Spectrum and vibrational predissociation of the HF dimer.
I. Bound and quasibound states

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We present full six-dimensional calculations of the bound states of the HF dimer for total angular momentum \( J = 0,1 \) and of the quasibound states for \( J = 0 \) that correspond with vibrational excitation of one of the HF monomers, either the donor or the acceptor in the hydrogen bond. Transition frequencies and rotational constants were calculated for all four molecular symmetry blocks. A contracted discrete variable representation basis was used for the dimer and monomer stretch coordinates \( R, r_A, r_B \); the generation of the monomer basis in the dimer potential leads to significantly better convergence of the energies. We employed two different potential energy surfaces: the SQSBDE potential of Quack and Suhm and the SO-3 potential of Klopper, Quack, and Suhm. The frequencies calculated with the SO-3 potential agree very well with experimental data and are significantly better than those from the SQSBDE potential. © 2003 American Institute of Physics. [DOI: 10.1063/1.1577111]

I. INTRODUCTION

One of the most important interactions in nature is the hydrogen bond. Quantitative information about the dynamics of hydrogen-bonded systems can be obtained by the study of small model systems, such as \((HF)_2, (HCl)_2\), and \((H_2O)_2\). The present paper focuses on the HF dimer, which has been widely studied. On the experimental side, much work has been done to determine its structure and tunneling dynamics, vibrational predissociation lifetimes, and rotational product state distributions. On the theoretical side, the dimer has also been studied in a variety of ways, using quantum Monte Carlo methods and four-dimensional rigid rotor and full six-dimensional calculations, as well as vibrational predissociation calculations.

In the theoretical work, several potential energy surfaces (PESs) have been used, of which the BJKKL surface by Bunker et al. and the empirically adjusted SQSBDE surface by Quack and Suhm have been the most popular. Recently, Klopper et al. published a new PES called SO-3, which is based on explicitly correlated second-order Møller–Plesset calculations, and which is adjusted to reproduce the experimental dissociation energy and monomer stretch frequencies. This potential has been used to describe the dimer dissociation in \( He(\text{HF})_2 \) clusters and the HF trimer, but so far no rigorous test of this potential for the dimer proper has been published.

In this paper we present the results of full dimensional (6D) variational calculations on the SO-3 surface. We have computed bound states for \((HF)_2\) with both monomers in their vibrational ground state and total angular momentum \( J = 0,1 \), as well as quasibound states where one of the monomers is vibrationally excited, for \( J = 0 \). The same calculations have been performed on the SQSBDE surface, to allow for a fair comparison between the new potential and an older, high quality potential.

In the accompanying paper (Paper II), we report results of 6D photodissociation calculations on vibrationally predissociating states of the SO-3 surface. We have calculated predissociation lifetimes and rotational state distributions upon excitation of the donor or the acceptor stretch, and combinations of these with excitations in the dimer stretch or the dimer geared bend modes. From the calculated rotational state distributions we have computed the theoretical photofragment angular state distributions, which allows us to compare with experimental data directly.

This paper is organized as follows: Section II will give the Hamiltonian for this system and the basis set used, Sec. III will deal with the details of the calculations. Results for both PESs will be presented and discussed in Sec. IV.

II. THEORY

The full-dimensional body fixed (BF) nuclear motion Hamiltonian for a dimer consisting of monomers \( A \) and \( B \) can be written as

\[
\hat{H} = \hat{H}_0 + V_f(R, r_A, r_B),
\]

where \( V_f \) is the interaction potential between the two molecules. In the two-angle embedded frame of Fig. 1, the term \( \hat{H}_0 \) is given by

\[
\hat{H}_0 = \hat{h}_A + \hat{h}_B - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{1}{2} R^2 \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial R^2},
\]

where \( \mu \) is the reduced mass of the dimer, \( \hat{j} \) is the total angular momentum operator, and \( \hat{j}_{AB} \) is the vector sum of the monomer angular momentum operators \( \hat{j}_A \) and \( \hat{j}_B \). The monomer Hamiltonians \( \hat{h}_X, X = A, B \) are given by

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where \( \mu_X \) denotes the reduced mass of monomer \( X \), and \( V_X \) are the monomer potentials.

A matrix representation of the total Hamiltonian was calculated in a BF basis

\[
|n_{v_A}v_B(j_{AB})j_{AB}K;JM\rangle = |n\rangle |v_Av_B\rangle |j_{AB}j_{AB}K;JM\rangle ,
\]

where \( |n\rangle = \varphi_n(R) \) denotes a dimer stretch basis function, and \( |v_Av_B\rangle = X_{v_A}(r_A)X_{v_B}(r_B) \) a product of monomer stretch functions. The angular basis functions are given by

\[
\langle n'v'_Av'_B(j_{AB})j_{AB}'K';JM|\hat{H}_0|n_{v_A}v_B(j_{AB})j_{AB}K;JM\rangle
\]

\[
= \delta_{j_{AB}}\delta_{j_{AB}'}\delta_{K}\delta_{K'}K\epsilon v_A v_B + \delta_{n'n}\delta_{v_A v_B}^n \delta_{v_A v_B}K\epsilon v_A + \epsilon(v_B) + \delta_{n'n}\delta_{K}\epsilon v_A v_B K\epsilon v_A
\]

\[
\times \int \frac{\hbar^2}{2\mu_A} \langle j_{AB}(j_{AB}+1)\delta_{v_A v_B} + \frac{\hbar^2}{2\mu_B} \langle j_{AB}(j_{AB}+1)\delta_{v_A v_B} \rangle \rangle + \delta_{v_A v_B} \delta_{v_A v_B} K\epsilon v_A v_B K\epsilon v_A v_B
\]

\[
\times [\delta_{K}\epsilon j_{AB}(j_{AB}+1)-2K^2] \delta_{K',K+1} C_{j_{AB}K'j_{AB}K} \delta_{K',K-1} C_{j_{AB}K'j_{AB}K},
\]

where \( \epsilon_{v_n} \) is the \( n \)th eigenvalue of the dimer stretch reference Hamiltonian of Eq. (6), and \( \epsilon v_A \) and \( \epsilon v_B \) are the monomer stretch energies. The kinetic energy is diagonal in the angular basis, except for the Coriolis coupling terms \( C_{j_{AB}j_{AB'}} \) that couple blocks with different \( K \). However, this coupling is neglected, because it is absent for \( J=0 \), and generally small in the HF dimer for low values of \( J \).

The interaction potential \( V_I \) was expanded in angular functions of the type of Eq. (5). Since the potential is invariant

\[
\langle j_{AB}j_{AB}K;JM \rangle
\]

\[
= \sqrt{\frac{(2J_A+1)(2J_B+1)(2J+1)}{64\pi^3}} D_{M\ell K}^{(j)}(\alpha,B,0)^n
\]

\[
\times \sum_{m_{AB}} C^{(j)}_{m_A}(\hat{\phi}_A) C^{(j)}_{m_B}(\hat{\phi}_B) \langle j_{AB}m_A; j_{AB}m_B | j_{AB}K \rangle,
\]

where the \( C^{(j)}(\hat{\phi}) \) denote Racah-normalized spherical harmonical functions of the body fixed angles of monomer \( X \), which are coupled with a Clebsch–Gordan coefficient

\[
\langle j_{AB}m_A; j_{AB}m_B|j_{AB}K \rangle.
\]

The Wigner rotation function \( D_{M\ell K}^{(j)}(\alpha,B,0)^n \) depends on the polar angles \( (\alpha, \beta) \) of the intermolecular vector \( R \) with respect to a space fixed frame.

The dimer stretch functions are given by \( \varphi_n(R) = \varphi_n(R)/R \), where the \( \varphi_n(R) \) are eigenfunctions of a reference Hamiltonian,

\[
\hat{H}_{\text{ref}} = \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V_{\text{ref}}(R),
\]

which will be specified further in the following. The eigenfunctions are obtained using a sinc-function discrete variable representation (DVR) method. The monomer stretch basis functions \( X_{v_A}(r_A) = \tilde{X}_{v_A}(r_A)/r_A \) are obtained in the same way.

Using these basis functions, the matrix elements of \( \hat{H}_0 \) are given by

\[
\langle n'v'_Av'_B(j_{AB})j_{AB}'K';JM|\hat{H}_0|n_{v_A}v_B(j_{AB})j_{AB}K;JM\rangle
\]

\[
= \delta_{j_{AB}}\delta_{j_{AB}'}\delta_{K}\delta_{K'}K\epsilon v_A v_B + \delta_{n'n}\delta_{v_A v_B}^n \delta_{v_A v_B}K\epsilon v_A + \epsilon(v_B) + \delta_{n'n}\delta_{K}\epsilon v_A v_B K\epsilon v_A v_B
\]

\[
\times [\delta_{K}\epsilon j_{AB}(j_{AB}+1)-2K^2] \delta_{K',K+1} C_{j_{AB}K'j_{AB}K} \delta_{K',K-1} C_{j_{AB}K'j_{AB}K},
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ant under overall rotations of the system, it does not depend on \( \alpha \) and \( \beta \), and not explicitly on both \( \phi_A \) and \( \phi_B \), but only on the difference angle \( \phi = \phi_B - \phi_A \). Only the terms with \( J=K=0 \) appear in the expansion, so that the expansion functions can be written as

\[
A_{L_A,L_B}(\theta_A, \theta_B, \phi) = (-1)^{L_A+L_B+L} \sum \frac{L_A \ L_B \ L}{M_A \ M_B} c_L(\theta_A) c_L(\theta_B, \phi).
\]

The corresponding expansion coefficients \( c_{L_A,L_B}(R, r_A, r_B) \) are then given by

\[
c_{L_A,L_B}(R, r_A, r_B) = \frac{(2L_A+1)(2L_B+1)(2L+1)}{16\pi^2} \times \int d\cos \theta_A \int d\cos \theta_B \times d\phi A_{L_A,L_B}(\theta_A, \theta_B, \phi) \times V(R, r_A, r_B, \theta_A, \theta_B, \phi).
\]

Substitution of this expansion for the potential results in the following expression for the potential matrix elements:

\[
\langle n'v'j_A'v_B'j_B'j_A''K'j_B''|JM|n_vj_Av_Bj_Aj_B|JM \rangle = \delta_{K'K}(2j_A+1)(2j_B+1)(2j_A^2+2j_B+1)(2j_A^2+2j_B^2+1)
\]

\[
\times (2j_{AB}+1)!^2 \sum_{L_{AB}, L} \langle n'v'j_A'v_B'|c_{L_{AB},L} |n_vj_Av_B \rangle \times (-1)^{j_A+j_B+j_{AB}+L_{AB}-K} \times \left( \begin{array}{ccc} j'_A & L & j_B \\ 0 & 0 & 0 \end{array} \right) \times \left( \begin{array}{ccc} j'_{AB} & 0 & 0 \\ -K & 0 & K \end{array} \right) \times \left( \begin{array}{ccc} j_A & L & j_B \\ 0 & 0 & 0 \end{array} \right) \times \left( \begin{array}{ccc} j_A & L & j_B \\ 0 & 0 & 0 \end{array} \right).
\]

The basis was adapted to the symmetry of the permutation-inversion group \( PI(C_2v) \), also called \( C_2v(M) \). The labeling of the irreducible representations (irreps) and the projection operators for this group are given in Table I.

### III. COMPUTATIONAL DETAILS

All calculations were done on two different potential surfaces, the SQSBDE potential by Quack and Suhm, and the more recent SO-3 potential of Klopper, Quack, and Suhm. In the calculation of the expansion coefficients \( c_{L_{AB},L} \) on the radial grid points, the integration over the angular coordinates \([7.6.0]\) was performed by means of a Gauss–Legendre quadrature with 12 points for \( \theta_A \) and \( \theta_B \), and a Gauss–Chebyshev quadrature with also 12 points for \( \phi \). Since for certain grid points the potential becomes strongly repulsive, one would need extremely high terms in the expansion. To avoid this, the potential was damped in these repulsive regions by means of a tanh function up to a value \( V_{\text{max}} \):

\[
\tilde{V} = \begin{cases} V, & V \leq V_0 \\ V_0 + \beta^{-1} \tanh(\beta(V-V_0)), & V > V_0, \end{cases}
\]

where \( \beta = [V_{\text{max}} - V_0]^{-1} \). With this scheme, the damped potential \( \tilde{V} \) is continuous around \( V_0 \) up to the second derivative. Care was taken to use sufficiently high values of \( V_0 \) and \( V_{\text{max}} \), so that the potential was affected only in regions without physical meaning. The actual values used were \( V_0 = 140,000 \text{ cm}^{-1} \), and \( V_{\text{max}} = 2V_0 \). The expansion of the potential was taken up to \( L_A, L_B \ll 11 \).

The dimer stretch basis functions were computed using a sinc function DVR on a reference potential, which was obtained by minimization of the potential in the monomer stretch coordinates, while keeping the intermolecular distance fixed at the grid points and the angles at their equilibrium values in the dimer. An equally spaced grid of 42 points in the range \( 4a_0 \leq R \leq 8a_0 \) was used for both potentials.

The monomer stretch basis functions were obtained in a similar way, but two different reference potentials were used. The first one was the pure monomer potential \( V^{(\text{mon})} \), obtained by making a cut through the PES at very large \( R \). The second was a dimer adapted potential \( V^{(\text{dim})} = [V^{(\text{mon})} + V^{(\text{dimer})}]/2 \), where \( V^{(\text{dimer})} \) was obtained by minimizing the potential by varying \( R, r_A, \theta_A, \phi_A \) and \( \phi_B \), while keeping \( r_B \) fixed on the grid points. Analogously, \( V^{(\text{dim})} \) was obtained by minimizing in all coordinates except \( r_B \). The average of the two monomer potentials was taken in order to preserve the exchange symmetry in the dimer. For the SQSBDE potential a grid of 20 equally spaced point between 1.0 and 2.9 \( a_0 \) was applied, whereas for the SO-3 potential a grid of 22 points between 1.0 and 3.1 \( a_0 \) was used.

Convergence was reached with an angular basis set with \( j_A \) and \( j_B \) up to \( j_{\text{max}}^{(\text{mon})} = 13 \), a dimer stretch basis up to \( n_{\text{max}}^{(\text{mon})} = 6 \), and a monomer stretch basis with \( v_A + v_B \leq 2 \), which lead to a maximum basis size of approximately 22,000 functions for the \( K = 0 \) states, and 38,000 for \( K = 1 \). For the monomer ground states, the lowest eigenstates were calculated with a direct variant of the Davidson algorithm. The procedure was not feasible for the monomer stretch excited states, however, since these states lie in the middle of the spectrum of the Hamiltonian in this basis. Therefore, we used a three-step procedure in each symmetry block, where in the first step the Hamiltonian was calculated in a basis with only the \( v_A + v_B = 1 \) monomer stretch functions, leading to a matrix with a dimension of half the total number of primitive basis functions (i.e., \( \approx 11,000 \)). Eigenstates of this matrix were calculated in an energy range of approximately 3800–4500 cm\(^{-1}\) above the ground state using the NAG routine f02fcf, which yielded approximately 500 eigenfunctions. These eigenfunctions were used as a new basis for the Hamiltonian, together with additional primitive basis functions with \( \vert v_A v_B \rangle = \langle 02 \rangle \) and \( \langle 20 \rangle \), resulting in a basis of approximately 7600 functions. The eigenstates in this basis were calculated in the same energy range. Finally, the resulting eigenfunctions were again combined with the \( \langle 11 \rangle \) func-
tions (yielding \( \approx 5500 \) functions), and the Hamiltonian matrix was diagonalized once more in the same energy range.

IV. RESULTS AND DISCUSSION

The first ten energy levels of the HF dimer with both monomers in their vibrational ground state are given for all four symmetry blocks in Tables II and III for total angular momentum \( J=0 \), and Table IV for \( J=K=1 \). For \( J=0 \), the antigeared bend \( (v_3) \) fundamental and its tunneling partner have also been added. The tables show the energy levels for both the SQSBDSE and the SO-3 potentials calculated in the dimer adapted monomer stretch basis. Also the expectation value and root mean square amplitude of the intermolecular distance \( R \) are given, as well as the rotational constant \( B = \langle 1/2 \mu R^2 \rangle \). These three values were calculated from the SO-3 wave functions. For the \( J=1 \), \( K=0 \) states too, energies and wave functions were calculated. We found that the difference between the resulting eigenvalues and the

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energies was $2B$ to within $10^{-4}$ cm$^{-1}$, while the expectation values and amplitudes of $R$ were virtually the same as for the $J=0$ states. Therefore, these results are not shown here.

The results in the monomer stretch basis from the free HF potential are not given, since we found that using the dimer adapted functions gives a systematic improvement of the energy. This effect is hardly noticeable on the SO-3 potential, where the difference does not exceed $10^{-3}$ cm$^{-1}$, but is much stronger on the SQSBDE potential where differences up to 0.4 cm$^{-1}$ occur. That the free monomer stretch functions are less than optimal for the SQSBDE potential has been shown before for the ground state by Mladenović and Lewerenz. 50

The states are labeled with the standard set of quantum numbers $(v_1 v_2 v_3 v_4 v_5 v_6)$, which correspond to the “free-H” monomer stretch $(v_1)$, “bound-H” monomer stretch $(v_2)$, in-plane antigeared (or cis) bend $(v_5)$, dimer stretch $(v_4)$, in-plane geared (or trans) bend $(v_3)$, and dimer torsion $(v_6)$ modes. Since interchange tunneling involves the same coordinate as the geared bend vibration, the $B$ states, which are odd with respect to interchange, contain an extra node in the $v_5$ tunneling path. Therefore, the ground $B$ state is labeled (000010), and all $B$ states have odd $v_5$, whereas $v_5$ is even for the $A$ states. It follows that the geared bending fundamental is labeled (000020).

Comparison of the SQSBDE results for $J=0$ with the 6D results of Zhang et al. 33 shows that the energy levels are generally similar. The difference of 0.55 cm$^{-1}$ in the dissociation energy may be explained by the fact that Zhang et al. used a monomer stretch basis obtained from the free HF potential, combined with the fact that they did not include the $v_A + v_B = 2$ functions. Indeed, we found a dissociation-

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<th>$\Gamma$</th>
<th>$n$</th>
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<th>SO-3</th>
<th>$\langle R \rangle$</th>
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FIG. 2. Square modulus of the wave function as a function of $R$, integrated over all other coordinates, calculated on the SO-3 potential. The upper panel is the $\sim 000120$ state, the lower the $\sim 000040$ state. Both are for total angular momentum $J=0$. 

TABLE IV. As in Tables II and III, for $J=K=1$. 

$A_1, B_1$
energy of 1057.46 cm$^{-1}$ when the free monomer basis was used, much closer to their value of 1057.33 cm$^{-1}$.

The assignment of the quantum numbers to the states was done on the basis of nodal patterns in the wave functions, combined with energy considerations. For the SQSBDE bound states, the assignment of the $v_4$ stretch quantum number was facilitated by the strong correspondence between this quantum number and the expectation value and root mean square amplitude of $R_s$, an effect that is much less pronounced on the SO-3 potential. An example of the weaker correspondence of $v_4$ with $\langle R \rangle$ on the SO-3 potential can be seen in the fifth and sixth $J=0$ states of the $A_1$ irrep, where the higher stretch quantum number is assigned to the fifth state, despite the fact that the expectation value of $R_s$, as well as the amplitude, are smaller. A radial plot of the density (Fig. 2) does not give direct evidence for the given assignment either. Angular cuts through the wave function are not very helpful, since they change very much with $R_s$ (see Fig. 3), so that this assignment can only be made on the basis of energy considerations. Similar situations occur for instance in the eighth and ninth states of the same $A_1$ irrep, as well as for their tunneling partners in the $B_2$ irrep.

An overview of the ground state energy splittings is given in Table V. Most of the splittings from the new SO-3 potential are in far better agreement with the available spectroscopic data than those obtained from the SQSBDE potential. The SO-3 dissociation energy of 1061.73 cm$^{-1}$ is well within the error bars of the experimental number of 1062 ± 1 cm$^{-1}$, as obtained by Bohac et al.$^{21}$ This should not come as a surprise, since the SO-3 surface was refined to reproduce this number.$^{43}$ More interesting are the vibrational frequencies. Unfortunately, for the monomer stretch ground state modes in $(\text{HF})_2$, the experimental data on the intermolecular frequencies are still scarce and rather uncertain, so that comparison between the two potentials is difficult. Looking at the data that are available, one can see that the performance of the PESs in this respect is rather alike, except for the $v_6$ (dimer torsion) frequency. The most reliable com-

![FIG. 3. Cuts through the wave function for the (000120) state (left), and the (000040) state (right) on the SO-3 potential for $J=0$. Both $r_A$ and $r_B$ are kept fixed at 1.769 $a_0$, and $\phi=180^\circ$. The cuts are made for $R=5.1$ $a_0$ (top), 5.3 $a_0$ (middle) and 5.7 $a_0$ (bottom).]
TABLE V. Comparison of calculated ground state energy splittings with experiment. Tunneling splittings between even (A) and odd (B) states with respect to monomer exchange are denoted by \( \Delta (\nu) = E_{\nu}^{A} - E_{\nu}^{B} \).

<table>
<thead>
<tr>
<th>( J = K = 0 )</th>
<th>SQSBDE</th>
<th>SO-3</th>
<th>Expt.</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>( D_0 )</td>
<td>1057.88</td>
<td>1061.73</td>
<td>1062</td>
<td>21</td>
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<tr>
<td>( \Delta (\nu_0) )</td>
<td>0.44</td>
<td>0.59</td>
<td>0.658690</td>
<td>11</td>
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<tr>
<td>( \nu_1 )</td>
<td>425.36</td>
<td>483.48</td>
<td>0.98</td>
<td>25</td>
</tr>
<tr>
<td>( \Delta (\nu_1) )</td>
<td>15.01</td>
<td>2.65</td>
<td>126.40</td>
<td>126.57</td>
</tr>
<tr>
<td>( 2 \nu_1 )</td>
<td>160.62</td>
<td>162.93</td>
<td>( \sim 161 )</td>
<td>54</td>
</tr>
<tr>
<td>( \Delta (2 \nu_1) )</td>
<td>7.47</td>
<td>7.19</td>
<td>378.82</td>
<td>420.83</td>
</tr>
<tr>
<td>( \nu_6 )</td>
<td>1.74</td>
<td>2.22</td>
<td>39.60</td>
<td>38.68</td>
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</table>

<table>
<thead>
<tr>
<th>( J = K = 1 )</th>
<th>( \nu_0 )</th>
<th>( \Delta (\nu_0) )</th>
<th>( \nu_1 )</th>
<th>( \Delta (\nu_1) )</th>
<th>( 2 \nu_1 )</th>
<th>( \Delta (2 \nu_1) )</th>
<th>( \nu_6 )</th>
<th>( \Delta (\nu_6) )</th>
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<tr>
<td>( \nu_0 )</td>
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<td>38.68</td>
<td>35.425</td>
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<td>( \Delta (\nu_0) )</td>
<td>0.78</td>
<td>1.05</td>
<td>1.0643</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>( \nu_1 )</td>
<td>168.59</td>
<td>175.47</td>
<td>1.30</td>
<td>3.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta (\nu_1) )</td>
<td>214.95</td>
<td>209.32</td>
<td>17.47</td>
<td>18.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>( 2 \nu_1 )</td>
<td>214.95</td>
<td>209.32</td>
<td>17.47</td>
<td>18.80</td>
<td></td>
<td></td>
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<tr>
<td>( \Delta (2 \nu_1) )</td>
<td>366.67</td>
<td>398.66</td>
<td>399.79</td>
<td>55</td>
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<tr>
<td>( \nu_6 )</td>
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<td>1.63</td>
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Comparison in this mode is made for the \( K = 1 \) state, since the experimental assignment of the \( \nu_6 \) mode for \( K = 0 \) is tentative.\(^{43}\) Looking at this \( K = 1, \nu_6 \) excitation, we see that the SO-3 result differs by only 0.3%, whereas the SQSBDE frequency is 8% off.

As another, more sensitive test we can compare the tunneling splittings between states of even (A\(_1\) and A\(_2\)) and odd (B\(_2\) and B\(_1\)) symmetry under monomer exchange. A tunneling pair is formed by a state of A\(_1\) symmetry and the corresponding state of B\(_2\) symmetry, or similarly between states of A\(_2\) and B\(_1\) symmetry. Note that the quantum numbers of the members of such a pair are equal, except for the \( \nu_5 \) quantum, which is one higher for the B state. We see that the new potential reproduces with 0.59 cm\(^{-1}\) around 90% of the ground state tunneling splitting of 0.66 cm\(^{-1}\).\(^{11}\) Although this 6D number is somewhat less than the (4 + 2)D result of Klopper \etal.,\(^{43}\) who reported a tunneling splitting of 0.63 cm\(^{-1}\), it is still a significant improvement over the SQSBDE potential, which only gives 67%. Also the tunneling splitting upon \( \nu_4 \) excitation is consistent with the experimental lower limit, whereas the SQSBDE result is not. Again the most striking are the results for the tunneling splitting in the \( K = 1, \nu_6 \)-excited state: whereas the SO-3 splitting is only 7% too low, the SQSBDE result is more than a factor of 3 too high.

Results for the monomer stretch excited states are given in Tables VI and VII. Several states in Tables VI and VII have been marked with an asterisk to indicate a relatively large mixing with vibrational ground state functions (>5%). Again the result for the free monomer basis is not shown, but since the choice of the monomer stretch basis has a greater effect for the excited states, the difference in results for the free monomer and dimer adapted basis sets are greater than in the ground state. The effect now also shows up for the SO-3 potential, with dimer adapted states that are up to 0.3 cm\(^{-1}\) lower than the corresponding free monomer states. It is still stronger on the SQSBDE potential, however, where differences up to 2 cm\(^{-1}\) occur.

The results for excited states of A\(_1\) and B\(_2\) symmetry on the SQSBDE surface may be compared with those of Wu \etal.,\(^{34}\) and those of Volobuev \etal.\(^{51}\) on the same surface. In general the results presented there are very similar to ours, with typical differences around 0.5 cm\(^{-1}\).

For the stretch excited states, there are more experimental data available, thanks to the experiments of Pine and co-workers\(^{16,18,19}\) and those of Anderson, Davis, and Nesbit.\(^{52,53}\) A comparison of our results with these data is given in Table VIII. We see again that the SO-3 potential

TABLE VI. As in Table II, for the first monomer stretch excited states \((\nu_1 + \nu_2 = 1)\).

<table>
<thead>
<tr>
<th>( \Gamma )</th>
<th>( n )</th>
<th>( \nu_1 \nu_2 \nu_3 \nu_4 \nu_5 \nu_6 )</th>
<th>SQSBDE</th>
<th>SO-3</th>
<th>( \langle R \rangle )</th>
<th>( \Delta R )</th>
<th>( B )</th>
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performs better than SQSBDE. The calculated donor stretch frequency of 3867.09 cm$^{-1}$ and the acceptor stretch at 3929.17 cm$^{-1}$ calculated with the SO-3 potential are in much closer agreement with the experimental values of 3868.079 and 3930.903 cm$^{-1}$ than their SQSBDE counterparts. Also the SO-3 dimer stretch ($v_1 + v_4$) and geared bend ($v_2 + v_5$) frequencies combined with excitation of either the donor or the acceptor stretch are very good. The errors between the results on this potential and experiment are 3.5–16 times smaller than the corresponding errors of the SQSBDE frequencies.

Also the tunneling splittings in these intramolecular stretch modes are better reproduced by the new potential. This effect can also be seen in the $v_1 + v_4$ combination band, but is less pronounced in states in which the geared bend is excited (in fact, the tunneling splitting in the $v_1 + 2v_5$ states is even worse on SO-3, although not much). It would be interesting to measure the experimental tunneling splitting upon $v_2 + v_4$ excitation, since the SO-3 splitting is more than twice as large as the SQSBDE result.

\section*{V. CONCLUSIONS}

We have investigated the HF dimer by means of variational calculations of bound and quasi-bound states using the SQSBDE and SO-3 potential energy surfaces. Our results on the SQSBDE surface are comparable to previous studies. The choice of the monomer stretch basis is of considerable importance. Using a dimer adapted monomer stretch basis leads to significantly lower energies in most cases. In addition, we find that although the energy gap between $v_X = 0$ and $v_X = 2$ monomer stretch function is huge, these overtone functions have to be included in the basis for a good description of the bound and quasi-bound states.

To our knowledge, no calculations on (HF)$_2$ using the SO-3 potential have been published. We have made a side-by-side comparison of this potential with the older SQSBDE potential on the (quasi) bound states calculated. We find that many of the interesting features of the dimer can be computed with remarkable accuracy using the SO-3 potential. For the ground state, the dissociation energy is in perfect agreement with experiment. Also the intermolecular vibrational frequencies agree well with the available experimental data, especially in the case of $v_6$ excitation, where the SQSBDE potential fails. Even the tunneling splittings, which are quite small, and very sensitive to the potential, are reproduced very well by the SO-3 potential, much better than by the older PES.

For the monomer stretch excited states, the difference between SO-3 and SQSBDE is even more striking. Not only are the $v_1$ and $v_2$ fundamental frequencies reproduced to within 2 cm$^{-1}$ (as opposed to $\sim 30$ cm$^{-1}$ for SQSBDE), also the intermolecular frequencies built upon these intramolecu-

\begin{table}[h]
\centering
\begin{tabular}{cccccc}
\hline
$\Gamma$ & $n$ & $v_1v_2v_3v_4v_6$ & SQSBDE & SO-3 & $\Delta R$ & $B$ \\
\hline
$A_2$ & 1 & 010001 & 4283.33 & 4303.00 & 5.27 & 0.23 & 0.2176 \\
& 2 & 100001 & 4312.91 & 4353.85 & 5.28 & 0.22 & 0.2172 \\
& 3 & 010101 & 4404.58 & 4431.93 & 5.38 & 0.37 & 0.2109 \\
& 4 & 100101 & 4425.12 & 4469.76 & 5.28 & 0.26 & 0.2171 \\
& 5 & 010201 & 4514.25 & 4551.14* & 5.51 & 0.51 & 0.2037 \\
& 6 & 100201 & 4592.57 & 4588.57* & 5.45 & 0.45 & 0.2073 \\
& 7 & 010121 & 4561.29 & 4594.26 & 5.53 & 0.48 & 0.2014 \\
& 8 & 100121 & 4600.35 & 4617.96 & 5.30 & 0.26 & 0.2158 \\
$B_2$ & 1 & 010010 & 3896.04 & 3899.01 & 5.22 & 0.21 & 0.2219 \\
& 2 & 100010 & 3940.81 & 4001.39* & 5.31 & 0.36 & 0.2163 \\
& 3 & 010101 & 4034.88 & 4001.39* & 5.31 & 0.36 & 0.2163 \\
& 4 & 100101 & 4063.67 & 4055.56 & 5.28 & 0.32 & 0.2180 \\
& 5 & 010030 & 4099.88 & 4094.15 & 5.29 & 0.29 & 0.2166 \\
& 6 & 100030 & 4067.57 & 4055.56 & 5.29 & 0.29 & 0.2166 \\
& 7 & 010210 & 4162.31 & 4130.62 & 5.37 & 0.42 & 0.2129 \\
& 8 & 100210 & 4180.19 & 4168.44 & 5.30 & 0.37 & 0.2174 \\
& 9 & 010130 & 4195.99 & 4181.23 & 5.38 & 0.42 & 0.2119 \\
& 10 & 000150 & 4208.28 & 4200.10 & 5.35 & 0.36 & 0.2130 \\
\hline
\end{tabular}
\caption{Comparison of calculated excited state energy splittings with experiment. Tunneling splittings between even (A) and odd (B) states with respect to monomer exchange are denoted by $\Delta (\nu) = E_\nu - E_{\nu^*}$.}
\end{table}
lar excitations all agree to within 1 or 2 cm$^{-1}$. The tunneling splittings in the excited states are not yet perfect, but are certainly an improvement over the SQSBEDE tunneling splittings, which are typically too low by a factor of 2.

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