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This paper presents the first *ab initio* attempt to reconstruct the observed band profile of the stretching fundamental v_{FX} (X = H,D) in the FX···O(CH₃)₂ hydrogen-bonded system. The two-dimensional potential energy surface $V(r_{FH}, R_{F\cdots O})$ is evaluated by means of large basis set SCF calculations. The related force constants up to the fourth order are obtained via the analytical fit to a polynomial expansion. The vibrational problem is solved by means of a variational treatment which includes the effects of mechanical anharmonicity. The side bands of the stretching fundamental v_{FX} are described in terms of the $v_{FX} \pm nv_{FX\cdots O}$ combination bands in excellent agreement with experiment.

I. INTRODUCTION

The hydrogen fluoride–dimethyl ether hydrogen-bonded complex and its deuterated analog have been a subject of several experimental[1-3] and theoretical[4] studies. The main feature of the gas-phase IR spectrum is a strong band assigned to the v_{FX} (X = H,D) transition accompanied by sidebands of weaker intensities. Several hypotheses have emerged in the last two decades to explain this peculiar band shape. Arnold and Millen[1] attempted to interpret the shoulders in terms of combination bands involving hydrogen stretching and bending vibrations of the FX···O group. Anharmonic coupling between two stretches v_{FX} and $v_{FX\cdots O}$, which dates back to the works of Stepanov,[5] has been confirmed by phenomenological calculations of Bouteiller and Guissani.[4] In these calculations the $v_{FX} \pm nv_{FX\cdots O}$ fundamental and the first overtone transitions along with their corresponding relative intensities were evaluated by assuming a certain form of the potential energy surface. Although the pattern of coupling was identified correctly, the particular parameters, such as force constants and anharmonic constants, were adjusted so as to best reproduce the experimental spectrum. The purpose of the present paper is to prove the existence of combination bands by starting from *ab initio* calculations.

In the present paper a solution of the two-dimensional vibrational Schrödinger equation is carried out in the potential $V(r,R)$ where r = FH and R = F···O, which is fully derived from the *ab initio* calculations. In the first step the SCF method is applied to evaluate $V(r,R)$; later investigations which are now in progress, will be devoted to the role of correlation effects. The SCF calculations apply a basis set which is flexible enough to distinguish between the two possible structures of the complex (the planar C_{2v} and bent C_s[6]) and at the same time provides a good description of hydrogen bonding. To do so, the surface should be corrected for basis set superposition effects. The potential energy surface $V(r,R)$ is then fit to a polynomial expansion up to the fourth

order in both variables. The $v_{FX} \pm nv_{FX\cdots O}$ transitions and intensities are computed using a variational method[7,8] which allows for a detailed study of the mechanical anharmonicity effects.

Finally, the results are compared with available experimental data.[1,3]

II. ELECTRONIC CALCULATIONS: SCF POTENTIAL ENERGY SURFACE

In choosing the basis set for the SCF calculations we followed the prescriptions set forth by van Duijneveldt.[9] For the HF molecule the double-zeta basis set contracted from the (9s5p/4s) set of van Duijneveldt,[10] with two sets of polarization functions: d_F (1.06,0.18) and p_H (0.87,0.078) was used. For the ether molecule we used the split-valence 6-31G basis set[11] augmented by the two sets of d functions on O (1.0,0.15) and a single diffuse set of p functions on all the H atoms with the exponent 0.15. For the C atoms, it was possible to add only a single set of d functions; therefore, we added an energy-optimized d function with the exponent d_C = 0.8. The pure d functions were used throughout.

This choice is similar to that of Huiszoon[12] for dimethyl ether except for omitting the second d set on Cs. The geometrical parameters of (CH₃)₂O were held fixed at their experimental values.[13]

The chosen basis set leads to very good values of the monomer dipole and quadrupole moments (see Table I) which assure a proper description of electrostatic interaction, thus leading to a correct dimer structure.

Geometry optimization involved the four parameters: R = O···F, r = H–F, the angle α between H–F and O···F, and the angle β formed by the plane of the ether molecule and the O···F vector. The equilibrium geometry belongs to the C_s point group with the angle $\beta = 177°$ and the angle $\alpha = 0°$. The barrier to planarity (C_{2v}) is very small (less than 5 cm⁻¹). Due to the fact that such a small barrier will most likely lie well below the ground vibrational level for the ether wagging mode,[17] in further calculations the planar C_{2v} structure was assumed. The equilibrium intersystem dis-

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TABLE I. Monomer properties.

	FH	(CH₃)₂O
E_{SCF}, a.u.	− 100.054 242	− 154.067 245
r_{eq}(FH),Å	0.902 5	⋯
μ, D	1.913[a,b]	1.451[b]
$Q_{2,0}$,[c] a.u.	1.619[a,d]	− 1.079[e]
$Q_{2,2}$,[c] a.u.	⋯	1.433[e]

[a] At the experimental $r_{FH} = 0.9168$ Å.

[b] The experimental value is 1.309 ± 0.01 D, Ref. 13 for ether and 1.93 D, Ref. 14 for HF.

[c] Quadrupole moments, for definitions see Ref. 15.

[d] With respect to the center of mass, the experimental value (in the same orientation) is 1.7 a.u. (Ref. 16).

[e] The orientation of the molecule is the same as in the paper by Huiszoon (Ref. 12); his values are $Q_{2,0} = -1.265$ and $Q_{2,2} = 1.320$ a.u.

tance was found to be $R = 2.661$ Å and the intrasystem distance $r = 0.9167$ which is 0.0142 Å longer than in the isolated HF molecule.

In supermolecular calculations of potential energy and dipole moment surfaces, one should keep in mind that the basis set superposition error is very strongly distance dependent and could affect considerably the parameters of PES. For example, the BSSE uncorrected H-bond energy is 9.939 kcal/mol whereas the corrected value amounts to 8.221 kcal/mol, as found by using the (full) counterpoise procedure of Boys and Bernardi.[18] It is necessary to add that there is a large body of evidence that this represents a correct means of calculating interaction energies in supermolecular treatments,[19] and no overcorrection occurs in this procedure.[20]

Molecular properties of monomers in a complex could also be affected by the presence of partner's orbitals.[21] For example, the dipole moment of $(CH_3)_2O$ derived in the basis set of the (equilibrium) dimer is equal to 1.478 vs 1.451 D in its own basis set. This will have its effect on calculated values of $\Delta\mu$, the change of dipole moment upon complexation.[22] For example, in our complex $\Delta\mu$ is equal to 0.964 D, if correction for the partner's orbitals is taken into consideration, and 1.007 D without correcting, which amounts to an error of 0.043 D. This is not much in absolute terms, but such an error will vary with geometry; hence, it should be eliminated entirely.

The grid of points for the two-dimensional surface

TABLE II. Expansion coefficients[a] of the potential energy surface for the hydrogen-bonded complexes FX···O(CH₃)₂.

$$V(r,R) = \Sigma_p \, \Sigma_q \, a_{pq} \, r^p R^q$$

a_{20}	4.7080	a_{40}	24.7140
a_{11}	0.1813	a_{31}	0.3744
a_{02}	0.1321	a_{22}	0.2707
a_{30}	− 15.3295	a_{13}	− 0.3256
a_{21}	0.6657	a_{04}	0.3446
a_{12}	0.1194		
a_{03}	− 0.3610		

[a] The results are given in mdyn/Å^{p+q-1}.

$V(r,R)$ was chosen so that the minimum can accommodate the fundamentals and first overtones of v_{FH} and $v_{FX···O}$, i.e., it was deep by about 8000 and 800 cm⁻¹, respectively. The parameter r was varied in the range $0.9167 + n0.08$ Å, where $n = -3, -2, -1, 0, 1, 2, 3$, and R likewise, in $2.661 + k0.18$ Å where $k = -2, -1, 0, 1, 2$. For every dimer point, the energy and dipole moment were also derived for both subsystems in dimer basis sets. The twelve coefficients of expansion of the potential energy surface are shown in Table II.

III. VIBRATIONAL CALCULATIONS

A. The method

The fundamental and first overtone of the v_{FX} (X = H,D) stretching modes of FX···O(CH₃)₂ hydrogen-bonded complexes as well as the $v_{FX···O}$ stretching mode have been calculated by using a previously reported variational method. For a review of this method, see Refs. 7 and 8. The infrared relative intensities $I_{mn \rightarrow m'n'}$ of v_{FX} and $v_{FX} \pm n v_{FX···O}$ modes have been reconstructed by using the following expression:

$$I_{mn \rightarrow m'n'} = v_{mn \rightarrow m'n'} \left| \int \psi_{mn} \, \mu(r,R)\psi_{m'n'} \, dr \, dR \right|^2 e^{-E/kT},$$

where $E = E_{0n} - E_{00}$, T represents the absolute temperature, and k the Boltzmann constant. The subscripts m and n describe the fundamental state while m' and n' describe the excited states; m and n refer to the v_{FH} and $v_{FX···O}$ stretching modes, respectively.

The variational method has been applied by using a 22×22 size vibrational basis set. An almost absolute convergence of the variational method is attained for the ten first eigenvalues and transitions which change by less than 1 cm⁻¹ in increasing the size of the basis set from 18×18 to 22×22. The eigenvalue corresponding to the v_{FH} transition changes by 2 cm⁻¹ under the same conditions. A detailed study of the convergence of the variational method reported previously[8] allows one to place a good deal of confidence in these results.

B. Comparison of the calculated values of the v_{FX} and $v_{FX···O}$ stretching fundamentals and their first overtones with experimental data

In Table III are reported the calculated values of the fundamental and first overtone transitions for the FH···O(CH₃)₂ complex and its deuterated analog as well as the corresponding experimental values.

The first result, 3756 cm⁻¹, for the v_{FH} transition differs markedly from the experimental 3470 cm⁻¹.[1,2] This discrepancy was shown to largely disappear when correlation effects are accounted for in electronic calculations.[8] The same conclusion is valid for the vibration associated with the deuterated analog. Concerning the overtone of the v_{FX} stretching fundamental only one experimental reference is available.[3] In this case the agreement between the experimental and calculated frequencies is slightly worse than for the v_{FH} stretching fundamental. This fact can be attributed to a less accurate convergence in the region of the overtone and, perhaps, to deficiencies in representing the area of the potential

TABLE III. The v_{FX} and $v_{F\cdots O}$ vibrational transitions of the FX···O(CH$_3$)$_2$ complexes. Fundamental and first overtone.

	FH···O(CH$_3$)$_2$		FD···O(CH$_3$)$_2$	
	Calculated	Experimental	Calculated	Experimental
v_{FH}	3756	3470[a]	2779	2540[a]
$v_{F\cdots O}$	174	185 ± 10[b]	165	185[b]
v_{FH}/v_{FD}	1.351	1.366[c]		
$2v_{FH}$	7374	6485[c]	5432	4860[c]
$2v_{FH}/2v_{FD}$	1.357	1.334[c]		

[a] References 1 and 2.
[b] Reference 23.
[c] Reference 3.

energy surface further removed from the equilibrium region (lack of electron correlation, a less accurate analytical fit, etc. ...). In the work of Bevan et al, two possible assignments are available for the first overtone of the v_{FH} stretching fundamental.[3] If the first assignment is considered (see Table II of Ref. 3), the isotopic ratio 1.334 is very close to the calculated value 1.357. The isotopic ratio of the v_{FH} stretching fundamental is represented with comparable accuracy.

On the other hand, the calculated value of the hydrogen bridge stretch $v_{FX\cdots O}$, 174 cm^{-1}, is in satisfactory agreement with the experimental value of 185 ± 10 cm^{-1}.[8] This agreement indicates that our theoretical treatment yields a balanced description of intermolecular forces in the complex.

C. Mechanical anharmonicity effects on the v_{FX} and $v_{FX\cdots O}$ stretching fundamentals

To gain further insight into the understanding of nuclear motion in the complex, the v_{FH} and $v_{FX\cdots O}$ stretching fundamentals are reported in Table IV with a brief analysis of the mechanical anharmonic effects. A first type of anharmonicity, labeled "uncoupled" anharmonicity (Type I), may be defined by adding only the a_{30}, a_{03}, a_{40}, a_{04} coefficients of the $V(r,R)$ expansion to a_{20} and a_{02}. That is, third

and fourth powers of r and R are considered but coupling between these two parameters is turned off. A second type of anharmonicity, labeled type II, couples r and R together by taking into consideration the a_{21}, a_{12}, a_{31}, a_{22}, a_{13} coefficients of the same expansion. It is seen from the first two rows of Table IV that the overall mechanical anharmonicity (I plus II) is responsible for decreasing v_{FH} and $v_{FX\cdots O}$ by 334 and 4 cm^{-1}, respectively, which represents an anharmonicity effect of 8.9% and 2.2%. For the deuterated analogs the corresponding values are 194 and 10 cm^{-1} (7% and 6%). Comparison of the first and third rows reveals that the anharmonicity of type II, involving the anharmonicity coupling between the two vibrations, decreases v_{FH} and v_{FD} by 31 and 16 cm^{-1}, respectively. Its effect is relatively more important for $v_{FX\cdots O}$ stretching modes of both complexes with an increase of 22 and 16 cm^{-1}, respectively. The anharmonicity of type I which roughly represents the difference between the overall anharmonicity and type II anharmonicity lowers v_{FH} and v_{FD} by 303 and 178 cm^{-1}, respectively. The corresponding values are 26 and 36 cm^{-1} for $v_{FX\cdots O}$ stretching modes. Quite surprisingly the complex does not prove to be very anharmonic. By looking at individual contributions to type II anharmonicity in the last several rows at Table IV, it is evident that none of the anharmonic coupling coefficients produce a large change in the transitions except a_{21} which affects strongly the $v_{FX\cdots O}$ stretching mode. The latter coefficient is of the same order of magnitude as estimated in previous phenomenological work.[4] Nevertheless, the ab initio a_{21} is about four times smaller than earlier estimates indicating that phenomenological calculations may eventually prove erroneous. On the other hand, inclusion of correlation in electronic calculations may change the potential energy surface along with the a_{21} coefficient. Similar conclusions might be drawn for the overtone of the stretching fundamental.

A final comparison is made between the experimental and present results, based on the computed value of $X_{12} = v_{combination} - (v_{FX} + v_{FX\cdots O})$. In the work of Bevan et al.,[3] this quantity (referred as X_{13}) has the value 70 cm^{-1} in the FH···O(CH$_3$)$_2$ complex. The corresponding quantity in the present paper may be defined as $X_{12} = (v_{00} \rightarrow v_{11}) - (v_{00} \rightarrow v_{10} + v_{00} \rightarrow v_{01})$. By referring to the results of Table

TABLE IV. Anharmonicity effects.[a]

	FH···O(CH$_3$)$_2$		FD···O(CH$_3$)$_2$	
	v_{FH}	$v_{F\cdots O}$	v_{FD}	$v_{F\cdots O}$
Full[b] (I + II)	3756	174	2779	165
Harmonic[c]	4090	178	2973	175
Uncoupled[d] (I)	3787	152	2795	149
Full ($a_{21} = 0$)	3772 (+16)	145 (−29)	2783 (+4)	144 (−21)
Full ($a_{12} = 0$)	3756 (0)	173 (−1)	2781 (+2)	166 (+1)
Full ($a_{31} = 0$)	3746 (−10)	175 (+1)	2776 (−3)	166 (+1)
Full ($a_{22} = 0$)	3758 (+2)	175 (+1)	2781 (+2)	166 (+1)
Full ($a_{13} = 0$)	3761 (+5)	174 (0)	2783 (+4)	166 (+1)

[a] The numbers in parentheses represent the difference with the full treatment in the first row.
[b] Calculated with all the coefficients of the expansion $V(r,R)$.
[c] Calculated in the harmonic approximation; i.e., including only a_{20}, a_{02}, and a_{11}.
[d] Calculated with anharmonicity of type I including only a_{20}, a_{02}, a_{11} ($p,q \leqslant 4$).

TABLE V. Infrared transitions and relative intensities of the FH···O(CH$_3$)$_2$ complex (fundamental of v_{FH}).

Transitions $mn \rightarrow m'n'$	v (cm^{-1})	Normalized relative intensities	
		A [a]	B [b]
00→01	174		
00→02	324		
00→03	460		
00→04	595		
00→10	3756	1.	
00→11	3973	(217)[c] 0.108	
00→12	4166	(193) 0.110	
01→10	3583	0.097	0.042
01→11	3799	(216) 0.754	0.330
01→12	3992	(193) 0.258	0.113
01→13	4165	(173) 0.015	0.006
02→10	3432	0.011	0.002
02→11	3649	(217) 0.203	0.044
02→12	3842	(193) 0.469	0.101
02→13	4015	(173) 0.403	0.086
02→14	4172	(157) 0.039	0.008
03→10	3297	0.000	0.000
03→11	3513	(216) 0.045	0.005
03→12	3706	(193) 0.273	0.031
03→13	3879	(173) 0.255	0.029
03→14	4036	(157) 0.486	0.055
03→15	4187	(151) 0.061	0.007
04→10	3161	0.000	0.000
04→11	3378	(217) 0.009	0.000
04→12	3571	(193) 0.091	0.005
04→13	3743	(172) 0.294	0.017
04→14	3900	(157) 0.154	0.009
04→15	4051	(151) 0.506	0.030

[a] Not weighted with Boltzmann factor.
[b] Weighted with Boltzmann factor.
[c] The numbers quoted in parentheses represent the increase relative to the transition listed directly above.

V, this difference is 43 cm^{-1}. Nevertheless, by looking at Fig. 1, it is seen that the maximum intensity of the positive combination band corresponds to the $(v_{01} \rightarrow v_{12})$ hot transition and not to the $(v_{00} \rightarrow v_{11})$. Since the $(v_{01} \rightarrow v_{12})$ transition is located at 3992 cm^{-1} the above difference turns out to be 62 cm^{-1}, a value very close to the work of Bevan *et al.*

D. Hydrogen bond progressions

In Tables V and VI are reported the studies of the v_{FX} $\pm$ $nv_{FX\cdots O}$ progressions together with the calculation of the infrared relative intensities. The successive transitions show quasiequally decreasing progressions due to the mechanical anharmonicity effect. This trend is more pronounced for FD···O(CH$_3$)$_2$ than for the FH···O(CH$_3$)$_2$ complex as qualitatively predicted by Stepanov.[5] This means that in excited vibrational states, the deuterated species is slightly more strongly coupled than the nondeuterated one. Tables VII and VIII report the progressions for the first overtone of the v_{FX} stretching fundamental. These progressions are also
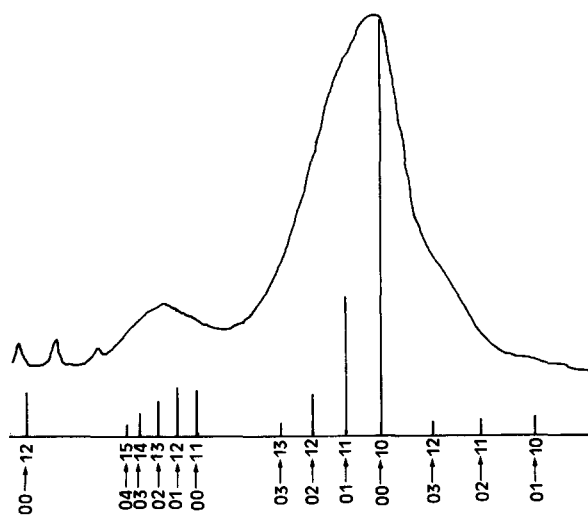
FIG. 1. The v_{FH} $\pm$ $nv_{FH\cdots O}$ stretching fundamental of the FH···O(CH$_3$)$_2$ complex.

quasiequally spaced and show the same trends as those for the v_{FX} stretching fundamental.

E. Relative intensities

Although the experimental and theoretical values of the stretching frequencies differ, it is instructive to construct a

TABLE VI. Infrared transitions and relative intensities of the FD···O(CH$_3$)$_2$ complex (fundamental of v_{FD}).

Transitions $mn \rightarrow m'n'$	v (cm^{-1})	Normalized relative intensities	
		A [a]	B [b]
00→01	165		
00→02	307		
00→03	437		
00→04	569		
00→10	2779	1.	
00→11	2978	(199)[c] 0.102	
01→10	2614	0.063	0.029
01→11	2812	(198) 1.176	0.537
01→12	2986	(174) 0.248	0.113
02→10	2472	0.006	0.001
02→11	2670	(198) 0.200	0.046
02→12	2844	(174) 0.893	0.208
02→13	2998	(154) 0.408	0.095
03→10	2342	0.000	0.000
03→11	2541	(199) 0.035	0.004
03→12	2714	(173) 0.296	0.037
03→13	2868	(154) 0.667	0.084
03→14	3011	(143) 0.503	0.063
04→10	2211	0.000	0.000
04→11	2409	(198) 0.000	0.000
04→12	2582	(173) 0.000	0.000
04→13	2737	(155) 0.337	0.023
04→14	2879	(142) 0.561	0.038
04→15	3021	(142) 0.528	0.035

[a] Not weighted with Boltzmann factor.
[b] Weighted with Boltzmann factor.
[c] The numbers quoted in parentheses represent the increase relative to the transition listed directly above.

TABLE VII. Infrared transitions and relative intensities of the FH···O(CH₃)₂ complex (first overtone of v_{FH}).

Transitions $mn \to m'n'$	v (cm^{-1})		Normalized relative intensities	
			A^a	B^b
00→20	7374		1.	
00→21	7622	(248)^c	0.297	
00→22	7849	(227)	0.039	
01→20	7201		0.288	0.126
01→21	7448	(247)	0.394	0.172
01→22	7675	(227)	0.522	0.228
01→23	7883	(208)	0.154	0.067
01→24	8072	(189)	0.017	0.007
02→20	7050		0.075	0.016
02→21	7298	(248)	0.400	0.085
02→22	7525	(227)	0.030	0.006
02→23	7733	(208)	0.478	0.102
02→24	7922	(189)	0.304	0.065
03→20	6915		0.022	0.002
03→21	7162	(247)	0.215	0.024
03→22	7390	(228)	0.258	0.029
03→23	7597	(207)	0.032	0.003
03→24	7786	(189)	0.292	0.033
03→25	7960	(174)	0.402	0.045
04→20	6779		0.000	0.000
04→21	7027	(248)	0.095	0.006
04→22	7254	(227)	0.285	0.017
04→23	7461	(207)	0.028	0.002
04→24	7650	(189)	0.137	0.008
04→25	7825	(175)	0.152	0.009
04→26	7990	(165)	0.421	0.025

^{a} Not weighted with Boltzmann factor.
^{b} Weighted with Boltzmann factor.
^{c} The numbers quoted in parentheses represent the increase relative to the transition listed directly above.

TABLE VIII. Infrared transitions and relative intensities of the FD···O(CH₃)₂ complex (first overtone of v_{FD}).

Transitions $mn \to m'n'$	v (cm^{-1})		Normalized relative intensities	
			A^a	B^b
00→20	5432		1.	
00→21	5656	(224)^c	0.217	
01→20	5267		0.220	0.100
01→21	5491	(224)	0.487	0.222
01→22	5692	(201)	0.414	0.189
02→20	5125		0.049	0.011
02→21	5348	(223)	0.334	0.078
02→22	5550	(202)	0.126	0.029
02→23	5732	(182)	0.488	0.113
03→20	4996		0.013	0.002
03→21	5219	(223)	0.146	0.018
03→22	5420	(201)	0.299	0.037
03→23	5603	(183)	0.004	0.000
03→24	5768	(165)	0.440	0.055
03→25	5921	(153)	0.221	0.028
04→20	4864		0.003	0.000
04→21	5087	(223)	0.055	0.004
04→22	5289	(202)	0.221	0.015
04→23	5471	(182)	0.203	0.014
04→24	5636	(165)	0.011	0.001
04→25	5790	(154)	0.379	0.025

^{a} Not weighted with Boltzmann factor.
^{b} Weighted with Boltzmann factor.
^{c} The numbers quoted in parentheses represent the increase relative to the transition listed directly above.

theoretical spectrum by combining calculated frequencies and intensities. Such a construction of the v_{FX} stretching fundamental and combination bands is shown in Figs. 1 and 2. Superimposed is the experimental spectrum, translated along the horizontal axis for coincidence of the absorption maxima. The agreement of the theoretical prediction with the experimental results may be considered remarkable. In Figs. 3 and 4 the same procedure is applied for the overtone of the v_{FX} stretching fundamental. In this case agreement with the experiment is quite poor. It should be recalled at this point that the experimental assignment of this spectrum by Bevan et al.[3] involves a coupling with a wagging bridge mode. The results presented here seem to support this interpretation.

IV. CONCLUSIONS

The results presented here demonstrate clearly that the variational method is suitable for the study of coupled vibrational modes and their intensities. It seems very likely that electric anharmonicity effects would change slightly the relative intensities to provide even better agreement with ex-

perimental data. Calculations to this effect are in progress in our laboratories.

The potential energy surface was calculated at the SCF level employing an extended basis set. The surface was corrected for basis set superposition effects. The frequencies derived from this surface seem to indicate that this is a very reasonable first approximation especially in the case of fun-
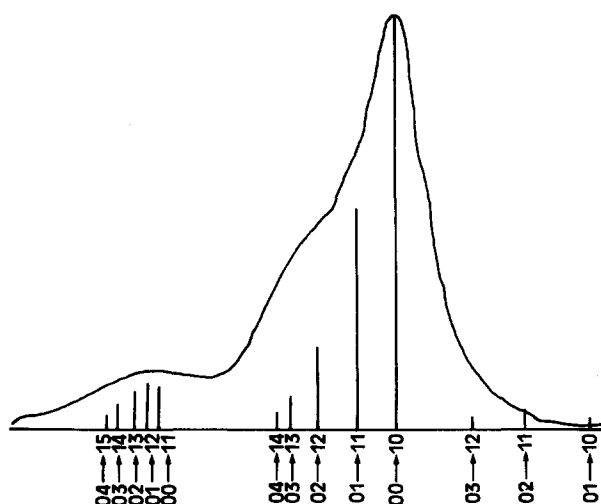
FIG. 2. The $v_{FD} \pm nv_{FD···O}$ stretching fundamental of the FD···O(CH₃)₂ complex.
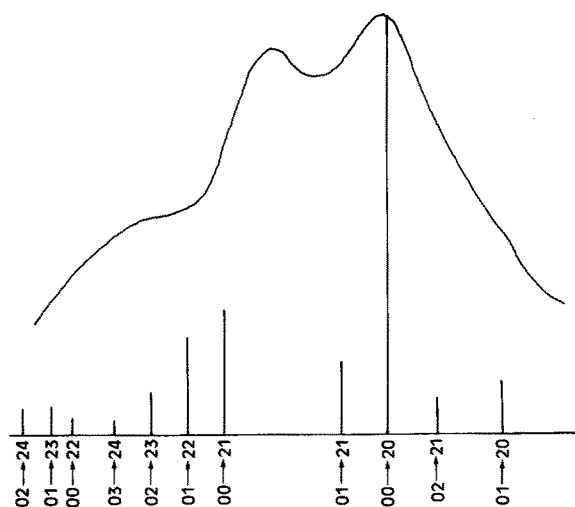
FIG. 3. Overtone of the $v_{FH} \pm n v_{FH\cdots O}$ stretching fundamental of the FH···O(CH$_3$)$_2$ complex.

damentals. However, it is not necessarily so with the overtone transitions which are too high at the SCF level. Clearly, an area of the potential energy surface which involves a partial bond dissociation is strongly affected by electron correlation. This problem will be examined in the next stage of this work.

The results presented here are the first to prove convincingly the existence of combination bands in hydrogen-bonded systems, as suggested by Stepanov some 40 years ago.[5]
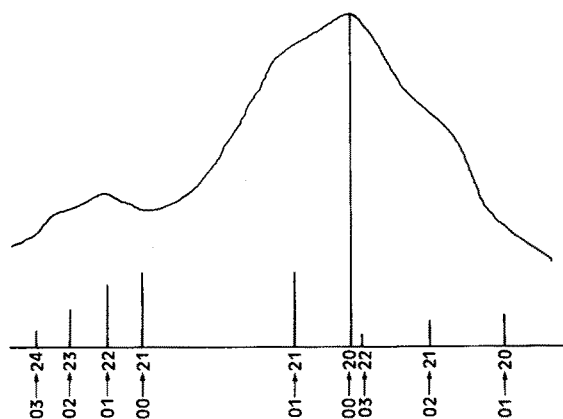

FIG. 4. Overtone of the $v_{FD} \pm n v_{FD\cdots O}$ stretching fundamental of the FD···O(CH$_3$)$_2$ complex.

The predicted band profile is in excellent agreement with the experimental one, except for the absolute position of the v_{FH} transition which occurs at slightly too high frequencies. This discrepancy can be largely reduced if correlation effects are accounted for, and indeed, was shown to disappear in large basis set CI calculations.[8] We believe that high-quality *ab initio* calculations, followed by the variational treatment of vibrational motions, can be used for quantitative reconstructions of the IR band shapes of hydrogen-bonded systems.

ACKNOWLEDGMENTS

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