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LETTERS

Tunneling Splittings in Predissociated HF Dimer

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We have calculated converged energies and tunneling splittings of the intramolecular stretching fundamentals and high-frequency, low-frequency combination levels of $(HF)_2$ on three potential energy surfaces. The resonance states are located against a broad background of continuum states by a moment-based stabilization method. The mean unsigned deviation from experiment for six tunneling splittings on the recently proposed S2 surface and on the BJKKL surface of Bunker *et al.* are 28% and 24%, respectively, as compared to 41% for the previously available results on the SQSBDE surface of Quack and Suhm. The results for the S2 surface are more accurate for excitation of the hydrogen-bond acceptor mode than for the hydrogen-bond donor mode, whereas those for the BJKKL surface are more accurate for the latter than the former.

Introduction

The HF dimer is the simplest hydrogen-bonded system; nevertheless, it exhibits a variety of quantum mechanical phenomena that present extant challenges to theory. These include the potential energy surface, the vibrational spectrum, and the dynamics. A review covering work in all three areas up to 1989 provides background,[1] and more recent reviews of selected aspects are also available.[2-4]

Early quantum mechanical calculations of the vibrational spectrum were based on reduced-dimensionality models in which some degrees of freedom were frozen. Recently it has become possible to calculate the low-lying energy levels of this four-body systems by complete quantal calculations including all degrees of freedom, for the ground state,[5-12] lowest excitation of the out-of-plane torsion,[5,6,8-12] and general excited states.[5,9-12] (For some states, approximate full-dimensional quantum calculations have also been carried out by making nonrigorous assumptions about the nodal hypersurfaces of the wave functions or by making quasiadiabatic assumptions.[6-8]) These low-lying states involve excitations of the bends (ν_3 and excitations of even numbers of quanta in ν_5), the hydrogen-bond exchange motion (excitations of odd numbers of quanta in ν_5), the van der Waals stretch (ν_4), and the torsion (ν_6). It is also of interest to consider high-lying predissociated states involving excitations of the high-frequency modes ν_1 and ν_2 corresponding to excitation of monomer stretches; Wu *et al.*[12] presented the first converged calculations of vibrational excitations involving monomer stretches. In these calculations, Wu *et al.* employed the SQSBDE[6] potential energy surface.

Several potential energy surfaces[1,6,8,11,13,14] have been proposed for $(HF)_2$, and in the present study we carried out calculations for three of these surfaces that are presumed to be among the most accurate:

BJKKL, an analytic fit[13] to the *ab initio* coupled-pair

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functional electronic structure calculations of Kofranek *et al.*[15] plus additional points;

SQSBDE, the semiempirically-adjusted (S) surface of Quack and Suhm[6] (QS) fitted to the *ab initio* data of Kofranek *et al.*[15] plus dispersion coefficients,[16] and then adjusted to reproduce the experimental rotational constants (B) and the dissociation energy (D_e);

S2, a second semiempirically-adjusted (S2) surface,[11] based on the earlier SQSBDE surface, further adjusted to retain good agreement with the equilibrium geometry of that surface and the experimental dissociation energy and theoretical vibrational frequencies and also to agree with the experimental ground-state tunneling splitting[17] due to hydrogen bond exchange.

Very recently Klopper *et al.* have developed a new surface called S-2.9, which is the culmination[8] of a line of work by Quack, Suhm, and co-workers[3,7,8,14] in which *ab initio* calculations are adjusted to produce semiempirical surfaces that agree well with several[6,18−23] experimental spectroscopic observations. The parameters of the S-2.9 surface are not yet available to us so we could not calculate the predissociated states for this surface.

We consider here both the stretching vibration ν_1 corresponding to the stretch of the base, H ↔ F···HF, and the stretching vibration ν_2 corresponding to the stretch of the acid, HF···H ↔ F, and we report results for both fundamentals and combination bands. Our results for the SQSBDE surface confirm the accuracy of the calculations of Wu *et al.*,[12] and our calculations for the other surfaces allow us to see for the first time the effect of variation of the potential energy surface on the results. The results are particularly timely in that experimental observations of combination bands involving monomer stretches are now available.[18,24] The monomer stretch fundamentals were observed earlier.[25]

The tunneling splittings in $(HF)_2$ have also been studied by approximate reaction-path methods. The reader is referred to previous publications for reaction-path models of the tunneling process.[26,27] The present communication is concerned entirely with accurate quantal calculations.

The binding energy of the dimer is $D_0 = 1062$ cm^{-1},[20] whereas the stretching fundamentals occur at ∼3900 cm^{-1}.[19,21] Thus, all states involving vibrational quantum numbers $v_1 > 0$ or $v_2 > 0$ are predissociated[28] states, also called decaying states, metastable states, quasibound states, or resonances.[29] In particular, since the dissociation of these complexes involves converting internal excitation energy of a subsystem into relative translational energy along a subsystem separation coordinate, the resonances are of a type called multichannel,[30] target-excited,[31] or Feshbach[32] resonances.

Computational Methods

The resonance energies are calculated by the stabilization method,[33] originally developed for electronic spectra, but also well-known[34−37] for Feshbach resonances in vibrational problems. In this method the Hamiltonian is diagonalized in a finite basis, which leads to an artificial discretization of the continuum above the dissociation energy. Most of the eigenvectors and eigenvalues above the dissociation energy correspond to approximations to scattering states, i.e., to collisions of two HF monomers. However, the resonances are also represented in the numerical spectrum. In our version of the stabilization method, the resonances are picked out of the dense background of scattering states by examining moments. In previous applications using moments, we considered moments $\langle q^2\rangle$ involving the hyperradius q and searched for small values—since the scattering states are delocalized and the resonance states localized.[36,37] In the present work we used a different strategy; in particular we calculated moments $\langle (R_1 - R_{1e})^2\rangle$ and $\langle (R_2 - R_{2e})^2\rangle$ of the acid stretch coordinate R_1 and the base stretch coordinate R_2, where R_{1e} and R_{2e} denote classical equilibrium values of these coordinates. Since the continuum corresponds to $v_1 = v_2 = 0$ but the resonances have $v_1 > 0$ or $v_2 > 0$, the resonances are identified by having considerably larger values of one or another of these moments than are found for the scattering states.

If x_i is a coordinate describing the motion in mode i and the corresponding potential in x_i is harmonic, i.e., equals 0.5 $k_i x_i^2$, where k_i is the force constant, then the relationship between the expectation value of x_i^2 in the eigenstate specified by quantum number v_i and the energy E_{v_i} of mode i in that eigenstate is easily obtained from the virial theorem, which yields

$$\langle x_i^2\rangle = \frac{1}{k_i}E_{v_i} \tag{1}$$

where

$$E_{v_i} = (v_i + {}^1\!/_2)hc\omega_i \tag{2}$$

and ω_i is the spacing in wavenumbers between successive energy levels in mode i. An approximate quantum number v_i is then obtained from the ratio of the expectation values in the eigenstate specified by v_i and the ground state

$$v_i = \frac{\dfrac{\langle x_i^2\rangle_{v_i}}{\langle x_i^2\rangle_0} - 1}{2} \tag{3}$$

The potential surfaces described in this work are anharmonic, and so we should not expect to get integers when we compute the right-hand side of eq 5, but nevertheless we do see patterns in the right-hand side of eq 5 that allow us to assign quantum numbers to individual states. The relevant variable to consider to locate the ν_2 fundamental is $x_2 = R_1 - R_{1e}$, where R_1 is the bond length of the monomer that in the equilibrium geometry corresponds to the hydrogen bond donor and R_{1e} is the equilibrium bond length of that monomer in the dimer on a given potential energy surface. Similarly $x_1 = R_2 - R_{2e}$, where R_2 is the bond length of the hydrogen bond acceptor.

The basis functions are taken to have the form of a symmetrized product of a sum of harmonic oscillator functions in the van der Waals stretch coordinate r, monomer eigenfunctions in the stretch coordinates R_1 and R_2, and laboratory-frame[38] rotational-orbital functions. Each monomer eigenfunction is a linear combination of m_{vib} harmonic oscillator functions for the monomer. Using symmetry considerations presented previously,[11] we calculate the tunneling splittings as the difference in energy of a state in the A_g representation of the symmetry group (which contains states with even values of v_5) and the corresponding state in the B_u representation of the symmetry group (which contains states with odd values of v_5).

We use the basis set truncation scheme defined by the inequalities

$$j_{\text{sum}}(n) \le j_{\text{sum,max}} \tag{4}$$

and

$$m_{\max}(n) = \min\begin{cases} m_{\max,\max} \\ \text{INT}[Q - Q_v v_{\text{sum}}(n) - Q_j j_{\text{sum}}(n)] \end{cases} \tag{5}$$

TABLE 1: Basis Set Parameters

	SQSBDE	S2	BJKKL
Q	17.0	17.5	16.8
$j_{\mathrm{sum,max}}$	16	16	16
$m_{\mathrm{max,max}}$	13	14	13
M (A_g)	9379	10958	13159
(B_u)	8786	10300	12428

In these expressions, n denotes a particular basis function (characterized by basis set parameters v_1, v_2, j_1, j_2, and m), $j_{\mathrm{sum,max}}$ is the maximum allowed value of the quantum number j_{sum}, where j_{sum} is the sum of the individual monomer rotational quantum numbers j_1 and j_2, v_{sum} is the sum of the individual monomer vibrational quantum numbers v_1 and v_2, $m_{\mathrm{max,max}}$ is the maximum allowed index m (1, 2, ..., not 0, 1, ...) on the harmonic oscillator basis functions in the translational coordinate, and Q_v, Q_j, and Q are parameters. The strategy we use is to fix Q_v and Q_j and increase $j_{\mathrm{sum,max}}$, $m_{\mathrm{max,max}}$, and Q until convergence is attained. In previous papers[10,11] we used simple estimates, $Q_v = 6.7$ and $Q_j = 1$. Although the results converge as Q, $j_{\mathrm{sum,max}}$, and $m_{\mathrm{max,max}}$ are increased for *any* fixed values of Q_v and Q_j, they converge faster if Q_v and Q_j are optimized. Therefore, in this work, we performed a rough optimization of Q_v and Q_j for the excitation of the acid-stretch fundamental for two of the surfaces. In this optimization we took advantage of the fact that although the calculated resonance energies do not strictly satisfy a variational bound theorem, in practical experience they do get lower as one adds basis functions in the monomer vibrational modes and/or the rotational-orbital modes with a fixed basis in the van der Waals stretch mode. Using this observation we obtain approximately optimized values of $Q_v = 3.9$ and $Q_j = 0.65$ for the BJKKL potential and $Q_v = 2.4$ and $Q_j = 0.8$ for the SQSBDE surface. We used these values for convergence tests, and we also used $Q_v = 2.4$ and $Q_j = 0.8$ for the S2 surface, because it is similar to the SQSBDE surface. The final run on the BJKKL surface used $Q_v = 2.4$ and $Q_j = 0.65$; excellent stability with respect to Q_v was exhibited. The values of the other basis set convergence parameters for the final calculations on each of the three surfaces are given in Table 1.

Results and Discussion

The supporting information shows that the fundamental excitation energies are converged within 1 cm^{-1}, and the ground-state tunneling splittings are converged within about 0.02 cm^{-1} over a broad range of basis set parameters and sizes. The fundamental excitation energies are lower than the isolated monomer values (3961 cm),[25] but except for ν_1, on the BJKKL surface, which is very accurate, are higher than the experimental values of 3931 and 3868 cm^{-1} for the dimer ν_1 and ν_2 modes, with errors for these fundamental excitations of 9−39 cm^{-1}. However, our focus here is on the tunneling dynamics, not on the shifts of the dimer with respect to the monomers. The ground-state tunneling splitting of the S2 surface is in excellent agreement with the experimental value[17] of 0.66 cm^{-1}. In fact, one of the primary design goals[11] of the S2 modification of the SQSBDE surface had been to improve this agreement; the SQSBDE surface has a ground-state tunneling splitting of[9] 0.44 cm^{-1}.

As an example of the performance of the stabilization method, consider the calculations on potential energy surface S2 with parameter set PS5, which is a parameter set defined in Table A-1 of the Supporting Information and used for calculations reported in Table A-3 of the Supporting Information. For A_g symmetry the ground state energy, 3017 cm^{-1}, and two fundamental resonance energies, 6914 and 6958 cm^{-1}, are eigenvalues 1, 1485, and 1512 in a matrix of order 9379. The values of v_2 calculated from eq 5 are 0, 1.11, and 0.30, respectively, whereas the values of v_1 are 0, 0.08, and 0.89, so the assignments as the v_1v_2 = 00, 01, and 10 states are reasonable. This is especially so when we consider that all eigenvalues from 1486 to 1511 and from 1513 to 1556 have v_1 and v_2 in the range 0.007−0.026. In contrast eigenvalue 1557 has $v_1 = 0.27$, $v_2 = 0.91$; this eigenvalue corresponds to the combination band with $v_1 = 0$ and $v_2 = v_4 = 1$. This eigenvalue is followed by 10 more eigenvalues approximating the continuum with v_1 and v_2 in the range 0.008−0.022. Thus the resonances are quite easy to identify. As one moves higher in energy one sometimes finds an eigenvalue with greater mixing of resonance and continuum or more mixing of acceptor and donor character, but with a little care the method continues to allow reasonable identification and assignment of resonances. We further checked the assignments in some cases by examining moments of $\langle (R - R_e)^2 \rangle$, where R is the intermolecular stretch coordinate and R_e is its equilibrium value; this moment is larger when v_4 is excited.

TABLE 2: Excitation Energies and Tunneling Splittings (cm^{-1}) of Ground State and Predissociated States[a]

v_1	v_2	v_4	v_5	SQSBDE[b]	SQSBDE[c]	S2[c]	BJKKL[c]	experiment[d]
0	0	0	0	0.00	0.00	0.00	0.00	0.00
			1	0.44	0.43	0.66	0.47	0.66
			Δ	0.44	0.43	0.66	0.47	0.66
1	0	0	0	3940.64	3939.77	3940.37	3930.50	3930.90
			1	3940.51	3939.64	3940.17	3930.35	3930.69
			Δ	−0.13	−0.13	−0.21	−0.15	−0.21
1	0	1	0	4064.87	4064.27	4060.62	4057.46	4058.47
			1	4064.07	4063.55	4059.29	4056.52	4056.81
			Δ	−0.79	−0.72	−1.33	−0.94	−1.66
1	0	0	2	4101.30	4100.72	4081.06	4100.12	4097.42
			3	4099.02	4098.47	4079.10	4097.25	4094.68
			Δ	−2.28	−2.25	−1.96	−2.87	−2.74
0	1	0	0	3896.39	3895.82	3896.49	3883.00	3868.08
			1	3896.48	3895.91	3896.64	3883.16	3869.39
			Δ	0.09	0.10	0.14	0.16	0.23
0	1	1	0	4034.87	4034.49	4026.28	4008.68	4000.69
			1	4035.28	4034.98	4028.00	4008.96	−
			Δ	0.41	0.49	1.72	0.28	−
0	1	0	2	4065.96	4065.56	4048.90	4055.05	4046.75
			3	4067.99	4067.57	4049.60	4058.77	4050.34
			Δ	2.03	2.01	0.70	3.72	3.59

[a] All states in this table have $v_3 = v_6 = 0$. [b] Wu *et al.*, ref 12. [c] Present calculations. [d] Dyke *et al.* (ref 17) for ground state; Anderson *et al.* (ref 18) for predissociated states.

Table 2 compares our results for five tunneling splittings to the recent experimental results of Anderson *et al.*;[18] these results were not available at the time that the S2 surface was created. Table 2 shows that the S2 surface provides considerable improvement over the SQSBDE surface for the tunneling splitting in both pure fundamental stretches and also in the $\nu_1-\nu_4$ combination band. However it does not improve agreement with the experiment for the $\nu_1-\nu_5$ and $\nu_2-\nu_5$ combinations. We note that the ν_4 motion is orthogonal to the tunneling path, whereas the ν_5 motion is parallel to it. This may indicate that the S2 surface is more accurate for the modes coupled to the tunneling mode than for the barrier height or shape in the tunneling mode itself. Barrier heights and shapes along rearrangement coordinates are typically the hardest quantities to converge in electronic structure calculations, so this situation provides a considerable challenge to electronic structure methodology to try to improve the surface by that means.

Agreement of the S2 results with experiment is much better for tunneling splittings with v_1 excited than for those with v_2 excited. The coupling of ν_2 to intermolecular coordinates is underestimated more by the SQSBDE and S2 surfaces than by the BJKKL surface, and these features may indeed turn out to be related.

The average unsigned percentage deviation from experiment for the six tunneling splittings for which comparison is possible is 28% for S2, while that for the SQSBDE surface is 41%. It is encouraging that modifying the SQSBDE surface semiempirically for the ground-state tunneling splitting has also reduced the average relative error in tunneling splittings of predissociated states at much higher energies. Interestingly, the average unsigned percentage deviation in the older, *ab initio* BJKKL surface is only 24%, which is smaller than for either semiempirical surface. The agreement for the BJKKL surface is especially better than the semiempirical surfaces for states with $v_2 = 1$.

Concluding Remarks

We have demonstrated good convergence of stabilization calculations for the energies and tunneling splittings of predissociated states of $(HF)_2$ with a three-parameter basis set selection scheme. We used this method to test the predictions of the two semiempirical potential energy surfaces for which these were previously unknown. Our calculations show that as compared to the one previously available calculations, both surfaces reduce the mean unsigned percentage deviation in six available tunneling splittings, in one case from 41% to 28% and in the other case to 24%. Very recently, more tunneling splittings have been reported;[39] continuing experimental and theoretical activity on this problem in our and other groups[2,3,8,12,18,40] may eventually lead to a quantitative understanding of this prototype hydrogen-bonded cluster.

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Supporting Information Available: Tables and text containing parameters of the basis sets and quadratures and convergence of the ground-state and resonance energies and tunneling splittings (7 pages). Ordering information is given on any current masthead page.

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