Variational analysis of HF dimer tunneling rotational spectra using an *ab initio* potential energy surface

Oleg L. Polyansky[1a,b], Roman I. Ovsyannikov[b], Jonathan Tennyson[a], Sergei P. Belov[b], Mikhail Yu. Tretyakov[b], Vladimir Yu. Makhnev[b], Nikolai F. Zobov[b]

[a] *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom*
[b] *Institute of Applied Physics, Russian Academy of Sciences, 46 Ulyanov Street, Nizhny Novgorod, 603950, Russia*

Abstract

A very accurate, $(HF)_2$ potential energy surface (PES) due to Huang *et al.*(*J. Chem. Phys.*, **150**, 154302 (2019)) is used to calculate the energy levels of the HF dimer by solving the nuclear-motion Schrödinger equation using variational program WAVR4. Calculations on an extended range of rotational states show very good agreement with experimental data. In particular the known empirical rotational constants for the ground and some observed excited vibrational states are reproduced with an accuracy of about 50 MHz. This level of accuracy is shown to extend to higher excited inter-molecular vibrational states v and higher excited rotational quantum numbers (J, K_a). These calculations allow the assignment of 3 new J-branches in an HF dimer tunneling-rotation spectra recorded 30 years ago. These branches belong to excited $K_a = 4$ state of the ground vibrational state, and $K_a = 0$ states of excited inter-molecular vibrational states.

Keywords: HF dimer; tunneling-rotation-vibration spectra; subterahertz experimental data; variational calculations.

[1]To whom correspondence should be addressed; email: o.polyansky@ucl.ac.uk

1. Introduction

The study of weakly bound molecular complexes with hydrogen bonds and Van der Waals bonding accounts for a large sub-branch of molecular spectroscopy [1]. High resolution spectroscopy can provide very accurate information on these complicated quantum systems but often requires theoretical support to provide interpretation and understanding. High precision study of hydrogen bonded species also extends beyond molecular physics to the study of biological systems, while still relying on a quantum mechanical interpretation.

Quantum chemical calculations of the HF dimer potential energy surface (PES) started in 1974 [2]. Already the 1991 review by Quack and Suhm [3] cites 35 papers reporting *ab initio* PESs. Further work on the *ab initio* $(HF)_2$ PESs is presented, for example, by Klopper, Quack and Suhm [4, 5]. The PES used here is due to Huang *et al.*[6] and is based on about 100 000 points calculated using a very high level of theory. The accuracy of this PES is demonstrated below in Section 2.

Most molecular complexes can only be observed experimentally in cold jets or molecular beams. In the gas phase at room temperature these complexes dissociate into monomers or condense into polymers on the gas cell walls. The HF dimer is one of the rare molecular complexes possessing a large dimerisation constant which therefore results in sufficient collisionally-formed complexes at pressures appropriate for high resolution spectroscopy at higher temperatures than achievable in molecular jets and beams. Other such examples include HF-H_2O [7] and HF-HCN [8]. A major reason for studying such complexes is that thermal occupation allows one to observe spectra involving highly excited vibrational and rotational states. That is the main reason why HF dimer spectra are so well studied [9]. On the other hand these gas phase observations highlight significant incompleteness in the theory of HF dimers. As discussed below, observations

made of HF dimer spectra in highly excited vibrational states remain unassigned due to the limitations of theory.

This paper presents a significant step forward in the accurate representation of highly excited energy levels of the HF dimer. We present first principles variational calculations of rotationally-excited HF dimer states and compare them with the high J energies, derived from line frequencies obtained from high resolution HF dimer spectra. Moreover, we use these calculations to provide first assignments to lines in the tunneling-rotation-vibration spectra of the HF dimer, recorded 30 years ago [10]. At the time of our recording this sub-millimeter spectrum of HF dimer at equilibrium in the gas phase, the theoretical tools for assigning high resolution HF dimer spectra were rather limited. The microwave spectrum of the HF dimer was first observed by Dyke *et al.* [11], and then Pine and Lafferty studied its mid infrared (IR) spectrum in the region of the HF monomer fundamental stretch [12]. Subsequently, a thorough study of the gas phase HF dimer millimeter region spectrum was performed by Lafferty *et al.* [13]. The spectrum of the HF dimer behaves in many respects like that of a linear molecule, as for certain vibrational states and K values the rotation-tunneling spectrum consists of the characteristic quasi-equidistant branches with increasing values of the total rotational quantum number J. This behavior can be described by a simple formula (see Eq. (1) of Section II). So although the HF dimer is an asymmetric top and, in principle, the asymmetric top quantum number K_a should be used, it is actually almost a symmetric top and one can use the designation K instead.

When in 1990 we recorded the spectrum of the HF dimer in what at the time was the more exotic and difficult to work in sub-millimeter wave region around 10 cm^{-1} [10], the first obvious thing to do was to continue the branches observed in the lower part of the millimeter region [13] to higher frequencies and, as we dealt mostly with the R-branches, to higher Js of the same K rotational quantum numbers. We did that and assigned the $K = 0, 1$ and 2 R-branches

of the tunneling-rotation spectrum. As the HF dimer is a floppy, quasi-linear system, the extrapolation to higher K's, first of all to $K = 3$, proved impossible using the standard effective Watson Hamiltonian. Fortunately, by that time the method of one-dimensional approximation of effective Hamiltonians in a Padé-Borel form had already been developed by one of us [14] and it was applied to the extrapolation to higher K's of the ground and first excited bending state of water monomer [15, 16]. Before that approximants in Padé form were used by Pine *et al.* [17] to assist assignment of the $K = 4$ branch in the ν_1 band of $(HF)_2$. The use of approximants allowed us to extrapolate [10] the B constants for $K = 0, 1$ and 2 to the B constant for $K = 3$. Using this prediction we identified the $K = 3$ branch of the tunneling rotation spectrum. However, since the Q-branch of this spectrum was in the millimeter region, beyond the capability of the spectrometer we used to record the spectrum, we had to ask our colleagues at the National Institute of Standards and Technology (NIST) to observe the $K = 3$ Q-branch we predicted, as well the continuation of our R-branch series of lines. Our colleagues at NIST successfully observed the Q-branch using our predictions. Thus, our extrapolation from $K = 0, 1$ and 2 to $K = 3$ was confirmed as being correct and the assignment of the $K = 3$ branch established [10].

Nevertheless, at that time we were unable to go further. We observed many unassigned lines belonging to the HF dimer, but could not do anything with them because of limitations in the effective Hamiltonian technique, even in its more sophisticated Padé-Borel form. Although the Padé approximation efficiently sums the divergent perturbation series of the effective Hamiltonian and extrapolates well to higher rotational quantum numbers, it can do nothing with the vibrational spectrum; the majority of unassigned lines in our spectrum were assumed to be due to the vibration-tunneling-rotation transitions in four low-lying intermolecular vibrational states ν_3, ν_4, ν_5 and ν_6. The values of the $J = 0$ energy levels of these bands are respectively about 475 cm^{-1} [5], 125 cm^{-1} [5], 160 cm^{-1}

[5] and 370 cm^{-1} [3]. These values are comparable with the ground state values of 116 cm^{-1} (for $K = J = 2$) and 235 cm^{-1} (for $K = J = 3$). It means that the Boltzmann factor of the low K ($K = 0$ and 1) lines in these excited vibrational states is comparable to the Boltzmann factor of the excited K lines in the ground vibrational state, so we should have been able to see them. This suggests that many of the observed unassigned lines belonged to these excited vibrational states and not, for example, to impurities.

Variational calculations on the HF dimer with $J = 0$ have a long history. Most *ab initio* PESs have been produced by Suhm, Quack and their co-workers, see Refs. [3–5, 18, 19] and references therein. These were full dimensional 6D calculations. There were also reduced dimensional (frozen monomer) calculations by Bunker and Jensen [20] and a (4,2)D calculation by Quack, Suhm and others [4]. So far all full 6D variational calculations only deal with $J = 0$ states; highly excited Js have been studied only using less accurate Quantum Monte Carlo (QMC) calculations [21]. The $J = 0$ calculations of Quack and Suhm augmented by their QMC excited K calculations helped them to assign many spectra in the ν_5 and ν_6 bands in the IR region [3]. However, in the tunneling rotation sub-millimeter region, where all the HF dimer lines belonging to various vibrational states are mixed together, $J = 0$ only calculations are not enough.

In this paper we present variational calculations on $(HF)_2$ for the excited J states; these are described in detail in the next section. Section 3 summarizes the 1990 experimental sub-millimeter spectrum of HF dimer. Section 4 describes the application of our calculations to the analysis of this spectrum. The first information on tunneling-rotational high resolution spectra in the $v_4 = 1$ and $v_3 = 1$ states is given. We also assigned the $K = 4$ branch of rotation-tunneling spectrum in the ground vibrational state. Section 5 presents our conclusions.

2. Variational calculations of HF dimer tunneling rotation-vibration energy levels

Variational calculations of excited rovibrational tunneling energy levels of the HF dimer are performed using the *ab initio* PES calculated by Huang *et al.* [6]. This PES is both of a high theoretical level, using CCSD(T) with an aug-cc-pvQZ basis set, and built on a very large number of calculated *ab initio* points – 100 000, which makes the resulting surface very smooth. Use of this gives highly accurate predictions of rovibrational-tunneling energy levels. In particular, the discrepancies between calculated and empirical values (Tables 1 and 2 below) are at least as accurate as the best empirical (*i.e.* spectroscopically determined or, in other words, adjusted to experimental data) PESs. The HF dimer empirical PES of Klopper, Quack and Suhm [5] reproduced the available experimental data on $K = 0$ and excited K energy levels better than any of the then available *ab initio* surfaces. This work used QMC calculations of excited rotational J and K levels to fit the $(HF)_2$ PES to experimental energy levels with $K > 0$ [5]. However, QMC calculations of nuclear motion energy levels lack accuracy; for example, this work only computed rotational B constants with 1 % accuracy. We are unaware of any previous variational calculations of highly excited J and K states; such calculations are necessary to obtain accurate energy levels beyond band origins. These energies are needed for many purposes, in particular to provide the more numerous theoretical counterparts to experimental measurements for accurate characterisation of the PES and also to assist assignment of the spectra.

For the variational solution of the nuclear motion problem we use the WAVR4 [22] program suite, developed especially for the calculation of energy levels and wavefunctions of tetratomic molecules with large amplitude internal motions. WAVR4 uses an exact, body-fixed kinetic energy operator [23, 24]. The program offers a choice of orthogonal (or polyspherical) coordinates. For the present work we used diatom – diatom Jacobi coordinates and discrete variable representation

(DVRs) based on Morse-oscillator-like functions to represent the three radial coordinates. Rotationally excited states are treated using a two-step procedure which involves solving an initial set of effective vibrational problems which excludes Coriolis coupling and then using the results as a basis to solve the full problem [25]. The original implementation of this procedure in WAVR4 [26] proved to be rather inefficient for higher rotational states [27] but has been improved so that for the present calculations the computer time taken only depends linearly on J. This new version of WAVR4, which includes the capability of computing dipole transition intensities, is currently being prepared for publication [28].

Calculations were performed for J up to 9. This allows us to calculate both B, the rotational constant, and D, the distortion constant, for corresponding branches of the HF dimer spectrum as well as many theoretical line frequencies directly (up to $J = 9$) without resorting to simplified treatments of rotational excitation, using formulae of the type

$$E = BJ(J+1) - DJ^2(J+1)^2. \tag{1}$$

However, energy levels with $J > 9$, if needed, could be obtained using this formula.

Before describing our excited J calculations, we consider the $J = 0$ calculations. These calculations provide the first step in the high J calculations and also illustrate the accuracy with which our adopted PES reproduces the empirical-determined frequencies of all four inter-molecular vibrations.

After the matching of the PES [6] with the program WAVR4, by transformation of coordinate systems and the units used, calculation of the vibration-rotation levels of the HF dimer consisted of the following steps:

1. Choice of an integration region where the potential is well defined, namely, for the HF monomer stretches 1.48 $a_0 < r_1, r_2 <$ 2.4 a_0 and for the HF

– HF stretch 3.5 $a_0 < R < 40\ a_0$ (where r_1 and r_2 are internuclear distances of the two HF monomers, and R is the distance between centers of mass of the monomers). To select a mesh extending to $R > 20$ a_0, it was necessary to modify WAVR4 by increasing the number of iterations in the LAGUER algorithm which selects the location and weights of integration points. The LAGUER algorithm in WAVR4 is an improved version of a LAGUER algorithm from DVR3D [29]. We used the following Morse-like oscillator parameters which are designed to give DVR grids over the appropriate integration range: for the monomer stretches we used $r_e = 1.03$ Å, $w_e = 7500$ cm^{-1}, $D_e = 43000$ cm^{-1} and for the inter-molecular stretch $R_e = 7.7$ Å, $w_e = 16$ cm^{-1}, $D_e = 5000$ cm^{-1}.

2. To ensure convergence, a sufficiently large basis must be used to represent the vibrational-rotational states of interest. Only 10 DVR points were needed for the stiff monomer r_1 and r_2 coordinates, while the inter-molecular stretch required 90 DVR points to obtain a good representation. For bending modes, $l_{max} = 16$ basis functions were used, and $k_{max} = 6$ basis functions for internal rotation, where l_{max} determines sizes of $H_1F_1F_2$ and $H_2F_2F_1$ bending basis sets and k_{max} gives the size of H_1F_1-H_2F_2 internal rotation basis set. The quality of convergence becomes apparent from the shift in energy levels with increasing basis parameters. Thus, with an increase in l_{max} to 20, the energies up to 500 cm^{-1} changed by no more than 10^{-4} cm^{-1}. With an increase in k_{max} to 10, the energies up to 500 cm^{-1} changed by no more than 10^{-3} cm^{-1}. Increasing the DVR grid along r_1 and r_2 to 16 points (with a change in the basis parameter $w_e = 12000$ cm^{-1} to maintain the same integration interval), the energies of fundamental inter-molecular vibrations changed by no more than 1 cm^{-1}. While increasing the DVR grid along R to 100 points (with a change in the basis parameter $w_e = 18$ cm^{-1} to maintain the same integration interval), the energies of

fundamental inter-molecular vibrations changed by no more than 0.5 cm^{-1}. A final vibrational Hamiltonian matrix of dimension 7200 was used. This size comes from truncation at 80 basis function for each of the 90 radial points. Increasing the truncation from 80 up to 120 basis functions leads to a test vibrational Hamiltonian matrix of dimension 10800, and shows the following convergence of the main Hamiltonian: 6×10^{-5} cm^{-1} for energies below 500 cm^{-1} and 2×10^{-4} cm^{-1} for energies below 1000 cm^{-1}.

Table 1 presents a comparison of our $J = 0$ calculations with values obtained empirically. Drawings of all six HF dimer fundamental vibrational modes are given, for example, in Fig. 2 of the paper by Quack *et al.* [3]. There are no accurate high resolution data on the frequencies of these modes. However, there have been several attempts to obtain relatively accurate indirect estimates of their values. In particular, Nesbitt and co-authors [30, 31] used high resolution combination band spectra to estimate the fundamental frequencies. In Table I of their paper [31] ν_4 and ν_5 fundamental frequencies are given with an estimated accuracy of 0.1 cm^{-1}. For ν_4 the frequency was given as 125 cm^{-1}, whereas for ν_5 it was estimated as 160 cm^{-1}. These two frequencies derived from extrapolation of high resolution spectra of combination bands $\nu_1 + \nu_4$, $\nu_2 + \nu_4$, $\nu_1 + \nu_5$ and $\nu_2 + \nu_5$. Less accurate extrapolations have been performed for the higher energy inter-molecular modes ν_3 and ν_6. Table II of paper [30] gives $\nu_3 = 475$ cm^{-1} and $\nu_6 = 395$ cm^{-1} with an estimated extrapolation accuracy of 3 and 8 cm^{-1}, respectively. These extrapolations were made using accurate values of $\nu_1 + \nu_3$, $\nu_2 + \nu_3$, $\nu_1 + \nu_6$ and $\nu_2 + \nu_6$. Since there are more than one estimated frequency for both ν_3 and ν_6 [5, 30], we present both values for comparison in Table 1.

The quality of the HF dimer PES we use is illustrated by the discrepancies between the inter-molecular vibrations energy levels and the results of our calculations described above. All these discrepancies are close to the error bars in

Table 1: Calculated and empirical values of inter-molecular vibrations with $(J, K) = 0$ given in cm^{-1}. Uncertainties in units of the final digit are given in parenthesis.

	calc.	empirical
$\Delta_{K=0}$	0.679	0.6587(1)[a]
ν_4	124.8	125.1(1)[b]
ν_5	162.7	160.6(6)[b]
ν_6	413.0	395(8)[c]
ν_6	413.0	420(5)[d]
ν_3	485.0	475(3)[c]
ν_3	485.0	480(10)[d]

[a] Ref. [32]
[b] Ref. [31]
[c] Ref. [30]
[d] Ref. [5]

Table 2: Calculated and experimentally determined values of band origins with $K > 0$ in cm^{-1}.

$(v_3 v_4 v_5 v_6)$	calc.	exp.
(0000) $K = 1$	36.4	35.4[a]
(0010) $K = 1$	37.5	36.5[a]
(0000) $K = 2$	118.0	116.1[a]
(0010) $K = 2$	120.0	118.1[a]
(0000) $K = 3$	235.4	232.6[a]
(0010) $K = 3$	239.3	236.5[a]
(0010) $K = 4$	390.5	386.7[a]
(0020) $K = 3$	394.0	393.6[b]
(0001) $K = 1$	399.4	399.8[c]
(0011) $K = 1$	401.3	400.8[c]
(0001) $K = 2$	467.2	465.3[c]
(0011) $K = 2$	471.7	468.8[c]
(0101) $K = 1$	507.5	508.1[d]
(0111) $K = 1$	511.8	507.3[d]

[a] Ref. [32]
[b] Ref. [33]
[c] Ref. [34]
[d] Value obtained from energy of $\nu_6 + \nu_4 - \nu_4$, $K = 1$ state [35] and ν_4

the extrapolation of the high resolution values of the experimental band origins. There is no way to improve further the PES based only on the $J = 0$ comparisons with experiment; therefore further developments need to use calculations that consider excited Js.

Table 2 presents a comparison between variationally calculated and experimentally-derived band origins of the J-branches of excited K levels of the ground and vibrationally excited inter-molecular modes. The values for the ground state were taken from our 1990 study [10] and the excited K values of the excited vibrational states are taken from various works by Quack and Suhm. The agreement between calculated and experimentally derived values shown in Table 2 is very good. It again confirms the high quality of the *ab initio* PES used. Even more so, since the information in Table 2 is directly derived from experiment, unlike the estimated values of Table 1, the much better agreement between calculations and experiment in Table 2 emphasises once more the importance of high K and thus excited J calculations. The comparisons given in Table 2 could not be made in the original paper reporting the *ab initio* PES [6] since that work only performed $J = 0$ calculations.

To calculate the rotational energy levels of the $(HF)_2$ dimer, we used parameters $J_{\max} = 9$ and $K_{\max} = 9$. We had to increase from 10 to 500 the number of levels written out by the program for each symmetry at the fourth stage, that is, when the Coriolis-decoupled $J > 0$ energy levels are calculated. Additionally, the angular vibrational basis set parameter with a rotational momentum l_{max} had to be increased from 16 to 20. The final ro-vibrational calculations involved diagonalisation of Hamiltonian matrices of dimension $40 \times (J + 1)$. This is sufficient to converge the energy levels of interest to better than 0.1 cm^{-1}. Our calculated $(HF)_2$ vibrational-rotational energy levels with $J \leq 9$ are given in Table A1 of the Supplementary Materials.

Experimental information on the excited J states of $(HF)_2$ is usually com-

pressed by fitting values of rotational constants (such as B, D and H, see Eq. (1) and Eq. (2)) to the observed line positions. This compression is possible because the HF dimer behaves like a nearly linear molecule and for a certain vibrational and K_a states, the lines of the HF dimer are grouped in regular progressions, similar in structure to the rotational series observed for diatomic or linear molecules. The observed rotational constants are obtained from experimental line positions and calculated constants from variational calculations using excited J energy levels. We determined B and D constants from the fit of calculated levels with J from 1 to 9 using Eq. (1).

Table 3 presents values for our computed B and D constants and, where possible, compares them with empirical values. We will refer to these collectively as 'spectroscopic constants' here and elsewhere. For convenience and completeness Table 3 also presents experimental values for $K = 4$ of the ground state and some excited inter-molecular vibrational states obtained in Section 4 of this paper; other experimental values are taken from the literature, mostly from the papers by Quack and Suhm.

Table 3: Calculated and experimental rotational constants (powers of ten are given in parenthesis).

State	Units	B_{calc}	B_{exp}	D_{calc}	D_{exp}	Exp. source
(0000)						
$K = 0$	cm^{-1}	0.2154	0.2167	2.26(−6)	2.06(−6)	Ref. [32]
	MHz	6457.5	6496.9	0.0633	0.0618	
$K = 1$	cm^{-1}	0.2158	0.2179	1.92(−6)	1.99(−6)	Ref. [32]
	MHz	6469.5	6531.3	0.0577	0.0596	
$K = 2$	cm^{-1}	0.2174	0.2186	1.89(−6)	1.94(−6)	Ref. [32]
	MHz	6517.4	6553.7	0.0567	0.0582	

State	Units	B_{calc}	B_{exp}	D_{calc}	D_{exp}	Exp. source
$K = 3$	cm^{-1}	0.2169	0.2181	1.47(−6)	1.76(−6)	Ref. [32]
	MHz	6502.4	6538.2	0.0441	0.0529	
$K = 4$	cm^{-1}	0.2150	0.2175	6.14(−5)	-6.01(−5)	This work
	MHz	6444.6	6498.6	1.84	-1.8	
(0010)						
$K = 0$	cm^{-1}	0.2153	0.2166	2.41(−6)	2.04(−6)	Ref. [32]
	MHz	6451.5	6492.8	0.0625	0.0612	
$K = 1$	cm^{-1}	0.2177	0.2177	2.08(−6)	1.97(−6)	Ref. [32]
	MHz	6525.5	6526.8	0.0625	0.0591	
$K = 2$	cm^{-1}	0.2173	0.2185	1.86(−6)	1.95(−6)	Ref. [32]
	MHz	6514.3	6551.1	0.0558	0.0586	
$K = 3$	cm^{-1}	0.2176	0.2188	1.60(−6)	1.87(−6)	Ref. [32]
	MHz	6522.7	6558.9	0.0479	0.0561	
$K = 4$	cm^{-1}	0.2181	0.2194	1.74(−6)	2.28(−6)	Ref. [32]
	MHz	6539.1	6576.9	0.052	0.068	
(0100)						
$K = 0$	cm^{-1}	0.2119	0.2140	3.04(−6)	4.34(−6)	This work
	MHz	6353.0	6415.5	0.0910	0.130	
(0110)						
$K = 0$	cm^{-1}	0.2104	0.2161	2.71(−6)	5.07(−6)	This work

State	Units	B_{calc}	B_{exp}	D_{calc}	D_{exp}	Exp. source
	MHz	6306.3	6478.5	0.0813	0.152	
(1000)						
$K = 0$	cm^{-1}	0.2052	0.2129	3.24(−6)	1.88(−4)	This work
	MHz	6350.2	6383.9	0.0971	5.63	
(1010)						
$K = 0$	cm^{-1}	0.2099	0.2002	2.97(−5)	1.52(−4)	This work
	MHz	5922.3	6000.4	0.890	4.57	
(0001)						
$K = 0$	cm^{-1}	0.2154		1.02(−5)		
	MHz	6460.1		0.306		
$K = 1$	cm^{-1}	0.2132	0.2105	1.13(−5)	2.5(−6)	Ref. [34]
	MHz	6393.7	6310.6	0.34	0.07	
$K = 2$	cm^{-1}	0.2127	0.2113	1.03(−5)	2.1(−6)	Ref. [34]
	MHz	6375.4	6334.6	0.31	0.06	
(0011)						
$K = 0$	cm^{-1}	0.2157		3.09(−6)		
	MHz	6466.9		0.0926		
$K = 1$	cm^{-1}	0.2132	0.2103	1.08(−5)	2.5(−6)	Ref. [34]
	MHz	6385.9	6304.6	0.324	0.07	

State	Units	B_{calc}	B_{exp}	D_{calc}	D_{exp}	Exp. source
$K = 2$	cm^{-1}	0.2140	0.2129	0.99(−6)	2.05(−6)	Ref. [34]
	MHz	6415.9	6382.5	0.30	0.0615	
(0101)						
$K = 1$	cm^{-1}	0.2080	0.2133	7.67(−6)	3.74(−6)	[a]
	MHz	6236.5	6334.6	0.23	0.112	
(0111)						
$K = 1$	cm^{-1}	0.2072	0.2114	9.54(−6)	5.03(−6)	[a]
	MHz	6211.3	6337.6	0.286	0.151	
(0020)						
$K = 3$	cm^{-1}	0.2227	0.2217	4.5(−6)	1.67(−6)	Ref. [33]
	MHz	6679.4	6646.3	0.13	0.050	

[a] Constants calculated from ν_4 constants determined in this work and values for ΔX $(X = B, D)$ in Ref. [34]

Table 3 shows that the ground state B constants taken from the Belov *et al.* [10] and calculated variationally in the present paper coincide to within about 30 – 50 MHz. This agreement between B_{obs} and B_{calc} is unexpectedly good.

The impressive accuracy of prediction of B and D constants associated with the tunneling rotation spectrum of the ground vibrational state of the HF dimer and also of the B values of some excited vibrational states taken from the papers by Quack and Suhm, paves the way for us to apply the results of these calculations

to an analysis of unassigned lines in the HF dimer tunneling-rotation spectra. These lines belong to excited inter-molecular vibrations and higher K states of the ground vibrational state; for instance, the high resolution spectra of tunneling-rotational lines in $v_4 = 1$ and $v_3 = 1$ vibrational states are assigned for the first time here (Section 4). For other vibrational states, high resolution spectra have been analysed by Quack and Suhm [19, 33–35].

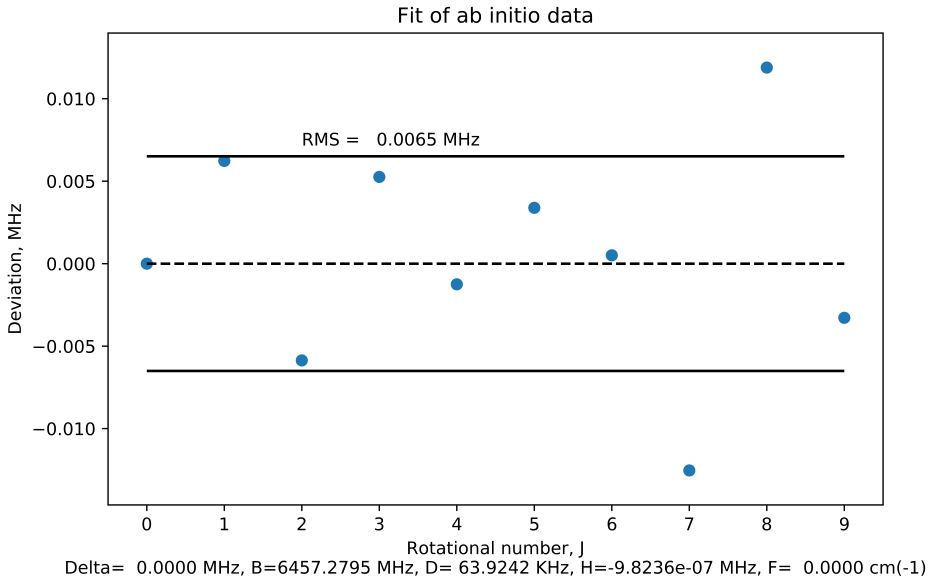

Figure 1: Difference between the *ab initio* energies and ones obtained from the fit for $(v_3 v_4 v_5 v_6) = (0\ 0\ 0\ 0)$ band of $(HF)_2$, $K = 0$

We also performed a least-squares fit to the *ab initio* energies using the formula of Belov *et al.* [10]

$$E(J,K,\nu) = \Delta_K \delta_{\nu,1} + F_K + B_J^\nu J(J+1) \\ -D_J^\nu J^2(J+1)^2 + H_J^\nu J^3(J+1)^3. \tag{2}$$

Results of this fit are presented in Figures 1 and 2. Small residuals (less than 100 kHz) confirm that the formula 1 used for the fit is appropriate and we can thus safely use the results of this fit to represent the energies obtained by our

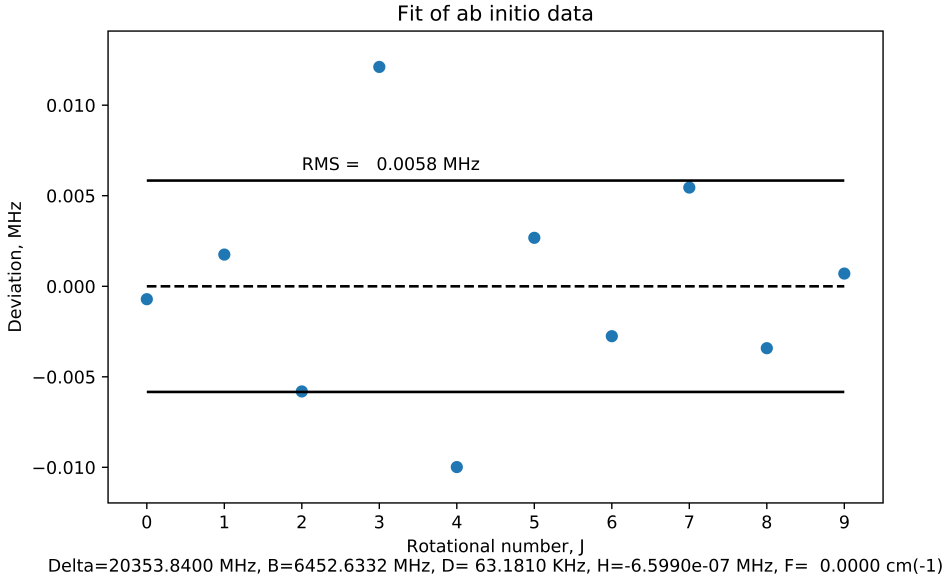

Figure 2: Difference between the *ab initio* energies and ones obtained from the fit for $(v_3 v_4 v_5 v_6) = (0\ 0\ 1\ 0)$ band of $(HF)_2$, $K = 0$

ab initio calculations. In other words the values of B and D given in Table 3 give an excellent representation of the values calculated when used with Eq. (2) and effect on energy levels related to H-constants may be omitted.

3. Experimental details of the observation of sub-millimeter spectrum of HF dimer in the gas phase

Thirty years ago some of us published a sub-millimeter study [10] of the $(HF)_2$ spectrum. At the time it was not possible to completely assign this spectrum. Before discussing new assignments we have been able to make using our variational calculations (Section 4), we first give some experimental details.

The broad-band (180-380 GHz) spectrum of the HF dimer was recorded at the end of eighties using a spectrometer with a backward wave oscillator (BWO) as a radiation source [36] and Radio-Acoustic Detection of absorption (RAD), which we call the RAD-3 spectrometer. A detailed description of the instrument can

be found on the Laboratory website[2] and in our report on a similar study of the H_2O-HF dimer [7]. A brief description of the experiment considered was given in the corresponding section of Ref. [10]. For the reader's convenience we repeat here the most important details with some other complementary information which was used in the present analysis of the spectrum.

Equilibrium gas-phase HF dimer spectra were observed at temperatures of about 200 - 220 K in a static pressure stainless steel cell at pressures between 0.5 – 1.5 Torr. HF vapor was obtained by thermal decomposition of KFHF. The intensity of the observed spectrum depended on pressure and temperature. The prominent spectral lines appeared and grew up only with cooling the cell down and their intensity also increased with increased pressure as expected from the general pressure and temperature dependence characterized by the dimerisation constant. The optimal temperature was found to be near 210 K. Neither the HF gas generator nor the cell thermostat allowed active control of experimental conditions. Because of this the spectral intensity in the repeated recordings varied from day to day but relative intensity of lines within one recording was preserved.

The spectrum was recorded continuously (without gaps) covering the range from 180 up to 385 GHz. The continuity is crucial for unambiguous assignment of observed lines. At the time of the experiment, such broadband continuous recordings were not possible in this spectral range as the radiation frequency was controlled using a phase locking loop systems with poor scanning ability (see review [37] and references therein). Frequency measurements in the spectrometer were calibrated using the lines from a SO_2 reference spectrum [38]. The mean square value of the frequency uncertainty was determined in preliminary tests as 0.5 MHz for strong isolated monomer lines. The uncertainty was somewhat larger in the case of weak and pressure broadened HF dimer lines. However,

[2] http://mwl.ipfran.ru

we consider a value of a few MHz as a reasonable estimate of the possible error in the frequency measurements for most lines. Figure 3 presents a portion of the observed HF dimer spectrum recorded simultaneously with a SO_2 reference spectrum. Unfortunately, only half of the recorded spectrum has survived the transition from large specialized counting machines to personal computers. Only recordings in the range of 268 – 385 GHz are now available. Analysis of this spectrum is given in the next section.

It is our view that repeating the experiment using a modern, more sensitive and more accurate apparatus alongside extension of the spectral range to higher frequencies, where the characteristic Q-branches are located, is now important for obtaining data for comparison with high accuracy *ab initio* calculations. However, this would have to be the subject of a specialized project with adequate funding.

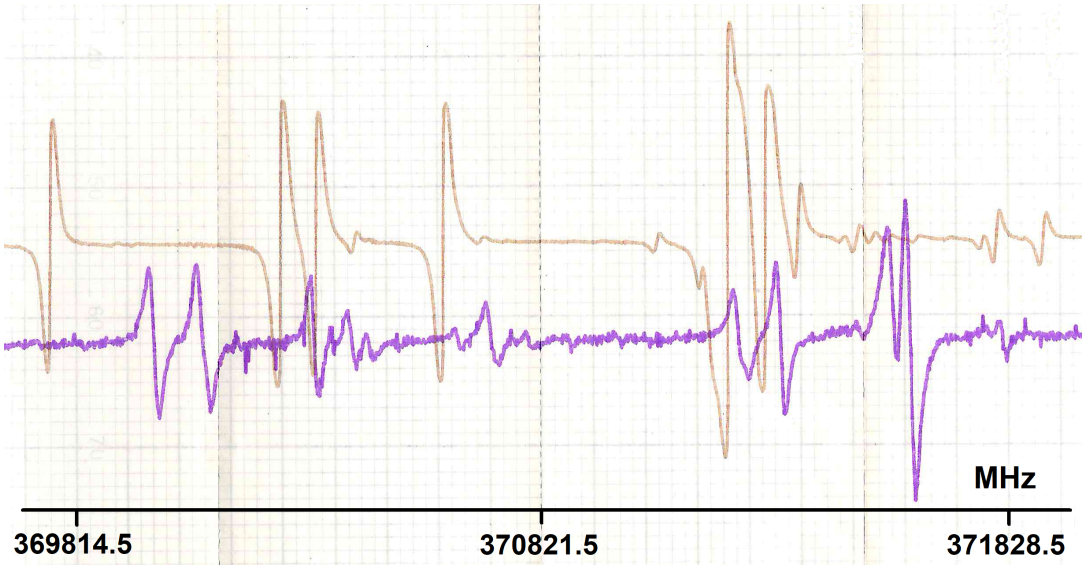

Figure 3: Small portion of recorded in the late 80-ties tunneling-rotation spectra of $(HF)_2$ in violet (lower spectrum) and calibration SO_2 in light brown (upper spectrum)

4. Analysis of the sub-millimeter spectrum

Accurate *ab initio* prediction of highly rotationally excited J and K energy levels are essential for the analysis of the sub-millimeter tunneling-rotation spectrum of the HF dimer in the limited region between 268 and 385 GHz. Quack and Suhm were able to assign the lines of the far IR HF dimer spectrum, [3, 34, 35] since the IR experimental spectra with much wider coverage provided information on all the P, Q and R branches. Moreover, ro-vibrational lines belonging to the different fundamental bands of the different inter-molecular modes, ν_3, ν_4, ν_5 and ν_6, occur in distinct, non-overlapping regions of the spectrum. Let us briefly summarise their assignments. Von Puttkammer and Quack [35] studied the region between 350 and 550 cm^{-1}, where the observation of two Q-branches helped them to assign the ν_6, $K = 1 \leftarrow 0$ band with a Q-branch at around 400 cm^{-1}. In the same paper they observed another clearly resolved P, Q, R structure with a Q-branch at 383 cm^{-1}. In a subsequent paper [3], Quack and Suhm attributed this structure to the $\nu_6 + \nu_4 - \nu_4$ hot band. Von Puttkammer *et al.* [34] analyzed the ν_6, $K = 2 \leftarrow 1$ subband at 465 cm^{-1}, and Quack and Suhm [33] investigated $K = 2$ and 3 subbands of the ν_5 band and predicted the 6.83 cm^{-1} sub-millimeter rotation-vibration tunneling band between excited vibrational states. Figure 4 of their paper [33] is a diagram of all known and estimated high K energy levels of ν_4, ν_5 and ν_6 bands of the HF dimer. This figure facilitates understanding of the energy levels presented in Tables 1 and 2.

To summarize the previously published work, mostly by Quack, Suhm and co-authors, experimental information on inter-molecular vibrations with $J = 0$ and excited K the following is known (Tables 1 and 2). $K = 0$ is unknown from analysis of high resolution spectra for all inter-molecular states. However, different extrapolation procedures have allowed frequencies of all four low-lying vibrations to be estimated with differing levels of accuracy (Table 1). In partic-

ular, for the ν_4 band indirect experimental information on the 125 cm^{-1} band origin, derived from $\nu_1 + \nu_4$ and $\nu_2 + \nu_4$ data extrapolation by Anderson *et al.* [31], and from an analysis of the $J \geq 30$ resonance between $K = 2$ of the ground state and $K = 0$ of the $v_4 = 1$ state by Quack and Suhm [3].

Comprehensive information on the $K \leftarrow K - 1$ bands for $K = 1$ and 2 was obtained by Quack and Suhm for ν_5 [33] and ν_6 [34] states. However, no high resolution information on ν_3 and ν_4 has been published. In what follows we present the first high resolution experimental assignment of lines belonging to these two states.

Table 4: Observed frequencies (in MHz) for the $K = 0$ branch of the tunneling-rotation spectrum of HF dimer in the ν_4 excited vibrational state.

Frequency	J'	J"	obs.-fit.
274791.3	15	14	-0.1
285878.5	16	15	-0.5
296872.7	17	16	1.5
307772.9	18	17	-0.7
318591.5	19	18	0.1
329329.8	20	19	-1.0
339995.3	21	20	-0.1
350590.3	22	21	0.4
361118.4	23	22	1.8
371574.7	24	23	-2.1
381970.6	25	24	0.6

Table 5: Values (in MHz) of the effective rotational B and D constants as well as the tunneling splitting constant Δ_K (Eq.(2)) of the $K = 0$ tunneling-rotation spectrum of ν_4.

	Calc.	Obs.
Δ_0	88659	94494
	Upper	
B	6306.3	6433.9
D	0.0813	0.167
	Lower	
B	6353.0	6488.8
D	0.091	0.172

Table 6: $K = 4$ branch of tunneling-rotation spectrum in the ground vibrational state in MHz.

Frequency	J'	J"	obs.-fit
280614.3	5	4	-0.1
294326.6	6	5	1.2
308144.8	7	6	-3.4
322151.6	8	7	4.9
336419.3	9	8	-3.7
351119.4	10	9	1.1
366409.2	11	10	0.2
382504.2	12	11	0.1

Table 7: Values (in MHz) of effective rotational B and D constants as well as the tunneling splitting constant Δ_K (Eq.(2)) of the $K = 4$ tunneling-rotation spectrum of HF dimer in the ground vibrational state.

	Calc.	Obs.
Δ_4	225051	213545
	Upper	
B	6539.1	6576.9
D	0.052	0.068
	Lower	
B	6444.6	6498.6
D	1.84	-1.8

Table 8: $K = 0$ branch of tunneling-rotation spectrum of HF dimer in the ν_3 state (in MHz)

Frequency	J'	J"	obs.-fit.
325666.6	1	0	1.5
336768.3	2	1	-6.3
346933.0	3	2	4.3
356077.7	4	3	8.1
364146.9	5	4	-14.2
371203.5	6	5	5.7
377198.7	7	6	0.8
382203.6	8	7	-0.9

As an example of the use of calculated HF dimer tunneling splittings, band origins and rotational constants, we assigned part of the $K = 0$ R-branch tunneling-rotational transitions within the exited fundamental inter-molecular vibration ν_4.

Table 9: Values (in MHz) of effective rotational B and D constants as well as the tunneling splitting constant Δ_K (Eq.(2)) of the $K = 0$ tunneling-rotation spectrum in the ν_3 state.

	Calc.	Obs.
Δ_0	317824	313681
	Upper	
B	5957.4	6000.5
D	0.89	4.57
	Lower	
B	6232.7	6383.91
D	0.097	5.63

The $K = 0$, ν_4 state lies at about 125 cm^{-1}, which is close to the ground state $K = 1$ (35 cm^{-1}) and $K = 2$ (116 cm^{-1}) states. So the Boltzmann factor suggests it should be the strongest of the remaining unassigned bands. Manually we have a set of 11 lines covering all the available experimental region of 268–385 GHz. Using seven constants (B, D and H rotational constants for upper and lower tunneling split states and the value of this splitting) as fitting parameters, the lines are described with a standard deviation of 1.7 MHz corresponding to an estimated experimental accuracy of 2-5 MHz. If we omit the two H constants, the standard deviation increases to 4.5 MHz which is still inside experimental accuracy. As the number of fitted lines is not much larger than the number of constants when H constants are included, the H constants are poorly determined. For this reason only fit with H constants fixed to zero are presented

The fit was made assuming that the inversion splitting of the $K = 0$, ν_4 state is close to the calculated value of about 3 cm^{-1} (90 GHz). This value, plus the values of the B rotation constants, determine the upper and lower J's of the measured transitions as in Eq. (2). Changing the splitting by 12 GHz leads to a change in the J's by one. The correct J values for the observed transitions could not be determined from available experimental transitions in the region 268–385 GHz. Fits to the experimental frequencies with J's differing

by one give practically the same standard deviation, and similar values for the rotation constants. To empirically determine the correct J values one has to observe either the Q-branch or the beginning of the R-branch in the centimeter wavelength region. Fit residuals for the tunneling-rotation $K = 0$ branch lines in the $v_4 = 1$ state are presented in Table 4. A comparison of experimentally derived B and D constants with those obtained variationally is given in Table 5. Table 3 presents a corresponding comparison for all known v and K states. The residuals of *ab initio* calculations for the observed frequencies are of order 0.1 cm^{-1} (3000 MHz).

This first determination of B and D constants for the ν_4 state helped us to obtain another important piece of experimental information. In their study on the first IR hot spectrum of combination band $\nu_6 + \nu_4 - \nu_4$ Von Puttkamer and Quack [35] could determine only ΔB and ΔD constants as they did not of a know the B and D constants of the lower state ν_4, so only differences between upper and lower state constants could be determined. Our determination of the ν_4 B and D constants allows us to determine the B and D constants of the upper combination state of $\nu_6 + \nu_4$. These newly determined values are used in Table 3 for comparison with the variationally determined B and D constants.

Let us now consider the assignment of tunneling-rotation lines in the ν_3 state. This mode is the highest energy inter-molecular vibration (about 480 cm^{-1}) and its lines should be among the weakest in the recorded spectrum. The inversion splitting of the $v_3 = 1$ state is calculated to be about 318 GHz.We were able to find a series of lines starting at 325 GHz. Fits to this series of 8 lines with 5 constants (B and D constants for upper and lower states and the tunneling splitting) gives a standard deviation of 6.7 MHz. Observed values of the frequencies and the residuals of the fit are given in Table 8 and constants obtained from the fit and our variational calculations are given in Table 9.

The last series of lines which we assign in the 268 - 385 GHz tunneling-rotation

spectrum was the $K = 4$ branch of the ground state. Table 7 gives lines of the branch for J ranging from 4 to 11 together with the residuals between observed and fitted frequencies using the B, D and Δ_K model. B and D constants of the upper state given in Table 7 were fixed to the values reported by to Quack and Suhm [32], obtained from the $K = 4 \leftarrow 3$ band. Δ_K, B and D constants are determined in the fit of Eq.(2) to the data of Table 6. The standard deviation of this fit is 4.7 MHz.

To summarize our new assignments of the tunneling rotation sub-millimeter spectrum: lines belonging to previously unobserved ν_3 and ν_4 states are found and assigned for their $K = 0$ branches. The $K = 4$ branch of the ground vibrational state had only a single known tunneling state [34] and now both tunneling states involved in the tunneling rotation band have been observed, assigned and B, D and Δ_K constants determined. The variationally calculated B and D constants together with the constants obtained from the fit are given in the tables of Section 2 and this section. It transpires that after assignment and analysis of these branches, the values of the experimental B and D constants are reproduced very well, with similar accuracies of tens of MHz, by our variational calculations. The planned further improvement of the *ab initio* PES should lead to the further improvement in the agreement between variational and experimental B and D constants as well as the agreement between calculated and observed band origins.

What remains to be observed in the HF dimer spectrum within the sensitivity of the existing experimental setup and the Boltzmann factor of the states to be observed is the following: $K = 5$ and 6 of the ground vibrational state, $K = 1$ and 2 of ν_3 and $K = 1, 2, 3$ and 4 of ν_4 as well as $K = 0$ of ν_6. These observations could be made using active thermal stabilization of an experimental gas cell and HF generator improving the signal-to-noise ratio of the observed spectra and an expansion of the region of observation to 180 - 260 GHz and 370 - 535 GHz (accessible with corresponding radiation sources [36]) in order to observe

Q-branches and expand the J ranges of the P and R branches. The resulting set of experimental Δ_K, B and D constants would serve as an excellent source of data for comparison with an improved *ab initio* HF dimer PES.

5. Discussion and Conclusions

We present calculations on the tunneling-rotation-vibration spectrum of the HF dimer performed using the variational nuclear motion program suite WAVR4 [22, 28] and an *ab initio* HF dimer PES [6]. We used the results of these calculations to analyze a 30-years old gas phase tunneling-rotation spectrum of the HF dimer, recorded using a RAD-3 spectrometer in the sub-millimeter region [10]. Excellent reproduction of the observed B constants of the previously assigned [10] $K_a = 0, 1, 2$ and 3 branches encouraged us to assign further branches of the HF dimer spectrum. In particular, the higher $K_a = 4$ branch of the ground vibrational state and the two $K_a = 0$ branches of the exited ν_4 and ν_3 fundamental vibrational inter-molecular modes were assigned for the first time. No previous high resolution study had identified transitions in the ν_4 and ν_3 states; we were able to identify lines of these states in our sub-millimeter spectrum on the basis of predictions obtained using high accuracy excited J variational calculations.

The present study paves the way for the further improvements of the *ab initio* HF dimer PES and application of it to the accurate calculation of HF dimer spectrum as well as the assignment of the further energetically higher lying branches. This should help fully characterise the HF dimer spectrum up to dissociation, provided the corresponding experimental tools are available. Further improvement of the *ab initio* calculations are necessary to achieve agreement with experiment. This work currently is in progress.

The drive for obtaining a more complete understanding of HF dimer spectra is not limited to an interest in the HF dimer itself. The HF dimer is similar in many respects to the water dimer which enhances the motivation for studying highly

excited rovibrational states of $(HF)_2$. The ability to accurately calculate highly excited J levels of the water dimer remains an unsolved problem but one which is important for both fundamental molecular spectroscopy and atmospheric physics. Developing viable theoretical methods for this is a prerequisite for the calculation of accurate water dimer line lists which would provide an important step towards a solution of various physical problems, not the least of which is the problem of the water continuum in the Earth's atmosphere [39, 40] and atmospheres of exoplanets. The unambiguous observation of rotational features of water dimers in equilibrium water vapor at close to atmospheric conditions [41–43] paves the way to a fuller understanding of the water dimer spectrum via a complete theoretical line list and further experimental observations, see [44, 45]. However, a reliable interpretation of such experimental observations requires an accurate theoretical line list, which includes treatment of highly excited vibrational and rotational states. This problem remains very challenging.

The HF dimer system has strong similarities with the water dimer: It has the same number of electrons and is similarly floppy. The tunneling-rotational spectrum of these two dimers are quite similar in terms of the adiabatic relations between the low energy and high energy motions. However, there are also a few significant differences. The water dimer is of much higher importance for applications to the atmospheric studies of the Earth and exoplanets, and to an understanding of liquid water. The second difference is the number of nuclear degrees of freedom: 6 for $(HF)_2$ and 12 for $(H_2O)_2$. Because of this it is much harder to calculate accurately both the PES and tunneling-rotation-vibration energy levels of $(H_2O)_2$, than in the case of $(HF)_2$. These similarities and differences open wide opportunities for the study of both dimers. Studies of $(HF)_2$ are of increased importance as a similar but easier to study system, which will teach us how to deal with the more important and more complicated water dimer. The third big difference between these two dimers is the relative ease of observing HF

dimer spectra under equilibrium and relatively warm gas phase thermodynamic conditions, as demonstrated by numerous studies in both the microwave and the IR regions, and the utter impossibility of observing spectra of similar high resolution for the water dimer. This fact makes studies of the HF dimer even more important, as high accuracy high resolution experimental data facilitates detailed comparison with theory. Such comparisons give guidance on how to achieve comparable accuracy of calculations for the water dimer, without having to actually compare these calculations with highly excited vibrational and rotational water dimer energy levels. Nevertheless, extensive data on the water dimer obtained in beams and jets allows such comparisons to be made for low-lying rotations and vibrations. These comparisons can confirm ideas about the similar accuracy of calculations of energy levels and line intensities for the water- and HF-dimers; this should allow one to extrapolate our understanding of the accuracy of highly excited HF dimer calculations to practical calculations of highly excited states of the water dimer.

The resulting observed minus calculated residuals for the HF dimer based on experimental and semi-experimental data, presented here and the corresponding variationally calculated values, provide valuable information for estimating the accuracy of a corresponding water dimer *ab initio* calculations of energy levels and line positions. Clearly this will be the case when *ab initio* calculations on the water dimer are performed at the same level of electronic structure theory. Thus our HF dimer study provides useful underpinning information for *ab initio* studies on the water dimer supporting our objective, which is to calculate a very accurate water dimer *ab initio* PES whose accuracy can be benchmarked by studies of the HF dimer.

There are two alternative approaches to further improving our HF dimer PES and hence spectrum calculations. The first is to produce an improved PES by fitting to experimental data, as Klopper *et al.* have done [5]. However, this

approach will not guide us to improved water dimer calculations. The other alternative is to increase the levels of electronic structure theory. Work along these lines is currently in progress paved by impressive results reported in this paper.

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Supplementary material

A text files giving the calculated HF dimer energy levels is given as supplementary data.

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