VIBRATIONAL DYNAMICS OF THE H_2O . HF COMPLEX. POTENTIAL ENERGY AND ELECTRIC DIPOLE MOMENT SURFACES

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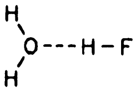
A total of 330 points on the potential energy and electric dipole moment surfaces of the ground electronic state of the H_2O . HF complex have been calculated *ab initio* using the SCF method and many-body perturbation theory (MBPT). To keep the calculations manageable, the geometry parameters of H_2O were fixed at their experimental values and only certain two-dimensional sections of the total surfaces have been evaluated. For each of the two-dimensional surface sections, analytic potential energy and electric dipole moment functions have been fitted through the points and corresponding vibration energy levels and effective electric dipole moments have been calculated using approximate vibrational Hamiltonians. The calculated values of resulting vibrational energies and effective electric dipoles form differently wide intervals for different vibrational modes. The intervals corresponding to the most interesting low frequency modes (out-of-plane and H_2O vs HF stretching) are very narrow and coincide satisfactorily with the corresponding experimental values. A very reasonable agreement has also been obtained for the equilibrium geometry, electric dipole moment and dissociation energy D_e of the complex. These findings lead us to believe that the calculated potential energy and electric dipole moment surfaces are sufficiently accurate for predicting purposes and rationalization of the so far unassigned spectral data of H_2O . HF.

The complex formed between one molecule of water and one of hydrogen fluoride, is the simplest possible hydrogen bonded complex in which water acts as the proton acceptor. For this reason it is of considerable chemical interest, and, not surprisingly, the subject of numerous experimental and theoretical studies throughout the years.

An early *ab initio* study of Kollman and Allen[1] has revealed that the complex may acquire four stable geometries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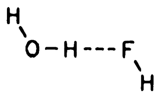
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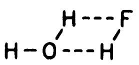
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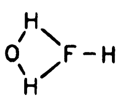
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Experimentally, the existence of the complex has been established through its microwave and infrared spectra[2,3], and, only structure *I*, which is predicted to have the most favourable stabilization energy, has been found to be consistent with the spectra. In subsequent microwave studies[4 – 12] many properties of H_2O . HF have been established quantitatively (e.g. geometry[5], effective electric dipole moments[8], effective potential energy function governing the out-of-plane bending mode[6,9], dissociation energies[12] D_e and D_0). Abundance of very precise experimental data has also stimulated activity of theorists[13 – 21]. Relative simplicity of H_2O . HF has made it possible to apply sophisticated theoretical treatments and, after accounting for the electron correlation effects[17 – 19] (included via second- and third-order Møller–Plesset perturbation theory), the equilibrium geometries and electric dipoles and dissociation characteristics were obtained in an excellent agreement with available experimental information. Fairly less satisfactory agreement, however, was obtained for the vibrational frequencies which probe a much bigger portion of the potential energy surface of H_2O . HF.

The reasons causing the failure of theory may be attributed to the fact that the vibrational analyses have been performed either in the harmonic approximation or within the frameworks of too-low-dimensional vibrational models. The aim of our effort is to overcome these limitations by accounting both for anharmonicity and the fact that certain vibrational motions of H_2O . HF exhibit collective features.

The complex H_2O . HF has nine independent vibrational degrees of freedom, some of which are related to strongly nonharmonic potentials. A complete theoretical study of this system, including the *ab initio* evaluation of the multi-dimensional potential energy and electric dipole moment surfaces and the solution of the complete dynamical vibrational problem, would thus represent an unfeasible task. Fortunately, since the vibrational frequencies of the H_2O and HF constituents are much higher than the frequencies of the intermolecular modes, the 9-dimensional dynamical problem can accurately be separated into two smaller problems (high and low frequency problems) by using the adiabatic approximation. Moreover, it appears that the same approximation may subsequently be used for similar separation of the intermolecular motions. To reduce the *ab initio* tedium, we keep the geometry parameters of H_2O at their experimental values and, with exception for the study of the interaction between the dissociation and HF stretching motions, we freeze the HF bond length at its equilibrium value in the complex. High quality of the adiabatic separation of the high (constituent) and low (intermolecular) frequency motions is a reliable guarantee for our assumption that the corresponding property surface sections should be highly parallel to the genuine ones. Secondly, we disregard from our *ab initio* calculations all the geometry configurations which are accessible only by more than two simultaneous vibrational displacements from the reference equilibrium configuration. Thirdly, we neglect completely the interactions between the H_2O and hydrogen bond bending motions possessing different symmetries. The latter neglections seem to be justified reasonably by the preliminary results we have obtained with global electrostatic empirical potentials.

In this paper, we concentrate our attention to the evaluation of the property surfaces and their testing by comparing with the experimental equilibrium characteristics and dissociation asymptotics, and to the investigation of the intermode couplings by performing calculations of the vibrational energies and effective electric dipoles within the frameworks of one- and two-dimensional vibrational Hamiltonians pertaining to the evaluated property surface sections. A proper "fully-dimensional" evaluation of the vibrational characteristics is postponed for a future study.

THEORETICAL

Coordinate System and Reference Configurations

The previous experimental and theoretical studies have established that the equilibrium geometry of H_2O . HF is pyramidal at the oxygen atom and that its hydrogen bond is slightly nonlinear. However, the height of the potential barrier to inversion through the planar C_{2v} form of the complex is very low. Thus, to classify the vibration-rotation energy spectrum of the complex it is convenient to use the point group C_{2v}. Accordingly, geometrical deformations of H_2O . HF can conveniently be described relative to a reference configuration of C_{2v} symmetry using the following symmetry coordinates (for definition of symbols see Fig. 1)

$$S_1(A_1) = R - R_e = \Delta R \qquad (1a)$$

$$S_2(A_1) = \gamma - \gamma_e = \Delta\gamma \qquad (1b)$$

$$S_3(A_1) = r - r_e = \Delta r \qquad (1c)$$

$$S_4(A_1) = (d_{13} + d_{23} - 2\,d_e)/\sqrt{2} \qquad (1d)$$

$$S_5(B_1) = \alpha_i \qquad (1e)$$

$$S_6(B_1) = \beta_i \qquad (1f)$$

$$S_7(B_1) = (d_{13} - d_{23})/\sqrt{2} \qquad (1g)$$

$$S_8(B_2) = \alpha_0 \tag{1h}$$

$$S_9(B_2) = \beta_0 . \tag{1i}$$

Earlier *ab initio* calculations[13,19] have also revealed that the high frequency ν_2, ν_4, and ν_7 vibrations of the complex are essentially almost the same as those of the isolated water molecule. The last high frequency motion, i.e. the HF stretching motion ν_3, appears to be affected considerably more by complexation. Still, it is opposed by a very deep and narrow potential. Thus, from the point of view of the low frequency (intermolecular) vibrational motions, the H_2O and HF fragments may be treated, to a high degree of approximation, as rigid units. If doing that (by fixing the water geometry parameters at the values corresponding to the equilibrium geometry of the isolated water molecule and the HF bond length at its optimal value for the planar C_{2v} geometrically defined reference configuration), then, any actual configuration of H_2O . HF can be described by the following components of the atomic position vectors of the Hougen–Bunker–Johns (HBJ) nonrigid reference configuration[22]

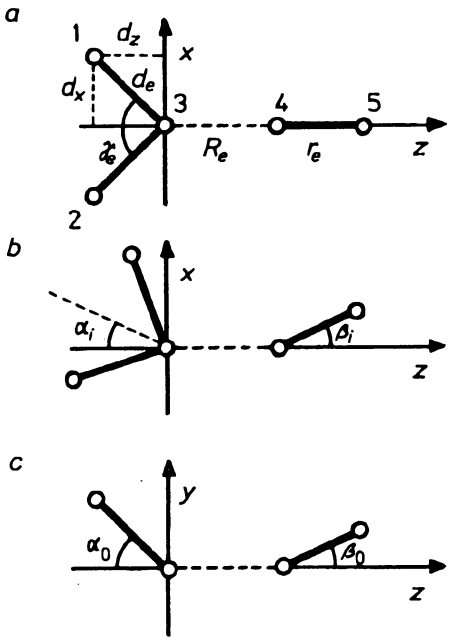

FIG. 1
Vibrational coordinates of H_2O . HF: *a* rigid reference configuration (C_{2v}), *b* in-plane bending coordinates, *c* out-of-plane bending coordinates

$$a_{1x} = d_x \cos\alpha_i + d_z \cos\alpha_0 \sin\alpha_i + D_x \tag{2a}$$

$$a_{1y} = a_{2y} = d_z \sin\alpha_0 + D_y \tag{2b}$$

$$a_{1z} = d_x \sin\alpha_i - d_z \cos\alpha_0 \cos\alpha_i + D_z \tag{2c}$$

$$a_{2x} = -d_x \cos\alpha_i + d_z \cos\alpha_0 \sin\alpha_i + D_x \tag{2d}$$

$$a_{2z} = -d_x \sin\alpha_i - d_z \cos\alpha_0 \cos\alpha_i + D_z \tag{2e}$$

$$a_{3x} = a_{4x} = D_x \tag{2f}$$

$$a_{3y} = a_{4y} = D_y \tag{2g}$$

$$a_{3z} = D_z \tag{2h}$$

$$a_{4z} = R_e + \Delta R + D_z \tag{2i}$$

$$a_{5x} = r_e \sin\beta_i \cos\beta_0 + D_x \tag{2j}$$

$$a_{5y} = r_e \sin\beta_0 + D_y \tag{2k}$$

$$a_{5z} = R_e + \Delta R + r_e \cos\beta_i \cos\beta_0 + D_z . \tag{2l}$$

The mass dependent quantities D_x, D_y, D_z in Eqs (2) are defined so that it holds

$$\sum_i m_i a_{i\alpha} = 0 \qquad (\alpha = x, y, z) , \tag{3}$$

where m_i is the mass of the i-th atom.

The HBJ reference configuration exactly follows all the intermolecular large-amplitude displacements. Consequently, the H_2O and HF vibrational displacements measured with respect to this reference remain small and can be processed using the Cartesian displacement coordinates $\boldsymbol{d}_i$ fulfilling the following constraints

$$\sum_i m_i \boldsymbol{d}_i = 0 \tag{4a}$$

$$\sum_i m_i [\boldsymbol{a}_i \times \boldsymbol{d}_i] = 0 \tag{4b}$$

$$\sum_i m_i \left(\frac{\partial \boldsymbol{a}_i}{\partial \rho_j} \right) \boldsymbol{d}_i = 0 \qquad (\rho_j = \Delta R, \alpha_i, \alpha_0, \beta_i, \beta_0)\,. \tag{4c}$$

Kinetic Energy Operator

With the above definition of the molecule-fixed position vectors (2) for the HBJ reference configuration and the vibrational displacement coordinates $\boldsymbol{d}_i$ the kinetic energy operator is obtained as

$$\mathbf{T} = \frac{1}{2} \mu^{1/4} \sum_{\alpha,\beta} (\mathbf{J}_\alpha - \mathbf{p}_\alpha)\, \mu_{\alpha\beta}\, \mu^{-1/2} (\mathbf{J}_\beta - \mathbf{p}_\beta)\, \mu^{1/4} + \frac{1}{2} \mu^{1/4} \sum_{i,j} \mathbf{P}_i\, \mu^{-1/2}\, \mathbf{P}_j\, \mu^{1/4} \tag{5}$$

with $\alpha,\beta = x,y,z,S_1,S_5,S_6,S_8,S_9$ and $i,j = S_2,S_3,S_4,S_7$.

All the quantities in Eq. (5) are formally defined by analogous relations as in ref.[22]. The explicit expressions for the components of the inertia tensor $\boldsymbol{I}$ and its inverse μ have been obtained with the aid of the computer algebra program MAPLE (see ref.[23]). Note that in deriving these terms, no attempt has been made to exclude or minimize any of the off-diagonal coupling terms in the μ tensor.

Ab initio Calculations

Methods. All calculations of the interaction potential in the H_2O . HF complex have been carried out in what is known as the supermolecule model (see ref.[24]) and all results were afterwards corrected for the basis set superposition effect by using the counterpoise correction method[24,25]. To obtain the interaction potential $V(R,r,\alpha_i,\alpha_0,\beta_i,\beta_0)$ in terms of the two-dimensional cross-sections, the point-wise calculations of the interaction energy have been carried out in several different approximations. We have employed the SCF HF method to obtain the electrostatic and inductive contributions to V, while the dispersion and intramolecular correlation effects have been accounted for at the level of the many-body perturbation theory (MBPT, see ref.[26]). The MBPT calculations of the electron correlation contribution have been performed at the level of the second-, third- and complete fourth-order approximations, which will be referred to as MBPT2, MBPT3, and MBPT4, respectively. We have also investigated the performance of the approximate fourth-order approach, referred to as the SDQ–MBPT4 method[26].

The main features of the interaction potential are correctly predicted already at the SCF level of approximation. For the H_2O and HF fragment geometries fixed at the experimental values of the free molecules, the optimal value of the H-bond distance, R(OH), acquires value 3.348 a.u. and the pertinent SCF interaction energy amounts to −12.466 mH; the corresponding experimental values are 3.267 a.u. and −11.4 mH, respectively. Including the electron correlation causes only small changes in both the equilibrium geometry and interaction energy. Moreover, in most cases different MBPT approaches lead to virtually same results. The mutual agreement between the results of the different MBPT approaches shows that the major part of the electron correlation contribution to the interaction potential is already recovered at the level of the MBPT2 approximation. The compatibility of different MBPT interaction potentials also supports our claim of a high accuracy of the interaction energies computed in this study.

Basis set. All calculations have been performed with the so-called polarized GTO/CGTO basis sets[27,28]. In order to avoid excessive basis set superposition contributions to the interaction energy, a series of high-quality GTO/CGTO basis sets for H, O and F has been generated following the method of refs[27,28]. The hydrogen polarized basis set of the form [11*s*6*p*/4*s*2*p*] has been derived by the polarization-oriented[27,28] extension of the (10*s*) GTO set of van Duijneveldt[29]. The same method[27,28] applied to the (13*s*8*p*) basis sets[29] for O and F has led to the [14*s*9*p*6*d*/6.4.2] polarized GTO/CGTO sets used in the present study. Those basis sets, by the method of their derivation, provide highly accurate results for the major electric properties (the dipole and quadrupole moments and dipole polarizabilities) of the isolated fragments. In this respect their quality is at least as high as that of the standard polarized basis sets[27,28]. However, in comparison with the standard polarized sets the present ones are more suitable for a simultaneous calculation of the geometry dependence of energy.

Another advantage of the extended polarized basis sets used in this study is that in comparison with the standard basis sets the size of the basis set superposition effects is considerably reduced at both the SCF and MBPT levels of approximation. In the vicinity of the complex equilibrium configuration the basis set superposition effect, as estimated by the counterpoise correction (refs[24,25]), amounts to about 0.5 mH for the SCF approximation and to about 2 mH for the MBPT2 approach. These numbers should be referred to the non-corrected interaction energies of the order of −12 mH and −14 mH, respectively. In higher orders of the MBPT approach the additional basis set superposition contribution is virtually negligible; its dominant part is accounted for at the MBPT2 level of approximation. Moreover, since the size of the basis set superposition effect at the most significant complex geometries does not exceed about 10 per cent of the total interaction energy, the use of the counterpoise correction appears to be reasonably justified[31].

The details of the extended polarized GTO/CGTO basis sets employed in this study are available from one of the authors (A. J. S.).

Computational details. In all calculations the geometry parameters of the water molecule has been kept fixed at the corresponding experimental values: $R(\mathrm{OH}) = 1.81117$ a.u., $\sphericalangle\,\mathrm{HOH} = 104.44°$. All other geometry parameters of the complex have been varied in a pair-wise way leading to two-dimensional cross-sections of the total interaction surface. At both the SCF and MBPT levels of approximation the *s*-components of the cartesian GTO/CGTO's have been removed from the molecular basis set. Moreover, in MBPT calculations no excitations were allowed from the 1*s* core orbitals of F and O. The calculations have been carried out by using the MOLCAS system of quantum chemistry programs[32 - 35].

Dipole moment surfaces. Along with the interaction energy surface we have also evaluated the electric dipole moment surface. Some pilot calculations have been carried out at the MBPT4 approximation by using the appropriate finite field perturbation approach[37]. It has been found that the MBPT4 dipole moment surfaces are essentially parallel to those obtained at the level of the SCF approximation. Thus, the interaction dipole surface can be obtained with a good accuracy from much less expensive SCF treatment based on the Hellmann–Feynman theorem. The absolute values of the dipole moments can be then obtained by simply adding the dipole moments of HF and H_2O computed within a high-level correlated approximation. Accordingly, the total electric dipole moment surface, $\boldsymbol{m}^{\mathrm{corr}}$, is constructed as the following sum

$$\boldsymbol{m}^{\mathrm{corr}} = \boldsymbol{m}^{\mathrm{SCF}} + \Delta\boldsymbol{m}^{\mathrm{corr}}_{\mathrm{H_2O}} + \Delta\boldsymbol{m}^{\mathrm{corr}}_{\mathrm{HF}}\,, \qquad (6)$$

where

$$\Delta\boldsymbol{m}^{\mathrm{corr}}_{\mathrm{H_2O}} = \boldsymbol{m}^{\mathrm{SDQ4}}_{\mathrm{H_2O}} - \boldsymbol{m}^{\mathrm{SCF}}_{\mathrm{H_2O}} \qquad (7a)$$

and

$$\Delta\boldsymbol{m}^{\mathrm{corr}}_{\mathrm{HF}} = \boldsymbol{m}^{\mathrm{SDQ4}}_{\mathrm{HF}} - \boldsymbol{m}^{\mathrm{SCF}}_{\mathrm{HF}}\,. \qquad (7b)$$

It is also worthwhile to mention that the dipole moment surface is virtually unaffected by the basis set superposition[38]. This is an additional advantage of the polarized basis sets used in the present study.

RESULTS AND DISCUSSION

Potential Energy and Electric Dipole Moment Surfaces

A total of 330 points were calculated covering an energy range up to approximately 13 000 cm^{-1} above equilibrium. This set of points was chosen in order to sample the full range of values of the intermolecular vibrational coordinates and the HF stretching coordinate and to probe, in full details, the following two-dimensional cross-sections of the total property surfaces: R vs r, R vs α_i, R vs α_0, R vs β_i, R vs β_0, α_i vs β_i, α_0 vs β_0, α_0 vs β_i, α_i vs α_0. No calculations were performed for the remaining α_i vs β_0 and β_i vs β_0 interactions as they have been found, within the framework of our preliminary analysis based on the Buckingham and Fowler electrostatic model[39], to be rather unimportant. The geometries and the energies and electric dipole moments of all the calculated points are collected in Table I.

For each of the calculated two-dimensional surface cross-sections, P_{ij}, analytic potential energy and electric dipole moment functions have been fitted through the corresponding points using the following power series

$$P_{ij} = \sum_{k,l} p_{kl}^{(ij)} x^k y^l \qquad (i,j = R,r,\alpha_i,\alpha_0,\beta_i,\beta_0)\,, \tag{8}$$

where x and y are $\exp(-\Delta R),\Delta r,\alpha_i,\alpha_0,\beta_i$ and β_0 for the potential energy functions, and x and y are $R,r,\alpha_i,\alpha_0,\beta_i$ and β_0 for the electric dipole moment functions.

The functional form (*8*) has turned out to be flexible enough to permit a practically quantitative fit of all the points. The expansion coefficients are available from the authors (O. B. and V. Š.). The fitted equilibrium and reference geometry parameters are collected in Table II. Typical representatives for the fitted functions are illustrated by Fig. 2.

Vibration Energies and Effective Electric Dipole Moments

To evaluate the vibration energies E and eigenfunctions Ψ_k for each of the two-dimensional problem it is necessary to solve the corresponding two-dimensional Schrödinger equation

$$\mathrm{H}^{(ij)} \Psi_k = E_k^{(ij)} \Psi_k \qquad (i,j = R,r,\alpha_i,\alpha_0,\beta_i,\beta_0)\,, \tag{9}$$

TABLE I
Ab initio MBPT4-SDQ energies and SCF dipole moment functions (E, m_x, m_y, m_z, R, r in a.u., α_0, α_i, β_0, β_i in deg)

R	r	E + 176	m_z
2.500	1.533	–.56649	–1.847
2.500	1.633	–.58638	–1.949
2.500	1.683	–.59248	–2.001
2.500	1.708	–.59475	–2.028
2.500	1.733	–.59658	–2.054
2.500	1.758	–.59799	–2.081
2.500	1.783	–.59902	–2.109
2.500	1.833	–.60008	–2.164
2.500	1.933	–.59897	–2.276
2.500	2.033	–.59471	–2.392
2.500	2.133	–.58834	–2.510
2.500	2.233	–.58059	–2.630
2.500	2.333	–.57196	–2.753
2.500	2.433	–.56282	–2.877
2.500	2.533	–.55344	–3.002
2.750	1.733	–.60630	–1.972
3.000	1.533	–.58821	–1.745
3.000	1.633	–.60427	–1.822
3.000	1.683	–.60854	–1.862
3.000	1.708	–.60992	–1.883
3.000	1.733	–.61086	–1.903
3.000	1.758	–.61140	–1.924
3.000	1.783	–.61158	–1.945
3.000	1.833	–.61097	–1.988
3.000	1.933	–.60667	–2.075
3.000	2.033	–.59943	–2.166
3.000	2.133	–.59028	–2.260
3.000	2.233	–.57994	–2.357
3.000	2.333	–.56891	–2.456
3.000	2.433	–.55756	–2.558
3.239	1.919	–.60774	–1.991
3.250	1.733	–.61257	–1.846
3.295	1.639	–.60760	–1.770
3.295	1.863	–.61071	–1.933
3.332	1.676	–.61053	–1.789
3.407	1.751	–.61302	–1.827
3.482	1.826	–.61184	–1.864
3.500	1.533	–.59277	–1.671
3.500	1.633	–.60747	–1.733
3.500	1.683	–.61107	–1.765
3.500	1.708	–.61212	–1.782
3.500	1.733	–.61274	–1.798
3.500	1.758	–.61295	–1.815
3.500	1.783	–.61280	–1.831
3.500	1.833	–.61156	–1.866
3.500	1.933	–.60602	–1.936
3.500	2.033	–.59760	–2.009
3.500	2.133	–.58733	–2.084
3.500	2.233	–.57593	–2.162
3.500	2.333	–.56392	–2.242
3.519	1.639	–.60803	–1.734
3.538	1.882	–.60914	–1.892
3.594	1.564	–.59864	–1.678
3.750	1.733	–.61214	–1.759
4.000	1.533	–.59225	–1.618
4.000	1.633	–.60644	–1.671
4.000	1.683	–.60979	–1.699
4.000	1.708	–.61072	–1.712
4.000	1.733	–.61120	–1.726
4.000	1.758	–.61129	–1.741
4.000	1.783	–.61102	–1.755
4.000	1.833	–.60953	–1.784
4.000	1.933	–.60341	–1.843
4.000	2.033	–.59463	–1.905
4.000	2.133	–.58391	–1.969
4.000	2.233	–.57209	–2.034
4.500	1.733	–.60916	–1.677
5.000	1.533	–.58906	–1.552
5.000	1.633	–.60294	–1.597
5.000	1.683	–.60614	–1.620
5.000	1.708	–.60698	–1.632
5.000	1.733	–.60740	–1.643
5.000	1.758	–.60741	–1.655
5.000	1.783	–.60706	–1.667
5.000	1.833	–.60542	–1.692
5.000	1.933	–.59910	–1.741
5.000	2.033	–.58993	–1.793
5.000	2.133	–.57894	–1.845
6.000	1.533	–.58686	–1.516
6.000	1.633	–.60066	–1.558
6.000	1.683	–.60381	–1.580
6.000	1.708	–.60463	–1.591
6.000	1.733	–.60502	–1.602
6.000	1.758	–.60501	–1.613
6.000	1.783	–.60464	–1.624
6.000	1.833	–.60295	–1.647
6.000	1.933	–.59655	–1.693
6.000	2.033	–.58730	–1.741
7.000	1.733	–.60370	–1.579
10.00	1.733	–.60216	–1.552
15.00	1.733	–.60156	–1.541

TABLE I
(*Continued*)

R	α_0	$E + 176$	m_y	m_z
2.500	0	–.59822	.000	–2.087
2.500	10	–.59831	.146	–2.075
2.500	20	–.59853	.288	–2.039
2.500	40	–.59931	.533	–1.906
2.500	60	–.59828	.713	–1.681
2.500	80	–.59493	.797	–1.403
2.500	100	–.58710	.781	–1.095
3.000	0	–.61147	.000	–1.928
3.000	10	–.61154	.142	–1.916
3.000	20	–.61172	.280	–1.881
3.000	40	–.61211	.523	–1.745
3.000	60	–.61179	.699	–1.531
3.000	80	–.60970	.785	–1.260
3.000	100	–.60476	.773	–0.962
3.376	0	–.61306	.000	–1.842
3.376	10	–.61312	.140	–1.830
3.376	20	–.61326	.276	–1.795
3.376	40	–.61356	.516	–1.660
3.376	60	–.61334	.691	–1.448
3.376	80	–.61178	.779	–1.181
3.376	100	–.60813	.770	–0.888
4.000	0	–.61127	.000	–1.743
4.000	10	–.61130	.138	–1.732
4.000	20	–.61137	.271	–1.697
4.000	40	–.61154	.509	–1.562
4.000	60	–.61134	.684	–1.352
4.000	80	–.61026	.773	–1.088
4.000	100	–.60785	.767	–0.802
5.000	0	–.60737	.000	–1.658
5.000	10	–.60738	.136	–1.646
5.000	20	–.60740	.268	–1.611
5.000	40	–.60740	.504	–1.475
5.000	60	–.60717	.678	–1.266
5.000	80	–.60643	.769	–1.005
5.000	100	–.60498	.765	–0.725

R	α_i	$E + 176$	m_x	m_z
2.500	10	–.59773	.127	–2.072
2.500	20	–.59625	.253	–2.027
2.500	30	–.59369	.372	–1.954
2.500	50	–.58444	.579	–1.738
3.000	10	–.61111	.130	–1.914
3.000	20	–.61005	.257	–1.871
3.000	30	–.60826	.377	–1.801
3.000	50	–.60210	.582	–1.592
3.376	10	–.61278	.132	–1.827
3.376	20	–.61194	.260	–1.786
3.376	30	–.61054	.380	–1.718
3.376	50	–.60586	.584	–1.515
4.000	10	–.61107	.133	–1.730
4.000	20	–.61049	.262	–1.690
4.000	30	–.60952	.383	–1.625
4.000	50	–.60641	.587	–1.430
5.000	10	–.60725	.134	–1.645
5.000	20	–.60691	.264	–1.607
5.000	30	–.60634	.386	–1.545
5.000	50	–.60456	.590	–1.359

R	β_0	$E + 176$	m_y	m_z
2.500	10	–.59736	–.149	–2.07
2.500	20	–.59469	–.294	–2.02
2.500	30	–.58990	–.427	–1.94
2.500	50	–.57103	–.641	–1.70
2.500	80	–.48585	–.750	–1.15
3.000	10	–.61104	–.140	–1.91
3.000	20	–.60972	–.275	–1.86
3.000	30	–.60737	–.401	–1.79
3.000	50	–.59835	–.604	–1.57
3.000	80	–.55877	–.730	–1.09
3.376	10	–.61280	–.136	–1.82
3.376	20	–.61199	–.268	–1.78
3.376	30	–.61058	–.390	–1.71
3.376	50	–.60525	–.591	–1.50
3.376	80	–.58297	–.726	–1.05
4.000	10	–.61114	–.133	–1.73
4.000	20	–.61074	–.262	–1.69
4.000	30	–.61005	–.383	–1.62
4.000	50	–.60759	–.582	–1.43
4.000	80	–.59845	–.729	–1.01
5.000	10	–.60731	–.132	–1.64
5.000	20	–.60713	–.261	–1.60
5.000	30	–.60683	–.381	–1.54
5.000	50	–.60581	–.581	–1.36
5.000	80	–.60280	–.737	–0.97

R	β_i	$E + 176$	m_x	m_z
2.500	10	–.59744	–.151	–2.07
2.500	20	–.59503	–.296	–2.02
2.500	30	–.59072	–.431	–1.94
2.500	50	–.57379	–.647	–1.69
2.500	80	–.49677	–.749	–1.12
3.000	10	–.61108	–.141	–1.91
3.000	20	–.60988	–.278	–1.86
3.000	30	–.60777	–.404	–1.79
3.000	50	–.59964	–.611	–1.57

TABLE I
(*Continued*)

R	β_i	$E + 176$	m_x	m_z
3.000	80	–.56383	–.743	–1.074
3.376	10	–.61283	–.137	–1.827
3.376	20	–.61210	–.270	–1.785
3.376	30	–.61082	–.394	–1.716
3.376	50	–.60604	–.597	–1.505
3.376	80	–.58592	–.739	–1.045
4.000	10	–.61115	–.134	–1.730
4.000	20	–.61079	–.264	–1.691
4.000	30	–.61018	–.385	–1.626
4.000	50	–.60798	–.586	–1.430
4.000	80	–.59975	–.738	–1.010
5.000	10	–.60731	–.132	–1.645
5.000	20	–.60715	–.261	–1.608
5.000	30	–.60688	–.381	–1.547
5.000	50	–.60597	–.582	–1.363
5.000	80	–.60323	–.741	–.972

α_0	β_0	$E + 176$	m_y	m_z
10	–80	–.58340	.864	–1.049
10	–50	–.60537	.730	–1.499
10	–30	–.61065	.530	–1.707
10	–20	–.61206	.408	–1.775
10	–10	–.61286	.276	–1.816
10	10	–.61285	.003	–1.815
10	20	–.61203	–.128	–1.773
10	30	–.61059	–.251	–1.704
10	50	–.60519	–.452	–1.493
10	80	–.58250	–.589	–1.039
20	–80	–.58363	.997	–1.017
20	–50	–.60547	.865	–1.466
20	–30	–.61075	.666	–1.673
20	–20	–.61217	.544	–1.741
20	–10	–.61299	.412	–1.782
20	10	–.61299	.139	–1.780
20	20	–.61217	.007	–1.737
20	30	–.61072	–.115	–1.667
20	50	–.60524	–.317	–1.455
20	80	–.58210	–.457	–.998
40	–80	–.58305	1.233	–.886
40	–50	–.60524	1.104	–1.333
40	–30	–.61077	.906	–1.540
40	–20	–.61230	.784	–1.607
40	–10	–.61321	.652	–1.647
40	10	–.61337	.379	–1.644
40	20	–.61260	.246	–1.600
40	30	–.61119	.122	–1.529
40	50	–.60569	–.081	–1.313
40	80	–.58188	–.225	–.848
45	–80	–.58262	1.283	–.840
45	–50	–.60503	1.155	–1.287
45	–30	–.61066	.957	–1.493
45	–20	–.61224	.836	–1.561
45	–10	–.61319	.704	–1.601
45	10	–.61343	.430	–1.597
45	20	–.61270	.298	–1.553
45	30	–.61132	.174	–1.481
45	50	–.60586	–.030	–1.265
45	80	–.58197	–.176	–.798
60	–80	–.58056	1.401	–.677
60	–50	–.60386	1.277	–1.123
60	–30	–.60990	1.080	–1.329
60	–20	–.61165	.959	–1.396
60	–10	–.61278	.828	–1.436
60	10	–.61334	.554	–1.431
60	20	–.61277	.422	–1.386
60	30	–.61154	.297	–1.314
60	50	–.60635	.092	–1.095
60	80	–.58248	–.056	–.623
80	–80	–.57608	1.476	–.417
80	–50	–.60079	1.357	–.859
80	–30	–.60745	1.164	–1.063
80	–20	–.60950	1.044	–1.130
80	–10	–.61092	.914	–1.169
80	10	–.61210	.643	–1.163
80	20	–.61184	.511	–1.118
80	30	–.61095	.387	–1.045
80	50	–.60644	.182	–.824
80	80	–.58299	.033	–.346
100	–80	–.56994	1.447	–.138
100	–50	–.59575	1.336	–.572
100	–30	–.60294	1.148	–.773
100	–20	–.60526	1.031	–.838
100	–10	–.60696	.903	–.877
100	10	–.60879	.636	–.870
100	20	–.60890	.506	–.824
100	30	–.60841	.384	–.751
100	50	–.60474	.183	–.529
100	80	–.58149	.042	–.045

α_i	β_i	$E + 176$	m_x	m_z
10	–80	–.58325	.865	–1.037
10	–50	–.60446	.726	–1.493
10	–30	–.60979	.524	–1.703
10	–20	–.61132	.401	–1.771
10	–10	–.61229	.269	–1.813
10	10	–.61280	–.005	–1.813

TABLE I
(*Continued*)

α_i	β_i	$E + 176$	m_x	m_z
10	-80	-.58325	.865	-1.037
10	-50	-.60446	.726	-1.493
10	-30	-.60979	.524	-1.703
10	-20	-.61132	.401	-1.771
10	-10	-.61229	.269	-1.813
10	10	-.61280	-.005	-1.813
10	20	-.61234	-.138	-1.771
10	30	-.61135	-.262	-1.701
10	50	-.60721	-.466	-1.489
10	80	-.58832	-.612	-1.027
20	-80	-.58057	.984	-1.004
20	-50	-.60253	.849	-1.454
20	-30	-.60828	.650	-1.662
20	-20	-.61002	.528	-1.730
20	-10	-.61122	.396	-1.772
20	10	-.61222	.123	-1.771
20	20	-.61203	-.009	-1.729
20	30	-.61135	-.132	-1.659
20	50	-.60790	-.337	-1.447
20	80	-.59016	-.485	-.982
30	-80	-.57800	1.094	-.947
30	-50	-.60030	.964	-1.391
30	-30	-.60632	.767	-1.596
30	-20	-.60822	.646	-1.664
30	-10	-.60961	.516	-1.704
30	10	-.61106	.244	-1.703
30	20	-.61114	.112	-1.660
30	30	-.61076	-.010	-1.591
30	50	-.60803	-.214	-1.378
30	80	-.59112	-.362	-.909
50	-80	-.57312	1.271	-.774
50	-50	-.59479	1.151	-1.202
50	-30	-.60090	.961	-1.400
50	-20	-.60297	.843	-1.465
50	-10	-.60460	.716	-1.504
50	10	-.60678	.451	-1.499
50	20	-.60735	.321	-1.455
50	30	-.60751	.201	-1.383
50	50	-.60597	.001	-1.166
50	80	-.58868	-.135	-.673

$\bar{\alpha}_0$[a]	$\bar{\alpha}_i$[a]	$E + 176$	m_x	m_y	m_z
10	10	-.61284	.132	.138	-1.816
20	10	-.61300	.132	.272	-1.782
40	10	-.61337	.133	.509	-1.649
60	10	-.61323	.134	.681	-1.441
80	10	-.61175	.135	.767	-1.178
100	10	-.60815	.137	.758	-0.890
10	20	-.61202	.260	.132	-1.775
20	20	-.61223	.260	.260	-1.743
40	20	-.61279	.262	.487	-1.618
60	20	-.61289	.265	.651	-1.421
80	20	-.61165	.267	.733	-1.172
100	20	-.60821	.270	.722	-0.896
10	30	-.61065	.380	.123	-1.708
20	30	-.61095	.381	.242	-1.680
40	30	-.61182	.384	.452	-1.567
60	30	-.61233	.387	.603	-1.389
80	30	-.61149	.391	.676	-1.161
100	30	-.60830	.395	.665	-0.907
10	50	-.60609	.584	.094	-1.509
20	50	-.60671	.585	.185	-1.490
40	50	-.60870	.589	.344	-1.415
60	50	-.61060	.595	.455	-1.292
80	50	-.61102	.600	.505	-1.128
100	50	-.60861	.605	.490	-0.939

[a] $\bar{\alpha}_0$, $\bar{\alpha}_j$ satisfy the following relations:

$$\alpha_0 = \arccos \frac{\cos \bar{\alpha}_0 \cos \bar{\alpha}_i}{\sqrt{1 - \cos^2 \bar{\alpha}_0 \cos^2 \bar{\alpha}_i}} \qquad \alpha_i = \arcsin (\cos \bar{\alpha}_0 \sin \bar{\alpha}_i) .$$

where the Hamiltonians $\mathbf{H}^{(ij)}$ may be written as[22]

$$\mathbf{H}^{(ij)} = \frac{1}{2}\sum_{i,j} \mu^0_{ij}\,\mathbf{J}_i\,\mathbf{J}_j + V_{ij} + H^{(ij)}_{\mathrm{hot}}\,, \qquad (10)$$

where μ^0_{ij} are the zeroth-order reduced masses, $\mathbf{J}_k$ the pertinent momenta, V_{ij} the pertinent potential energy functions and $H^{(ij)}_{\mathrm{hot}}$ higher order energy terms. The higher order terms $H^{(ij)}_{\mathrm{hot}}$ contain energies comparable to the contributions corresponding to the neglected intermode interactions. Hence, we have decided to neglect them and postpone

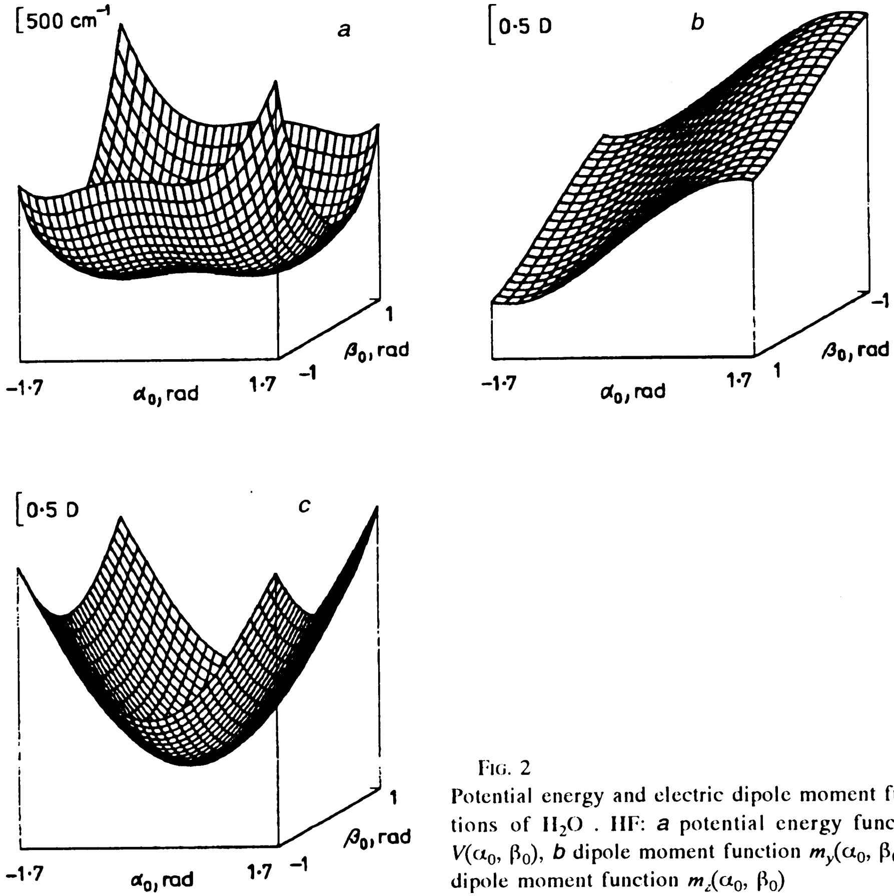

FIG. 2
Potential energy and electric dipole moment functions of H_2O . HF: *a* potential energy function $V(\alpha_0, \beta_0)$, *b* dipole moment function $m_y(\alpha_0, \beta_0)$, *c* dipole moment function $m_z(\alpha_0, \beta_0)$

their respecting for a future study which will be devoted to a fully-dimensional study of the discussed problem.

The approximate eigen-characteristics have been obtained variationally by diagonalizing the simplified Hamiltonians (*10*) as matrices over basis set functions expressed as products $\Phi_i(v_i)\,\Phi_j(v_j)$. The functions $\Phi_i(v_i)$ and $\Phi_j(v_j)$ were obtained numerically by solving the corresponding uncoupled one-dimensional Schrödinger equations. The lowest energies evaluated in this way are collected in Table III.

TABLE II
The geometry parameters[a] and dissociation energy of the H_2O . HF complex

R_{OF}, Å	r, Å	d, Å	γ_0, deg	α_0, deg	D_e, kcal mol^{-1}	Origin
			Equilibrium C_s geometry			
2.704	0.933[b]	0.958[b]	104.44[b]	45.5	7.78	This paper
2.642	0.935	0.960	105.0	52.1		Ref.[19]
2.662				46.0	7.2	Experiment[3,6]
			Planar C_{2v} geometry			
2.719	0.933	0.958[b]	104.44[b]	0.0[b]		This paper

[a] See Fig. 1; [b] held fixed.

TABLE III
The vibrational frequencies of the H_2O . HF complex (in cm^{-1}) obtained with one- and two-dimensional models

Mode	1-D	2-D Calculations	Experiment[a]
$\nu_1(R)$	200	204(α_0), 196(α_i), 189(β_0), 189(β_i), 205(r)	176 ± 15
$\nu_3(r)$	3 661	3 660(R)	3 608 ± 2
$\nu_5(\alpha_i)$	357	350(R), 197(β_i), 378(α_0)	157 ± 10
2 $\nu_5(\alpha_i)$	715	696(R), 394(β_i), 756(α_0)	330 ± 30
$\nu_6(\beta_i)$	587	540(R), 733(α_i)	696 ± 30
$\nu_8(\alpha_0)$	82	83(R), 70(β_0), 92(α_i)	64 ± 10
2 $\nu_8(\alpha_0)$	283	283(R), 229(β_0), 294(α_i)	267 ± 35
$\nu_9(\beta_0)$	617	567(R), 645(α_0)	666 ± 30

[a] Refs[3,6].

The effective electric dipole moments, $\langle \boldsymbol{m}(v_i,v_j)\rangle$, have been evaluated as the following averages

$$\langle \boldsymbol{m}(v_i,v_j)\rangle = \langle v_i,v_j|\boldsymbol{m}_{ij}|v_i,v_j\rangle . \qquad (11)$$

The values of these effective constants of the lowest vibrational states are given in Table IV.

A brief inspection of Table III reveals that in addition to the three water vibrational motions the H_2O . HF complex possesses three more rather characteristic motions. Namely the H_2O vs HF and HF stretching and the H_2O out-of-plane bending motions. The energies corresponding to the remaining bending motions exhibit very strong model dependences indicating thus their collective behaviour. Especially the interaction between the α_i and β_i bending motions appears to be of crucial importance as its respecting shifts the only "really improperly" behaving α_i and β_i energies in the proper direction. In any case, the calculated energies are in a much closer agreement with experimental values than those which are available from the previous *ab initio* studies (compare Tables III and V). A similar conclusions can also be derived from inspection of the Table IV comprising the effective electric dipole moments. The failure of the

Table IV
The effective electric dipole moments of the H_2O . HF complex (in Debye) obtained with two-dimensional models

State[a] $|1,3,5,6,8,9\rangle$	$\langle \boldsymbol{m}(\nu_1, \nu_3, \nu_5, \nu_6, \nu_8, \nu_9)\rangle$	Experiment[b]
0 0 0 0 0 0	4.082($R\alpha_0$), 4.352($R\alpha_i$), 4.297($R\beta_0$), 4.073 ±	
0.007		
	4.293($R\beta_i$), 4.526(Rr), 4.019($\alpha_0\beta_0$),	
	4.293($\alpha_i\beta_i$), 4.079($\alpha_0\alpha_i$)	
1 0 0 0 0 0	4.056($R\alpha_0$), 4.320($R\alpha_i$), 4.262($R\beta_0$), 3.91 ± 0.04	
	4.258($R\beta_0$), 4.488(Rr)	
0 1 0 0 0 0	4.780(Rr)	
0 0 1 0 0 0	4.238($R\alpha_i$), 4.189($\alpha_i\beta_i$), 4.044($\alpha_0\alpha_i$)	4.074 ± 0.016
0 0 0 1 0 0	4.059($R\beta_i$), 4.146($\alpha_i\beta_i$)	
0 0 0 0 1 0	3.815($R\alpha_0$), 3.756($\alpha_0\beta_0$), 3.817($\alpha_0\alpha_i$)	3.802 ± 0.007
0 0 0 0 0 1	4.068($R\beta_0$), 3.944($\alpha_0\beta_0$)	
0 0 0 0 2 0	3.764($R\alpha_0$), 3.693($\alpha_0\beta_0$), 3.754($\alpha_0\alpha_i$)	
0 0 1 0 1 0	3.798($\alpha_0\alpha_i$)	3.76 ± 0.04

theory in describing the variation of the dipole moment with the H_2O vs HF stretching excitation may be attributed to the rotational-vibrational interactions which are completely neglected in this study.

CONCLUSIONS

Molecular potential energy and electric dipole moment surfaces of the H_2O . HF complex have been probed by performing highly accurate *ab initio* calculations for all the two-dimensional cross-sections of these surfaces which are important for description of the complexation dynamics. From these data, approximate vibrational energies and effective electric dipole moments have been evaluated using approximate two-dimensional HBJ vibrational Hamiltonians. A comparison of these quantities with available experimental data has revealed that the present theory closely describes both the highest-frequency motion of the HF fragment and the lowest-frequency H_2O vs HF stretching and H_2O out-of-plane bending motions. The characteristics corresponding to the medium-frequency bending motions, however, exhibit strong model dependences indicating thus unusually strong inter-mode kinematic interactions. Nevertheless, the quantities vary within the intervals which are in accord with the present assignment of the experimental data. Moreover, the evaluated static characteristics (equilibrium geometry, equilibrium dipole moment, dissociation energy) seem to be in a close harmony with their experimental counterparts. Hence, we believe that the present property surfaces are very reliable approximations to the genuine ones and that might be useful for unambiguous experimental identifications of the so far unassigned transitions and for rationalization of yet unprobed properties of the H_2O . HF complex.

TABLE V
Literature data on the calculated vibrational frequencies of the H_2O . HF complex (in cm^{-1})

Mode	Ref.[13]	Ref.[16]	Ref.[19]	Ref.[17]	Ref.[20]	Experiment
ν_1	254	247	270	236	223	176[a], 180[a]
ν_3	3 599	3 858	3 791	3 764	4 250	3 608[b]
ν_5	250		252		223	157[a], 170[b]
ν_6	913		862		793	696[b]
ν_8	265		232	96	168	70[c], 64[a]
2 ν_8				255		267[a]
ν_9	740		742		656	666[b]

[a] Ref.[6]; [b] ref.[3]; [c] ref.[9].

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