J. Am. Chem. Soc. **1993**, *115*, 9596–9601

Is Protonated Ammonium Fluoride an Ion–Neutral Complex in the Gas Phase?

M. Mark Midland and Thomas Hellman Morton*

Contribution from the Department of Chemistry, University of California, Riverside, California 92521-0403

Received August 17, 1992[⊗]

Abstract: The two-dimensional rotation of the ammonium ion within $NH_4^+\cdots FH$ is compared with hindered internal rotations in ethane. Both have bound levels below their internal rotation barriers as well as higher lying free rotor levels. Rotation in $NH_4^+\cdots FH$ is the large-amplitude limit of bending vibrations, whereas free rotations in ethane are the large-amplitude limits of torsional oscillations. The accuracy of *ab initio* computations is calibrated using another tetrahedral–diatomic complex, $CH_4\cdots FH$, for which MP4(SDTQ) calculations using the 6-311G** basis set reproduce experimentally determined spectroscopic properties. The calculations predict that the internal rotation barrier for $NH_4^+\cdots FH$ is 13 kJ mol^{-1}, much lower than the calculated dissociation energy, $D_0 = 48$ kJ mol^{-1}. From the quantization of the two-dimensional rotation, statistical mechanics predicts that $NH_4^+\cdots FH$ exists as an ion–neutral complex for a significant fraction of the time at temperatures above 300 K. We therefore propose that it represents a paradigm for ionic bonding between polyatomic partners in the gas phase.

Conformationally mobile molecules are widely viewed as being highly fluxional. Nearly 120 years ago, Le Bel and van't Hoff proposed that free rotation occurs around single bonds. This description is satisfactory for many purposes, although most chemists are well aware that even the simplest example, ethane, has a 12 kJ mol^{-1} barrier to internal rotation.[1] An ethane molecule has four bound levels corresponding to torsional oscillations. The energy gap between the zero point and the highest bound torsional level is 9 kJ mol^{-1}. The next level, which is approximately 10 kJ mol^{-1} above the zero point, corresponds to free internal rotation of one methyl with respect to the other. At sufficiently elevated temperatures, ethane behaves as though the methyl groups turn freely.

We wish to draw a comparison between the behavior of ion–neutral complexes and internal rotations in molecules with low torsional barriers, such as ethane. Ion–neutral complexes have been proposed as gaseous analogues of ionic bonding. They are widely involved in gas-phase ion chemistry, both in unimolecular (ion decomposition) and in bimolecular (ion–molecule reaction) regimes.[2] The partners in such complexes are held together electrostatically such that at least one of them exhibits little directionality in its bonding to the other. In some instances ion–neutral complexes appear to be discrete intermediates, separated by energetic or entropic barriers from their covalently bonded isomers. For example, SCF calculations on ammonia plus isopropyl cation show local minima corresponding to a hydrogen-bonded structure, $H_3N\cdots H_3CCHCH_3^+$, and an "electrostatic" complex, $[(CH_3)_2CH^+\ NH_3]$, in addition to the covalent structure $(CH_3)_2CHNH_3^+$.[3] The center-of-mass distance between the isopropyl cation and the ammonia molecule is calculated to be nearly the same for the first two geometries, but the electrostatic complex is lower in energy. The cation is expected to rotate easily in all directions within the electrostatic complex, but the existence of stable isomeric structures makes it difficult to assess quantitatively the effects of this kind of internal rotation. Clearer insight is to be gained by theoretical examination of a system in which isomerism is not anticipated.

This paper examines a situation where ion–neutral complexes appear simply to be highly vibrationally excited states of a more conventional species. Here we describe a theoretical study of protonated ammonium fluoride ($NH_4^+\cdots FH$), which in its equilibrium geometry looks as though it is held together by a proton bridge. With increasing internal energy, $NH_4^+\cdots FH$ takes on the character of an ion–neutral complex: the NH_4^+ rotates so that no single proton is hydrogen bonded to the fluorine. Whatever bonding remains must be viewed as being purely ionic in character.

In ethane the carbon–carbon bond is the axis for internal rotation, whereas in $NH_4^+\cdots FH$ the axis is orthogonal to the proton bridge. In a room temperature sample of ethane, only a small fraction of the molecules are hot enough to populate a level corresponding to a free internal rotor. As the energy available for distribution increases, the probability for putting ≥ 10 kJ mol^{-1} into a given internal degree of freedom goes up. In microscopic terms the density of states corresponding to free internal rotation, $\rho^*(E)$, rises, on average, faster than does the total density of states, $\rho(E)$, where E designates the internal energy above the zero point. Such behavior has been known for a long time and accounts for the peculiar temperature dependence of the heat capacity of ethane.[4] The energetics for $NH_4^+\cdots FH$ are much the same as for ethane.

This paper discusses internal rotations that are not compatible with chemical bonds that require directed balance. Van der Waals molecules represent a case in point. Spectroscopic evidence leads to the conclusion that methane behaves like a two-dimensional free rotor within the methane–hydrogen chloride complex.[5] The equilibrium geometry resembles structure **1** (X = Cl), but if **1** were not fluxional, there would be two isomers when one of the methane hydrogens is isotopically substituted. Experimentally there is no evidence for isomerism in $CH_3D\cdots HCl$. This supports the view that the methane enjoys unrestricted rotations, as

---

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1993.

[1] (a) Weiss, S.; Leroi, G. E. *J. Chem. Phys.* **1968**, *48*, 962–967. (b) Moazzen-Ahmadi, N.; Gush, H. P.; Halpern, M.; Jagannath, H.; Leung, A.; Ozier, I. *J. Chem. Phys.* **1988**, *88*, 563–577. (c) Fernández-Sánchez, J. M.; Valdenebro, A. G.; Montero, S. *J. Chem. Phys.* **1989**, *91*, 3327–3334. (d) Bermejo, D.; Santos, J.; Cancio, P.; Fernández-Sánchez, J. M.; Montero, S. *J. Chem. Phys.* **1992**, *97*, 7055–7063.

[2] (a) McAdoo, D. J.; Morton, T. H. *Acc. Chem. Res.* **1993**, *26*, 295–302. (b) Morton, T. H. *Org. Mass Spectrom.* **1992**, *27*, 353–368. (c) Longevialle, P. *Mass Spectrom. Rev.* **1992**, *11*, 157–192. (d) Bowen, R. D. *Acc. Chem. Res.* **1991**, *24*, 364–371. (e) Hammerum, S. In *Fundamentals of Gas Phase Ion Chemistry*; Jennings, K. R., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1990; pp 379–390. (f) McAdoo, D. J. *Mass Spectrom. Rev.* **1988**, *7*, 363–393. (g) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195–3243.

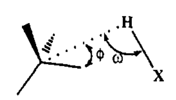
[3] Audier, H. E.; Morton, T. H. *Org. Mass Spectrom.*, in press.

[4] Lewis, G. N.; Randall, M.; Pitzer, K. N.; Brewer, L. *Thermodynamics*, 2nd ed.; McGraw-Hill: New York, 1961.

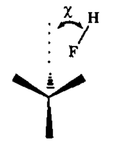
[5] Oshima, Y.; Endo, Y. *J. Chem. Phys.* **1990**, *93*, 6256–6265.

0002-7863/93/1515-9596$04.00/0

1



2



3

represented by the curved arrows.[6] Whatever potential barriers exist (corresponding to structure **2**) must be very low. It is no great heresy to suggest that what holds this van der Waals molecule together is neither covalent nor hydrogen bonding.

The van der Waals complex of methane with hydrogen fluoride behaves as if "internal rotation of the methane substituent is quenched."[6] This complex has an equilibrium geometry that resembles structure **2** (X = F), and the top of the internal rotation barrier should look like **1** or **3**. One may speculate that internal rotation has not been detected because the barrier is higher than the dissociation energy of the complex. Here we present *ab initio* calculations for the isoelectronic system $NH_4^+\cdots FH$, which possesses (like ethane) bound levels corresponding to restricted rotation and higher levels corresponding to free internal rotation (which are still below the dissociation threshold). We calibrate these calculations by showing that the computational level comes close to fitting experimentally measured spectroscopic values for $CH_4\cdots FH$. The goal of this work is to examine the extent to which rotations of the NH_4^+ (treated as a spherical top) are accessible internal degrees of freedom. Unlike the case of ethane, however, the classical motions corresponding to the bound levels below the rotation barrier are bends rather than torsions, and the free rotor levels correspond to a two-dimensional rather than a one-dimensional internal rotor. $NH_4^+\cdots FH$ represents a situation intermediate between $CH_4\cdots HCl$ (free internal rotation in its ground vibrational state) and $CH_4\cdots HF$.

Protonated ammonium fluoride, in the published SCF structure, appears to contain a hydrogen bond.[2b] Because of a large ion–dipole attractive force, $NH_4^+\cdots FH$ holds together even when internal energy is great enough for the microscopic probability that free rotor levels are occupied, $P = \rho^*(E)/\rho(E)$, to be significant. Free rotation of the NH_4^+ abolishes the directional nature of hydrogen bonding. At energies where two-dimensional internal rotation becomes probable, protonated ammonium fluoride behaves like an ion–neutral complex.

Computational Methods

Ab initio calculations were performed using the SPARTAN software on a Silicon Graphics 4D/35 Personal Iris computer[7] or using GAUSSIAN[8] on the Cray YMP 8/864 at the San Diego Supercomputing Center. Unless otherwise specified the 6-311G** basis set was used.[9] The normalization coefficients for the zero-order determinants in post-SCF computations were in the range 1.046–1.047 for the tetrahedral–diatomic systems. Basis set superposition errors (BSSE) were estimated using the counterpoise method.[10] Values of BSSE for tetrahedral–diatomic systems were found to be on the order of 300 cm^{-1} for the SCF calculations using 6-311G** and in the range 650–800 cm^{-1} for MP4. Energy levels for hindered internal rotations (E_v) were computed by established methods[11] on a VAX 8820. Coriolis coupling was taken into account for a given angular momentum quantum number K by setting the energy levels for the doubly degenerate internal degree of freedom equal to $E_{v_1} + E_{v_2} + A(2K\delta K + \Delta K^2)$, where A is the molecular rotational constant about the figure axis. For $NH_4^+\cdots HF$, conservation of momentum requires that $\Delta K = v_1 - v_2$, and nuclear spin statistics require that ΔK be a multiple of 3. Coriolis coupling was taken into consideration only for the $N–H\cdots F$ bends and the corresponding NH_4 internal rotation that represents their large-amplitude limit. Densities of states were enumerated by means of a direct counting program (DSC)[12] and used to calculate partition functions. The centrifugal elongation of a van der Waals complex, Δr, was calculated for a nonharmonic stretching potential $V(\Delta r)$ by setting the centrifugal force for a given value of J equal to the value of V and solving for Δr. The rotational energy for that value of J was then equated to $V(\Delta r) + \bar{B}J(J+1)/(r_{cm} + \Delta r)^2$, and the centrifugal distortion constant u was determined by fitting it to the form $\bar{B}J(J+1)[1 + uJ(J+1)]$.

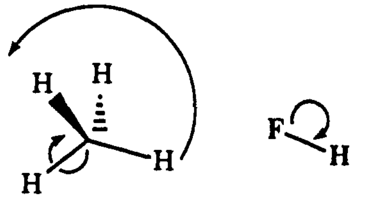


Figure 1. Large-amplitude limit of a bending vibration in a complex containing a tetrahedral molecule and a diatomic: the large arrow corresponds to a rotation of the tetrahedral molecule (treated as a spherical top), and the small arrows correspond to revolutions of the centers of mass of the molecular fragments.

Results

The object of these calculations has been to compute the vibrational partition function for protonated ammonium fluoride *ab initio* and to evaluate the contribution from populating levels that correspond to free internal rotations about axes perpendicular to the hydrogen bond. Tunneling was not considered in this work, and free rotation here designates a level at or above the internal barrier. Coupling to end-over-end rotation is neglected, which simplifies the enumeration of states without introducing large errors. The equilibrium geometry is represented in Figure 1, and the type of internal rotation under consideration is portrayed schematically by the large circular arrow.

Because the *ab initio* methods used here have not had a reputation for great accuracy in computing energies of hydrogen bonds, we have performed a couple of benchmark calculations on weakly bonded systems for which experimental data are available. The $H_3N\cdots HF$ dimer has been studied in the gas phase, and the force constant for stretching the hydrogen bond is reported to be 32.8 N m^{-1}.[13] A 6-31G** SCF calculation predicts the complex to have C_{3v} symmetry with a hydrogen bond length $N\cdots H$ = 1.83 Å. The SCF force constant, calculated by reoptimizing at 1.93 Å and comparing the electronic energies, is 14 N m^{-1}. Geometry optimization at MP4/6-311G** gives nearly the same hydrogen bond length (1.82 Å), but the energy to stretch the hydrogen bond by 0.1 Å corresponds to a force constant of 35 N m^{-1}. Thus MP4 appears to be satisfactory for the uses to which standard *ab initio* methods are applied in the present work.

Calculational accuracy is further assessed below by comparing *ab initio* results for the van der Waals molecule $CH_4\cdots HF$ with the two experimental measurements that have been reported, *viz.* the microwave frequencies for the $J = 0 \rightarrow J = 1$ and the $J = 1 \rightarrow J = 2$ transitions for overall rotation. It turns out that MP4/6-311G** comes close to fitting the experimentally reported moment of inertia. Treating the van der Waals complex as though it were a diatomic also gives reasonable agreement between the calculated energy for elongating the $F\cdots C$ distance and the experimental value for centrifugal distortion.

Calculations are then presented for $NH_4^+\cdots FH$ and used to estimate vibrational partition functions in which internal rotation

---

[6] Legon, A. C.; Roberts, B. P.; Wallwork, A. L. *Chem. Phys. Lett.* **1990**, *173*, 107–114.

[7] SPARTAN, Wavefunction Inc., Irvine, CA.

[8] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92, Revision B, Gaussian, Inc., Pittsburgh, PA.

[9] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.

[10] (a) Mo, O.; DePaz, J. L. G.; Yanez, M. *Theor. Chim. Acta* **1988**, *73*, 307–316. (b) Gutowski, M.; van Duijnveld-van de Rijdt, J. G. C. M.; van Lenthe, J. V.; van Duijnveld, F. B. *J. Chem. Phys.* **1993**, *98*, 4728–4737.

[11] (a) Lewis, J. D.; Malloy, T. B.; Chao, T. H.; Laane, J. *J. Mol. Struct.* **1972**, *12*, 427–449. (b) Stams, D. A.; Johri K. K.; Morton, T. H. *J. Am. Chem. Soc.* **1988**, *110*, 699–706. We are grateful to Prof. D. F. Bocian for providing us with his computer code for performing these calculations.

[12] Grant, E. R., Department of Chemistry, Purdue University. Personal communication.

[13] Legon, A. C. *Chem. Soc. Rev.* **1993**, *22*, 153–163.

Table I. Geometrical Parameters for Optimized Structures of $CH_4\cdots HF$ and Protonated Ammonium Fluoride[a]

	$CH_4\cdots HF$ global minimum			$NH_4^+\cdots FH$ global minimum	
	MP2/ 6-31G**	SCF/ 6-311G**	MP4/ 6-311G**	SCF/ 6-311G**	MP4/ 6-311G**
r_{cm}, Å	3.42	3.79	3.62	2.88	2.79
ϕ, deg	22.8	24.4	20.8	4.7	4.3
ω, deg	90.1	96.8	100.7	5.7	19.0
χ, deg	15.5	8.1	11.8	0.2	0.0
$\bar{B}$, GHz	4.55	3.86	4.20	6.15	6.51

[a] Angles ϕ, ω, and χ are shown in structures **2** and **3**.

is treated as independent of overall (external) end-over-end rotation. At room temperature and above, separation of internal and external rotation introduces errors on the order of the ratio of moments of inertia, $I_{internal}/I_{external}$, which turns out to be no more than a few percent (comparable to the effect of neglecting coupling between internal and external rotation in computing vibrational partition functions for ethane[1c]). Coriolis coupling to rotations about the N–F axis, however, are considered explicitly. One important consequence of this is that nuclear spin statistics turn out to play the same sort of role in $NH_4^+\cdots FH$ as they do in the internal rotation within ethane.[14]

Methane–Hydrogen Fluoride. Published computations on $CH_4\cdots HF$ have imposed a mirror plane of symmetry.[6] In terms of structure **2**, this corresponds to the plane of the paper. When that constraint is removed, we find that the optimized geometries deviate from C_s symmetry, with the F atom 0.1 Å and the H atom 0.2–0.3 Å below the paper. If the H–F did happen to lie in an H–C–H plane (as in the previously published calculations), the orientation of the two molecules could be uniquely specified by the distance between their centers of mass, the CH and HF bondlengths, and the angles ϕ and ω. But since the HF is not coplanar with any other two atoms, additional angles, one of which we shall call χ, must be given. This stands for the angle the HF axis makes with one of the H–C–H planes, and the calculated value varies somewhat with the level of computation, as do the optimized center-of-mass distance, r_{cm}, and the angles ϕ and ω. This variation is summarized in Table I for the level at which previous calculations have been reported (MP2/6-31G**, frozen core[6]) and for the 6-311G** basis set. A 6-311G** the SCF electronic energy difference between the isolated molecules and $CH_4\cdots FH$ is 3.9 kJ mol^{-1} without correction for basis set superposition error (BSSE). When BSSE is approximated using counterpoise the estimate of D_e is less than zero, both at SCF and at MP4.

At the MP4 level the optimized geometry agrees with the spectroscopic data: the complex is nearly a prolate symmetric top whose two lowest rotational constants are 4.19 and 4.21 GHz, which have an average value $\bar{B}$ less than 1% different from the experimental value $\bar{B}$ = 4.24 GHz.[6] While no vibrational spectroscopy has been reported for $CH_4\cdots HF$, we can gauge estimates of the value of D_e using the reported experimental centrifugal distortion constant, $u = 8.09 \times 10^{-6}$. If we treat $CH_4\cdots HF$ as though it were a diatomic, this is related to the harmonic stretching frequency ν as shown in eq 1, where $\bar{B}$ stands for the rotational constant of the pseudodiatomic.[4]

$$u = \frac{\bar{B}^2}{\pi^2 \nu^2} \tag{1}$$

At MP4 we have calculated the energetic cost of elongating the C–F distance by Δr = 0.1 Å. Viewed as a pseudodiatomic, $CH_4\cdots HF$ would have (in the harmonic oscillator approximation) a C–F stretching frequency of 45 cm^{-1}. Substituting that *ab initio* value into eq 1 leads to a value for the centrifugal distortion $u\bar{B}$ = 4.2 kHz. This is about 8 times smaller than the experimental value, and the discrepancy illustrates the hazard of treating such a weak bond as though it were a harmonic oscillator. If instead we use the same MP4 calculation to fit a Morse curve for the stretching potential, V, as a function of elongation Δr

$$V = D_e[1 - e^{-a\Delta r}]^2 \tag{2}$$

the calculated rotational energies of $J = 1$ and $J = 2$ give (using the SCF value of D_e without correction for BSSE and fitting the MP4 calculation with a = 2.01 $Å^{-1}$) a value of $u\bar{B}$ = 28.3 kHz. The level of agreement with the experimental value, $u\bar{B}$ = 34.3 kHz, suggests that the van der Waals bonding is even weaker than this estimate, *i.e.* the value of D_e is less than the SCF difference in electronic energy between the complex and free CH_4 plus HF.

Protonated Ammonium Fluoride. We now turn to the case where the tetrahedral molecule is a positive ion. The proton affinity of $H_3N\cdots HF$ is calculated to be slightly greater than that of ammonia. The electronic energy change for eq 3 is 919 kJ

$$H_3N\cdots HF + H^+ \rightarrow NH_4^+\cdots FH \tag{3}$$

mol^{-1} at the SCF level (6-311G**) and 915 kJ mol^{-1} at MP4. The change in SCF zero-point energies is 34 kJ mol^{-1} (uncorrected). The counterpoise corrections are large: 13 kJ mol^{-1} (SCF) and 35 kJ mol^{-1} (MP4). When a proton is deposited on the fluorine, the HF distance increases by 0.82 Å (MP4), and the geometry distorts from C_{3v} to C_s symmetry. The SCF proton affinity of $H_3N\cdots HF$ is 10 kJ mol^{-1} greater than the SCF proton affinity calculated for NH_3. Equation 3 is exothermic by approximately 870 kJ mol^{-1} (0 K) at the SCF level, but the MP4 calculation gives a value about 20 kJ mol^{-1} less exothermic. While there is a discrepancy between the two calculated proton affinities, there is excellent agreement between the two levels of calculation with respect to the hydrogen bond strength of $NH_4^+\cdots FH$.

Optimized geometries for protonated ammonium fluoride ($NH_4^+\cdots FH$) are summarized in Table I for the 6-311G** basis set. Because hydrogen fluoride has a large permanent dipole moment, its negative end is much closer to the center of charge of the ion than the positive end, leading to small values for the angles ϕ, ω, and χ. At the SCF level, the H and the F are only 0.05 Å out of the HNH plane; at MP4, they are in the plane (χ = 0), and the global minimum has C_s symmetry, even though no symmetry constraint was imposed. Thus there are three types of N–H bonds: that of the bridging hydrogen (whose rms equilibrium position is 0.2 Å away from the N–F axis), those of two equivalent nonbridging hydrogens (represented above and below the plane of the paper in Figure 1), and that of the unique, nonbridging hydrogen (drawn in the plane of the paper in Figure 1).

The geometry shown in Figure 1 corresponds to the global minumum, but there is a nonequivalent geometry, in which ϕ and ω are both negative, that has a nearly identical energy. In this second minimum, the F–H bond eclipses the unique nonbridging N–H bond. The structure in between these two minima, which has C_{3v} symmetry and a linear $N–H\cdots F–H$ arrangement, corresponds to a local maximum. Comparatively small reorientations of the NH_4^+ and FH convert one minimum geometry to the other *via* this linear structure. Calculations for other points along the NH_4^+ torsional coordinate were performed with additional symmetry constraints. The electronic energy differences between the global minima and separated ion and diatomic are 4643 cm^{-1} (SCF) and 5009 cm^{-1} (MP4). When counterpoise[10] is used to correct for BSSE, the SCF-calculated value of D_e (4347 cm^{-1}) agrees well with the MP4 value (4353 cm^{-1}). We use the SCF harmonic frequencies for all the vibrations (scaled by 0.9) to estimate the dissociation energy for $NH_4^+\cdots FH$ (D_0 = 48 kJ mol^{-1}). We use MP4 calculations for the geometry of the global minimum and the potential energy surface for internal rotation.

---

[14] Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; van Nostrand: Princeton, NJ, 1945.

Internal rotation is examined by using an upper bound estimate for the barrier. The potential energy surface was calculated by neglecting coupling between internal rotation and overall rotation. The constraints that the center of mass remain fixed and angular momentum is conserved were maintained. For internal motions not to produce torque about the center of mass, the Eckart condition[6] must be met:

$$\sum^{\text{all atoms}} \text{atomic mass(atomic displacement vector} \times \text{atom position vector)} = 0 \quad (4)$$

In the limit where coupling between internal and external rotation is neglected, rigid torsions of a spherical top within a complex can satisfy eq 4 by having the centers of mass of the two constituent fragments follow circular orbits in directions contrary to the internal rotation. In this fashion, net zero torque is exerted at all phases of large-amplitude torsions. This type of motion is represented by Figure 1, where the tetrahedral fragment is twisting about an axis perpendicular to the plane of the paper (large circular arrow). As this motion approaches free internal rotation, the centers of mass of both molecules come close to revolving in the plane of the paper about axes that are parallel to one another. The circular orbits defined by revolution of the centers of mass have the same helical sense; hence, the net result can be called conrevolution. If we draw the line between the centers of mass of two molecular fragments in the equilibrium geometry (which corresponds to the distance of closest approach), the axes for conrevolution are perpendicular to this line, and the orbits of conrevolution are centered about points that lie on this line of centers but are displaced outward by distances we shall call the radii of conrevolution. Conrevolution of the molecular fragments compensates for the torque of large-amplitude displacements while maintaining the center of mass of the entire complex fixed in the laboratory frame. Rotation contrary to conrevolution corresponds to the large-amplitude limit of a bending vibration in which one fragment maintains a fixed orientation while the other turns. This motion is used to define the potential energy surface for a bound torsion of NH_4^+ in one dimension.

When the moment of inertia of the tetrahedral molecule is much larger than that of the diatomic, conrevolution still provides a useful picture even if the diatomic reorients. The moment of inertia of NH_4^+ is 6 times greater than that of HF; even if ω changes when NH_4^+ turns 180°, Figure 1 does not substantially change. Because of the dynamical constraints imposed by eq 4, the top of the barrier need not represent a saddle point on the potential energy surface, and diagonalization of the Hessian gives more than one negative force constant (the NH_4^+–FH stretch in addition to the two-dimensional rotor).

When the mirror plane of symmetry is maintained, rotating the NH_4^+ by 360° passes four times through a geometry where HF is collinear with the nitrogen atom. To facilitate computation, ω was set equal to zero for all of them (*i.e.* HF collinear with an N–H bond). The first case, where $\phi = 0$, corresponds to a small local maximum near the global minimum. There are two almost equivalent minima on either side of $\phi = 0$. Both have nearly the same absolute values of ϕ and ω, but the one that is slightly higher in energy has negative values for both these angles.

The spacing of bending vibrations below the internal rotation barrier is determined using a potential energy surface that follows the path corresponding to rotation with conrevolution. Potential energy relative to the global minimum is shown in Figure 2 as a function of the angle made by the NF vector with an N–H bond. As the figure depicts, the lowest energy level within this potential is near the top of the $\phi = 0$ barrier. This means that the nonequivalent two global minima are not orientational isomers but are simply different phases of the zero-point vibration. In the limit where external rotation is neglected, the constraint of eq 3 requires that the radii of conrevolution be 0.069 Å for the center of mass of the HF and 0.077 Å for the center of mass of the NH_4^+. The second geometry where HF and N are collinear corresponds to ϕ being nearly a tetrahedral angle. For simplicity this is treated as a local minimum along the bending coordinate. These first two structures have an N–H pointing toward fluorine and will be called linear geometries. The other two collinear geometries are trifurcated, where an N–H points away from the HF. One is the top of the barrier ($\phi = 180°$), where the center-of-mass distance has its largest value, $r_{cm} = 3.08$ Å. The other trifurcated geometry occurs where ϕ is nearly a tetrahedral angle minus 180°. The linear geometries and the trifurcated geometries all have C_{3v} symmetry imposed as a constraint. The two linear geometries have different energies because conrevolution requires that the N–F distances not be the same when large-amplitude angular distortions have different absolute values. Likewise the two trifurcated geometries have different energies, even though they have the same symmetry.

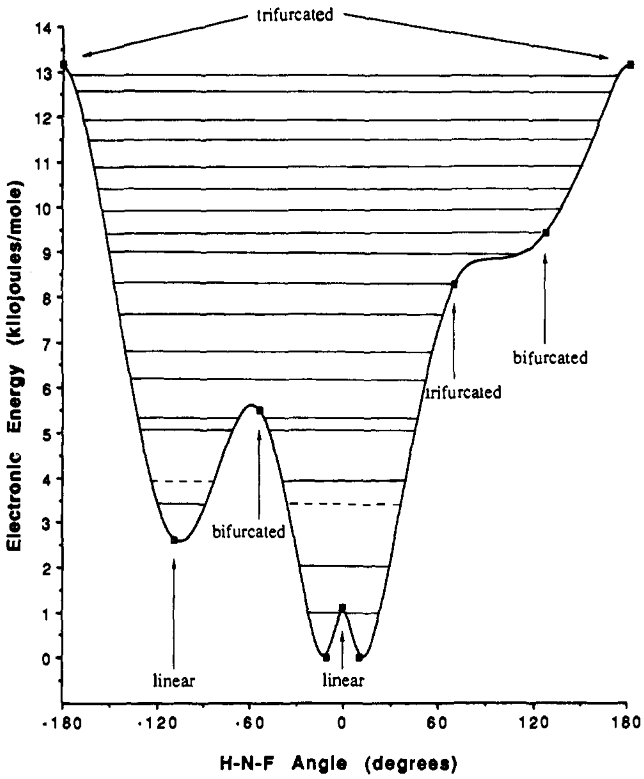


Figure 2. Potential energy surface and bound energy levels for a one-dimensional rotation of NH_4^+ within the plane of symmetry of $NH_4^+\cdots FH$ (MP4/6-311G**, no correction for BSSE) subject to the constraints of eq 4 in the absence of external rotation. Except for the two data corresponding to global minima, other calculated points represent geometries where the constraint ∠HNF = $-\phi$ is imposed.

Two other structures correspond to high-symmetry geometries, in which the HF is aligned with the bisector of an HNH angle. These are bifurcated geometries (with imposed C_{2v} symmetry), where ϕ is approximately one-half a tetrahedral angle or has that value minus 180°. The energies of the six symmetrical structures are shown in Figure 2 with a curve interpolated among the eight calculated points. The top of the barrier has an energy 13 kJ mol^{-1} above the global minima.

This is on the order of 1 kJ mol^{-1} higher than if we were to allow the trifurcated structure to optimize the value of r_{cm} without concern for the constraint imposed by eq 3. The curve was fitted as a periodic potential by a Fourier series, and the bound energy levels for one dimension are shown in Figure 2. As can be seen from Figure 2, the zero-point level for the $NH_4^+\cdots F$ bending vibration is so high that the effective geometry for $NH_4^+\cdots FH$ must be treated as a C_{3v} symmetric top. The potential energy curve in Figure 2 should therefore be treated in the same fashion as (for example) the doubly degenerate CCN bend in acetonitrile (ν_8) or one of the doubly degenerate bends (ν_9 and ν_{10}) in propyne.[14]

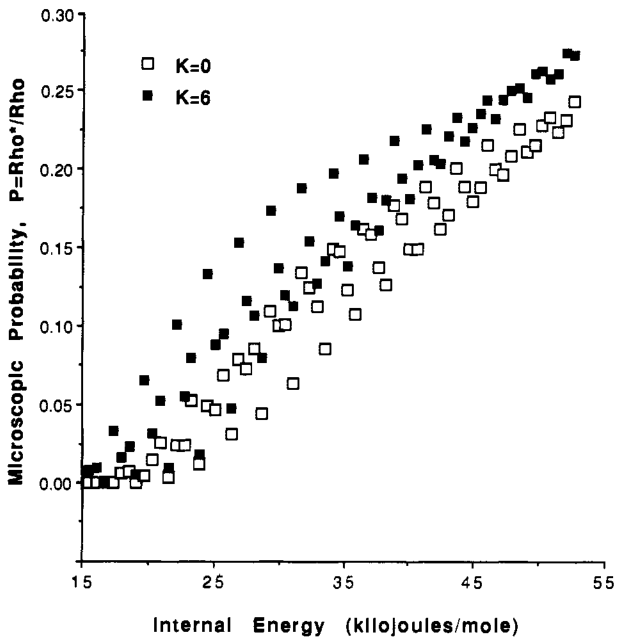


Figure 3. Microscopic probability P (taken as the fraction of the density of states for internal degrees of freedom) for occupying at least one free rotor level in $NH_4^+\cdots FH$ as a function of internal energy for two different rotational states, $K = 0$ (open squares) and $K = 6$ (filled squares).

For the two-dimensional internal rotation of the ammonium ion within $NH_4^+\cdots FH$, the potential energy surface will look like that in Figure 2 rotated 360° about a vertical axis. For oscillations that have no angular momentum, the quantization is taken to be the same as for the one-dimensional potential energy curve, but with each bound level being doubly degenerate. Vibrations that do contribute angular momentum experience large Coriolis coupling[6] with overall molecular rotation about the N–F axis (which corresponds to the 3-fold symmetry axis of the average geometry). This external rotation (angular momentum quantum number K) has a calculated rotational constant A = 171 GHz (5.7 cm^{-1}). For the purposes of state counting, additional coupling with end-over-end rotation (rotational constant B = 0.2 cm^{-1}) was neglected.

Densities of states were computed using the calculated quantization for the two-dimensional internal rotor and scaled SCF harmonic frequencies for the other $3N - 8$ internal degrees of freedom. (While the two-dimensional rotations of HF might also have been treated anharmonically as a dipole in a homogeneous strong electric field,[15] it is not obvious that this would have been an improvement for $NH_4^+\cdots FH$.) Coriolis coupling was neglected for the enumeration of other doubly degenerate vibrations (the FH bend and NH_4 rocking and stretching motions). The results of a direct state count for two different angular momentum states, $K = 6$ (whose rotational energy in the absence of Coriolis coupling is about the same as kT at room temperature) and $K = 0$, are summarized by the scatter plot in Figure 3. The microscopic probability of having a populated free rotor level, $P = \rho^*/\rho$, fluctuates, but the overall trend is for P to increase with internal energy.

The energy of the molecular system cannot be neatly divided into vibrational and rotational components. We simplify the problem by considering the rotational energy about the effective symmetry axis in the absence of Coriolis coupling (AK^2), neglecting the other overall rotations, and treating the remainder as the internal energy of the molecular system. At first glance the points corresponding to $K = 6$ in Figure 3 (filled squares) look as though they might simply be shifted by $\Delta E = AK^2$ = 2.5 kJ mol^{-1} from the points corresponding to $K = 0$ (open squares). However, a closer inspection suggests this is not the case, particularly since the average displacement of one scatter plot relative to the other is closer to 5 kJ mol^{-1}. Thus, the effect of overall angular momentum on the density of states is not negligible, although it is not very large.

Discussion

Recent theoretical studies of neutral atom–molecule van der Waals complexes suggest that, at high enough internal energies, the atom behaves as though it is in orbit around the molecule. For the $Ar\cdots CO_2$ cluster, a "dynamical transition" has been described when there are >6 quanta in the bending coordinate corresponding to motion of the argon atom relative to the CO_2 linear axis.[16] In the present work we discuss analogous behavior in protonated ammonium fluoride, a charged cluster that, in its vibrational ground state, can be described as a tetrahedral ion (NH_4^+) hydrogen bonded to the fluorine of HF. As internal energy is increased, the probability of its behaving like a diatomic in orbit around an ion increases in a fashion that we assess statistically using density-of-states calculations.

Loosely held complexes containing hydrogen fluoride and another neutral molecule do not, in general, permit either molecular species to rotate in all directions independently of the other. The T-shaped complex of hydrogen with hydrogen fluoride, $(H–H)\cdots HF$, has been closely examined theoretically,[17] and the computational results indicate that, if one diatomic is held fixed, the other cannot rotate without exceeding the value of the dissociation energy. While the two diatomics can rotate in a correlated fashion, one needs to move out of the way of the other so as not to arrive at a repulsive geometry. For an ion–neutral complex the binding energy is typically much greater. The charged fragment can rotate independently of the reorientation of its neutral partner. While *ab initio* calculations at the level presented here are not expected to give highly accurate results for dissociation energies, the agreement between MP4(SDTQ)/6-311G** calculations and the spectroscopic data for $CH_4\cdots FH$ provides a justification for applying this level of computation to the isoelectronic ion–dipole complex.

For protonated ammonium fluoride ($NH_4^+\cdots FH$) the energetics of internal motion resemble those in the case of ethane. *Ab initio* calculations of the barrier height were chosen so as to provide an upper bound. Because the moment of inertia for end-over-end rotation of the whole molecule (I_{external}) is 27 times greater than that of the internal rotor (I_{internal}), neglect of coupling between these two motions introduces only a small error. Because the internal rotor has virtually the same rotational constant as external rotation about the effective C_3-symmetry axis, Coriolis coupling is large and has been taken into account.

The present work does not require a high degree of accuracy in order to provide an approximation suitable for a statistical description. Free rotor levels start 13 kJ mol^{-1} above the zero point, at energies well below the dissociation threshold for the complex. When a free rotor level is occupied, the complex does not correspond to a classically hydrogen-bonded species. Instead it is better described as an ion–neutral complex, in which the orientation of the ion with respect to the neutral is fluxional.[2] Although the librations of HF are highly constrained (a 180° rotation leads to a repulsive part of the potential energy surface), the large-amplitude motions of the tetrahedral ion have relatively low energy barriers in the gas phase (as compared to tetrahedral ions in crystals[18,19]).

While $NH_4^+\cdots FH$ has not yet been reported experimentally in the gas phase, it provides a focus for discussion. Hydrogen bonds between NH_4^+ and neutral molecules often have low barriers for large-amplitude bending distortions. This has been ascribed to

---

(15) (a) Kryachko, D. S.; Yanovitskii, O. E. *Int. J. Quantum Chem.* **1991**, *40*, 33–53. (b) Rost, J. M.; Griffin, J. C.; Friedrich, B.; Herschbach, D. R. *Phys. Rev. Lett.* **1992**, *68*, 1299–1302.

(16) Horn, T. R.; Gerber, R. B.; Ratner, M. A. *J. Phys. Chem.* **1993**, *97*, 3151–3156.

(17) Clary, D. C.; Knowles, P. J. *J. Chem. Phys.* **1990**, *93*, 6334–6339.

(18) Hirota, E. *J. Mol. Spectrosc.* **1992**, *153*, 447–465.

(19) Weier, J. E.; Strauss, H. L. *J. Chem. Phys.* **1993**, *98*, 4437–4445.

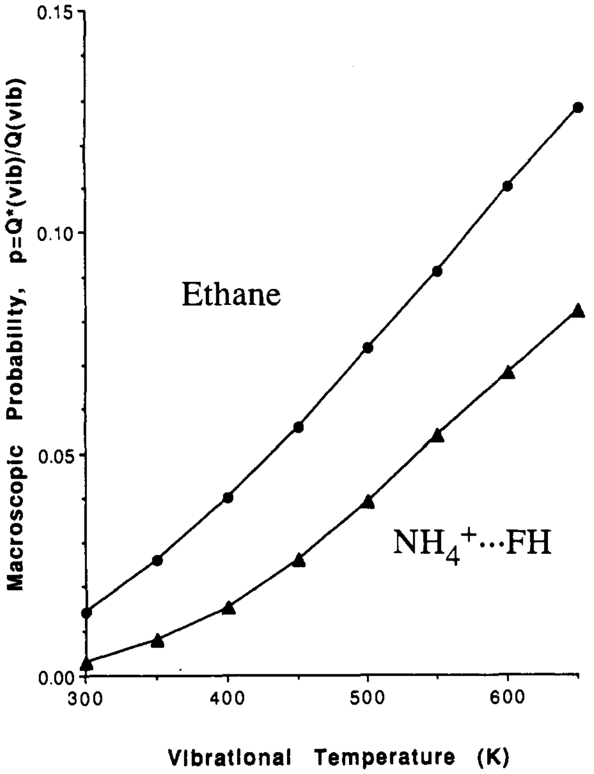


Figure 4. Macroscopic probabilities, *p*, for free internal rotation (as fractions of the vibrational partition function as a function of temperature) for $NH_4^+\cdots FH$ (filled triangles) and ethane (filled circles, vibrational frequencies taken from ref 14). Contributions from the doubly degenerate $N-H\cdots F$ bending motions were convolved with the strongly Coriolis-coupled portion of the rotational partition function for $NH_4^+\cdots FH$.

a large, purely electrostatic contribution to the bond energy. Nevertheless, the barrier for two-dimensional internal rotation can be significant, calculated on the order of 50 kJ mol^{-1} for turning the NH_4^+ 180° within $NH_4^+\cdots NH_3$ from a linear to a trifurcated geometry.[20] On one hand, the proton-bound dimer of ammonia is held together by a strong hydrogen bond (for which the experimental dissociation energy is approximately 105 kJ mol^{-1}) that possesses directed valence to a significant extent. On the other hand, the bond in $NH_4^+\cdots FH$ is calculated to be about half as strong as in $NH_4^+\cdots NH_3$, but the barrier for internal rotation of the NH_4^+ is only about one-fourth as high. Protonated ammonium fluoride can therefore be said to have directed valence to a lesser degree. Near its dissociation threshold, protonated ammonium fluoride should, for all practical purposes, behave like an ion–neutral complex on any time scale long enough for internal energy to be completely randomized.

Microscopic probabilities for finding protonated ammonium fluoride with a free internal rotation are summarized in Figure 3. A microscopic picture (*i.e.* where internal energy is the independent variable) is useful for studying unimolecular decompositions in collision-free regimes. But for comparison with other internal rotations, such as the well-understood case of ethane, a macroscopic picture (*i.e.* where temperature is the independent variable) is easier to discuss. Transformation from a microscopic to a macroscopic domain is straightforward, and the result is summarized in Figure 4. Vibrational and rotational partition functions cannot be factored apart, but (as in the case of ethane[1c]) the error introduced by a partial factorization is small for temperatures ≥300 K. Effective vibrational partition functions, Q_{vib}, have been computed for $3N-6$ internal degrees of freedom (with the two-dimensional motions corresponding to Figure 2—both bound and unbound—coupled to external rotation about the unique axis). These partition functions (as well as those, Q^*_{vib}, that correspond to populating at least one of the internal rotor levels above the top of the barrier) were calculated for internal degrees of freedom corresponding to angular momentum quantum numbers $K = 0, 3, 6, 9$, and 12 (with respect to overall rotation about the effective C_3 axis along the N–F direction) and Boltzmann-averaged. Figure 4 plots the macroscopic probability of finding a molecule with an occupied free rotor level, $p = Q^*_{vib}/Q_{vib}$, as a function of temperature for protonated ammonium fluoride and for ethane. In the domain of Figure 4 the probability for $NH_4^+\cdots FH$ follows the same trend as that for ethane, but at a temperature shifted approximately 100 K higher. The slope for $NH_4^+\cdots FH$ is less than that for ethane at higher temperatures because dissociation of the complex cuts off the contribution of very high vibrational states in the case of protonated ammonium fluoride.

Consider the question posed by the title of this article. An isolated $NH_4^+\cdots FH$ with enough energy to fragment (as in a metastable ion decomposition) is statistically likely to spend (in the absence of tunneling) at least one quarter of its lifetime as a complex in which NH_4^+ rotates freely. If it is isotopically labeled, discrete rotamers such as $DH_2NH^+\cdots FH$ and $H_3ND^+\cdots FH$ may correspond to isomers distinguishable at low temperatures, but they should interconvert very quickly at room temperature or above. Our calculations have not considered the effects of tunneling (which has been reported to be important for partially deuterated ammonium ions in crystals[19]). Nevertheless, the present work suggests that, when compared to another example of a rapid unimolecular isomerization, switching the deuterium in and out of the bridging position in $NDH_3^+\cdots FH$ ought to have a rate that is of the same order of magnitude as that of the conversion of *anti*- to *gauche*-CH_2DCH_2D.

Conclusion

In the large-amplitude limit, bending motions become hindered internal rotations. At this limit the barrier for NH_4^+ rotation within $NH_4^+\cdots FH$ is comparable to the torsional barrier in ethane. In $NH_4^+\cdots FH$ this degree of freedom corresponds to a two-dimensional rotor about axes perpendicular to the classical hydrogen bond. Above room temperature the likelihood of finding thermally equilibrated $NH_4^+\cdots FH$ occupying a level above the internal rotation barrier is nearly the same as in the case of ethane at a temperature 100 K lower. Internal rotation in $NH_4^+\cdots FH$ abolishes the directionality of hydrogen bonding. When it has a sufficiently high probability of internal rotation, protonated ammonium fluoride is better described as an ion–neutral complex than as a proton-bridged species. We suggest that this example offers a paradigm for ionic bonding between two molecules in the gas phase.

Acknowledgment. This work was supported by Grant CHE92-03066 from the NSF and a block grant from the San Diego Supercomputing Center. The authors are grateful to Professor D. F. Bocian for helpful discussions and to IBM for loan of an RS6000 Model 530.

Supplementary Material Available: Listings of Cartesian coordinates and SCF vibrational frequencies for the species in Table I (5 pages). Ordering information is given on any current masthead page.

---

(20) (a) Cybulski, S. M.; Scheiner, S. *J. Phys. Chem.* **1989**, *93*, 6565–6574. (b) Liebman, J. F.; Romm, M. J.; Mautner, M.; Cybulski, S. M.; Scheiner, S. *J. Phys. Chem.* **1991**, *95*, 1112–1119. (c) Reported *ab initio* rotational barriers for $NH_4^+\cdots OH_2$ lie between the value reported for $NH_4^+\cdots NH_3$ and the value presented here for $NH_4^+\cdots FH$ (Kassab, E.; Evleth, E.; Hamou-Talvia, Z. D. *J. Am. Chem. Soc.* **1990**, *112*, 103–108).