) than for $(H_2O)_3$ (17%, [37, 39]). Consequently, the elongation of the hydrogen bonded H–F stretch, r, is ~0.01 Å/molecule from the monomer to the tetramer, larger than that found for the analogous water clusters [37, 40]. The effect of vibrational averaging on the optimal geometries is also shown in table 6. This amounts to elongations of 0.060 Å, 0.053 Å and 0.022 Å for the intramolecular F–F separations of the dimer through tetramer clusters, respectively. Our results for the equilibrium geometrical parameters are in good agreement with those published earlier [41] at comparable levels of theory and basis sets. To the best of our knowledge the vibrationally averaged geometries and corresponding spectroscopic constants, discussed below, are the first ones reported for those clusters.

The calculated rotational constants and the constants in the symmetrically reduced Hamiltonian (D_J, D_{JK} and D_K) are listed in table 7 for the equilibrium (subscript 'e') and vibrationally averaged (subscript '0') geometries and compared with available

Table 7. Effect of vibrational averaging (estimated at the MP2/aug-cc-pVDZ level of theory) on the rotational constants of $(HF)_n$, $n = 2$–4, and comparison with experimental values for the ground state. Constants in the symmetrically reduced Hamiltonian (D_J, D_{JK} and D_K) are also listed. Subscripts 'e' and '0' denote equilibrium and vibrationally averaged quantities, respectively.

Cluster		This work	Experiment
$(HF)_2$	A_e (cm^{-1})	23.09511	
	A_0 (cm^{-1})	27.05708	
	B_e (cm^{-1})	0.22447	
	B_0 (cm^{-1})	0.21530	0.21671[a]
	C_e (cm^{-1})	0.22231	
	C_0 (cm^{-1})	0.21275	
	D_J (cm^{-1})	1.650×10^{-6}	
	D_{JK} (cm^{-1})	-3.587×10^{-5}	
	D_K (cm^{-1})	1.542×10^{-1}	
$(HF)_3$	$A_e = B_e$ (cm^{-1})	0.250596	
	$A_0 = B_0$ (cm^{-1})	0.241355	0.23978[b]
	C_e (cm^{-1})	0.125298	
	C_0 (cm^{-1})	0.120234	0.11992[b]
	D_J (cm^{-1})	1.416×10^{-6}	
	D_{JK} (cm^{-1})	-2.192×10^{-6}	
	D_K (cm^{-1})	9.363×10^{-7}	
$(HF)_4$	$A_e = B_e$ (cm^{-1})	0.133255	
	$A_0 = B_0$ (cm^{-1})	0.131030	0.132081(7)[c]
	C_e (cm^{-1})	0.066628	
	C_0 (cm^{-1})	0.065448	
	D_J (cm^{-1})	3.774×10^{-7}	$7.1(2) \times 10^{-7}$[c]
	D_{JK} (cm^{-1})	-6.620×10^{-7}	$-9(2) \times 10^{-7}$[c]
	D_K (cm^{-1})	3.078×10^{-7}	

[a] References [42, 43].
[b] Reference [44].
[c] Reference [45].

experimental data [42–45]. When comparing the calculated with the experimentally measured quantities (for instance for the rotational constants) the effects of higher electron correlation and the truncation of basis set should be taken into account. As noted earlier our calculations are currently restricted at the MP2 level of theory due to the availability of analytic second derivatives at that level and they are performed with the aug-cc-pVDZ basis set but even those provide satisfactory results for the rotational constants when compared to experiment (cf. table 7).

3.3. *Anharmonic frequencies*

As noted earlier the Miller group has studied the vibrational predissociation lifetime of the HF dimer [46], the photodissociation of cyclic HF complexes pentamer through heptamer [47] and recently the growth of HF polymers inside He droplets [42, 48] providing experimental probes of the HF stretching vibrations [49] and their change in different media. In addition, many of the vibrations of various HF clusters have been studied experimentally by Nesbitt and coworkers [50–52] via high-resolution infrared spectroscopy. Other groups have also provided experimental data for the fundamental

Table 8. Harmonic and anharmonic vibrational frequencies, zero-point energies (in cm^{-1}) and infrared (IR) intensities (in km/mol) for the $(HF)_n$, $n = 2$–4 clusters.

				Anharmonic (cm^{-1})		
Cluster	Symmetry	Harmonic (cm^{-1})	IR intensity (km/mol)	This work	CC-VSCF[a]	Exp. (cm^{-1})
$(HF)_2$	A'	158	12.8	121		125[b]
	A'	214	148.3	148		161[b]
	A''	471	175.8	401		395 (8)[b]
	A'	576	152.8	440		475 (3)[b]
	A'	3940	462.8	3784		3868[c]
	A'	4039	136.2	3853		3931[c]
	ZPE, cm^{-1}	4698.1		4571.0		4591
$(HF)_3$	E'	197	24.1	163	162, 170	
	A'	219	0.0	182	187	
	E''	503	0.0	423	417, 445	
	E'	603	351.2	496	458, 485	446[d]
	A''	704	390.5	609	643	
	A'	990	0.0	786	835	
	A'	3664	0.0	3494	3575	
	E'	3782	687.7	3602	3655, 3659	3702[d]
	ZPE, cm^{-1}	7874.0		7676.7		
$(HF)_4$	B_u	44	0.0	40	76	
	B_g	95	0.0	85	81	
	A_g	224	0.0	194	183	
	E_u	288	48.7	258	241	195[e]
	B_g	303	0.0	275	254	
	B_u	653	0.0	588	631	
	B_g	677	0.0	623	635	
	E_g	696	0.0	626	693	
	A_u	799	487.6	732	824	714.8[f]
	E_u	891	331.3	781	773	752.7[f]
	A_g	1149	0.0	975	1023	
	A_g	3333	0.0	3127	3338	
	E_u	3527	1795.4	3323	3426	3445[g]
	B_g	3602	0.0	3408	3562	
	ZPE, cm^{-1}	10841.2		10593.5		

[a] Reference [57].
[b] References [50, 52].
[c] Reference [43].
[d] Reference [55].
[e] Reference [56].
[f] Reference [45].
[g] Reference [53].

bands of HF clusters by means of FTIR spectroscopic [53], size-selected IR absorption [54], pulsed supersonic expansion pulsed IR experiments [45] as well as experiments in an Ar matrix [55, 56]. Those experimental studies provide a useful database for the benchmarking of theoretical methods used to compute the anharmonic frequencies of these systems. Chaban and Gerber have previously reported [57] the anharmonic vibrational frequencies for the $n = 3$ and 4 clusters at the CC-VSCF level based on a PES computed at the MP2/TZP level of electronic structure theory.

The calculated harmonic (ω) and anharmonic (ν) frequencies (in cm^{-1}) and IR intensities (in km/mol) for the dimer through tetramer clusters are listed in table 8 together with the previous experimentally measured band origins and the results of the

CC-VSCF//MP2/TZP of Chaban and Gerber [57] for the trimer and tetramer. We note that our calculations overestimate the experimentally observed frequencies for the HF stretches in the dimer by ca. 80 cm^{-1}, whereas differences of ~100 cm^{-1} are found for the HF stretches of the larger trimer and tetramer clusters with respect to experiment. These differences are larger with respect to recent CC-VSCF calculations (albeit with the different TZP basis set), which yield differences with respect to experiment of 63 cm^{-1} for the trimer and just 20 cm^{-1} for the tetramer [57]. Given the results of the previous section on the comparison between the two methods for model systems with the same basis sets, the observed difference might be due to the different basis sets used, however further investigation of this proposition is needed.

4. Conclusions

The present study provides a comparison between the accuracy of mean-field grid-based methods and those based on higher energy derivatives for the calculation of anharmonic vibrational frequencies. Several model systems were used at the same level of theory (level of electron correlation and basis set) in order to compare the results between the two approaches. We found that, except in some special cases, which may require the use of larger grids and more points in the numerical calculation of higher order derivatives, the agreement between the two approaches is satisfactory. In this study we have demonstrated this ability by presenting the results of clusters as large as $(HF)_4$. Forthcoming results will be presented for molecular clusters as large as $(H_2O)_6$.

The computational efficiency and the time-to-solution for the two approaches are constantly being improved. For instance, the use of symmetry [58] in constructing the grids for VSCF and VCI calculations greatly reduces the number of *ab initio* points needed to represent the underlying PES whereas recent implementations [59] of the CC-VSCF method have improved its scaling by a factor of N^2. On the other hand the approach via higher energy derivatives can become more competitive, especially for larger ($n > 15$ atom) molecular systems, following the efficient implementation of the numerical computation of the higher order energy derivatives on parallel architectures.

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