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On hydrogen-bonded complexes: the case of $(HF)_2$

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Abstract. The hydrogen fluoride dimer $(HF)_2$ is the most completely characterized hydrogen bonded species incorporating a donor molecule and an acceptor molecule. We provide a summary of experimental and theoretical information pertinent to the fundamental and harmonic vibrational frequencies, equilibrium geometry and dissociation energies D_e and D_0 as well as a brief critical discussion including some new results on the potential function and current "best estimates" of experimental quantities.

Key words: Anharmonicity – Dynamics – Density functionals – Infrared – Structure

1 Introduction

In a recent paper [1], Mele et al. have presented some calculations on molecular complexes, in particular also $(HF)_2$. A substantial body of experimental and some theoretical information over the last decade has been overlooked by the authors of Ref. [1], which renders their comparison of experiment and theory less useful and informative than it might have been. In particular, we have studied the low frequency fundamentals of this complex over the last decade using high resolution FTIR spectroscopy [2–5]. Extensive theoretical analysis of our results using quantum Monte Carlo calculations [5] in combination with *ab initio* data [6] have led to empirical potential energy functions defining both harmonic frequencies and structural parameters to a reasonable degree of accuracy, which may be compared with the theoretical results of Ref. [1] and further theoretical results.

2 Summary of experimental and theoretical results on $(HF)_2$

Tables 1–3 give a compact summary of experimentally determined dynamical, structural and energetic properties of $(HF)_2$ in comparison to selected theoretical results [5–17] and the findings in Ref. [1], which we shall discuss very briefly. While five gas phase fundamental vibrations ν_i of $(HF)_2$ have been experimentally characterized in a more or less direct way for some time [2–5], and intermolecular modes have also recently been seen [18] as combination bands

Table 1. Predicted $(HF)_2$ harmonic (ω) and anharmonic (ν) wavenumbers and vibrational shifts $\Delta\nu_{1,2}$ relative to the monomer wavenumber in cm^{-1} compared to experimental gas phase transitions, which refer in part to higher angular momemtum K around the major axis

	ν_1	ν_2	ν_3	ν_5	ν_4	ν_6	$-\Delta\nu_{1,2}$
Experiment							
Refs. [2, 4, 5, 20–22] (see also [18])	3931 [20, 21]	3868 [20, 21]		394 (K = 3[a]) [4]	≈ 125 [5]	400 [2] (K = 1[a]) 467 [22] (K = 2[a]) (570) [5] (K = 3[a])	31, 93
Band origin of fundamental estimated	3931	3868		≈160	≈125	≈380	
SQSBDE [5]							
QMC [5]					130 (10)	381 (6)	
(4 + 2)D [7]	3942	3900		162	126	382	16, 58
6D [9]	3941	3896	(425)[c]	161	126	379	17, 62
SNB [8]							
(4 + 2)D [7]	3930	3867	(412)[c]	152	125	378	28, 91
	ω_1	ω_2	ω_3	ω_5	ω_4	ω_6	$-\Delta\omega_{1,2}$
Empirical potentials							
BH [16] (4*D*)			520	337	178		
SQSBDE [5]	4100	4048	485	211	151	401	38, 90
SNB [8]	4099	4055	484	203	150	409	34, 78
Best empirical estimate	4100	4050	—	210	150	410	38, 88
Ab initio potentials							
MP2 (DZP) [23]	4181	4117	593	221	168	482	40, 104
MP2 ([8*s*6*p*2*d*/6*s*3*p*]) [8]	4100	4017	574	222	157	450	43, 126
CPF [6]	4103	4052	510	216	150	413	32, 83
ACCD [24]	4103	4056	420	127	167	—	64, 111
CCSD (T) [11]	4119	4050	567	210	157	458	38, 107
DFT potentials							
LDA [15]	3947	3718	730	292	203	550	65, 294
BLYP [15]	3902	3787	577	222	157	452	40, 155
B3LYP [15]	4059	3960	581	221	160	461	43, 143
PP [1]	3864	3706	639	253	187[b]	513	106, 264

[a] Exact high angular momemtum predictions remain to be made [5]

[b] Erroneously denoted as bend in Ref. [1]

[c] Strongly mixed character prevents clear quantum number assignment

with HF stretching modes (see Table 1), the rotationless band centers remain approximate in several cases. Anharmonic contributions typically exceed the experimental uncertainty. This calls for global treatments beyond the standard harmonic approximation (ω_i), as was also noted in Ref. [1]. Using global treatments [5, 7], the SQSBDE surface [5] (adjusted to binding energy and expectation value of the B rotational constant), the SQSRAB surface [5] (as SQSBDE, but adjusted to the experimentally estimated hydrogen

Table 2. Planar $(HF)_2$ geometries of potential minima from theory and experiment. r_{HF} denotes monomer bond lengths, R_{FF} the fluorine distance and θ_{HFF} the corresponding angles between the HF units and the F–F axis. Corrections for basis set superposition error are indicated as -BSSE. See the indicated references for details of the electronic structure approaches. Primed quantities refer to the "free" HF unit

Potential surface	r_{HF} (pm)	r'_{HF} (pm)	R_{FF} (pm)	θ_{HFF} (°)	θ'_{HFF} (°)
Experimental [25]			272(3)	10(6)	63(6)
Experimental [26]			—	7(3)	60(2)
Empirical BH surface [16]			270	11	68
SQSBDE [5]	92.3	92.1	275(1)[a]	8	65
SQSRAB [5]	92.3	92.1	273(1)	8	65
SNB [8]	92.0	91.8	275(1)[a]	8	66
MP2 (DZP) [23]	92.4	92.3	274	8.2	67.3
MP2 ([8*s*6*p*2*d*/6*s*3*p*]) [8]	92.3	92.1	275	6.7	69.3
CCSD(T) (aug-cc-pVTZ) [10]	92.7	92.4	274	7	69
CCSD(T) (aug-cc-pVTZ)-BSSE [10]	92.6	92.4	277	7	69
CCSD(T) (aug-cc-pVQZ) [10]			273		
CCSD(T) (aug-cc-pVQZ)-BSSE [10]			275		
CCSD(T) (TZ2P (*f*, *d*)) [11]	92.3	92.1	274	7	70
CPF [6]	92.4	92.2	279	6.8	65.6
ACCD [24]	92.6	92.4	277	6.4	59.9
LDA [15]	94.5	93.6	256	10	73
BLYP [15]	94.1	93.6	277	8	66
B3LYP [15]	92.9	92.5	275	9	65
PP [1]	95.3	94.7	269.5	7	62

[a] Subtract 1.5(1) pm for an estimated anharmonic Coriolis correction [16, 5]

bond length) and the SNB surface [8] (S(emiempirical), N(ew), one of a series of potentials (A, B, C) which are further adjusted to the HF stretching levels and hydrogen bond exchange tunneling [7], a purely anharmonic effect) have been constructed from comprehensive *ab initio* data [6] and provide the first reliable assessment of anharmonic contributions [5, 9]. To some degree, these anharmonic effects will be transferable to harmonic potential energy surfaces from more sophisticated electronic structure calculations [10, 11]. As illustrated in Table 1 and investigated by us in much more detail using a wide variety of gradient correction schemes and numerical approaches [12, 13], potential surfaces derived from gradient corrected density functional theory (DFT) such as in Ref. [1] do not belong to the latter category. Some of the deficiencies become more pronounced in larger HF clusters [12, 13]. This is true for the frequency shifts induced in the HF stretching mode upon complexation (Table 1), which must be compared *consistently* at the harmonic or better anharmonic level, rather than in a mixed way [1]. On an absolute scale, the DFT stretching frequencies also deviate strongly from their experimental and correlated *ab initio* counterparts. Only through admixture of exact Hartree Fock exchange contributions in hybrid methods, currently best represented by the B3LYP approach [14, 15], a globally satisfactory description of the HF cluster dynamics is achieved [13]. For structural properties (see Table 2), the deficiencies of DFT are less pronounced except for an unusual HF bond length and elongation upon complexation, which is of course tied to the frequency shift anomaly discussed above. The currently best empirical estimate of the equilibrium FF distance is 273–274 pm, based on substantial vibrational averaging [5] and

Table 3. Electronic (D_e), harmonically zero point energy corrected (D_0^h) and fully anharmonic (D_0) binding energies of $(HF)_2$ with respect to separated monomers from theory and experiment

Potential surface	D_e (kJ/mol)	D_0^h (kJ/mol)	D_0 (kJ/mol)
Experimental [17]			12.70(1)
Best estimate	18.9(2)	12.0(2)	
SQSBDE [5, 7]; [9]	18.7	11.96	12.65
SNB [8]	18.5	12.0	12.67
MP2 (DZP) [23]	24.1	16.1	
MP2 ([$8s6p2d/6s3p$]) [8]	18.5	11.1	
CCSD(T) (aug-cc-pVQZ) [10]	19.8		
CCSD(T) (aug-cc-pVQZ)-BSSE [10]	18.8		
CCSD(T) (extrapolation [10])	19.2		
CCSD(T) (TZ2P (f,d)) [11]	19.8	12.3	
CPF [6]	18.1	11.1	
ACCD [24]	19.1		
LDA [15]	37.4	28.9	
BLYP [15]	19.8	12.5	
B3LYP [15]	21.1	13.7	
PP [1]	27.6	20.3	

additional Coriolis corrections [16, 5] in the empirically adjusted surfaces [5]. It agrees very well with the currently best theoretical extrapolations of 273 pm [10] to 274 pm [11].

Accurate energetic discussions of hydrogen bonding must also include anharmonicity effects, which are easily captured by quantum Monte Carlo (QMC) techniques [5]. The fully anharmonic dissociation energy D_0 exceeds the harmonic estimate D_0^h by $\approx 6\%$ and has been used in our adjustment of the SQSBDE and SNB surfaces to the most recent experimental data [17], accurate to 0.01 kJ/mol. As the ν_3 frequency appears to be underestimated in these surfaces [18], the currently best experimental estimate of the electronic binding energy D_e is probably 18.9(2) kJ/mol. The "excellent agreement" of density functional results for the binding energy (see Table 3, last row) with experiment stated in Ref. [1] is based on early thermodynamic modelling results (see Ref. [19] and references cited therein), which are now known to be incorrect (for accurate equilibrium constants see Ref. [5]).

In conclusion, the combined experimental and quantum dynamical progress on HF dimer achieved during the last decade and summarized in Tables 1–3 is approaching a level which allows the quantitative characterization of various electronic structure approaches to the important phenomenon of hydrogen bonding. Density functional theory at the level presented in Ref. [1] does not perform satisfactorily, unless exact exchange terms [14] are incorporated [12, 13, 15]. Further experimental work is in progress in our laboratory to even better characterize both the low energy parts and also the high energy aspects of the highly anharmonic potential of $(HF)_2$ and its isotopomers.

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