

# Vibrational dynamics of $(\text{HF})_n$ aggregates from an ab initio based analytical (1+2+3)-body potential

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We have fitted an analytical 12-dimensional three-body potential type hypersurface for the hydrogen fluoride system with a weighted root mean square deviation of  $62.8\text{cm}^{-1}$  at 1004 geometries for  $(\text{HF})_3$ , selected by a quantum sampling technique, calculating electronic potential energies by correlated ab-initio techniques at the DZP+MP2 level. Extensive test calculations with larger basis sets and for larger  $(\text{HF})_n$  aggregates show that the analytical three-body term gives an excellent description of the  $(\text{HF})_3$  potential hypersurface and a good approximation for clusters up to at least the pentamer, when used in combination with the experimental high quality pair potential previously obtained by us. We have calculated for the first time a reliable, fully anharmonic binding energy with respect to 3 HF to be  $D_0[(\text{HF})_3]=43.34\text{kJmol}^{-1}$  by means of vibrational quantum Monte Carlo calculations using this potential (nuclear dynamical error  $< 0.1\text{kJmol}^{-1}$ , electronic error estimate  $< 1\text{kJmol}^{-1}$ ). This is compared to  $D_0$  for other  $(\text{HF})_n$  aggregates ( $n = 2$  to  $7$ ). We systematically explore energetic effects from D isotope substitution on the dissociation energies and vibrational predissociation channels. Anharmonic predictions for the infrared spectrum of  $(\text{HF})_3$  are made.

## 1. INTRODUCTION

The structure and dynamics of hydrogen bonded clusters, polymers, liquids, and crystals remain among the most challenging problems in kinetics and spectroscopy, indeed, in chemical physics in general [1, 2]. We have pursued over the last decade an experimental and theoretical project on the hydrogen bonded dimer  $(\text{HF})_2$  with the aim to contribute in this particularly simple system to the understanding of the fundamental dynamical properties of the hydrogen bond [3–9]. In continuation and extension of this investigation to larger clusters and possibly the liquid we have undertaken ab initio (electronic potential energy) and vibrational quantum Monte Carlo (QMC) calculations for  $(\text{HF})_3$  and some of its isotopomers and report here the first results from this study.

While most investigations of the structure and dynamics of molecular clusters and condensed matter are still based on pairwise interactions between the constituents, the importance of three- and possibly higher body contributions for many properties and classes of substances is increasingly confirmed by spectroscopic and theoretical techniques [10–12]. The cooperative phenomena observed in hydrogen bonded networks

suggest particularly pronounced many-body effects [13]. Hydrogen fluoride is therefore an obvious model candidate for the systematic study of non-pairwise interactions. Section 2 summarises briefly our approach to many-body contributions in the hydrogen fluoride system. A more detailed description including the analytical three-body potential representation will be published elsewhere [14]. Some effects of this analytical HF three-body potential on the structural properties and vibrational dynamics of  $(\text{HF})_3$  and higher oligomers are presented in section 3. Comparisons with local, vibrationally harmonic ab initio approaches [15–18], with the vibrational dynamics in empirical potentials [10, 12, 19] and with the still limited, in part quite contradictory experimental body of information on HF trimer and oligomers [6, 8, 10, 20–24] are made. These topics are dealt with in much more depth elsewhere [14, 25].

## 2. AB INITIO CALCULATIONS AND ANALYTICAL POTENTIAL

We choose a many-body partition scheme for the description of HF clusters to exploit the available empirically refined one and two-body potentials (SQSBDE [9] and the intermolecularly sim-

Table 1

Comparison of  $(HF)_n$  ( $n = 3, 4$ )  $C_{nh}$  minimum geometries, well depths  $D_e$ , harmonic and anharmonic binding energies ( $D_0^h$  and  $D_0$ ) with respect to dissociation into  $n$  HF predicted by the analytical HF3B term (added to the empirically refined accurate ab initio pair potential SNC [25]) with results from the literature. BSSE-corrected energies are given in parentheses and ab initio trimer energies which have been corrected proportional to their dimer error (dimer scaled results) are given in square brackets. Note the good agreement of ab initio binding energies with the independent results from the analytical surface, when the former are either BSSE-corrected or dimer-scaled.

$r_{HF}$ pm	$R_{FF}$ pm	$\angle / ^\circ$ (FFH)	$D_e$	$D_0^h$ kJmol $^{-1}$	$D_0$	approach + literature
(HF) $_3$						
92.9	258	24.4	60.7	41.8	43.3	SNC pair + HF3B potential
92.3	273	26.5	50.9	34.3	36.0	SNC pair potential only
91.1	269	27.4	60 (52)			MP2 [16]
93.3	259	21.4	67 (62) [61]	46 (42) [41]		[5s4p2d/3s2p1d]+MP2 (this work)
93.4	262	21.6	61 (60) [61]			[8s6p2d/6s3p]+MP2 (this work)
93.2	262	23.6	64 [59]	44 [40]		ACPF [18]
(HF) $_4$						
93.2	254	13.4	104.8	77.7	79.3	SNC pair + HF3B potential
92.4	268	14.2	87.0		63.6	SNC pair potential only
94.3	252	11.6	121 [111]	85 [79]		ACPF [18]

ilar SNC-surface [25]), to go beyond simple polarizability effects [11–13], to have a modular approach, and to profit from small basis size, basis set superposition error (BSSE), and electron correlation dependences for three-body forces [17]. Extensive tests at the MP2 level with basis sets beyond TZ quality (see table 1 and ref. [14]) support the use of a standard DZP basis for the systematic exploration of the three-body potential, whereas satisfactory dimer properties were only achieved with the large [8s6p2d/6s3p] basis set of table 1. Using a quantum sampling technique based on QMC [9, 14], 1004 important trimer configurations were evaluated and their ab initio BSSE-corrected three-body energies were fitted to an analytical expression consisting of angular terms and radial exponentials (hereafter called HF3B) with two free parameters and an energy weighted rms deviation of 62.8cm $^{-1}$ . Full weights were given to all configurations up to 5000cm $^{-1}$  above the trimer minimum. The distribution of sampled three-body energies is dominantly stabilizing, concentrating in the range of  $-1500$  to  $+100$ cm $^{-1}$ . Agreement with pointwise ab initio literature data [16, 17] is good.

### 3. RESULTS

Table 1 shows results for the trimer and tetramer  $C_{nh}$  minima from several approaches. The influence of the three-body term on the FF distance and on binding is strong. Comparison of energetic quantities requires careful corrections for unsaturated basis sets to yield coherent results. (HF) $_3$  anharmonicity effects for  $D_0$  from QMC calculations [9, 14] amount to  $\approx 4\%$ , while we find  $\approx 15$ -20% for the intermolecular fundamental transitions [25], with obvious consequences for the far IR band assignment problem [8]. Other (high-lying) stationary points located both on the analytical trimer surface and via ab initio gradient search include a chainlike  $C_s$  and a  $C_{2v}$  [10] saddle point as well as a  $C_{2v}$  minimum in which the central HF acts as a twofold hydrogen bond acceptor. Hydrogen bond interconversion tunneling in (HF) $_3$  is predicted to be complex and quite slow.

Table 2 contains fully anharmonic (QMC) maximum energy gaps  $\Delta_{exc}$  between IR stretching excitations and predissociation fragment channels. Fragmentation into three monomers or into a monomer and a dimer is possible and the analysis of possible mechanisms requires an accurate

Table 2

Fully anharmonic maximum excess wavenumbers  $\Delta_{exc}$  of the lowest type I (monomer+dimer) and type II (monomers) predissociation channels for H,D-isotopomers of  $(\text{HF})_3$  excited in infrared-active stretching fundamentals (excitation wavenumbers from [23], in part only estimates). While the dynamical uncertainties are  $\pm 10\text{cm}^{-1}$ , the overall electronic potential error may be up to about  $100\text{cm}^{-1}$ . Negative  $\Delta_{exc}$  values represent channels that are calculated to be closed. Dimer fragment binding energies are taken from ref. [9]. Trimer zero point energies refer to the HF3B + SNC potential.

parent species	$(D_0 D_0^h)/hc$ $\text{cm}^{-1}$	excitation wavenumbers	fragments type I/II	$\Delta_{exc}$ $\text{cm}^{-1}$
$(\text{HF})_3$	3623 3493	3712	3HF	89
$(\text{HF})_2\text{DF}$	3726 3615	3712 3645 2700	$(\text{HF})_2+\text{HF}$ 2HF+DF	1151 -14 -81 -1026
$\text{HF}(\text{DF})_2$	3837 3738	3678 2720 2670	$(\text{HF})_2+\text{DF}$ HFDF+HF 2DF+HF	1048 981 36 1131 1064 119 -159 -1117 -1167
$(\text{DF})_3$	3933 3861	2720	HFDF+DF $(\text{DF})_2+\text{HF}$ 3DF $(\text{DF})_2+\text{DF}$	986 28 -22 1010 52 2 -1213 -44

knowledge of such energy gaps. One can see that a large fraction of the gaps is zero within the estimated ab initio accuracy, with possible lifetime consequences on the stretching states. The most interesting prediction refers to  $(\text{DF})_3$ , which appears to be stable with respect to any fundamental excitation, while stretch-excited  $(\text{HF})_3$  is relatively short-lived [23]. As the maximum energy gap is still within the possible ab initio error bar, we predict that spectroscopy of this molecule near  $2720\text{cm}^{-1}$  can lead us to an accurate determination of the trimer binding energy. A similarly favourable situation arises for the mixed isotopomers when using DF stretching excitation of the trimer (see table 2).

Our results for higher oligomers  $(\text{HF})_n$  with  $n = 4 \dots 7$  rest on the neglect of higher than three-body potential contributions. We have tested and confirmed this assumption for selected close to minimum pentamer and hexamer geometries. A more detailed investigation of this subject is planned. We find that the global minimum structure starts to fold out of planarity beyond  $n = 5$ . Figure 1 contains results for both classical and fully quantal stepwise cluster evaporation as a measure of relative oligomer stability. Vibrational quantum effects (from QMC) and electronic three-body effects (from HF3B) are large and similar in size (but opposite in sign) for

$n = 3, 4$ , which are the two most stable species up to  $n = 7$ .

#### 4. CONCLUSIONS

i) The three-body potential for HF oligomers is economic to calculate, now for the first time analytically available (at a  $< 1\text{kJmol}^{-1}$  error level), significant for structure and dynamics and clearly the dominant cooperativity term, thus suggesting a compact (1+2+3)-body approach to HF vapour, applicable to some extent even to condensed phases [12, 26, 27].

ii)  $(\text{HF})_3$  and its isotopomers are strongly bound. The anharmonically calculated lowest dissociation energy is predicted to be very close to the DF-stretching quantum for the DF containing isotopomers, thus allowing easy study of the dissociation threshold by vibrational predissociation spectroscopy. Our 12-dimensional anharmonic predictions for the FIR active vibrations are  $140 \pm 20\text{cm}^{-1}$ ,  $390 \pm 50\text{cm}^{-1}$  ( $E'$ ) and  $510 \pm 30\text{cm}^{-1}$  ( $A''$ ) [25].

iii) The relative stability of HF oligomers reaches a pronounced maximum for  $n = 4$ , in agreement with findings for pair potentials and for the water system. Early, more uniform thermodynamic oligomerization models require revision.

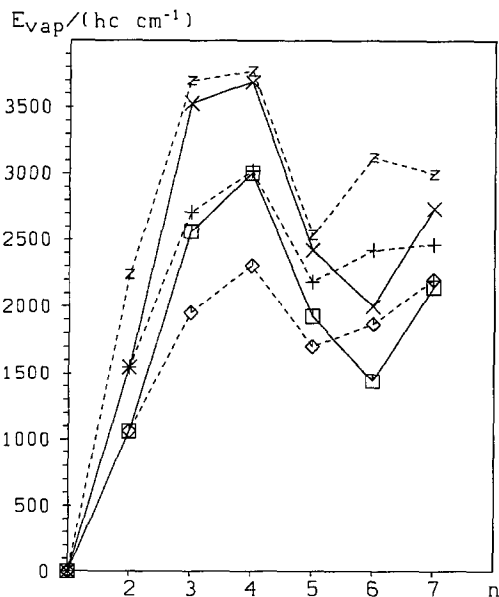


Figure 1. Evaporization energies  $E_{\text{vap}}(n)$  at 0K corresponding to the process  $(\text{HF})_n \rightarrow (\text{HF})_{n-1} + \text{HF}$  obtained classically (+, x, z) and including anharmonic zero point energy ( $\diamond$ ,  $\square$ ) for pure pair potentials (dashed) and with inclusion of the HF3B three-body potential (full lines). '+, x,  $\diamond$ ,  $\square$ ' correspond to the potentials presented in this work, while 'z' marks the results for the extended effective pair potential HF2-X described in [19]. Note the  $\approx 45\%$  overestimate of the  $(\text{HF})_2$  evaporization energy of the HF2-X potential due to the inappropriate effective inclusion of many-body effects.

## REFERENCES

- 1 P. Schuster, G. Zundel, and G. Sandorfy, editors. *The Hydrogen Bond*, volume 1-3. North-Holland, Amsterdam, (1976).
- 2 P. Schuster, editor. *Hydrogen Bonds, Topics in Current Chemistry Vol. 120*. Springer, Berlin, (1984).
- 3 K. v. Puttkamer and M. Quack, *Chimia*, **39**, 358-360 (1985).
- 4 K. v. Puttkamer and M. Quack, *Mol. Phys.*, **62**, 1047-1064 (1987).
- 5 K. v. Puttkamer, M. Quack, and M. A. Suhm, *Mol. Phys.*, **65**, 1025-1045 (1988).
- 6 K. v. Puttkamer and M. Quack, *Chem. Phys.*, **130**, 31-53 (1989).
- 7 M. Quack and M. A. Suhm, *Mol. Phys.*, **69**, 791-801 (1990).
- 8 M. Quack and M. A. Suhm, *Chem. Phys. Lett.*, **171**, 517-524 (1990).
- 9 M. Quack and M. A. Suhm, *J. Chem. Phys.*, **95**, 28-59 (1991).
- 10 K. D. Kolenbrander, C. E. Dykstra, and J. M. Lisy, *J. Chem. Phys.*, **88**, 5995-6012 (1988).
- 11 J. Detrich, G. Corongiu, and E. Clementi, *Chem. Phys. Lett.*, **112**, 426-430 (1984).
- 12 H. Sun, R. O. Watts, and U. Buck, *J. Chem. Phys.*, **96**, 1810-1821 (1992).
- 13 H. Saint-Martin, C. Medina-Llanos, and I. Ortega-Blake, *J. Chem. Phys.*, **93**, 6448-6452 (1990).
- 14 M. Quack, J. Stohner, and M. A. Suhm, to be published.
- 15 S. Liu, D. W. Michael, C. E. Dykstra, and J. M. Lisy, *J. Chem. Phys.*, **84**, 5032-5036 (1986).
- 16 Z. Latajka and S. Scheiner, *Chem. Phys.*, **122**, 413-430 (1988).
- 17 G. Chałasinski, S. M. Cybulski, M. M. Szcześniak, and S. Scheiner, *J. Chem. Phys.*, **91**, 7048-7056 (1989).
- 18 A. Karpfen, *Int. J. Quantum Chem.: Quant. Chem. Symp.*, **24**, 129-140 (1990).
- 19 C. Zhang, D. L. Freeman, and J. D. Doll, *J. Chem. Phys.*, **91**, 2489-2497 (1989).
- 20 W. Strohmeier and G. Briegleb, *Z. Elektrochemie*, **57**, 662,668 (1953).
- 21 E. U. Franck and F. Meyer, *Z. Elektrochemie*, **63**, 571-582 (1959).
- 22 J. Janzen and L. S. Bartell, *J. Chem. Phys.*, **50**, 3611-3618 (1969).
- 23 D. W. Michael and J. M. Lisy, *J. Chem. Phys.*, **85**, 2528-2537 (1986).
- 24 L. Andrews. In J. R. Durig, editor, *Applications of FT-IR spectroscopy, Vol 18 in Vibrational Spectra and Structure*, pages 183-216. Elsevier, (1990).
- 25 D. Luckhaus, M. Quack, and M. A. Suhm, to be published.
- 26 M. L. Klein and I. R. McDonald, *J. Chem. Phys.*, **71**, 298-308 (1979).
- 27 M. Springborg, *Phys. Rev. B*, **38**, 1483-1503 (1988).