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A theoretical study of the structure, bonding, and vibrational frequency shifts of the H_2–HF complex

David E. Bernholdt, Shi-yi Liu, and Clifford E. Dykstra
Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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The complex formed from hydrogen fluoride and the hydrogen molecule has been investigated theoretically in two ways. Large basis, well-correlated *ab initio* electronic structure calculations have been used to map out regions of the potential energy surface and an electrical interaction model has been used to find the classical intermolecular interaction effects. From the *ab initio* potential surface, the fundamental vibrational transition frequencies of hydrogen and hydrogen fluoride are predicted to be red shifted by 20 and 15 cm^{-1}, respectively. The Liu and Dykstra theory of vibrational frequency shifts that uses the intermolecular electrical interaction yields shifts of 31 and 19 cm^{-1}, respectively. The equilibrium structure of the molecule is *T* shaped, a feature that is determined by electrical interaction, and the well depth is around 300 cm^{-1}. A significant fraction of the well-depth results from electron correlation effects.

INTRODUCTION

Experimental and theoretical investigation of hydrogen bonding and weak intermolecular interaction in simple complexes is currently providing a wealth of new understanding that is spawning new efforts to connect isolated molecule and condensed phase chemistry. From detailed studies of dimer (two molecule) complexes, the working knowledge is becoming available to design experiments and to formulate calculational strategies for investigating trimers, tetramers, and so on in just as detailed a way as for dimers. The microscopic connection between isolated molecule interaction and the dynamics of large clusters and extended molecular systems is thereby emerging in ever clearer form.

Ab initio electronic structure calculations, when carried to sufficiently high level, have proven their predictive power for hydrogen bonded complexes. The hydrogen fluoride vibrational frequency shifts obtained from calculation[1] are only several cm^{-1} different from observed values[2,3] in the HF dimer. The calculated dissociation energy and dissociation pathways of the HF trimer[4] correspond nicely to vibrational predissociation data.[5] The calculated well depths[6–9] for a number of systems appear to be in satisfactory agreement with available experimental data. What this means is that electronic structure technology is capably of making meaningful determinations of those features of a hydrogen-bonded complex that are measured through experiment. These include structural parameters, vibrational frequencies, and bond strengths.

While it is satisfying to a computational chemist that electronic structure calculations of suitably high level can be correct in specific hydrogen bonded complexes, it is even more satisfying when the system-specific information from such calculations can be unified. The question to be asked is if there are common transferable elements of hydrogen bonding that can be extracted from the detailed quantum mechanical picture. If so, or even if nearly so, then such elements should provide what is needed to know more than the near-equilibrium properties of hydrogen bonded systems and to investigate large aggregations of molecules by calculational means. The practical application here is meeting the need for accurate interaction potentials in molecular dynamics simulations.

In our recent studies of hydrogen bonding and weak intermolecular interactions,[4,10–13] we have focused attention on the intermolecular electrical interaction as a key element, one long recognized as important in hydrogen bonding.[14] While there are other elements, the electrical forces are distinguished as the ones that persist to longest range. In that sense, there is at least some limiting region where electrical interaction comprises the whole picture. Our concern is seeing if other elements are overwhelming the electrical influences in the vicinity of a hydrogen-bonded complex's equilibrium structure. In thinking about this, it should be remembered that in many hydrogen halide complexes the typical equilibrium separation between nearest nonhydrogen centers is generally about three times the length of a carbon–hydrogen, nitrogen–hydrogen, or oxygen–hydrogen chemical bond.

The complete electrical interaction between two species consists of the interaction of the molecular electrical fields arising from all the permanent and (infinite-order) induced electrical multipoles. This interaction depends on the isolated molecular charge distributions and on the multipole polarizabilities, hyperpolarizabilities, and so on of those charge distributions. This electrical interaction may be regarded as entirely classical. Truncated to some finite order of multipoles and polarizabilities, it can be evaluated very simply from the moments and polarizabilities of charge distributions of any sort. It does not include intermolecular quantum effects, especially those developing as charge clouds overlap. However, the interaction is perhaps better thought of as semiclassical since the moments and polarizabilities of the monomer constituents of a complex have to be quantum mechanical properties. Using powerful *ab initio* techniques, it is possible to obtain monomer electrical properties about as far as desired. This facilitates virtually exhaustive evaluation of the electrical interaction, something we have done for a number of systems.[4,10–13]

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In principle, an *ab initio* calculation of a hydrogen-bonded complex's potential energy surface can incorporate all hydrogen bonding elements. (Not every *ab initio* calculation will, though, since some elements require correlation effects or certain basis set augmentations.) There have been ideas for partitioning Hamiltonians and for enforcing such partitioning in the course of a calculation[15–20] so as to extract the contributing elements. There is, however, a degree of arbitrariness in such partitioning, and this is affirmed by the fact of existence of *different* partioning schemes. On the other hand, the ability to exhaustively calculate electrical interactions separately from *ab initio* treatment of a complex suggests an unambiguous partitioning into electrical and nonelectrical factors. The latter is merely the difference between a proper *ab initio* result and the electrical result. The long range persistence of the electrical interaction means that typically the nonelectrical part will vanish first with increasing intermolecular separation, but exceptions will be those complexes that simply have little or no classical electrical interaction, e.g., two rare gas atoms.

An important nonelectrical element is exchange repulsion. It gives rise to the repulsive walls between molecules that prevent their total coalescence, something that would result with just classical electrical interaction. Other elements that my be nonelectrical are dispersion and charge transfer, both of which are usually regarded to be attractive. However, charge transfer cannot always be entirely distinct from an electrical interaction, if that electrical interaction provides for the *shifting* of charge density via multipole polarization of charge density. Electron correlation includes dispersion and more, and the evaluation of dispersion alone is somewhat subject to definition. While these are important subtleties, our focus on electrical factors draws us back to the separation into electrical and nonelectrical parts only, and partial justification for paying attention to that separation is how well the electrical part can account for certain features of a complex.

Specific studies of hydrogen-bonded complexes are the testing ground for the ideas mentioned, and the complex of hydrogen and hydrogen fluoride is an especially good choice. It has not yet been the subject of experimental investigation, and so it is first an unbiased test of the predictive power of *ab initio* technology. It is a relatively simple system from a computational standpoint, and so sufficient *ab initio* calculations can be carried out to make all the necessary comparisons with the computationally trivial electrical model. Also, preliminary results indicated a relatively sizable correlation contribution to the complex's stability, and for reasons discussed later, that could make it a case to challenge the electrical picture.

The *ab initio* calculations that were carried out for the HF–H_2 complex were used for the determination of the equilbrium structure, the vibrational frequencies, transition moments, deuterium quadrupole coupling, bond strength, and rotational constants. The electrical model was used to obtain the orientational parameters of the complex at equilbrium, the intramolecular vibrational frequency shifts, and transition moments. The results support our optimism of earlier studies about the usefulness of electrical interactions for understanding hydrogen bonding and for developing accurate, transferable potentials.

AB INITIO CALCULATIONS

The *ab initio* potential energy surface was searched and mapped out in certain regions through calculations at specific points on the surface. The wave functions at those points were calculated at the self-consistent field (SCF) level and at the ACCD level,[21–23] which is a double substitution coupled cluster approach[24–28] that neglects certain small Hamiltonian matrix elements that tend to partly cancel. This is well suited for hydrogen bonding studies because it accounts for pair correlation and high order correlation effects alike, in a size-extensive manner.[26,29] This is important in describing the dissociation energy of the complex and is also important in the anharmonicities of stretching potentials.[30] A direct, matrix-formulated procedure,[27] following the method of self-consistent electron pairs (SCEP),[31–34] was used to calculate the ACCD wave functions. Single substitutions were incorporated linearly and the florine 1*s* orbital was frozen to substitution.

A relatively large basis set, flexible in the valence region and suitable for electrical properties and interactions, was used in the *ab initio* calculations. The fluorine core/valence basis was the triple-zeta, Dunning-contracted[35] Huzinaga (10*s*5*p*/6*s*3*p*) set.[36] The hydrogen basis started with the (6*s*/3*s*) triple-zeta Huzinaga set.[36] Diffuse *s* and *p* functions were added to the fluorine set, and a diffuse *s* function was added to the hydrogen basis. Finally, two sets of polarization functions were used for each center. The augmented functions, beyond TZ, are listed in Table I.

Potential energy curves were generated for isolated H_2 and isolated HF and vibrational analysis was carried out by exact, Numerov–Cooley[37,38] numerical solution of the vibrational Schrödinger equation. From these wave functions vibrational averaging was performed by numerical integration. The monomer properties obtained are in Table II. The agreement in vibrational frequencies is extremely good, the error being at most a few cm^{-1} for the fundamental transitions. The transition frequency for HF is better than previously obtained at the ACCD level, even with certain larger basis sets. As will be reported elsewhere, these other basis sets suffered from a slight imbalance or an inappropriate augmentation which has been corrected here.

The permanent multipole moments of HF and H_2 were calculated from the ACCD wave functions by expectation

TABLE I. Basis set augmentation.

Atomic center	Exponents of supplemental uncontracted functions		
	s	*p*	*d*
H	0.06	1.9	
		0.12	
F	0.10	0.05	0.9
			0.15

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TABLE II. *Ab initio* monomer properties.

	H_2		HF	
	ACCD calc.	Comparison value	ACCD calc.	Comparison value
R_e (Å)	0.7432	0.7414[a]	0.9256	0.91680[b]
μ_e (D)	0.0	0.0	1.807	1.803[c]
$\langle R \rangle_{00}$ (Å)[d]	0.7526	0.7511[a]	0.9339	0.92559[e]
$\langle R \rangle_{11}$ (Å)[d]	0.7719	0.7705[a]	0.9512	0.94348[e]
$\langle \mu \rangle_{00}$ (D)	0.0	0.0	1.844	1.826[c]
$\langle \mu \rangle_{11}$ (D)	0.0	0.0	1.891	1.872[c]
$\langle \mu \rangle_{01}$ (D)	0.0	0.0	0.09915	0.0985[f]
$\langle \mu \rangle_{02}$ (D)	0.0	0.0	−0.01131	−0.0127[f]
ω_e (cm^{-1})	4376.3[g]	4402.2[a,g]	4136.0[g]	4138.32[h]
$\omega_e\chi_e$ (cm^{-1})	103.0[g]	121.4[a,g]	89.93[g]	89.88[h]
$\omega_e y_e$ (cm^{-1})	−1.85[g]	0.82[a,g]	1.58[g]	0.90[h]
ω_{01} (cm^{-1})	4164.2	4162.1[a]	3961.4	3961.4[e]
ω_{12} (cm^{-1})	3941.5	3926.7[a]	3794.9	3789.4[e]
D_2 and Df				
ω_{01} (cm^{-1})	2993.3	2994.0[a]	2905.3	2906.8[h]
ω_{12} (cm^{-1})	2881.9	2874.8[a]	2817.4	2815.5[h]

[a] Calculated values of Kolos and Wolniewicz (Ref. 47), which are virtually exact results. Agreement with experimental values for vibrational frequencies is to tenths of wavenumbers.
[b] Experimental value from Ref. 48.
[c] Experimental values from Ref. 49.
[d] Calculated values obtained as $\langle R^{-2} \rangle^{-1/2}$, as in the averaging of a moment of inertia.
[e] Experimental values from Ref. 50.
[f] Experimental values from Ref. 51.
[g] Values were obtained from a fit of ω_{01}, ω_{12}, and ω_{23} to the functions $(v + 1/2)$, $(v + 1/2)^2$, and $(v + 1/2)^3$.
[h] Based on experimental $G(v)$ fit in Ref. 48.

with the expansion truncated at double substitutions.[39] The multipole polarizabilities and hyperpolarizabilities were obtained with the derivative Hartree–Fock (DHF) approach.[40,41] DHF is a completely open-ended procedure for the analytical evaluation of SCF energy derivatives to all orders. An even larger, triply polarized basis set was used for the DHF calculations of monomer properties. It has been specified elsewhere,[11] and was developed from basis set tests on several species.[10,41,42]

ELECTRICAL INTERACTION

The details of our calculation of electrical interaction energies have been given elsewhere.[11] To summarize the procedure, fields arising from the multipole moments of the monomers (truncated at the octupole) are allowed to interact and to induce moments in the other monomers via the polarizabilities we find to be most important. These are the dipole, quadrupole, and dipole–quadrupole polarizabilities and the dipole hyperpolarizability and the dipole–dipole–quadrupole hyperpolarizability. The fields of induced moments are taken to induce moments in each bonding partner and this is continued to convergence (infinite order induction). The energy, which can be computed many ways, is obtained in our calculation from the total moments of the monomers and the fields they give rise to. This represents a very complete accounting of the electrical interaction. Again, the energy is a classical interaction energy, though one involving polarizable, *quantum mechanical* charge distributions.

Incompleteness in the electrical interaction comes from truncation in the order of multipoles and in the set of polarizabilities. In a few representative HF complexes, we have tested the effects of hexadecapole moment and dipole–quadrupole–quadrupole hyperpolarizabilities. Their contribution to the interaction energy was not large, and their relative effect is local regions of the surface is ignorable.[11] At closer range, this may not be true. Also, larger molecules, such as diacetylene, would naturally require higher moments. The distributed multipole analysis used by Buckingham and Fowler[43] and by Stone and Alderton[44] offers an attractive concept for general problems. Moments are associated with atomic or bond centers in this analysis, and so implicitly the expansion includes more than a single-center expansion would with the same multipoles. Stone has also developed a distributed polarizability analysis[45] which should be quite useful. We have found a two-center expansion of a different sort useful in more completely treating the vibrational effect of hydrogen bonding.[11] The two centers are the positive and negative charge centers of a monomer. However, in H_2–HF, this two-center analysis gives results essentially the same as the analysis using a single center, the center of mass. The *ab initio* electrical properties of the monomers have been reported in full elsewhere[10,11,41] and have been recently compared with electrical properties of other small molecules.[46]

RESULTS AND DISCUSSION

Equilibrium structure and spectroscopic parameters

The ACCD-determined equilibrium is a *T*-shaped structure. Using the parameters defined in Fig. 1, the struc-

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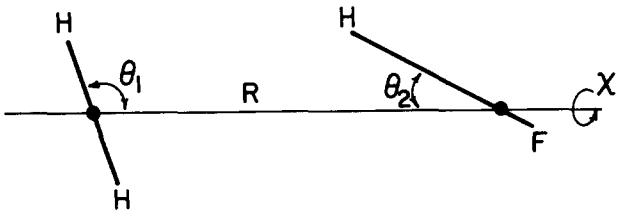

FIG. 1. Definition of the structural parameters of the H_2–HF complex. θ_1 and θ_2 are angles measured respective to the line connecting the centers of mass. χ is the out-of-plane twist of one monomer relative to the other.

ture is found to be $\theta_1 = 90°$, $\theta_2 = 0°$, and $R = 2.794$ Å. A potential curve was calculated for the pseudo-diatomic intermonomer vibrational motion along R at $\theta_1 = 90°$ and $\theta_2 = 0°$. Numerov–Cooley analysis[37,38] was used to compute the intermolecular vibrational frequencies and to vibrationally average the intermolecular separation distance. Vibrational wave functions were also calculated for the monomer stretches from ACCD potential surface slices where all parameters except one or the other monomer bond length were held fixed at their equilibrium values. These same types of potential curves were used successfully in studying the vibrational motion of the HF dimer.[1] In that study, relaxing the other structural parameters to account for the coupling of motions through the potential affected transition frequencies by less than 3 cm^{-1}. That coupling should be even smaller in the weaker H_2–HF complex. Table III shows how vibrational averaging affects the bond lengths. For the weak intermolecular bond, averaging effects are around 0.1 Å, depending on the isotopic substitution, while for the monomer bonds, averaging effects are around 0.01 Å. The equilibrium bond length of HF is increased slightly upon complex formation, but the H_2 bond length is unchanged to an accuracy of 0.0001 Å.

At the calculated equilibrium structure, the rotational constants given in Table IV were obtained. Partly vibrationally averaged rotational constants were also obtained and are listed in Table IV as well. These were found using the ACCD, averaged intermolecular center of mass separations, where the averaging was over R^{-2}. Averaging over bending and torsional motions was neglected. The monomer bonds were set to their averaged values, but corrected slightly according to the differences between calculated and known equilibrium values for the isolated monomers (see Table II).

TABLE III. Bond length changes[a] due to complex formation and vibrational averaging.

	Relative to isolated monomer	Relative to complex equilibrium
$\Delta r_e(H_2)$	0.0	...
Δr_e(HF)	0.0007	...
$\Delta r_0(H_2)$	0.0018	0.0108
Δr_0(HF)	0.0008	0.0084
ΔR_0 (H_2–HF)[b]	...	0.106
ΔR_0 (H_2–DF)[b]	...	0.106
ΔR_0 (D_2–HF)[b]	...	0.072
ΔR_0 (D_2–DF)[b]	...	0.072

[a] All values are in Å.
[b] Equilibrium center of mass separation is 2.974 Å.

TABLE IV. Rotational constants of isotopic forms of H_2–HF.

	$\overline{B}$(GHz)[a]	A(GHz)	B(GHz)	C(GHz)
Equilibrium				
H_2–HF	29.50	1825	29.74	29.26
HD–HF	20.85	1366	21.01	20.69
H_2–DF	28.92	1825	29.14	28.69
HD–DF	20.66	1362	20.82	20.50
D_2–HF	16.45	913.0	16.60	16.30
D_2–DF	16.38	913.0	16.52	16.23
Vibrationally averaged[b]				
H_2–HF	27.43	1773	27.64	27.22
HD–HF	19.64	1331	19.79	19.50
H_2–DF	26.98	1773	27.19	26.78
HD–DF	19.51	1327	19.65	19.37
D_2–HF	15.61	892.9	15.75	15.48
D_2–DF	15.58	892.9	15.71	15.44

[a] $\overline{B} = (B + C)/2$.
[b] Averaged over stretching vibrations in the ground state.

By comparison with the calculations on the HF dimer, we expect the $\overline{B}_0$ values to be accurate to at least 4%. The main source of error is the neglect of averaging over torsional motions. While this averaging may be noticeable in terms of the structural parameters that might be inferred from rotational spectral data, one can easily demonstrate that the rotational constant $\overline{B}_0$ is much more sensitive to averaging in R than in θ_1 and θ_2.

The calculated intermolecular stretching frequencies are listed in Table V. The $v = 0 \rightarrow 1$ transition frequency is roughly one-third of the well depth D_e. Anharmonicity is very significant as shown by the $v = 0 \rightarrow 1$ spacing being ~ 120 cm^{-1} while the $v = 1 \rightarrow 2$ spacing is ~ 70 cm^{-1}. The next level, $v = 3$, cannot be as well determined because it is so near the top of the well and very sensitive to the potential curve over a long distance. It does appear, though, that $v = 0$ and $v = 1$ are bound in all isotopic forms and $v = 2$ is a bound state for the D_2–HF and D_2–DF complexes, at least.

The electrical model potential energy surface gives a global minimum at the T-shaped orientation of the monomers in complete agreement with the fully quantum mechanical results. A further test of its ability to account for orientational features of the intermolecular interaction is its prediction that the linear forms are saddle points and that the lowest of these is HH--FH. This was confirmed by ACCD calculations which place the linear form 130 cm^{-1}

TABLE V. Intermolecular stretching frequencies of H_2–HF.

	Vibrational state energies (cm^{-1})			$v = 0 \rightarrow 1$ transition frequency (cm^{-1})
	$v = 0$	$v = 1$	$v = 2$	
H_2–HF	82.3	201.2	270.4	119
HD–HF	70.0	177.0	248.0	107
H_2–DF	82.1	200.9	270.2	119
HD–DF	69.9	176.8	247.8	107
D_2–HF	62.7	161.5	231.0	99
D_2–DF	62.5	161.0	230.5	99

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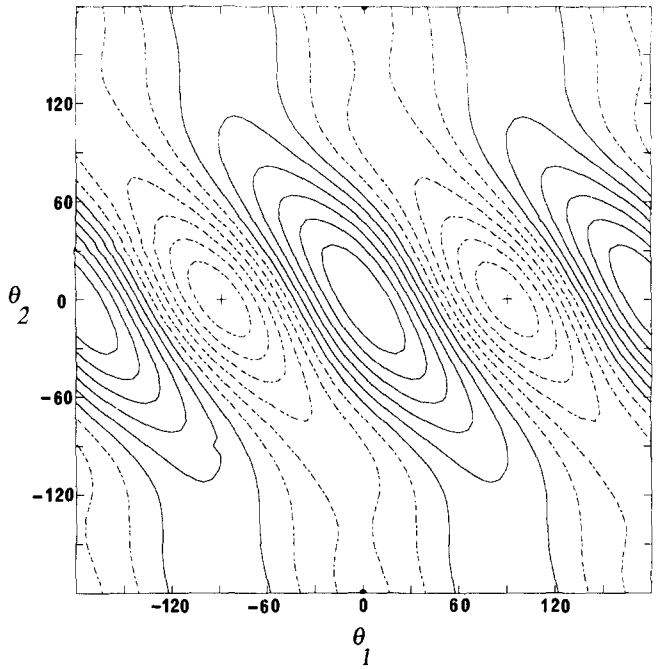

FIG. 2. The electrical model potential energy surface of H_2–HF for the coordinates θ_1 and θ_2. R was held at 3.0 Å and χ at 0° (planar). Contours are at 50 cm^{-1} steps. The minimum is at "+."

above the equilibrium, which is nicely in line with the electrical model's value of 113 cm^{-1}. A slice through the electrical model's potential energy surface is shown in Fig. 2.

The stability of the H_2–HF complex is analyzed in Table VI. From the *ab initio* calculations, over one-third of the well depth is found to arise from correlation effects. Dispersion, which involves intermolecular electron correlation, is probably of relative importance in the 300 cm^{-1} bond strength especially because of the shallowness of this potential well in comparison to complexes such as N_2–HF[6] or $(HF)_2$.[1] The electrical model results in Table VI are broken down to show the electrical contributions to the well depth. Charge polarization effects (i.e., the induced moments) are about one-third as sizable as the permanent moment interaction effects. Correlation effects, through their changes in the permanent moments, are small in the electrical model. The total electrical model's interaction energy happens to be simlar to the total *ab initio* value; it is about 10% greater. Were the values the same, it could be argued that dispersion and exchange repulsion were roughly in-check. The 10% difference suggests exchange repulsion is probably larger at the minimum energy separation. All effects weigh against each other, and it is fair to say that dispersion and exchange repulsion are not entirely negligible in the bonding region. That makes this complex a good testing ground for seeing the limitations of the electrical model in describing potential surface features. At this point in the discussion the electrical model has given a good accounting of the equilibrium orientation and the transition state orientation.

Vibrational red shifts

The potential curves generated about the ACCD equilibrium and the subsequent vibrational analyses indicate that for both H_2 and HF the fundamental transitions are shifted lower in energy. These types of curves were found to be very close to those obtained with all parameters relaxed (i.e., minimum energy paths for stretching) in the *ab initio* study of the HF dimer.[1] H_2–HF is a much weaker complex than the HF dimer and there should be even less difference between the pure stretch curves and minimum energy path curves. What is accomplished from analyzing vibrations this

TABLE VI. Stability contributions for the H_2–HF complex.

	Contribution (cm^{-1})	Total (cm^{-1})
Ab initio		
SCF level	186[a]	186
Correlation (ACCD) effect	120	306
Electrical[b]		
SCF permanent moments		
dipole–dipole	0	0
dipole–quadrupole	120	120
quadrupole–quadrupole	97	217
others	42	259
ACCD permanent moments		
difference (dipole–dipole, dipole–quadrupole, etc.)	−32	227
Induced moments		
contribution (with SCF permanent moments)[c]	126	353
Induced moments		
difference from using ACCD permanent moments	−11	342

[a] At the SCF equilibrium $R = 2.281$ Å. At the ACCD equilibrium, this is 165 cm^{-1}.
[b] At $R = 3.0$ Å.
[c] Only about 40% of this contribution arises via the dipole polarizabilities.

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way is an accurate incorporation of the anharmonicity effects on frequencies. However, as discussed in previous studies,[1,11] kinetic coupling of the intramolecular stretches with other modes is neglected in this pseudo-diatomic treatment, since that seems to have a small effect. The calculated red shifts in transition frequencies are given in Table VII. The estimated reliability of these shifts is $\pm 5\ \mathrm{cm}^{-1}$.

The theory of Liu and Dykstra[11] directly relates the transition frequency shifts in hydrogen bonded complexes to the intrinsic anharmonicities of the monomer stretching potentials and to the monomer electrical properties. Thus, frequency shifts can be estimated directly from monomer properties, without calculations on the whole complex. In this theory, the electrical model is used to compute the slope of the "interaction potential," which is the modification of the intramolecular stretching potential that occurs upon complex formation. From that slope and information related to the intrinsic anharmonicity of each unperturbed potential, first order perturbation theory yields the corrections in the vibrational state energies and thereby the shifts in transition frequencies. Results of applying this simple theory show satisfactory agreement with the *ab initio* values (Table VII). That this theory should work for the variety of systems that it has been applied to[11] is a strong indication that electrical interaction is a most important factor in how the potentials are modified in a complex.

Ab initio values were obtained for the dipole moment of the complex at most of the potential energy surfaces points. Using the numerical intramolecular and intermolecular stretching vibrational wave functions, the dipole moment surface was integrated to give the transition moments shown in Table VIII. For HF there is the characteristic enhancement of the fundamental transition moment, while the overtone is slightly enhanced. This can be related to the dipole induced in HF by H_2, since that increases the slope $d\mu/dr$ of the total dipole moment function in HF. The electrical model was used to compute the change in the HF dipole moment function due to polarization of charge by H_2. With this function, the transition moments were computed, and as shown in Table VIII, they agree well with the entirely *ab initio* results, though undervaluing the hydrogen-bonding effect slightly. The extent of the agreement is important because it says that something as characteristic as the enhancement of a fundamental transition intensity can be largely explained by simple, intermolecular electrical interaction.

TABLE VII. Comparison of *ab initio* and electrical model predictions of intramolecular vibration red shifts upon formation of H_2–HF.

Constituent monomer stretch	$v=0\rightarrow1$ vibrational transition frequency shifts (cm^{-1})	
	ab initio (ACCD)	Electrical
H_2	20	31
D_2	15	22
HF	15	19
DF	11	14

TABLE VIII. Transition moments for the H_2–HF complex (in D).

	$\langle\mu\rangle_{01}$	$\langle\mu\rangle_{02}$
HF monomer	0.099 15	−0.011 31
HF (*ab initio*) complex	0.123 87	−0.012 82
HF (electrical model) complex	0.119 25	−0.012 14
H_2–HF stretch (*ab initio*)	0.047 89	0.022 34

Quadrupole coupling constants

Structural information from rotational spectra is sometimes based on nuclear quadrupole splittings.[52] The nuclear quadrupole coupling constants lead to values for on-average orientational parameters, and this has been employed for species such as NN–HF[53] and the ammonia dimer.[54] The nuclear quadrupole coupling constant for a monomer is related to the nuclear quadrupole moment eQ and the field gradient at the nucleus q:

$$\chi = -eQq. \tag{1}$$

The field gradient may change due to complex formation, and often this is done simply as[55]

$$\chi^c = \chi + \Delta\chi, \tag{2a}$$

$$q^c = q + \Delta q, \tag{2b}$$

where χ^c is the coupling constant in the complex, and q^c is the field gradient in the complex both at equilibrium. The relationship between χ^c and the vibrationally averaged value χ_0^c is obtained by taking[55,56] the vibrational averaging over one angular direction γ to be an average of $(3\cos^2\gamma - 1)/2$. This assumes that χ^c is independent of γ, which will be true at least if $\Delta\chi$ is quite small. The resulting expression

$$\chi^c = \chi_0^c\langle 3\cos^2\gamma - 1\rangle/2 \tag{3}$$

serves to give a value of $\cos^2\gamma$, and thus γ, when χ_0^c is measured and χ^c is known. χ^c is not usually known, and so the approximation $\chi^c \approx \chi$ is used. From Eq. (3), an opertional expression for an averaged angle based upon measured values of the quadrupole coupling constants in the complex and the monomer is obtained.

$$\gamma_{\mathrm{ave}} \approx \cos^{-1}[(2\chi/\chi_0^c + 1)/3]^{1/2}. \tag{4}$$

TABLE IX. Electric field gradient changes in H_2–HF.

Orientational angle θ_2 (see Fig. 1)	Angle with respect to a axis, γ	Field gradient q in a.u. at H center of HF	$\Delta q = q_{\mathrm{monomer}} - q$ in a.u.
0 (eq.)	0.0	0.611 08	0.006 31
5	5.235	0.611 24	0.006 15
10	10.465	0.611 70	0.005 69
30	31.201	0.614 84	0.002 55
50	51.412	0.616 92	0.000 47
70	70.950	0.617 52	−0.000 13
90	90.0	0.617 66	−0.000 27
120	118.738	0.617 75	−0.000 36
160	159.120	0.617 67	−0.000 28
180	180.0	0.617 63	−0.000 24
Monomer		0.617 39	

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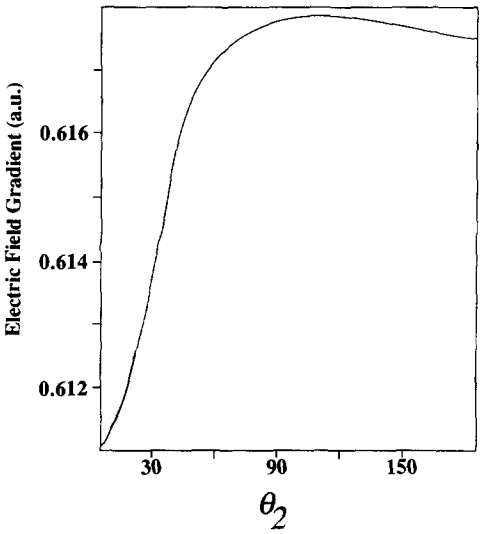

FIG. 3. The electric field gradient at the deuterium center in H_2–DF as a function of θ_2, the orientation angle for DF.

One of the assumptions in this expression can be tested for the H_2–HF complex.

Using the ACCD wave functions for the complex, the electric field gradient was evaluated at the HF's proton center. This gradient would manifest itself in quadrupolar coupling upon deuteration, e.g., H_2–DF. The HF was rotated about its center of mass with the H_2 molecule held fixed at the equilibrium structural parameters of the complex. This maps out the angular dependence of χ^c. Table IX lists the field gradients obtained, which are simply proportional to the quadrupole coupling constants. The values are plotted in Fig. 3. At the equilibrium, q^c or χ^c is about 1% smaller than q or χ, the coupling constant in isolated DF. Interestingly, $\Delta\chi$ [Eq. (2)] is strongly dependent on the angle θ_2.

Since $\Delta\chi$ (or Δq) is changing sharply around the equilibrium, vibrational averging could have a sizable effect. Thus, any usual spectroscopic value of $\Delta\chi$ should be designated $\Delta\chi_0$ since it would be a vibrationally averaged value that is likely to be much different from the change in the coupling constant at equilibrium. Should this be a common feature for other complexes, and there is every reason to believe it is within our picture of hydrogen bonding, then conclusions drawn from rotational spectra about how the field gradient changes, and then how the monomer electronic structure changes upon complex formation, are quantitatively wrong. Perhaps they may not even be qualitatively meaningful.

The often used assumption that $\Delta\chi$, at any angle, is small relative to χ is valid for H_2–HF where $\Delta\chi$ is $\sim 1\%$ of χ at the most. For more strongly bound complexes, such as HCN–DF, $\Delta\chi$ has been found to be $\sim 8\%$ of χ.[57] We can test the effect of assuming that $\Delta\chi = 0$ on γ_{ave} in Eq. (4) by recomputing γ_{ave} after $\chi^c \approx \chi$ is altered by a few percent. This is a sensitivity test for how meaningful experimentally inferred angles are under the assumption that $\Delta\chi = 0$. Making the substitution, $\chi^c = \chi + \Delta\chi$ in Eq. (4) and differentiating with respect to $\Delta\chi$ shows that the greatest sensitivity will occur when $\gamma_{ave} \sim 0°$.[58] Then, changing χ^c by 1% is found to change γ_{ave} from 0° to 4.7°; changing it by 5% changes γ_{ave} to 10.5°. That means that a value of γ_{ave} inferred with the assumption that $\Delta\chi = 0$ can be off by several degrees for typical hydrogen-bonded complexes.

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