Asymmetry in angular rigidity of hydrogen-bonded complexes

Zhenhong Yu and William Klemperer*

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138

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The asymmetry in angular rigidity of the proton donor and proton acceptor of hydrogen-bonded hydrogen fluoride binary complexes is investigated. The intermolecular bending frequency of HF, as the proton donor, is linearly proportional to the square root of the dissociation energy, whereas that of the proton acceptor is always much lower. The asymmetry, measured by the ratio of bending elastic constants of HF to that of the proton acceptor, is generally >2 , and varies pronouncedly with the acceptors reaching values >20 . Molecules with nitrogen as the bridged acceptor atom show an angular rigidity nearly one order of magnitude greater than the group with oxygen as the proton acceptor.

hydrogen bonding | hydrogen fluoride | intermolecular interactions

The noncovalent interaction between individual molecules or molecular units is a determining factor for molecular organization and polymeric shape. A rich diversity of such interactions exists. Often, the dominant intermolecular interaction is the hydrogen bond. Among the reasons for this structural importance is the rigidity that it confers upon the system. It has been known for half a century that hydrogen bonding is highly directional. The hydrogen bond consists of two units: proton donor and proton acceptor. Thus, the rigidity in the system may be analyzed as angular rigidity of the proton donor, angular rigidity of the proton acceptor, and radial rigidity of the binding pair. Traditionally, the strength of the hydrogen bond has been correlated with the readily measured red shift of the proton donor stretching frequency (1, 2). Photofragment translational spectroscopy by Miller and coworkers (3) has provided precise values for the hydrogen bond strength. Occasionally radial rigidity is used as an indicator of hydrogen bond strength, but the angular rigidities have rarely been discussed, mainly because of the lack of systematic experimental and theoretical investigations and the complexity of hydrogen bonded systems. Recently, the Saykally group (4) discovered that the lifetime of the hydrogen bond for water trimer decreases by three orders of magnitude with single excitation of an out-of-plane librational vibration, showing the significance of angular motions. Luzar and Chandler (5), using molecular dynamic simulation, found that the librational motions play a more significant role than does translation in breaking the hydrogen bond in liquid water.

Correlation Between Proton Donor Bending Frequency and Hydrogen Bond Strength

Although water hydrogen bonding is the most studied, hydrogen fluoride is probably the simplest molecule readily forming hydrogen bonds. The intermolecular bending frequencies of both the proton donor and proton acceptor of a number of HF complexes are available from high-resolution laser spectroscopy of molecular beams or infrared absorption spectroscopy of matrix-isolated complexes. The spectral measurements at the vibrational excited states are frequently obtained as combination bands.

The intermolecular bending frequencies (ν_D) of HF, as proton donor, range from 271 cm^{-1} for $\text{N}_2\text{-HF}$ to 694 cm^{-1} for $\text{H}_2\text{O-HF}$, as listed in Table 1 (6–24). For the strong hydrogen-bonded HF clusters, this vibration contributes the most to the zero-point

Table 1. Intermolecular bending frequencies ν_D and ν_A (in cm^{-1}) of proton donors and acceptors, dissociation energies D_0 (in cm^{-1}) of some hydrogen-bonded HF complexes, and their corresponding asymmetric parameter α of angular rigidity

Proton acceptor	ν_{HF}^*	D_0	ν_A	ν_D	α
N_2	0	398 (6)	59.2 (7)	271 (8)	2.0
	3	550 (7)	68.5 (7)	328.6 (7)	2.5
CO	0	732 (9)	75 (10)	348 (11)	2.0
	3	1,210 (12)		538.2 (12)	
HCN	0	1,970 (13)	73.6 (14)	550 (14)	4.0
CH_3CN	0	2,182 (15)	45 (16)	620 (15)	2.8
HCCCN	0	1,705 (15)	30 (17)	555 (15)	2.5
CO_2	0	672 (18)	9.1 (19)	313 (11)	22
	3	870 (20)	24.8 (20)	362.5 (20)	4.5
HF	0	1,060 (21)	161 (22)	400 (22)	6.2
H_2O	0	2,867 (23)	157 (24)	694 (11)	26

The numbers in the parentheses are the references for the experimental results.

*The vibrational state of HF as proton donor.

energy of the complex. From experimental data, we observe that there exists a nearly linear correlation between ν_D and $D_0^{1/2}$, as shown in Fig. 1, where D_0 is the dissociation energy of the cluster. We find that a useful one-dimensional potential for this bending vibration is

$$V(\theta_D) = A(e^n - e^{n\cos\theta_D}).$$

This provides essentially the linear correlation, because the leading term of a power series expansion is $An\theta_D^2/2$. It has been noted (12) that the vibrational red shift of the hydrogen fluoride combined with the value of D_0 provides the dissociation energy for the vibrationally excited state, ν_{HF} . The increase in ν_D with HF valence excitation further illustrates the good correlation of donor bending frequency with binding energy of the complex. We find that the bending frequency is a more reliable indicator of binding energy than the traditional red shift. For example, the red shifts of $\text{N}_2\text{-HF}$, OC-HF , and $\text{CO}_2\text{-HF}$ are 43, 117, and 53 cm^{-1} , whereas the corresponding dissociation energies of the hydrogen bond are 398, 732, and 672 cm^{-1} , respectively.

Unlike the quite rigid proton donor, the proton acceptor of the hydrogen bond appears to be much “softer” or less rigid, as demonstrated by the bending frequencies ν_A presented in Table 1. The most dramatic display of this asymmetry in angular rigidity between proton donor and proton acceptor occurs for $\text{CO}_2\text{-HF}$. At $\nu_{\text{HF}} = 0$, the CO_2 intermolecular bending frequencies are measured to be merely 9.1 cm^{-1} (19), whereas the bending frequency of the HF unit is 313 cm^{-1} . For $\nu_{\text{HF}} = 3$, the rigid CO_2 unit assumes a bent orientation of 30° with respect to line connecting the centers of mass, with the bending frequency of HF of 362.5 cm^{-1} . The bending mode of the CO_2 unit has a

*To whom correspondence should be addressed. E-mail: billk@otto.harvard.edu.

Fig. 1. The observed correlation between intermolecular bending frequencies (ν_D) of HF as proton donor and the square root of dissociation energies (D_0) for some hydrogen-bonded HF complexes. The data are listed in Table 1.

frequency of 24.8 cm^{-1} (20). This dramatic asymmetry in angular rigidity between proton donor and proton acceptor is an interesting and likely important facet of hydrogen bonding. We note further that there appears to be virtually no correlation between binding energy of the complex and the bending frequency of the proton acceptor. It appears that one simple consequence of this asymmetry of the hydrogen bond is the lack of correlation between dimer geometry and that of higher polymers. For instance, $(\text{HF})_2$ has the proton acceptor oriented near 120° , whereas the structure of $(\text{HF})_3$ is cyclic. The binding energy of $(\text{HF})_3$ with respect to dissociation to monomers is three times that of the dimer or essentially constant per bond. It would appear likely that the hydrogen bonds in $(\text{HF})_3$ are nearly linear, requiring the angular geometry of the proton acceptor not to reflect that of the acceptor in the dimer of 120° .

Asymmetry in Angular Rigidity of Hydrogen Bond

The consequences of the low frequency of ν_D upon the thermodynamic and kinetic properties of the complex are to increase the level density of the cluster and its entropy, thus lowering its chemical potential. The flat bending potential surface of the proton acceptor would lead to a shallow transition barrier, as in the case of formation of sulfuric acid from sulfur trioxide and water dimer (25) or even functioning as a chiral catalyst (26). The low-barrier hydrogen bond has been claimed to play a critical role in HIV protease and aspartic protease, because of the conformational flexibility of the active carboxyl groups (27, 28).

To quantify this asymmetry of angular rigidity, we define the parameter

$$\alpha = \left(\frac{\nu_D^2}{B_D} \right) / \left(\frac{\nu_A^2}{B_A} \right).$$

Here, ν_D and ν_A are the frequencies of the proton donor and acceptor bending vibration, B_A and B_D are rotational constants of the monomers. This parameter is equivalent to the conventional ratio of bending force constants for harmonic oscillation. The values of α for some HF complexes are listed in Table 1. A number of the results are obtained from infrared spectra in noble gas matrices.

To provide detailed physical insight into this asymmetry of angular rigidity in the hydrogen-bonded clusters, we again use the HF complexes as the prototype and separate them into two

Fig. 2. The *ab initio* calculated two-dimensional bending potential energy surfaces of $\text{N}_2\text{-HF}$. Here, θ_A and θ_D are the internal rotation coordinates for proton acceptor and HF, respectively.

major groups: the semirigid linear N-bridged, in which a nitrogen atom is the proton acceptor, including OC-HF ; and the floppy quasilinear O-bridged.

The N-bridged group with linear configuration at the ground state shows larger angular rigidity, with $\alpha \approx 2\text{--}4$. For example, the high-resolution spectroscopic study (14) of HCN-HF gives rise to $\alpha = 4.0$. For the simple system, $\text{N}_2\text{-HF}$, the two-dimensional bending potential shown in Fig. 2 is obtained by a high-level electronic structure calculation (29). θ_A and θ_D are the internal rotation coordinates for the proton acceptor and donor. The approximate perpendicularity of the two bending coordinates demonstrates the local-mode character of the intermolecular benders, whose motions will be adiabatically separable. The potential gradient along the HF bending coordinate is much greater than along that of the acceptor, providing a value of α considerably greater than 1.

The O-bridged hydrogen-bonded group yields the least directional proton acceptor, with $\alpha \approx 20\text{--}25$ for the complex with CO_2 . The vibration frequency, ν_A , is so low that in principle there should be no appreciable coupling to other vibrational modes. The one-dimensional *ab initio* potential for the CO_2 intermolecular bending of OCO-HF successfully predicts the vibrational frequency (19, 20, 30, 31). The origin of the quasilinear character is the effect of electron correlation, which is not, however, the dominant component of the intermolecular interaction. It is the combination of electrostatic and dispersion interactions that gives rise to a very flat angular potential for the proton acceptor. Furthermore, the lack of angular rigidity of this group depends highly upon the vibrational level of HF. For example, at $\nu_{\text{HF}} = 3$, the asymmetry parameter for OCO-HF decreases to 4.5 despite the increased HF angular rigidity.

Dynamically, the larger the difference in frequency of two coupled vibrations is, the weaker is the coupling between them. For the planar hydrogen-bonded complex, such as HF dimer, the two in-plane bending vibrations vary by a factor of three and are weakly correlated. Numerous theoretical investigations of $(\text{HF})_2$ exist, from the simplified bound state calculations to the full-dimensional quantum dynamical treatment. The most recent study, by Vissers *et al.* (32), offers the value $\alpha = 7.0$ when using an empirically modified six-dimensional potential energy surface (SO-3) (33), in good agreement with experiment.

Summary

We have examined several correlations of the bending frequencies in hydrogen bonded complexes of HF. There is an excellent

correlation between the HF bending frequency and the square root of the dissociation energy of the complex. The angular rigidity of the proton donor and proton acceptor in these complexes has been found to be very different, with that of the proton donor always considerably greater. Complexes with fluorine and oxygen as the proton acceptor show the greatest asymmetry in the bending potential for the two hydrogen-bonded units. Although high-level electronic structure calculations can capture this asymmetry, a facile predictive physical explanation is not readily apparent.

We have not attempted to extend this examination of angular asymmetry of hydrogen bonding to other proton donors, in particular water. Nor have we examined the consequences for the nature and pathways of vibrational energy redistribution of the hydrogen-bonded complexes. We note that the asymmetry in angular rigidity of the donor and acceptor in $(\text{HF})_2$ may be the briefest rationalization for the strong asymmetry in rotational product distribution observed by Miller *et al.* (21) in its vibrational predissociation. This was essentially the argument of Halberstadt *et al.* (34), who modeled the vibrational predisso-

ciation of $(\text{HF})_2$ as essentially Rg-HF complex. The spherical rare gas (Rg) is their model for the proton acceptor HF.

The large asymmetry in angular rigidity appears to persist even for relatively poor proton donors. The HCN dimer has linear equilibrium geometry. The proton donor bending frequency is estimated (35) to be $\nu_D = 120 \text{ cm}^{-1}$, whereas that of the acceptor is precisely measured (36) to be $\nu_A = 40.75 \text{ cm}^{-1}$. This yields $\alpha = 9$ for the asymmetry. Note that HCN is not a particularly good proton donor but certainly is a strong acceptor. This angular rigidity asymmetry is further illustrated by the triangular equilibrium geometry of $(\text{HCN})_3$. Although water clusters are the most frequently considered hydrogen-bonded system, there are too few experimental results on intermolecular bending vibrations to readily summarize the asymmetry of angular rigidity for such clusters. It will be interesting to see whether the linearity of the hydrogen bond is the same in the higher polymers as it is in the dimer of these species, so that the change in interaction angle always occurs at the proton acceptor.

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