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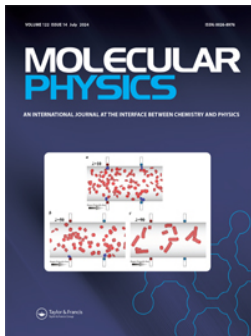
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## High-resolution FTIR spectroscopy and analysis of the $K_a = 0 \leftarrow 1$ subbands of the fundamentals $\nu_3$ and $\nu_6$ of the dimer $(\text{HF})_2$

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# High-resolution FTIR spectroscopy and analysis of the $K_a = 0 \leftarrow 1$ subbands of the fundamentals $\nu_3$ and $\nu_6$ of the dimer $(\text{HF})_2$

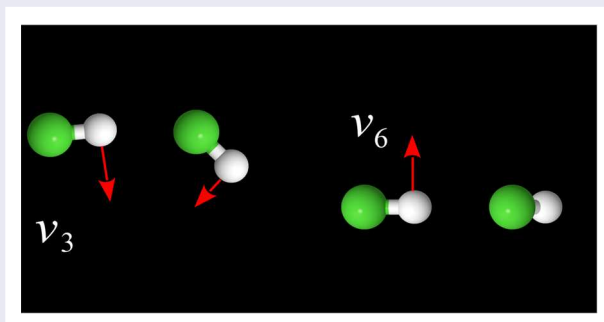
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## ABSTRACT

We report new far-infrared spectra of  $(\text{HF})_2$  obtained by high resolution long-path Fourier Transform-Infrared (FTIR) spectroscopy. The origins of the two tunneling components of the  $K_a = 0 \leftarrow 1$  subband of the in-plane symmetric bending fundamental  $\nu_3$  were found to be at  $450.4546 \text{ cm}^{-1}$  ( $\Gamma_t: A^+ \leftarrow B^+$ ) and at  $451.4583 \text{ cm}^{-1}$  ( $B^+ \leftarrow A^+$ ), and of the  $K_a = 0 \leftarrow 1$  subband of the out-of-plane bending fundamental  $\nu_6$  at  $382.0802 \text{ cm}^{-1}$  ( $A^+ \leftarrow A^+$ ) and at  $383.2245 \text{ cm}^{-1}$  ( $B^+ \leftarrow B^+$ ). The  $K_a = 0$  term values with respect to the ground state  $\Gamma_t = A^+$  term are  $486.9442 \text{ cm}^{-1}$  for the  $A^+$  and  $486.8834 \text{ cm}^{-1}$  for the  $B^+$  tunneling levels of  $\nu_3$ . They are  $417.5053 \text{ cm}^{-1}$  for the  $A^-$  and  $419.7140 \text{ cm}^{-1}$  for the  $B^-$  vibration-tunneling sublevels of  $\nu_6$ . The results are discussed in relation to full-dimensional quantum dynamics and predictions based on recent *ab initio* calculations and our empirically refined potential energy hypersurfaces.

Graphical abstract



## ARTICLE HISTORY

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## KEYWORDS






FTIR spectroscopy; HF dimer; potential energy hypersurfaces; vibration-tunneling dynamics; hydrogen bonding

## 1. Introduction

In contrast to early theoretical analyses of high-resolution spectra of polyatomic molecules and clusters based on perturbation theory and approximate vibration rotation Hamiltonians, recent progress has focused on quasi-exact vibration rotation calculations on full-dimensional potential hypersurfaces (see for instance the reviews in [1]). Attila Császár has been a pioneer in the development of exact numerical methods and computational approaches towards such molecular rovibrational eigenstate calculations [2,3]. In particular the highly non-rigid hydrogen bonded clusters are candidates for such

approaches and an early example for vibration-tunneling quantum dynamics on full-dimensional potential hypersurfaces is the prototypical dimer HFHF [4]. Some of the historical development can be found summarized in the recent Refs. [5,6].

Indeed, the hydrogen bonded clusters  $(\text{HF})_n$  can be considered to be the simplest prototypes for studies of multidimensional potential hypersurfaces and the quantum dynamics of hydrogen bond tunneling rearrangement and hydrogen bond formation and dissociation processes in hydrogen-bonded clusters in general [7–9]. Such clusters in increasing size (with  $n = 2, 3, 4, \dots$ ,

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up to very large nanoclusters [10–14]) can serve as a role model for the transition from molecules in the gas phase to liquids and solids also for more complex hydrogen-bonded systems such as water, alcohols and even biomolecular systems such as proteins and DNA [15–21]. They can also serve in relation to effects such as quasiadiabatic channel above barrier tunneling to an understanding of some of the most fundamental aspects of tunneling spectra [5,22].

Although the hydrogen bond in the HF dimer is relatively strong, with electronic dissociation energy corresponding to  $D_e = 1597 \text{ cm}^{-1}$  by theory [4,7,23] and  $D_0 = 1062 \text{ cm}^{-1}$  ( $\Delta H_0^\ominus = 12.70 \text{ kJ mol}^{-1}$ ) by experiment [24,25], this molecule is very flexible and the description of its dynamics is quite complicated. Considering its degrees of freedom, we may distinguish between the so-called intramolecular vibrations  $\nu_1$  (*free* HF stretching) and  $\nu_2$  (*bonded* HF stretching), and the intermolecular modes  $\nu_3$  (in-plane symmetric bending or in-plane libration or ‘antigear’ bend or conrotatory bend),  $\nu_4$  (FF stretch or van der Waals stretch),  $\nu_5$  (in-plane antisymmetric bend or ‘geared’ bend or hydrogen bond exchange disrotatory in-plane vibration) and  $\nu_6$  (out-of-plane bend or out-of-plane libration or out-of-plane torsion). The intermolecular fundamentals are expected below about  $600 \text{ cm}^{-1}$ , *i.e.* in the far infrared region. The far-infrared spectrum therefore represents a particularly rich source of information on structure and dynamics of this molecule. Early investigations of the far-infrared spectrum could identify the  $K_a = 1 \leftarrow 0$  [26] and  $2 \leftarrow 1$  [27] subbands of the  $\nu_6$  fundamental as well as excited  $K_a$  levels of the vibrational ground state  $\nu_0$  [27,28],  $\nu_5$  [29], and an approximate value of  $\nu_4$  [4]. Many structures in the far-infrared spectrum remained unexplained. In particular, the band centers ( $K_a = 0$  levels) of the in-plane symmetric bending fundamental  $\nu_3$  and of the out-of-plane bending fundamental  $\nu_6$  were not experimentally assigned and analyzed in earlier work.

This lack of direct evidence motivated us to reinvestigate the far-infrared region of the spectrum by high resolution FTIR spectroscopy under improved conditions using a new long path absorption cell. We report the detailed analysis of two subbands centered near  $380$  and  $450 \text{ cm}^{-1}$ , which could be assigned to the  $K_a = 0 \leftarrow 1$  subbands of the fundamentals  $\nu_6$  and  $\nu_3$ , respectively. The results of the present investigation are particularly timely in view of recent efforts of generating improved *ab initio* potential energy hypersurfaces [7,23,29–31]. The interaction potential of the two HF molecules in  $(\text{HF})_2$  has been repeatedly studied already from the early days of accurate *ab initio* quantum chemistry [32–35]. A large set of *ab initio* potential energies for various structures calculated by Kofranek, Lischka and Karpfen [36] was

used as starting point for developing fully six dimensional analytical potential hypersurface representations by Quack and Suhm [4,37] (labeled QSKLK, QSBDE *etc.*, where the S in front indicates potentials which were semi-empirically adjusted to selected experimental data such as rotational constants  $B$  or the dissociation energy corresponding to  $D_e$ ). These surfaces were used for full-dimensional eigenstate calculations by Quantum Monte Carlo techniques [4] as well as vibrational variational approaches [38,39]. In comparison with experiment it was noted that *ab initio* calculations needed improvement and a substantial effort led to new *ab initio* calculations using an MP2-R12 approach to generate accurate potential energy and dipole hypersurfaces [23,29]. At the same time, new high level CCSD(T) calculations were carried out for selected structures and properties [40,41]. It was realised that for some aspects of the empirical adjustment of the hypersurfaces the accurate spectroscopic basis was still lacking [4,23]. However, we have recently shown that the empirically adjusted potential hypersurface SO-3 from [7,29] provides a very satisfactory description of the HF-stretching overtone polyads including the tunneling and symmetry substructures [6,42]. Nevertheless, an accurate empirical basis for an adjustment notably for the properties related to the mode  $\nu_3$  is lacking and the present work intends to fill this gap.

## 2. Experimental

The high-resolution spectra have been measured on our BOMEM DA002 spectrometer in the  $125\text{--}680 \text{ cm}^{-1}$  range (see Refs. [26–28,43,44]). We used a Globar light source, a  $3\mu$  Mylar beam splitter and a liquid Helium cooled Si bolometer which was equipped with a  $12.5 \mu\text{m}$  cut-on long wave pass filter. The sample cell had been purchased from *Portmann Instruments AG, Switzerland*. It is a coolable long-path cell with internal White optics. The base length is  $1.37 \text{ m}$  and the path length can be varied in steps of about  $10 \text{ m}$ . The cooling of the cell can be performed by passing a refrigerant through a cooling-jacket. All materials of the cell have been carefully selected to be resistant to HF. The cell body is made of stainless steel and the White optics inside the cell consists of gold coated  $\text{CaF}_2$  mirrors. The cell was equipped with polyethylene windows and was cooled to  $243 \text{ K}$  by passing cryogenic liquid from a thermostat (Lauda Kryomat RUK90, Instrumentengesellschaft AG, Zürich). The optical path length was set to  $30 \text{ m}$  and the HF pressure was chosen in the  $15\text{--}20 \text{ mbar}$  range. Under these conditions the spectra taken at a resolution of  $0.01 \text{ cm}^{-1}$  are limited by pressure broadening. In order to improve the signal-to-noise ratio, we co-added 100

scans in a typical measurement. The wavenumber calibration was done with *in situ* H<sub>2</sub>O lines (see [44–46]). The estimated wavenumber uncertainty, given by the root-mean-square (rms) deviation of 57 calibration lines in the range 200–530 cm<sup>-1</sup> with respect to a linear calibration function, was  $d_{\text{rms}} = 1.2 \times 10^{-3} \text{ cm}^{-1}$ .

### 3. Term formulae and selection rules

The dimer (HF-HF) is a slightly bent, near symmetric top. As it is fairly flexible, each sublevel of a given symmetric top quantum number  $K$  ( $= K_a$ ) is best characterised by an individual set of spectroscopic parameters [26]. For the rotational analysis of vibration-tunneling  $K$ -subbands involving  $K_a$  up to 2 the following term formula (1) proved successful in previous studies [26,27,28,43,47] and will be used in the present analyses (see in particular [47] also for the symmetry selection rules):

$$\begin{aligned} \frac{E_{vK}^{(\pm)}}{hc} = & \tilde{\nu}_{vK} + \left( \bar{B}_{vK} \pm \frac{1}{4} \delta_{K1} b_{vK} \right) J(J+1) \\ & - [D_{vK} \mp (\delta_{K1} + \delta_{K2}) d_{vK}] J^2 (J+1)^2 \\ & + (H_{vK} \pm \delta_{K2} h_{vK}) J^3 (J+1)^3 \end{aligned} \quad (1)$$

The constant term  $\tilde{\nu}_{vK}$  describes a hypothetical vibration-tunneling level for a fixed  $K$ , and  $J$  extrapolated to zero.  $\bar{B}_{vK} = \frac{(B_{vK} + C_{vK})}{2}$  is an average rotational constant,  $D_{vK}$  and  $H_{vK}$  are centrifugal distortion constants, and  $b_{vK} = (B_{vK} - C_{vK})$ ,  $d_{vK}$  and  $h_{vK}$  are asymmetry splitting constants of different order. The  $\delta_{Ki}$  ( $i = 1, 2$ ) are the conventional Kronecker delta. The upper signs in the above equation apply to levels with  $K_a + K_c = J$ , the lower to  $K_a + K_c = J + 1$ , where  $K_a$  and  $K_c$  are the usual asymmetric top quantum numbers [48] (see also Refs. [26–28,43,47] for further explanation of the origin and symbols used in Equation (1)).

The molecular symmetry group of (HF)<sub>2</sub> and its implications on the classification of the level structure and the electric dipole selection rules was subject of early studies by Dyke, Howard and Klempner [49] and by Hougen and Ohashi [50] and a detailed discussion in relation to the analysis of the far-infrared spectra has been given in Refs. [26–28,47]. We follow here Refs. [26,47] and the notation defined in [51] and give for definiteness the relevant character tables in Table 1 (see also Refs. [5,6,52]). There is experimental and theoretical evidence for the *trans tunneling path* to be dominant with a  $C_{2h}$  saddle point or transition state structure and low barrier of about 350 cm<sup>-1</sup> [7,28]. The group theoretical scheme for this path is therefore adequate and the corresponding approximate point group notation for  $C_{2h}$  has been frequently used [50], which we give here in parentheses. It should be noted, however, that the classification

**Table 1.** Character tables for the symmetry groups of the HF dimer ( $H^{(1)}F^{(2)} H^{(3)}F^{(4)}$ ) [5,6,26].

(a) Character table and species of the molecular symmetry group  $M_{S_4}$  of (HF)<sub>2</sub>. The approximate point group ( $C_{2h}$ ) species notation is given in parentheses (see also Refs. [52,54,55] and references cited therein for conventions and notation).

Species	$E$	$E^*$	$(ab) (13)(24)$	$(ab)^* (13)(24)^*$	$\Gamma(M_{S_4}) \uparrow S_{2,2}^*$
$A^+ (A_g)$	1	1	1	1	$A_1^+ + A_2^+$
$A^- (A_u)$	1	-1	1	-1	$A_1^- + A_2^-$
$B^+ (B_g)$	1	1	-1	-1	$B_1^+ + B_2^+$
$B^- (B_u)$	1	-1	-1	1	$B_1^- + B_2^-$

(b) Character table and symmetry species for  $S_{2,2}$ .

Species	$E$	$(13)$	$(24)$	$(13)(24)$	$(S_{2,2}) \downarrow M_{S_2}$
$A \times A \equiv A_1$	1	1	1	1	A
$B \times B \equiv A_2$	1	-1	-1	1	A
$B \times A \equiv B_1$	1	-1	1	-1	B
$A \times B \equiv B_2$	1	1	-1	-1	B

of eigenstates with symmetry labels from the molecular symmetry group  $M_{S_4}$  of permutation-inversion operations is independent of any assumption of the tunneling path, as tunneling is in any case multidimensional. For symmetry considerations we can assume the total (rovibrational-tunneling-nuclear spin) wavefunctions to be given by product-wavefunctions  $\Psi_{\text{total}} = \psi_{rtv} \psi_n$  with  $\psi_{rtv} = \psi_r \psi_t \psi_v$ . The ‘tunneling mode’ is the disrotatory in-plane bending vibration  $\nu_5$ , for which a number of tunneling and  $K$ -sublevels were observed and analysed already in 1990 [53], where also a survey of the low energy level structure of HFHF is given. The symmetry of the tunneling wavefunctions,  $\Gamma_t$ , is either  $A^+$  or  $B^+$ , the symmetry of the vibrational wavefunctions,  $\Gamma_v$ , is  $A^+$  for  $\nu_2, \nu_3$  and  $\nu_4$ ,  $B^+$  for  $\nu_1$  and  $A^-$  for  $\nu_6$ , and the symmetry of the rotational wavefunctions  $\Gamma_r$  is  $A^+$  (even  $K_c$ ) or  $B^-$  (odd  $K_c$ ). The symmetry of the nuclear spin wavefunctions,  $\Gamma_n$ , is either  $A^+$  or  $B^+$ . The allowed combinations are determined by the generalised Pauli principle, which requires  $\Gamma_{\text{total}} = \Gamma_r \Gamma_t \Gamma_v \Gamma_n = A^+$  or  $A^-$ . The nuclear spin statistical weights  $g_i$  of  $\Gamma_n$  are  $g_B = 6$  and  $g_A = 10$ , as the  $A$  species are symmetric with respect to monomer exchange and the  $B$  species are antisymmetric. The superscript indicates parity (‘+’, positive, symmetric with respect to inversion at the origin, or ‘-’, negative, antisymmetric with respect to inversion). We give also the induced representation for the full permutation-inversion group in the last column of Table 1 (see also [51,52] for an in-depth discussion of the symmetry aspects).

For allowed electric dipole moment transitions the following selection rules hold:  $\Delta J = 0, \pm 1$  and  $+$   $\leftrightarrow$   $-$  (change of parity);  $A \leftrightarrow A$  and  $B \leftrightarrow B$  for  $\Gamma_n$  (nuclear spin symmetry conservation) and therefore for  $\Gamma_{rtv}$ . Since (HF)<sub>2</sub> is nearly a prolate symmetric top, we have in addition approximate selection rules for the quantum

number  $K$  ( $= K_a$ ):  $\Delta K = 0$ , giving rise to parallel bands ( $\mu_a$  transition moment), or  $\Delta K = \pm 1$ , giving rise to perpendicular bands ( $\mu_b$  or  $\mu_c$  transition moment). The in-plane fundamentals  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  give rise to  $a$ ,  $b$ -hybrid bands ( $\Delta K = 0, \pm 1$ ), the out-of-plane fundamental  $\nu_6$  to a type  $c$  band ( $\Delta K = \pm 1$ ). In the case of the in-plane fundamentals with  $A^+$  symmetry, the upper and lower tunneling states involved must belong to different symmetry species  $A^+$  and  $B^+$ . This is in contrast to  $\nu_6$  where the two tunneling sublevels connected by the transition must belong to the same symmetry species. Figure 1 illustrates the selection rules for the two subbands the present investigation is concerned with. In the case of the  $\nu_3$  subband, the Q-branch transitions start from the higher component of  $K_c$ -doublets, in contrast to the  $P$ - and  $R$ -branch transitions which start from the lower component. For the  $\nu_6$  subband, the reverse is true.

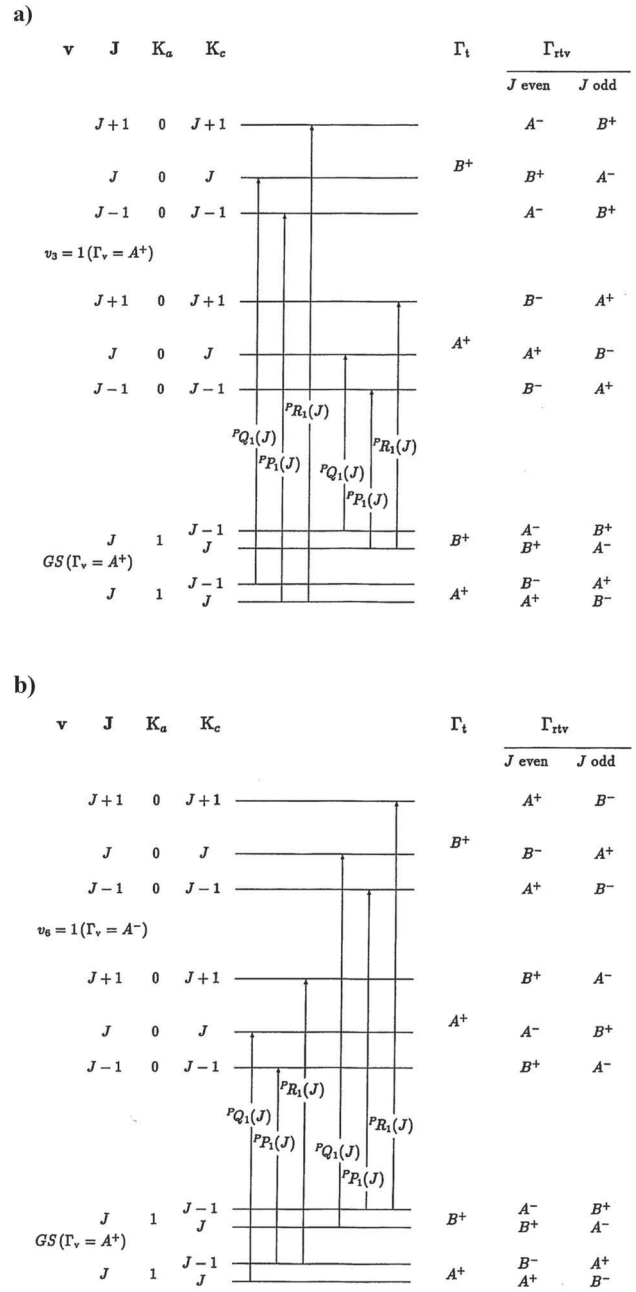
## 4. Results, analysis and assignments

### 4.1. The $K_a = 0 \leftarrow 1$ subband of $\nu_6$

The line-structure of two Q-branches near  $380 \text{ cm}^{-1}$  had been analysed and tentatively assigned in a previous investigation at our laboratory early on [26]. At that time, the assignment of the  $J$  quantum numbers was not unambiguous, however, and the corresponding  $P$ - and  $R$ -branch transitions had not been identified. The assignment of vibrational-tunneling quantum numbers as well as of  $K_a$  quantum numbers was therefore not uniquely possible, neither for the lower nor the upper states. Nevertheless, already then the first option of several possible assignments mentioned was the  $K_a = 0 \leftarrow 1$  transition in  $\nu_6$ , which we confirm here. However, in 1987 other optional assignments could not be excluded [26].

The new spectra yield more accurate peak wavenumbers and a more extended range of valuable Q-branch lines. From a plot of wavenumber-differences of adjacent Q-branch peaks we established a hypothetical  $J$ -assignment. Predictions based on the SO-3 potential energy surface [29,56] favour the assignment to the two tunneling components of the  $K_a = 0 \leftarrow 1$  subband of the  $\nu_6$  fundamental. Since the spectroscopic constants of the  $K_a = 1$  ground state levels are very accurately known [28], we tested this hypothesis by means of combination differences. Using lower state energies as given by Equation (1), combination differences for the two tunneling components of this  $\nu_6$  subband can be expressed as follows:

$${}^P R_1(J-1) - {}^P P_1(J+1) = E_{01}^{(+)}(J+1) - E_{01}^{(+)}(J-1) \quad (2)$$



**Figure 1.** Schematic representation of the allowed transitions for the  $K_a = 0 \leftarrow 1$  subbands of  $\nu_3$  (a) and  $\nu_6$  (b).  $\Gamma_t$  and  $\Gamma_v$  refer to the tunneling and vibrational states involved, and  $\Gamma_{rtv}$  is the overall species ('motional', rotation-vibration species apart from nuclear spin symmetry [52]).

$${}^P Q_1(J) - {}^P P_1(J+1) = E_{01}^{(+)}(J+1) - E_{01}^{(-)}(J) \quad (3)$$

$${}^P R_1(J-1) - {}^P Q_1(J) = E_{01}^{(-)}(J) - E_{01}^{(+)}(J-1) \quad (4)$$

We used Equations (3) and (4) to predict the  $P$ - and  $R$ -progressions belonging to the tentatively assigned Q-structure. By this procedure we were able to identify  $P$ -

and  $R$ -branch transitions and to definitely identify the lower state labels. Using the intensity alternation due to the nuclear spin weights as a further indication, we could verify the symmetry species of the upper vibrational state to be  $A^-$  and therefore definitely assign these subband structures to the  $A^- \leftarrow A^+$  and  $B^- \leftarrow B^+$  components of the  $K_a = 0 \leftarrow 1$  subband of the fundamental  $\nu_6$ . We determined upper state constants according to equation (1) by a least squares fit. We omitted critical data when strong overlapping with neighbouring structures occurred and limited the input to transitions with lower state  $J$  quantum numbers smaller than 34. The reason for this restriction were systematic deviations of the residuals for larger  $J$  quantum numbers. The adjusted parameters and details of the statistics of the fit are listed in Table 2. Table 3 contains a listing of the observed transition wavenumbers used in the fit as well as the difference  $\Delta$  between observed and calculated values (in  $\text{cm}^{-1}/10^{-3}$ ). Figure 2 compares experimental and simulated survey spectra of this subband, and Figure 3 illustrates the region of the  $Q$ -branch origins on an expanded scale.

#### 4.2. The $K_a = 0 \leftarrow 1$ subband of $\nu_3$

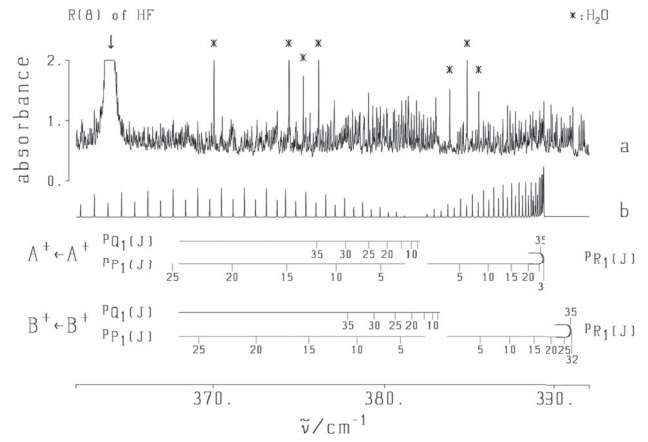
Theoretical 6D-calculations based on the SO-3 potential energy surface [57–59] predict the tunneling sublevels of the symmetric bending vibration  $\nu_3$  at  $483.54 \text{ cm}^{-1}$  ( $A^+$  tunneling component) and  $486.12 \text{ cm}^{-1}$  ( $B^+$ ). According to the dipole selection rules, we expect an  $ab$ -hybrid band for this fundamental. The dipole component  $\mu_b$  gives rise to a perpendicular band with a widely spaced and therefore well separated  $K$ -structure. Using the calculated values given above and ground state levels from [28], the centers of the tunneling components of the  $K = 0 \leftarrow 1$  subband of  $\nu_3$  are predicted at  $447.05 \text{ cm}^{-1}$  ( $A^+ \leftarrow B^+$  component) and at  $450.70 \text{ cm}^{-1}$  ( $B^+ \leftarrow A^+$  component). The measured spectrum shown in Figure 4 reveals an accumulation of features in the region around  $450 \text{ cm}^{-1}$ . By comparing spacings between neighbouring lines we were able to identify two  $Q$ -branch progressions in this range. In the following we could assign corresponding  $P$ - and  $R$ -progressions by means of combination differences valid for the case of a  $K_a = 0 \leftarrow 1$  subband of an  $A^+$  fundamental, given by

$${}^P R_1(J-1) - {}^P P_1(J+1) = E_{01}^{(-)}(J+1) - E_{01}^{(-)}(J-1) \quad (5)$$

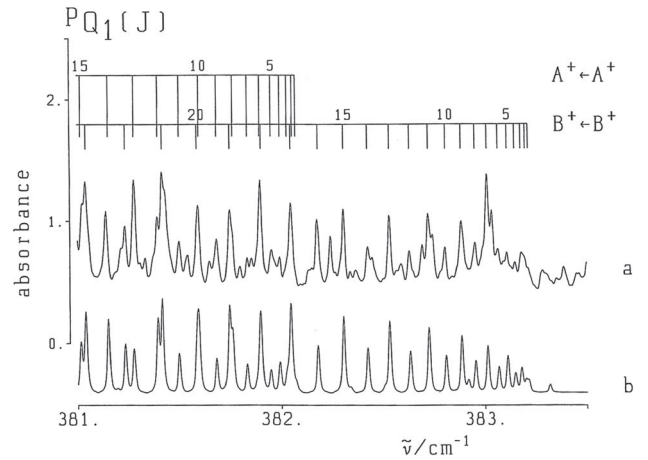
$${}^P Q_1(J) - {}^P P_1(J+1) = E_{01}^{(-)}(J+1) - E_{01}^{(+)}(J) \quad (6)$$

$${}^P R_1(J-1) - {}^P Q_1(J) = E_{01}^{(+)}(J) - E_{01}^{(-)}(J-1) \quad (7)$$

and thereby verify the identity of the lower states involved as well as the assignment of the rotational quantum



**Figure 2.** The  $K_a = 0 \leftarrow 1$  subband of  $\nu_6$  of  $(\text{HF})_2$ . (a) Experimental spectrum (pressure = 20 mbar, temperature = 243 K, resolution apodized  $\Delta\tilde{\nu}$  (FWHM) =  $0.01 \text{ cm}^{-1}$ ), (b) simulated spectrum and assignments.



**Figure 3.** Low  $J$  part of the  $Q$ -branches of the two tunneling components of the  $K_a = 0 \leftarrow 1$  subband of  $\nu_6$ . (a) Experimental spectrum, conditions see Figure 2. (b) simulated spectrum and assignments.

numbers. Furthermore the intensity alternation arising from nuclear spin statistical weights indicates the upper vibrational level belong to either the species  $A^+$  or  $B^+$ . The predicted values hardly leave any doubt that the upper vibrational state corresponds to  $\nu_3$  ( $A^+$ ). The adjusted upper state constants are collected in Table 2. Again we excluded data which are problematic due to overlapping lines and restricted the least-squares fit to transitions with lower state  $J$  quantum numbers smaller than 34 for the same reasons as discussed above with the corresponding  $\nu_6$  subband. The transition wavenumbers used in the fit are listed in Table 4. Figure 4 shows experimental and simulated survey spectra of this subband, together with assignments, and Figure 5 illustrates a characteristic part of the  $Q$ -branch region in more detail.

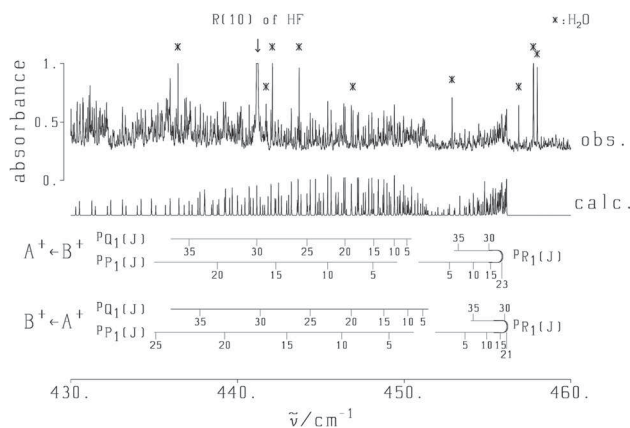
**Table 2.** Spectroscopic parameters for the  $K_a = 0 \leftarrow 1$  subbands of the fundamentals  $\nu_3$  and  $\nu_6$  of (HF)<sub>2</sub>.

	$\nu_3$		$\nu_6$	
	$A^+$	$B^+$	$A^+$	$B^+$
$\Gamma_t$	$A^+$	$B^+$	$A^+$	$B^+$
$\Gamma_{tv}$	$A^+$	$B^+$	$A^-$	$B^-$
$\Delta\tilde{\nu}_0^{(a)} / \text{cm}^{-1}$	450.4546(8)	451.4583(6)	382.0802(6)	383.2245(4)
$\tilde{\nu}_{v0}^{(b)} / \text{cm}^{-1}$	486.9442	486.8834	417.5053	419.7140
$\tilde{B}_{v0} / \text{cm}^{-1}$	0.208894(10)	0.207288(7)	0.212695(5)	0.213222(4)
$D_{v0} / 10^{-6} \text{cm}^{-1}$	1.435(37)	1.009(18)	2.1990(96)	2.3358(88)
$H_{v0} / 10^{-10} \text{cm}^{-1}$	-11.43(37)	-5.48(12)	-0.767(56)	-0.645(53)
<i>Statistics of the fit:</i>				
number of data	45	54	52	63
$J_{\text{max}}$	28	31	36	34
$d_{\text{rms}} / 10^{-3} \text{cm}^{-1}$	1.75	1.74	1.45	1.33
<i>Ground state combination differences<sup>(c)</sup>:</i>				
number of differences	29	33	43	34
$d_{\text{rms}} / 10^{-3} \text{cm}^{-1}$	1.95	1.93	1.93	1.91

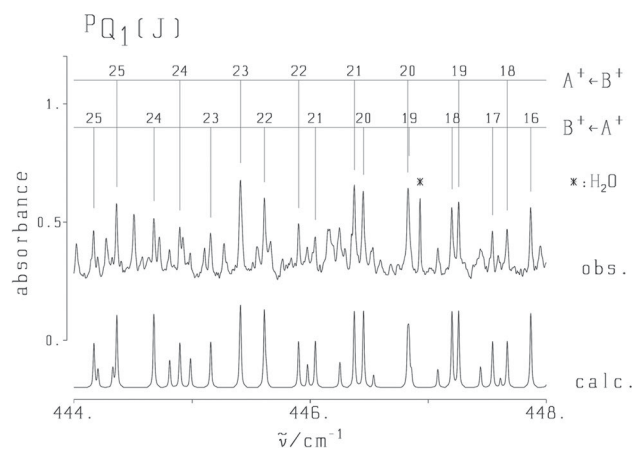
Ground state parameters for $K_a = 1$ [28]:		
$\Gamma_t$	$A^+$	$B^+$
$\tilde{B}_{01} / \text{cm}^{-1}$	0.217860181	0.217709222
$D_{01} / 10^{-6} \text{cm}^{-1}$	1.98814	1.96985
$H_{01} / 10^{-12} \text{cm}^{-1}$	-39.27	-40.85
$b_{01} / 10^{-3} \text{cm}^{-1}$	3.175940	3.041534
$d_{01} / 10^{-9} \text{cm}^{-1}$	-42.591	-36.913

- (a) Center of  $K_a = 0 \leftarrow 1$  subband tunneling component;  
(b) term value with respect to ground state  $K_a = 0, A^+$  term;  
(c) statistics of prediction using ground state parameters from Ref. [28].

**Figure 4.** The  $K_a = 0 \leftarrow 1$  subband of  $\nu_3$  of (HF)<sub>2</sub>. (a) Experimental spectrum (pressure = 20 mbar, temperature = 243 K, resolution apodized  $\Delta\tilde{\nu}$  (FWHM) = 0.01 cm<sup>-1</sup>), (b) simulated spectrum and assignments.

## 5. Discussion of the results and comparison with theory

The analysis of the two  $K_a = 0 \leftarrow 1$  subbands provide accurate term values of both tunneling components of the fundamentals  $\nu_3$  and  $\nu_6$ . The fits based on the term formula given by Equation (1) which includes contributions up to the sixth power in  $J$  approaches the experimental accuracy. For transitions with  $J'' > J_{\text{max}}$  systematic deviations occur. We consider this deficiency to be an indication for the limited validity of the theoretical model used. Due to the high flexibility of this molecule interactions

**Figure 5.** Details of the  $Q$ -branches of the two tunneling components of the  $K_a = 0 \leftarrow 1$  subband of  $\nu_3$ . (a) Experimental spectrum, conditions see Figure 4. (b) Simulated spectrum and assignments.

between internal motion and rotation may become very strong for higher  $J$  quantum numbers and can hardly be described by a term formula appropriate for quasi-rigid molecules.

The identification of the lower states involved in the transitions of these subbands is based on combination differences. For both tunneling components of both subbands investigated, a representative number of ground state combination differences could be formed. Using accurate ground state parameters from Ref. [28], these

**Table 3.** Rovibrational Tunneling Transitions of the  $K_a = 0 \leftarrow 1$  subband of  $\nu_6$  of (HF)<sub>2</sub>.

$\Gamma'_t$	$J'$	$K'_c$	$\Gamma_t$	$J$	$K_c$	$\tilde{\nu}_{\text{obs}} / \text{cm}^{-1}$	$\Delta / 10^{-3}$
Q-branch transitions:							
A <sup>+</sup>	4	4	A <sup>+</sup>	4	4	381.9929	0.19
A <sup>+</sup>	7	7	A <sup>+</sup>	7	7	381.8358	1.14
A <sup>+</sup>	9	9	A <sup>+</sup>	9	9	381.6850	0.23
A <sup>+</sup>	10	10	A <sup>+</sup>	10	10	381.5924	-3.91
A <sup>+</sup>	11	11	A <sup>+</sup>	11	11	381.4987	-0.07
A <sup>+</sup>	12	12	A <sup>+</sup>	12	12	381.3905	-1.56
A <sup>+</sup>	16	16	A <sup>+</sup>	16	16	380.8721	0.26
A <sup>+</sup>	17	17	A <sup>+</sup>	17	17	380.7184	0.47
A <sup>+</sup>	18	18	A <sup>+</sup>	18	18	380.5543	0.05
A <sup>+</sup>	19	19	A <sup>+</sup>	19	19	380.3807	0.06
A <sup>+</sup>	20	20	A <sup>+</sup>	20	20	380.1959	-1.08
A <sup>+</sup>	22	22	A <sup>+</sup>	22	22	379.7987	-0.13
A <sup>+</sup>	24	24	A <sup>+</sup>	24	24	379.3578	-0.59
A <sup>+</sup>	26	26	A <sup>+</sup>	26	26	378.8744	0.36
A <sup>+</sup>	27	27	A <sup>+</sup>	27	27	378.6143	-0.54
A <sup>+</sup>	28	28	A <sup>+</sup>	28	28	378.3452	1.25
A <sup>+</sup>	29	29	A <sup>+</sup>	29	29	378.0601	-1.02
A <sup>+</sup>	30	30	A <sup>+</sup>	30	30	377.7658	-0.24
A <sup>+</sup>	31	31	A <sup>+</sup>	31	31	377.4586	0.18
B <sup>+</sup>	4	4	B <sup>+</sup>	4	4	383.1514	1.61
B <sup>+</sup>	5	5	B <sup>+</sup>	5	5	383.1113	-1.02
B <sup>+</sup>	6	6	B <sup>+</sup>	6	6	383.0669	-0.35
B <sup>+</sup>	8	8	B <sup>+</sup>	8	8	382.9545	0.44
B <sup>+</sup>	9	9	B <sup>+</sup>	9	9	382.8867	0.90
B <sup>+</sup>	10	10	B <sup>+</sup>	10	10	382.8074	-2.24
B <sup>+</sup>	11	11	B <sup>+</sup>	11	11	382.7250	-0.48
B <sup>+</sup>	12	12	B <sup>+</sup>	12	12	382.6320	-1.22
B <sup>+</sup>	13	13	B <sup>+</sup>	13	13	382.5331	0.37
B <sup>+</sup>	14	14	B <sup>+</sup>	14	14	382.4256	1.71
B <sup>+</sup>	15	15	B <sup>+</sup>	15	15	382.3071	0.56
B <sup>+</sup>	16	16	B <sup>+</sup>	16	16	382.1765	-4.03
B <sup>+</sup>	17	17	B <sup>+</sup>	17	17	382.0473	1.59
B <sup>+</sup>	22	22	B <sup>+</sup>	22	22	381.2321	-0.46
B <sup>+</sup>	23	23	B <sup>+</sup>	23	23	381.0396	-1.01
B <sup>+</sup>	24	24	B <sup>+</sup>	24	24	380.8400	1.68
B <sup>+</sup>	25	25	B <sup>+</sup>	25	25	380.6244	-1.03
B <sup>+</sup>	26	26	B <sup>+</sup>	26	26	380.4001	-1.53
B <sup>+</sup>	27	27	B <sup>+</sup>	27	27	380.1651	-1.54
B <sup>+</sup>	28	28	B <sup>+</sup>	28	28	379.9210	0.87
B <sup>+</sup>	29	29	B <sup>+</sup>	29	29	379.6617	-0.07
B <sup>+</sup>	30	30	B <sup>+</sup>	30	30	379.3918	0.58
B <sup>+</sup>	32	32	B <sup>+</sup>	32	32	378.8132	1.16
B <sup>+</sup>	33	33	B <sup>+</sup>	33	33	378.5018	-0.82
P-branch transitions:							
A <sup>+</sup>	5	5	A <sup>+</sup>	6	5	379.2790	-0.22
A <sup>+</sup>	6	6	A <sup>+</sup>	7	6	378.7733	2.01
A <sup>+</sup>	9	9	A <sup>+</sup>	10	9	377.1772	-0.40
A <sup>+</sup>	10	10	A <sup>+</sup>	11	10	376.6257	2.58
A <sup>+</sup>	11	11	A <sup>+</sup>	12	11	376.0540	-3.04
A <sup>+</sup>	12	12	A <sup>+</sup>	13	12	375.4787	-0.63
A <sup>+</sup>	16	16	A <sup>+</sup>	17	16	373.0529	0.68
A <sup>+</sup>	17	17	A <sup>+</sup>	18	17	372.4174	1.14
A <sup>+</sup>	18	18	A <sup>+</sup>	19	18	371.7681	-0.46
A <sup>+</sup>	19	19	A <sup>+</sup>	20	19	371.1094	0.31
A <sup>+</sup>	20	20	A <sup>+</sup>	21	20	370.4377	-0.07
A <sup>+</sup>	21	21	A <sup>+</sup>	22	21	369.7556	1.04
A <sup>+</sup>	22	22	A <sup>+</sup>	23	22	369.0595	0.12
A <sup>+</sup>	23	23	A <sup>+</sup>	24	23	368.3522	0.05
A <sup>+</sup>	25	25	A <sup>+</sup>	26	25	366.8978	-3.37
A <sup>+</sup>	26	26	A <sup>+</sup>	27	26	366.1599	2.70
A <sup>+</sup>	27	27	A <sup>+</sup>	28	27	365.3985	-2.25
A <sup>+</sup>	28	28	A <sup>+</sup>	29	28	364.6336	1.91
A <sup>+</sup>	31	31	A <sup>+</sup>	32	31	362.2470	-0.19
A <sup>+</sup>	32	32	A <sup>+</sup>	33	32	361.4268	0.82
A <sup>+</sup>	34	34	A <sup>+</sup>	35	34	359.7424	-0.37
B <sup>+</sup>	1	1	B <sup>+</sup>	2	1	382.3395	-0.68
B <sup>+</sup>	4	4	B <sup>+</sup>	5	4	380.9376	1.87
B <sup>+</sup>	5	5	B <sup>+</sup>	6	5	380.4476	0.72

(continued).

**Table 3.** Continued.

$\Gamma'_t$	$J'$	$K'_c$	$\Gamma_t$	$J$	$K_c$	$\tilde{\nu}_{\text{obs}} / \text{cm}^{-1}$	$\Delta / 10^{-3}$
<i>P</i> -branch transitions:							
$B^+$	6	6	$B^+$	7	6	379.9444	-3.32
$B^+$	7	7	$B^+$	8	7	379.4385	0.27
$B^+$	8	8	$B^+$	9	8	378.9188	0.39
$B^+$	9	9	$B^+$	10	9	378.3893	1.05
$B^+$	11	11	$B^+$	12	11	377.2949	-1.87
$B^+$	12	12	$B^+$	13	12	376.7350	-0.39
$B^+$	14	14	$B^+$	15	14	375.5809	-0.20
$B^+$	15	15	$B^+$	16	15	374.9883	0.24
$B^+$	16	16	$B^+$	17	16	374.3833	-1.03
$B^+$	17	17	$B^+$	18	17	373.7691	-0.72
$B^+$	19	19	$B^+$	20	19	372.5079	-0.17
$B^+$	20	20	$B^+$	21	20	371.8617	1.09
$B^+$	21	21	$B^+$	22	21	371.2023	0.37
$B^+$	22	22	$B^+$	23	22	370.5331	1.21
$B^+$	23	23	$B^+$	24	23	369.8502	-0.15
$B^+$	24	24	$B^+$	25	24	369.1576	0.47
$B^+$	25	25	$B^+$	26	25	368.4526	0.52
$B^+$	26	26	$B^+$	27	26	367.7364	1.40
$B^+$	27	27	$B^+$	28	27	367.0066	0.90
$B^+$	28	28	$B^+$	29	28	366.2636	-0.38
$B^+$	29	29	$B^+$	30	29	365.5089	-0.70
$B^+$	30	30	$B^+$	31	30	364.7416	-0.73
$B^+$	32	32	$B^+$	33	32	363.1660	-2.10
$B^+$	33	33	$B^+$	34	33	362.3625	1.90
<i>R</i> -branch transitions:							
$A^+$	16	16	$A^+$	15	14	387.4104	0.77
$A^+$	18	18	$A^+$	17	16	387.8477	2.85
$A^+$	19	19	$A^+$	18	17	388.0430	0.93
$A^+$	20	20	$A^+$	19	18	388.2258	0.31
$A^+$	21	21	$A^+$	20	19	388.3937	-1.22
$A^+$	22	22	$A^+$	21	20	388.5486	-1.60
$A^+$	23	23	$A^+$	22	21	388.6905	-0.63
$A^+$	24	24	$A^+$	23	22	388.8175	0.00
$A^+$	25	25	$A^+$	24	23	388.9299	0.80
$A^+$	26	26	$A^+$	25	24	389.0281	2.39
$A^+$	27	27	$A^+$	26	25	389.1049	-2.17
$A^+$	28	28	$A^+$	27	26	389.1731	0.16
$B^+$	5	5	$B^+$	4	3	385.2487	-1.76
$B^+$	6	6	$B^+$	5	4	385.6255	2.08
$B^+$	8	8	$B^+$	7	6	386.3369	0.53
$B^+$	9	9	$B^+$	8	7	386.6786	2.45
$B^+$	10	10	$B^+$	9	8	387.0048	0.16
$B^+$	13	13	$B^+$	12	11	387.9204	-0.57
$B^+$	19	19	$B^+$	18	17	389.4290	1.01
$B^+$	22	22	$B^+$	21	20	390.0097	1.57
$B^+$	24	24	$B^+$	23	22	390.3255	-0.86
$B^+$	25	25	$B^+$	24	23	390.4646	0.49
$B^+$	27	27	$B^+$	26	25	390.6942	-1.16
$B^+$	29	29	$B^+$	28	27	390.8659	0.44

combination differences can be predicted very accurately. As summarised in Table 2, the rms-deviations amount to about  $d_{\text{rms}} = 0.0019 \text{ cm}^{-1}$  for all of the four subband-tunneling components analyzed. This value compares well with the experimental uncertainty, which amounts to  $0.0012 \text{ cm}^{-1}$  for a single transition, and therefore  $0.0012 \sqrt{2} \approx 0.0017 \text{ cm}^{-1}$  for the difference of two transitions. In view of this good consistency, the identity of the lower state assignments is strongly confirmed.

In Figures 2 and 4 we compare measured and calculated spectra. The clearly smaller  $\bar{B}$  constants in the excited  $\nu_3$  and  $\nu_6$  states as compared to the ground state

lead to band heads in the *R*-branches of all subband-tunneling components. In the case of  $\nu_3$  the branch turns near  $J'' \approx 20$ , and in the case of  $\nu_6$  at a higher value of  $J'' \approx 30$ . The details of the *Q*-branches shown in Figures 3 and 5 demonstrate the excellent agreement between experimental and calculated spectra. The intensity alternation arising from the nuclear spin statistical weights is unambiguously established and confirms the assignment of the symmetry of the vibrational-tunneling states involved. The figures also show that there still remains a considerable amount of structure in these regions which does not belong to the identified subbands. The centrifugal distortion constants  $D_{\nu_0}$  differ

**Table 4.** Rovibrational tunneling transitions of the  $K_a = 0 \leftarrow 1$  subband of  $\nu_3$  of  $(\text{HF})_2$ .

$\Gamma'_t$	$J'$	$K'_c$	$\Gamma_t$	$J$	$K_c$	$\tilde{\nu}_{\text{obs}} / \text{cm}^{-1}$	$\Delta / 10^{-3}$
Q-branch transitions:							
$A^+$	4	4	$B^+$	4	3	450.2603	-3.02
$A^+$	5	5	$B^+$	5	4	450.1723	4.47
$A^+$	6	6	$B^+$	6	5	450.0517	-1.67
$A^+$	7	7	$B^+$	7	6	449.9220	2.02
$A^+$	8	8	$B^+$	8	7	449.7669	-0.82
$A^+$	9	9	$B^+$	9	8	449.5986	1.96
$A^+$	11	11	$B^+$	11	10	449.1997	1.64
$A^+$	12	12	$B^+$	12	11	448.9729	2.35
$A^+$	13	13	$B^+$	13	12	448.7248	0.66
$A^+$	14	14	$B^+$	14	13	448.4593	0.56
$A^+$	15	15	$B^+$	15	14	448.1741	-0.06
$A^+$	16	16	$B^+$	16	15	447.8706	0.44
$A^+$	17	17	$B^+$	17	16	447.5457	-0.72
$A^+$	18	18	$B^+$	18	17	447.2019	-0.63
$A^+$	20	20	$B^+$	20	19	446.4511	-0.93
$A^+$	21	21	$B^+$	21	20	446.0441	0.10
$A^+$	22	22	$B^+$	22	21	445.6146	1.68
$A^+$	23	23	$B^+$	23	22	445.1581	0.43
$A^+$	24	24	$B^+$	24	23	444.6780	1.04
$A^+$	25	25	$B^+$	25	24	444.1685	-0.79
$B^+$	3	3	$A^+$	3	2	451.3265	4.48
$B^+$	4	4	$A^+$	4	3	451.2332	1.85
$B^+$	5	5	$A^+$	5	4	451.1192	1.02
$B^+$	6	6	$A^+$	6	5	450.9816	-1.05
$B^+$	7	7	$A^+$	7	6	450.8269	2.03
$B^+$	8	8	$A^+$	8	7	450.6466	1.60
$B^+$	9	9	$A^+$	9	8	450.4414	-1.80
$B^+$	10	10	$A^+$	10	9	450.2170	-2.65
$B^+$	12	12	$A^+$	12	11	449.7076	-0.45
$B^+$	15	15	$A^+$	15	14	448.7818	-0.36
$B^+$	16	16	$A^+$	16	15	448.4322	0.23
$B^+$	17	17	$A^+$	17	16	448.0619	0.64
$B^+$	18	18	$A^+$	18	17	447.6701	-0.03
$B^+$	19	19	$A^+$	19	18	447.2600	1.32
$B^+$	21	21	$A^+$	21	20	446.3756	0.67
$B^+$	22	22	$A^+$	22	21	445.9040	1.40
$B^+$	23	23	$A^+$	23	22	445.4110	1.18
$B^+$	24	24	$A^+$	24	23	444.8969	0.48
$B^+$	25	25	$A^+$	25	24	444.3613	-0.85
$B^+$	26	26	$A^+$	26	25	443.8046	-2.06
$B^+$	27	27	$A^+$	27	26	443.2276	-1.92
$B^+$	28	28	$A^+$	28	27	442.6273	-2.89
$B^+$	29	29	$A^+$	29	28	442.0069	-1.12
$B^+$	30	30	$A^+$	30	29	441.3622	-0.02
$B^+$	31	31	$A^+$	31	30	440.6948	2.92
P-branch transitions:							
$A^+$	4	4	$B^+$	5	5	448.1219	-3.29
$A^+$	5	5	$B^+$	6	6	447.6105	-1.17
$A^+$	6	6	$B^+$	7	7	447.0842	1.72
$A^+$	8	8	$B^+$	9	9	445.9769	-0.51
$A^+$	10	10	$B^+$	11	11	444.8100	-0.59
$A^+$	11	11	$B^+$	12	12	444.2024	-1.76
$A^+$	12	12	$B^+$	13	13	443.5849	2.50
$A^+$	14	14	$B^+$	15	15	442.2919	-0.76
$A^+$	15	15	$B^+$	16	16	441.6242	-0.25
$A^+$	16	16	$B^+$	17	17	440.9418	1.38
$A^+$	17	17	$B^+$	18	18	440.2380	-2.26
$A^+$	18	18	$B^+$	19	19	439.5218	-1.78
$A^+$	20	20	$B^+$	21	21	438.0367	-1.79
$A^+$	21	21	$B^+$	22	22	437.2689	0.21
$A^+$	23	23	$B^+$	24	24	435.6725	2.57
$A^+$	24	24	$B^+$	25	25	434.8392	0.59
$B^+$	5	5	$A^+$	6	6	448.5644	1.76
$B^+$	6	6	$A^+$	7	7	448.0138	0.86
$B^+$	7	7	$A^+$	8	8	447.4442	-0.26
$B^+$	9	9	$A^+$	10	10	446.2505	-1.41

(continued).

**Table 4.** Continued.

$\Gamma'_t$	$J'$	$K'_c$	$\Gamma_t$	$J$	$K_c$	$\tilde{\nu}_{\text{obs}} / \text{cm}^{-1}$	$\Delta / 10^{-3}$
<i>P</i> -branch transitions:							
$B^+$	11	11	$A^+$	12	12	444.9853	-1.29
$B^+$	12	12	$A^+$	13	13	444.3235	-3.66
$B^+$	17	17	$A^+$	18	18	440.7727	2.05
$B^+$	19	19	$A^+$	20	20	439.2322	2.03
$B^+$	20	20	$A^+$	21	21	438.4366	1.48
$B^+$	21	21	$A^+$	22	22	437.6238	0.24
$B^+$	22	22	$A^+$	23	23	436.7977	2.24
$B^+$	25	25	$A^+$	26	26	434.2108	0.32
$B^+$	26	26	$A^+$	27	27	433.3167	2.28
$B^+$	27	27	$A^+$	28	28	432.3989	-1.63
$B^+$	29	29	$A^+$	30	30	430.5172	0.25
$B^+$	30	30	$A^+$	31	31	429.5446	-1.24
<i>R</i> -branch transitions:							
$A^+$	12	12	$B^+$	11	11	454.3997	0.36
$A^+$	13	13	$B^+$	12	12	454.6199	-2.17
$A^+$	14	14	$B^+$	13	13	454.8288	0.74
$A^+$	15	15	$B^+$	14	14	455.0189	1.83
$A^+$	16	16	$B^+$	15	15	455.1872	-1.58
$A^+$	18	18	$B^+$	17	17	455.4779	-0.70
$A^+$	20	20	$B^+$	19	19	455.6909	-2.15
$A^+$	22	22	$B^+$	21	21	455.8276	1.92
$A^+$	26	26	$B^+$	25	25	455.8049	-1.76
$B^+$	7	7	$A^+$	6	6	453.9487	-1.08
$B^+$	8	8	$A^+$	7	7	454.2250	-2.96
$B^+$	10	10	$A^+$	9	9	454.7234	-3.42
$B^+$	11	11	$A^+$	10	10	454.9483	0.57
$B^+$	12	12	$A^+$	11	11	455.1488	-0.98
$B^+$	13	13	$A^+$	12	12	455.3335	0.41
$B^+$	15	15	$A^+$	14	14	455.6432	-0.71
$B^+$	18	18	$A^+$	17	17	455.9721	0.30
$B^+$	19	19	$A^+$	18	18	456.0446	0.24
$B^+$	21	21	$A^+$	20	20	456.1323	-1.84
$B^+$	26	26	$A^+$	25	25	456.0269	-0.40
$B^+$	29	29	$A^+$	28	28	455.7203	0.02
$B^+$	30	30	$A^+$	29	29	455.5747	1.22

considerably from the ground state values. They also differ strongly for the different tunneling components. The values of the sextic constants vary even more strongly. We consider this to be an indication for a stronger influence of the flexibility of this molecule in the vibrationally excited states. As one can hardly give a simple physical interpretation for these parameters, we consider them primarily as effective fitting variables, which do, however, allow for a compact and accurate representation of the experimental energy level structure of HFHF.

Table 5 shows a comparison of experimental and calculated vibrational-tunneling term values for various types of potential energy surfaces and approximations. Whereas predictions based on the SQSBDE potential energy surface [4,39] are considerably off, we find rather good agreement for the more recent calculations based on the SO-3 surface [29,56,57] and on the most recent HYZX [30] and RPB surfaces [31] which, however, give even a little less good predictions than the SO-3 surface of [29], which still can be considered to be the ‘best compromise’ potential hypersurface. Concerning the tunneling splitting, the agreement is generally excellent in the case of the out-of-plane fundamental

$\nu_6$ , but differs in part considerably in the case of  $\nu_3$ , where we observe a very small negative shift. In the region of  $\nu_3$ , the density of bound states having symmetry  $A^+$  or  $B^+$  as also the tunneling components of  $\nu_3$ , is much higher than in the region of  $\nu_6$ . In particular, there are 5 additional bound states with  $\Gamma_{vt} = A^+$  or  $B^+$  in the interval 400–550  $\text{cm}^{-1}$ , one of them being in near coincidence with the corresponding tunneling level of  $\nu_3$  (an  $A^+$  state at 478.32  $\text{cm}^{-1}$ , 6D calculation, and a  $B^+$  state at 481.78  $\text{cm}^{-1}$ , respectively, both representing highly excited FF-stretching states). A small change in the form of the potential energy surface is therefore expected to have a strong effect on the mixing of zeroth-order states and therefore on the tunneling splittings which may strongly depend on this composition. The present result for  $\nu_6$  also confirms the unusual sequence of the levels for  $K_a = 0$  and 1, the level for  $K_a = 0$  lying above the one for  $K_a = 1$ . This agrees with the calculations on the SO-3 surface. This unusual level sequence was already surmised in 1987 in our early work [26] as a realistic possibility due to Coriolis coupling and was traced to strong  $a$ -axis Coriolis interaction between the in- and out-of-plane bending modes in [29]. This special situation for

**Table 5.** Comparison of experimental and calculated term values and tunneling splittings (in  $\text{cm}^{-1}$ ) for  $K_a = 0$ . The term values are relative to the ground state  $A^+$  tunneling level.

Vibration	$\Gamma_t$	Experimental	SO-3 <sup>(a)</sup> 6D Refs. [6,57]	SO-3 (4+2)D Ref. [56]	SQSBDE 6D Refs. [4,39] <sup>(b)</sup>	HYZX 6D Ref. [30]	RPB 6D Ref. [31]
$\nu_3$	$A^+$	486.9442	483.48	482.73	425.30	481.647	490.5 (484.4) <sup>(c)</sup>
	$B^+$	486.8834	486.12	485.21	440.32	481.322	491.7
$\Delta\nu_t(\nu_3)$		-0.0608	2.65	2.48	15.02	-0.325	1.21
$\nu_6$	$A^+$	417.5053	420.83	420.48	378.72	413.271	418.6 (418.4) <sup>(c)</sup>
	$B^+$	419.7140	423.10	422.84	380.47		
$\Delta\nu_t(\nu_6)$		2.2087	2.22	2.36	1.75	2.284	2.13

<sup>(a)</sup> See also further references in [6] and Ref. [29] for the potential hypersurface;

<sup>(b)</sup> See also [60] for differing results;

<sup>(c)</sup> Ref. [31], values taken from the supplementary tables, the values in parentheses from the respective columns Pall in the tables of [31], including all corrections by calculating  $\bar{\nu}_{\text{calc}} = \bar{\nu}_{\text{obs}} - \text{Pall}$ .

$K_a = 1$  also shows up in the  $K_a$  dependence of the tunneling splitting as well as the rotational constant  $\bar{B}$  [26,27] which reveal local extrema at  $K_a = 1$ . We might mention here also approximate full-dimensional quantum results on SQSBDE, which differ slightly [60].

A  $K_a = 0$  combination level experimentally known involving  $\nu_3$  is  $\nu_1 + \nu_3$  [61]. An interesting question concerns the degree of additivity of spectroscopic parameters of the levels  $\nu_1$  and  $\nu_3$  to obtain estimates of corresponding quantities for the combination level. In particular we tested the additivity of the vibrational term values, of the tunneling-splittings and of the dependence of the rotational constants  $\bar{B}$  upon vibrational state  $\nu$  expressed by the  $\alpha_i^{\bar{B}}$  constants defined by [62]

$$\bar{B}_\nu = \bar{B}_e - \sum_i \alpha_i^{\bar{B}} \left( \nu_i + \frac{1}{2} \right) \quad (8)$$

The values collected in Table 6 reflect a high degree of additivity. The vibrational term values and tunneling splitting agree reasonably well. The very small cross anharmonicities between the intramolecular  $\nu_1$  mode on one hand and the intermolecular mode  $\nu_3$  on the other hand is not too surprising since  $\nu_1$  corresponds to the free HF stretching mode which obviously does not strongly influence the dynamics of the intermolecular (low-frequency) modes. In the case of the  $\alpha_i^{\bar{B}}$  constants,

**Table 6.** Comparison of parameters of the combination level  $\nu_1 + \nu_3$  with the sum of the corresponding parameters of the separate levels  $\nu_1$  and  $\nu_3$  listed in column ' $\nu_1$  plus  $\nu_3$ '.

	$\Gamma_t$	$\nu_1$ Ref. [47] <sup>(a)</sup>	$\nu_3$ this work	$\nu_1$ plus $\nu_3$	$\nu_1 + \nu_3$ Ref. [61]
$\bar{\nu}_{\nu_0}$	$A^+$	3930.903	486.9442	4417.8472	4418.0629
	$B^+$	3931.118	486.8834	4418.0014	4417.9183
$\Delta\nu_t$		0.2150	-0.0608	0.1542	-0.1446
$\alpha_{\nu_0}^{\bar{B}}$	$A^+$	-0.001225	0.007819	0.006594	0.007453
	$B^+$	-0.001293	0.009287	0.007994	0.007705

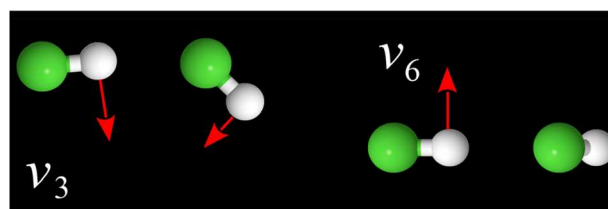
<sup>(a)</sup> See also Ref. [63].

the additivity is less perfect although the tendency is clearly indicated.

## 6. Conclusions

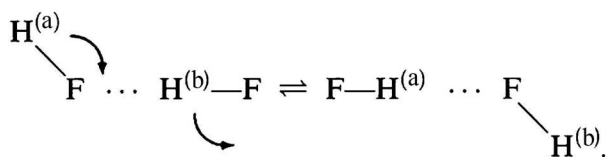
The present work has as main experimental result a first assignment and analysis of the  $K = 0 \leftarrow 1$  transitions for the in-plane fundamental  $\nu_3$  and the out-of-plane fundamental  $\nu_6$  of the hydrogen bonded dimer (HFHF). Together with the very accurate knowledge of the  $K = 1$  level in the vibrational ground state from our previous work [28,53], this provides highly accurate values for the purely vibrational term values (with  $K = 0$ ) of the tunneling sublevels of these two fundamentals (see Table 5). For  $\nu_6$  this result agrees with a tentative assignment mentioned already in the very first investigation of high-resolution spectra of (HFHF) in the far infrared where an accurate term value for the  $K = 1$  level of  $\nu_6$  was obtained [26]. However, based on the data available then, the assignment of the position of the  $K = 0$  level of  $\nu_6$  remained ambiguous, allowing either for a 'high' value of  $\nu_6$  (the  $K = 0$  level being then above the  $K = 1$  level as found in the present work) or else for a 'low' value for the  $\nu_6 = 1, K = 0$  level, below the  $K = 1$  level of  $\nu_6$ . The new experimental results presented here establish the high value for  $\nu_6$  without ambiguity.

The situation was even more difficult for the fundamental  $\nu_3$  which resisted an accurate analysis for a long time. Again, both 'high' and 'low' values were discussed

**Figure 6.** Qualitative graphical representation of the vibrational modes  $\nu_3$  and  $\nu_6$  in (HFHF).

as possible alternatives for this fundamental. From the limited theoretical and experimental information available early on, we favoured a ‘high’ value, for instance in [43] (for the harmonic wavenumber  $\omega_3$  and by inference for  $\nu_3$ ). However, in the design of the later widely used full-dimensional SQSBDE potential hypersurface [4] a ‘low’ value for  $\nu_3$  (and for  $\omega_3$ ) resulted from a fit to low level *ab initio* potential points and some empirical adjustment. As the ambiguity was recognized already then, this led to several theoretical efforts with higher level *ab initio* calculations which all preferred ‘high’ values for  $\omega_3$  (and by inference for  $\nu_3$ ) [23,29,40,41]. Finally a whole group of newly designed full-dimensional potential hypersurfaces based on new high level *ab initio* results and some empirical adjustment provided predictions of the ‘high’ values for both  $\nu_3$  and  $\nu_6$  [7,23,29]. The present experimental results provide proof without ambiguity also for the ‘high’ values of  $\nu_3$  (Table 5). Figure 6 provides a qualitative picture of the motion related to these two vibrational modes, an in-plane and out-of-plane ‘bending’ mode, which most importantly involve displacements of the hydrogen atoms from the equilibrium geometry, with  $\nu_3$  corresponding to a conrotatory in-plane motion.

One might on the basis of the atomic motions in these vibrational modes address the question of mode-selective enhancement or inhibition of tunneling by vibrational excitation of  $\nu_3$  and  $\nu_6$ , which in a normal mode picture are separable from the in-plane disrotatory bending mode, which represents the tunneling mode for the hydrogen bond switching process,



As the electronic barrier at the  $C_{2h}$  saddle point along the switching path is about  $350 \text{ cm}^{-1}$  ( $\pm 20 \text{ cm}^{-1}$  according to a best estimate from [7], and  $337 \text{ cm}^{-1}$  in the SO-3 surface [29]) the excitation of either  $\nu_3$  or  $\nu_6$  with one quantum leads to quasiadiabatic channel above barrier tunneling [5,6,22] (see also the discussion on the fully anharmonic quasiadiabatic channel potential by Diffusion Quantum Monte Carlo methods [28]). The excitation of  $\nu_6$  leads to enhancement of tunneling (with tunneling splitting of  $0.659 \text{ cm}^{-1}$  in the ground state and  $2.209 \text{ cm}^{-1}$  in  $\nu_6 = 1$ ), and all theoretical treatments summarized in Table 5 are consistent with this experimental result. On the other hand, the excitation of  $\nu_3$  leads to an inverted and in absolute value much reduced tunneling splitting (by the definition of  $\Delta\tilde{\nu} = \tilde{\nu}_{B^+} - \tilde{\nu}_{A^+} = -0.061 \text{ cm}^{-1}$ , being then negative).

The theoretical splittings are variable, depending on the potential hypersurface used (one with negative  $\Delta\tilde{\nu}$  and three with positive  $\Delta\tilde{\nu}$  in Table 5), none of them being very close to the experimental result. This indicates very complex multidimensional dynamic effects on the tunneling, which one might interpret in terms of vibrationally non-adiabatic couplings with close lying ‘perturber’ states. This complex situation was already discussed for (HFHF) in [28,53] and furthermore there is a strong dependence of tunneling on the quantum number  $K$ . This behaviour is quite different from tunneling in HOOH and similar molecules, where tunneling can be well described with the quasiadiabatic channel reaction path Hamiltonian treatment [64–66]. However, complex vibrationally nonadiabatic effects are also found in the prototypical molecule  $\text{NH}_3$  for inversion tunneling ([67] and references cited therein).

As part of a larger project of spectroscopic studies covering the whole infrared range from the far-infrared to the visible ranges [5–13,26–29,43,44,47,53,58,59,70] the present investigations of  $\nu_3$  and  $\nu_6$  aim also at providing benchmark results for *ab initio* calculations, which are, indeed, numerous for this prototypical hydrogen bonded dimer (see Refs. [23,29–36,40,41,68,69], this list being by no means complete). Furthermore the potential hypersurfaces based on the spectroscopic and *ab initio* results have also been used for benchmark studies of quantum eigenstate calculations. In this context notably the older SQSBDE potential [4] has been widely used as basis for such benchmark studies [8,38,39,56–58,60,70–83]. More recently also the improved potential SO-3 has been used as well by some authors [29,57–59,71,84,85]. We have shown in recent work completing the overtone HF-stretching polyad analyses to  $N = 2$  in the near infrared that, indeed, SO-3 is able to reproduce well the experimental results [6,42,59]. For the recent *ab initio* surfaces [30,31] the  $N = 2$  polyad overtone tunneling sublevels have not yet been computed. However, as summarized in Table 5 for  $\nu_3$  and  $\nu_6$  and more completely also for the other modes in Ref. [6], for the low frequency modes the SO-3 surface performs overall as well or even better than the most recent *ab initio* potentials. The dynamically very important hydrogen bond dissociation energy corresponding to  $D_0 = 1062 \text{ cm}^{-1}$  is perfectly represented by SO-3 (being adjusted to this value). There are still sizable differences in  $D_0$  for the HYZX surface (Ref. [30],  $D_0 = 1037.5 \text{ cm}^{-1}$ ) and for the RPB surface (Ref. [31],  $D_0 = 1065.6 \text{ cm}^{-1}$ ). Thus we may conclude that in consideration of the present and previous results the SO-3 potential hypersurface can be considered to be the best compromise currently available for use in quantum dynamical calculations of HFHF.

We might mention also the significance of such spectroscopic experiments combined with full-dimensional theoretical benchmark results in relation to the quantum dynamics of hydrogen bonded clusters in general including the particularly important water clusters  $(\text{H}_2\text{O})_n$  [86–91]. For instance, the early full-dimensional potential and quantum dynamical results for (HFHF) demonstrated the importance of a fully 6D treatment for the tunneling-rotation-vibration problem [4], as it showed large differences compared to the common reduced dimensional treatments with keeping the HF bond lengths as intramolecular degrees of freedom fixed [92]. Such reduced dimensional treatments with frozen intramolecular degrees of freedom were commonly used for more complex clusters such as  $(\text{H}_2\text{O})_2$ . The findings with full dimensional dynamics of  $(\text{HF})_2$  motivated then full dimensional treatments also for  $(\text{H}_2\text{O})_2$ , showing important effects on the dimer properties [87–89], including the ground state dissociation energy  $D_0$  as compared to the dissociation energy  $D_e$  from electronic structure theory for  $(\text{H}_2\text{O})_2$  [91], as well as other eigenstate properties. In an even broader context the spectroscopic results for HFHF dynamics can be considered as simple prototypes for the dynamics of rotors in molecular machines [93,94] or for understanding hydrogen bonding in general [95–97].

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