Scholarship and Professional Work - LAS   College of Liberal Arts & Sciences

1987

Determination of Dissociation Energies and Thermal Functions of Hydrogen-bond Formation using High Resolution FTIR Spectroscopy

B. A. Wofford

M. E. Eliades

Shannon Lieb
Butler University, slieb@butler.edu

J. W. Bevan

Recommended Citation

B. A. Wofford, M. E. Eliades, S. G. Lieb, and J. W. Bevan

Articles you may be interested in

Hydrogen bonding at grain surfaces and boundaries of nanodiamond films detected by high resolution electron energy loss spectroscopy
Appl. Phys. Lett. **91**, 103104 (2007); 10.1063/1.2779848

High-resolution ultraviolet spectroscopy of p -fluorostyrene-water: Evidence for a σ -type hydrogen-bonded dimer
J. Chem. Phys. **122**, 244312 (2005); 10.1063/1.1937370

Accurate dissociation energies of O–H ··· O hydrogen-bonded 1-naphthol·solvent complexes
J. Chem. Phys. **116**, 1850 (2002); 10.1063/1.1431282

Erratum: Determination of dissociation energies and thermal functions of hydrogen bond formation using high resolution FTIR spectroscopy [J. Chem. Phys. 8 7, 5674 (1987)]
J. Chem. Phys. **88**, 6678 (1988); 10.1063/1.454763

Dissociation energies of the hydrogen-bonded dimers RCN···HF (R=CH3, HCC) determined by rotational spectroscopy
J. Chem. Phys. **86**, 2530 (1987); 10.1063/1.452106

Determination of dissociation energies and thermal functions of hydrogen-bond formation using high resolution FTIR spectroscopy

B. A. Wofford, M. E. Eliades, S. G. Lieb, and J. W. Bevan

Chemistry Department, Texas A&M University, College Station, Texas 77843

A technique which employs high resolution Fourier transform infrared spectroscopy is demonstrated for evaluation of hydrogen bond dissociation energies D_0 and D_e. Results for HCN--HF give a $D_0 = 20.77(22)$ and $D_e = 28.77(45)$ kJ/mol which are compared with previously determined values obtained from microwave absolute intensity measurements and *ab initio* molecular orbital calculations. Rovibrational band information available for HCN--HF also permits evaluation of thermal functions of dimer formation in kJ/mol: $\Delta U^{\circ}_{298.2} = 20.1(2)$, $\Delta H^{\circ}_{298.2} = 22.6(2)$, $\Delta G^{\circ}_{298.2} = 59.4(2)$, $\Delta S^{\circ}_{298.2} = -0.1235$.

INTRODUCTION

The ground state dissociation energy D_0 and particularly the equilibrium dissociation energy D_e are regarded among the most significant parameters in the characterization of a hydrogen-bonded interaction.[1,2] For this reason a wide range of experimental techniques have been used to estimate the dissociation energies of these interactions.[3–6] Among these investigations are numerous spectroscopic studies which have employed low resolution infrared methods and integrated band intensities.[6] Direct methods of precise determination of D_0 and D_e have been restricted to two techniques which have exploited rotationally resolved spectra.[7–10] Initially, Stark microwave spectroscopic techniques were used to measure the absolute intensities in the evaluation of D_0 for the linear hydrogen-bonded complex HCN--HF.[7] Vibrational frequencies evaluated from low resolution infrared spectroscopy and predictions based on microwave spectroscopy (or on reasonable assumptions) also enabled an estimation of D_e for this complex within the harmonic approximation. The values for D_0 and D_e were 1580(90) and 2183(135) cm^{-1}, respectively. More recently microwave spectroscopy[8,9] has been used to study the related complexes of H–C≡C–C≡N--HF, CH$_3$C≡N--HF, and H$_2$O--HF. Subsequently, Pine *et al.*[10] determined D_0 for the dimers (HF)$_2$ and (HCl)$_2$. In this latter technique, a narrowband difference frequency infrared laser was used to determine absolute intensities for rotationally resolved transitions of these dimers in static gas equilibrium mixtures. This approach has provided the information necessary for evaluation of D_0. Using experimental vibrational frequency data and estimates of the remaining frequencies from the predictions of *ab initio* molecular orbital calculations, Pine *et al.*[10] were also able to estimate D_e for (HF)$_2$ and (HCl)$_2$. For (HF)$_2$, they obtained $D_0 = 1038(43)$ cm^{-1} and $D_e = 1657(103)$ cm^{-1}, while in the case of (HCl)$_2$, they obtained $D_0 = 431(22)$ cm^{-1} and $D_e = 817(82)$ cm^{-1}.

These aforementioned techniques have been particularly significant as they have provided experimental determinations of D_0 and D_e which are available for comparison with the predictions of an ever increasing number of sophisticated *ab initio* molecular orbital calculations.[11] However, there is a need to extend these evaluations of D_0 and D_e to a wider

range of hydrogen-bonded complexes. Furthermore, the development of alternative high resolution spectroscopic techniques which are capable of facilitating this objective is also highly desirable.

In this paper, D_0 and D_e for the HCN--HF complex are determined by using high resolution Fourier transform infrared spectroscopy. Recently, this technique has been used extensively to resolve the rotational fine structure of fundamental, overtone, combination, and hot bands in this hydrogen-bonded complex.[12] Such analyses result in precisely determined band origin frequencies, ground and excited state rotational and distortion constants for HCN--HF.[13] From these data, it is possible to directly determine the zero point energy correction needed in the evaluation of D_e. Furthermore, the thermal functions of hydrogen-bonded formation $\Delta U^{\circ}_{298.2}$, $\Delta H^{\circ}_{298.2}$, $\Delta G^{\circ}_{298.2}$, and $\Delta S^{\circ}_{298.2}$ can be evaluated. Using statistical mechanics, these properties are evaluated both within the harmonic and anharmonic approximation. Thus the effects of anharmonicity can be quantitatively determined for these thermal functions.

The dissociation energies obtained in this work have been compared with those previously determined by absolute microwave intensity measurements[7] and with recent predictions of *ab initio* molecular orbital theory.[11]

EXPERIMENTAL METHOD

Rotationally resolved transitions in ν_1 HF, ν_1 HCN, and ν_2 HCN--HF are selected for determination of the ground state concentration of each component of the dimer equilibrium. This choice is restricted by the requirement that each measured transition could be recorded within the bandwidth of the FTIR spectrometer. In this particular case, transitions from each of these three vibrational bands occurred in the range of 3292–3492 cm^{-1}. All measurements are carried out using a Bomen DA3-002 interferometer interfaced to a temperature controlled White cell as described previously.[14] In these experiments a liquid nitrogen cooled InSb detector is used with an instrumental resolution of 0.005 cm^{-1}. Measurements are carried out at two temperatures, 243(1) and 233(1) K. The temperature gradient along the White cell is measured to be ⩽1 K and the gas

temperature is monitored directly at the center and two extremes of the multipass cell.

HCN was obtained from Fumico (Amarillo, Texas) and HF from Matheson Inc. Both gases are vacuum distilled before use in order to remove impurities. Absolute pressure measurements are made by a Baratron MKS 2226A vacuum gauge.

As in the previously described techniques,[7-10] the present method is dependent on the evaluation of the equilibrium constant K_{00} which is related to the dissociation energy D_0, through the van't Hoff equation[15]:

$$K_{00} = \frac{N_{00}(\text{HCN--HF})}{N_{00}(\text{HCN})N_{00}(\text{HF})}$$

$$= \left(\frac{h^2}{2\pi\mu kT}\right)^{3/2} \exp(D_0/RT), \qquad (1)$$

where K_{00} is the ground state equilibrium constant, N_{00} (HCN--HF) is the concentration in the ground state of the complex, and N_{00} (HCN), N_{00} (HF) are the corresponding concentrations in the ground states of the proton acceptor and proton donor, respectively. The reduced mass μ is defined as

$$\frac{1}{\mu} = \frac{1}{m(\text{HCN})} + \frac{1}{m(\text{HF})} \qquad (2)$$

and D_0, h, k, and T are, respectively, the ground state dissociation energy, Planck's constant, the Boltzmann constant, and absolute temperature.

Pine *et al.*[10] used absolute infrared intensity measurements of rotationally resolved complex transitions at a single temperature to evaluate D_0. This particular technique involved a narrowband difference frequency laser spectrometer with an instrumental laser linewidth of approximately 1 MHz. In our case however, the instrumental linewidth of the Fourier transform interferometer is $\sim$150 MHz which is comparable to the 170 MHz Doppler limited transition full width at $1/e$ maximum intensity of the ν_2 HCN--HF transitions. Under such circumstances direct absolute intensity measurements become unreliable, and thus a different approach has been devised to determine concentrations of each component in the equilibrium mixture.

The concentration of each monomer component HCN and HF in the mixture is determined by comparison of their integrated line intensities with the integrated line intensities obtained for each component monomer, individually. Each monomer component is recorded under identical instrumental and temperature conditions to that of the mixture and each component's absolute pressure is measured using a Baratron gauge. The ground state concentrations of the equilibrium monomer components are determined by comparison of the integrated line intensities of the pure monomer components to those of the equilibrium mixture. Thus, this comparison serves as a calibration for the ground state concentration of each monomer component in the mixture. This procedure is accomplished through the use of standard expressions in statistical mechanics.[15] A number of independent verifications of this procedure have shown it to be reproducible to within 0.2%.

The ground state concentration of the complex itself re-

mains to be determined. This is evaluated by choosing a HCN transition to match the integrated intensity of the selected complex line and applying the minimally perturbed local mode behavior of the ν_2 C–H stretching vibration in the complex HCN--HF. N_{00} (HCN--HF) can then be determined by applying the integrated line strength expression to both transitions,[16] i.e.,

$$S_{if} = \frac{8\pi^3}{3hv} f_i v_{if} g_i A_J F_J e^{-E_i/kT} \langle \mu_v \rangle^2$$

$$\times \frac{N}{Q_R Q_V} \cdot [1 - e^{-E_V/kT}], \qquad (3)$$

where f_i is the isotopic fractional abundance of the species measured, v_{if} is the transition wave number, and g_i is the nuclear spin statistical weight. A_J is the Hönl–London factor which is equal to $J+1$ for an $R(J)$ branch transition and J for a $P(J)$ transition. $F(J)$ is the Herman–Wallis factor and represents the influence of Coriolis rotation-vibration and centrifugal distortion corrections to the vibrational transition moment $\langle \mu_v \rangle$. E_i is the rotational energy state. Q_J and Q_V are the respective rotational and vibrational partition functions defined as

$$Q_J = \sum_J (2J+1)\exp(-E_J/kT) \qquad (4)$$

and

$$Q_v = \sum_v g_v \exp(-E_v/kT) \qquad (5)$$

with g_v being the degeneracy of the vibrational state. These quantities were determined by direct summation over all states. The contribution from emission is negligible so that the factor $[1 - e^{-E_v/kT}]$ is set to 1. The rotational energy expression is

$$E(J) = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 \qquad (6)$$

and the vibrational energy relative to the ground state is given by the familiar expression

$$G(v_1,...,v_n) = \sum_i \omega_i v_i + \sum\sum_{i>j} X_{ij}(v_i v_j + \tfrac{1}{2}d_i v_j + \tfrac{1}{2}d_j v_i)$$

$$+ \sum\sum_{l>l} g_{ll'} \cdot ll'. \qquad (7)$$

The minimally perturbed local mode behavior of the ν_2 C–H stretch[17] in the HCN--HF complex is then applied. This approximation is supported experimentally by the very small band origin change upon complex formation[12] and confirmed by the recent results of a CEPA *ab initio* molecular orbital calculation.[11(d)] On this basis, the rotationless transition dipole moment matrix element of HCN--HF is expressed as $\langle \mu_v \rangle_D = f \langle \mu_v \rangle_{\text{HCN}}$, where f is the enhancement factor associated with complex formation. This latter factor has not been determined experimentally; however, it has been evaluated to be 1.13 by the previously mentioned CEPA calculations.[11(d)] As these calculations have precisely reproduced so many of the experimentally determined mo-

lecular parameters for this complex, the value of 1.13 is used with confidence for f. Also, the dissociation energy has a logarithmic dependence[18] on f, thereby minimizing any errors this estimation may introduce.

After using this new technique to evaluate N_{00} (HCN--HF), one can calculate D_0 through the use of Eq. (1). Measurements were carried out at two separate temperatures 243.2 K and 233.2 K. In each case a background spectrum is taken for the empty cell in order to obtain integrated transition intensities. Measurements of each component were made in the frequency range 3290–3490 cm^{-1} with an instrumental resolution of 0.005 cm^{-1}. Transitions were very carefully selected to minimize spectral interference so that the integrated intensities of the selected transitions could be determined as precisely as possible. Based on a previous investigation of ν_2 HCN--HF and its hot bands,[19] three transitions $P(5)$, $P(17)$, and $R(38)$ are selected for this purpose. Furthermore, to ensure that the transitions in ν_1 HF and ν_1 HCN were not saturated but still occurred within the frequency bandwidth quoted, the $P(10)$ transition of ν_1 HF (Ref. 20) and the $R(36)$ transition of ν_1 HCN (Ref. 21) are chosen. Care is taken to ensure that the measurement is carried out in the linear part of the response curve of the detector. Furthermore, during the component calibration procedure, great care is taken to evacuate the cell to prevent contamination due to outgassing. Carrying out the calibrations at 243.2 and 233.2 K also had the additional advantage of removing transition overlap due to water vapor which has caused pronounced problems for absolute intensity measurements made at higher temperatures.[22]

RESULTS

The ground state concentrations of each of the monomer components, HCN and HF, and the hydrogen-bonded species HCN--HF are given in Table I. This table shows results determined at two temperatures 243.2 and 233.2 K. These values are determined using integrated intensity measurements on the $P(10)$ transition in ν_1 HF, the $R(36)$ transition in ν_1 HCN, and the $P(5)$, $P(17)$, and $R(38)$ transitions in ν_2 HCN--HF. Thus, three values for K_{00} are determined for each given temperature. These latter values

are presented in Table I. The corresponding value of D_0 calculated for each measurement is also given in Table I.

The average value of the ground state dissociation energy D_0 evaluated from measurements at 243.2 K is 20.91(22) kJ mol^{-1} and the value at 233.2 K is 20.63(13) kJ mol^{-1} where the reported errors are one standard deviation. Both values are within one standard deviation of each other. For that reason the results are combined to yield an average value of $D_0 = 20.77(22)$ kJ mol which corresponds to 1737(18) cm^{-1}. The value of the equilibrium dissociation energy D_e is related to the ground state dissociation energy through the relationship[23]

$$D_e = D_0 + U_0^0(\text{HCN--HF})$$
$$- U_0^0(\text{HCN}) - U_0^0(\text{HF}), \qquad (8)$$

where U_0^0 represents the vibrational zero point energy for each component.

The band origin frequency of each fundamental vibration in HCN--HF is known and an extensive number of anharmonicity and anharmonic cross terms have been evaluated.[13] Unfortunately, there is insufficient data to enable a complete characterization of the anharmonic potential energy surface of HCN--HF. Assuming that the undetermined anharmonic cross terms X_{12}, X_{13}, X_{15}, X_{26}, and X_{36} have negligible influence on evaluation of the zero point energy, an approximate value of D_e can be determined within the second-order approximation. This should be a valid approximation as states involving such cross terms occur at energies greater than 2000 cm^{-1} and do not contribute to the partition function of the complex. The behavior of other determined anharmonic cross terms leads to the conclusion that the modulus of such terms, $|X_{ij}| \leqslant 1$ cm^{-1} for the first four terms above and $|X_{36}| \leqslant 3$ cm^{-1}. These terms are assumed to be zero and are included in the estimated errors. In addition, the anharmonic cross terms X_{16}, X_{34}, and X_{56} have not been evaluated. However, in these cases, the magnitude of these constants are expected to be larger and will have significant influence on the determination of the zero point energy of the complex. The combination band $\nu_5 + \nu_6$, which is necessary to evaluate X_{56}, has not yet been observed despite successfully detecting $2\nu_6^0$ and its series of hot bands[24] which

TABLE I. Calculation of the dissociation energy.

Transition	N_{00} (molecules/cm^{-3})	$K_{00}(m^3)$	D_0 (kJ/mol)
At 233 K			
HCN $R(36)$	$7.75 \times 10^{+14}$	$\cdots$	$\cdots$
HF $P(10)$	$8.23 \times 10^{+15}$	$\cdots$	$\cdots$
HCNHF $P(5)$	$6.27 \times 10^{+9}$	9.83×10^{-28}	20.65
HCNHF $P(7)$	$7.69 \times 10^{+9}$	1.21×10^{-27}	21.06
HCNHF $R(38)$	$7.49 \times 10^{+9}$	1.17×10^{-27}	21.01
At 243 K			
HCN $R(36)$	$7.36 \times 10^{+14}$	$\cdots$	$\cdots$
HF $P(10)$	$7.87 \times 10^{+15}$	$\cdots$	$\cdots$
HCNHF $P(5)$	$8.67 \times 10^{+9}$	1.50×10^{-27}	20.49
HCNHF $R(17)$	$9.37 \times 10^{+9}$	1.62×10^{-27}	20.64
HCNHF $R(38)$	$9.92 \times 10^{+9}$	1.71×10^{-27}	20.75

occur in the same frequency region. The expected values are $|X_{56}| \leqslant 3$ cm^{-1} and similarly $|X_{34}| \leqslant 3$ cm^{-1}. However, the estimation of $|X_{16}|$ is a more difficult proposition. A conservative estimate is $|X_{16}| \leqslant 10$ cm^{-1}. In the evaluation of the zero point energy of the complex, X_{16}, X_{34}, and X_{56} are assumed to be zero and estimates of their frequencies are included as errors in the evaluation of the zero point energy. These assumptions result in a contribution of 20 cm^{-1} in the estimated uncertainty of the zero point energy and therefore in the evaluation of D_e. The influence of Fermi resonance and Coriolis interactions are neglected in the calculations as there is inadequate information currently available to correct for such effects. Using the data for the monomer components HCN and HF,[20,21] the zero point energy correction is evaluated which yields $D_e = 1737(18) + 668(20)$ cm^{-1}. The error in the zero point correction has been augmented to reflect the maximum possible error due to the as yet unavailable anharmonicity terms. The most recent evaluation of D_e is 2405(38) cm^{-1} or 28.77(45) kJ mol^{-1}. These values of D_0 and D_e given in Table II can be compared with the average values of 1580(90) and 2183(135) cm^{-1} determined using absolute microwave intensity measurements.[7] The present value of D_0 agrees within error with individual microwave values of D_0 determined at higher temperatures. In these microwave measurements there appears to be a trend to lower D_0 as the temperature of measurement is lowered and these latter results show increased deviation from our observations. A number of *ab initio* molecular orbital calculations of D_e for HCN--HF exist with a variety of basis sets. A value for D_e is also calculated using the pseudodiatomic approximation. These results are tabulated for comparison in Table II.

The information currently available enables determination of other thermal functions for the HCN--HF complex. In particular, within the previously stated approximations, the thermal functions of complex formation can be determined within both approximate harmonic and anharmonic limits. This is particularly interesting as it presents the opportunity of assessing the effects of anharmonicity associated with the low frequency large amplitude motions.

Thermal functions associated with dimer formation can be evaluated through the use of the following expressions[15]:

Energy of dimer formation

$$\Delta U_T^0 = D_0 + U^0_{\text{HCN--HF}} - U^0_{\text{HCN}} - U^0_{\text{HF}},$$

where

$$\Delta U_0^0 = (U_T^0 - U_0^0) = \sum_i g_i \epsilon_i e^{-E_i/kT} \tag{9}$$

Gibbs free energy of dimer formation

$$\Delta G_T^0 = -RT \ln Kp = \Delta H_T^0 - T\Delta S_T^0. \tag{10}$$

Enthalpy of dimer formation

$$\Delta H_T^0 = \Delta U_T^0 + RT. \tag{11}$$

Entropy of dimer formation

$$\Delta S_T^0 = (\Delta H_T^0 - \Delta G_T^0)/T. \tag{12}$$

Constant pressure heat capacity of dimer formation

$$\Delta C_p = C_p(\text{HCN--HF}) - C_p(\text{HCN}) - C_p(\text{HF}). \tag{13}$$

Macroscopic equilibrium constant

$$K_p = \frac{Q_{\text{HCN--HF}} N_{00}(\text{HCN--HF})}{Q_{\text{HCN}} N_{00(\text{HCN})} Q_{\text{HF}} N_{00(\text{HF})}}. \tag{14}$$

The individual constant heat capacities are computed as the difference between the mean squared thermal energy and the square of the mean thermal energy divided by RT^2, and R is added to convert from C_v to C_p. Results for these five thermal functions are given in Table III both within harmonic and anharmonic approximations. In addition, the thermal functions are calculated using only the band origin frequencies in the harmonic limit. Table IV, on the other hand, displays the temperature dependence of these thermal functions within the anharmonic approximation.

DISCUSSION

High resolution Fourier transform infrared spectroscopy is demonstrated to be an effective technique for determining the ground state dissociation energies in simple hydrogen bonded dimers. In contrast to previously developed techniques, this method allows for the direct determination of the equilibrium concentration of each component of the dimer equilibrium. This advantage is made possible by the broadband capability of the Fourier transform technique. The latter characteristic is also advantageous for selecting the component transitions free from transition overlap and spectral interference. The technique does not have the high instrumental resolution capability of the previous approaches.[7-10] However, in this study an independent mea-

TABLE II. Comparison of dissociation energies.

	Species	D_0/kJ mol^{-1}	D_e/kJ mol^{-1}
Absolute microwave	CH$_3$CN$\cdots$HF	26.1(6)	29.0(9)
Intensity measurements	HCN$\cdots$HF	18.9(1.1)	26.1(1.6)
	HCCCN$\cdots$HF	20.4(7)	23.4(9)
Current FTIR work	HCN$\cdots$HF	20.77(22)	28.77(45)
Work of Botschwina [Ref. 11(d)]	HCN$\cdots$HF	$\cdots$	28.66
The results of Handy *et al.* [Ref. 11(c)]	HCN$\cdots$HF	16.7	25.9
Work of Benzel and Dykstra [Ref. 11(a)]	HCN$\cdots$HF	$\cdots$	28.9
Pseudodiatomic approximation	HCN$\cdots$HF	$\cdots$	21.8

TABLE III. Comparison of thermal functions of hydrogen-bond formation at various levels of approximation.

	$\Delta U^\circ_{298.16}$	$\Delta H^\circ_{298.16}$	$\Delta G^\circ_{298.16}$	$\Delta S^\circ_{298.16}$	$\Delta C^\circ_{P\,298.16}$
Anharmonic approx.	20.1(2)	22.6(2)	59.4(2)	$-0.1235(2)$	0.0021(3)
Harmonic approx.	19.6(2)	22.1(2)	59.9(2)	-0.1268	-0.0131
Observed frequencies	19.8(2)	22.3(2)	59.3(2)	-0.1242	-0.0132

surement of monomer integrated transition intensities under comparable partial pressure conditions to that in the complex mixture is used, thereby precisely calibrating absolute ground state equilibrium concentrations. This approach is found to be both reliable and reproducible. This method has the additional advantage of circumventing the problems associated with attempting to exploit direct absolute intensity measurements in order to determine these concentrations. Such problems would have been encountered because the instrumental resolution of the Fourier transform technique is comparable to the Doppler limited full width at $1/e$ maximum intensity of the transitions associated with equilibrium components. The sensitivity and broadband capability of the Fourier transform instrument when used in conjunction with a temperature controlled White cell should make this approach applicable to similar determinations of dissociation energies and thermal functions for a wide range of complexes.

The value of D_0 in HCN--HF was determined from three different transitions in the complex $P(5)$, $P(17)$, and $R(38)$ at two different temperatures. The average value of $1737(18)$ cm^{-1} indicates the precision of the technique. This value agrees within experimental error with the corresponding values determined by absolute microwave measurements[7] determined at 192 K, but shows significant variation from corresponding values determined at lower temperatures.

The rovibrational analyses of vibrational band spectra do not permit the evaluation of all of the anharmonic cross terms which are necessary to determine precisely the zero point energy in HCN--HF.[13] Expected limits for the undetermined constants have been estimated and incorporated as errors in the evaluation of the zero point energy. Within this approximation and limitations imposed by considering the energy expansion to second order, the zero point energy is determined to be $668(20)$ cm^{-1}. This yields $D_e = 2405(38)$ cm^{-1}. Experimental evaluation of the undetermined X_{16} anharmonic constant and to a lesser extent X_{56}, X_{34}, and X_{36}

TABLE IV. Results for the five thermal functions using the anharmonic potential model.

Temperature (K)	ΔU°	ΔH°	ΔG°	ΔS°	ΔC°_P
298.16	20.1	22.6	59.4	-0.1235	0.0021
250	20.2	22.3	52.7	-0.1219	-0.0057
200	19.9	21.6	45.8	-0.1212	-0.0020
150	19.7	20.9	39.0	-0.1203	-0.0048
100	19.6	20.4	32.2	-0.1172	-0.0105

terms should permit a more precise evaluation of D_e. A sensitive laser spectrometer is currently under construction and should have the capability of providing this information. Sensitivity restrictions of the present equipment have prevented the determination of such information and have thus placed limitations on the accuracy of the quoted D_e. Assumptions and approximations in the evaluation of D_e have been kept to a minimum allowing realistic estimates concerning the errors involved in its determination. In particular, the influence of the low frequency vibrations on the evaluation of D_e are explicitly taken into account.

It is interesting to compare the current value of D_e with those predicted on the basis of *ab initio* molecular orbital calculations (Table II).[11] It appears that the recent CEPA calculations done by Botschwina,[11(d)] which are now regarded as the most accurate currently available, are in remarkably good agreement with the determined D_e value in this work. Also, the work of Benzel and Dykstra[11(a)] is similarly in excellent agreement with this D_e. The current results can also be compared with the recent microwave results of Millen *et al.*[8] The methyl group is a stronger electron donor than a hydrogen atom and in turn the hydrogen atom is a stronger electron donor than the HCC group. On this basis the expected ordering of the equilibrium dissociation energies is $D_e\,(CH_3\,CN--HF) > D_e\,(HCN--HF) > D_e\,(HCCCN--HF)$. Both the ground and equilibrium dissociation energies determined in this work for HCN--HF fall between the values obtained for the complex with CH_3 and HCC substituents in place of H on the cyanide (Table II).

It is pertinent to note that investigations of predissociation from the excited states in common[12] and isotopic species[25] of HCN--HF should permit an independent approach to determining the upper and lower bounds to D_0. In particular, the investigation of predissociative characteristics in fundamental, overtone, and combination band transitions involving ν_3, $2\nu_5^0$, and $3\nu_6^1$ should place strict limitations on the upper and lower bounds to D_0 in this complex. Such studies would be most useful as they would give an alternative assessment of the accuracy for the evaluation of D_0.

The present measurements of D_0 and the extensive rovibrational band analyses of HCN--HF provide an unusual opportunity for evaluating macroscopic thermal functions for complex formation. $\Delta U^\circ_{298.16}$, $\Delta H^\circ_{298.16}$, $\Delta G^\circ_{298.16}$, and $\Delta S^\circ_{298.16}$ are evaluated within the previously described limitations. These values are subject to the limitations imposed by the second-order expansion in the energy expression and thus neglect higher anharmonic cross terms. However, previous microwave[26] and infrared[12] spectroscopic techniques have provided detailed quantitative studies of the low lying states of the HCN--HF complex which make the most signif-

icant contributions to the molecular partition function of the species. Furthermore, the as of yet undetermined X_{12}, X_{13}, X_{15}, X_{16}, X_{34}, and X_{36} anharmonic constants involve states which are above the dissociation energy of the complex and do not contribute to the evaluation of such thermodynamic parameters.

The availability of anharmonicity and anharmonic constants in HCN--HF provide an opportunity of evaluating $\Delta U^\circ_{298.16}$, $\Delta H^\circ_{298.16}$, $\Delta G^\circ_{298.16}$, $\Delta S^\circ_{298.16}$, and $\Delta C^\circ_{p\,298.16}$ within several levels of approximation. The levels of approximation are (i) anharmonic, i.e., all the information available within the second-order expansion in energy; (ii) based on the harmonic approximation only; (iii) with observed fundamental frequencies only used in the harmonic approximation.

The initial calculation is the best that can be proposed at the current time and makes an attempt to take into account the effects of anharmonicity on determination of the thermal functions of complex formation. The second set of calculations is determined within the corresponding harmonic approximation, an approximation often used in many *ab initio* calculations so these calculations provide an interesting comparison with the previous anharmonic determinations. The third level of calculation is often made in the absence of sufficient empirical data. The results are given in Table III. The band origin frequency calculations are closer to the thermodynamic values based on the model calculation. This is easily understood when one considers that the fundamental harmonic frequencies are uniformly higher than the observed band origins. Therefore, as the contributions from the excited vibrational states are added together, the band origin frequencies contribute more to the thermal energy than the harmonic frequencies. Both of those approximations uniformly underestimate the excited state vibrational energy contributions obtained through a proper anharmonic potential calculation. The band origin frequency calculations give good estimates of the thermal functions (see Table III) in this low temperature regime (i.e., less than 500 K). Indeed, the values are only slightly outside one standard deviation of the anharmonic corrected thermal functions. In the particular case of HCN--HF, this approximate technique would have provided reliable values of these latter parameters and anharmonicity does not appear to make unduly large contributions to their evaluation. This is a consequence of the fact that the anharmonicity and anharmonic cross terms associated with the low frequency vibrations of the complex are small leaving the Boltzmann distribution relatively unaffected.

Previously, the $\Delta S^\circ_{298.16}$ for this dimer formation was estimated[6] to be -95 J mol^{-1} K^{-1}. It is interesting to compare that rather conservative estimate with a formation of a linear compound from linear reactants[27]:

$$C\!\!=\!\!O + C\!\!=\!\!C\!\!=\!\!O \rightarrow O\!\!=\!\!C\!\!=\!\!C\!\!=\!\!C\!\!=\!\!O.$$
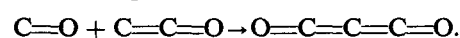
The entropy contribution due to electronic degeneracy in $C\!\!=\!\!C\!\!=\!\!O$ is removed: $S^*_{298}(C_2O) = S^\circ_{298}(C_2O) - R(\ln 3) = 223.9$ J mol^{-1} K^{-1}, and the contribution due to degeneracy arising from symmetry is removed: $S^*_{298}(C_3 O_2) = S^\circ_{298}(C_3O_2) + R(\ln 2) = 281.9$ J mol^{-1} K^{-1}. The

$S^\circ_{298}(CO)$ equals 227.2 J mol^{-1} K^{-1} which gives a $\Delta S^\circ_{298} = -139.5$ J mol^{-1} K^{-1} for compound formation. The $\Delta S^*_{298.16}$ dimer formation (i.e., HCN--HF formation) is -123.5 J mol^{-1} K^{-1} of which -139.2 J mol^{-1} K^{-1} is due to a translational entropy loss. The remaining entropy gain of 15.9 J mol^{-1} K^{-1} is a trade off between the loss of two rotational degrees of freedom from the monomer units for the gain of five vibrational degrees of freedom of the complex (i.e., the two hydrogen-bond bending modes and the hydrogen-bond stretching mode). The temperature dependence of ΔS° is shown in Table IV.

Also tabulated in Table IV are the results for the five thermal functions calculated at temperatures ranging from 100 to 298.16 K. Over the relatively small temperature range of current calculations, the deviation from linearity is greater than the estimated errors of the evaluated parameters. Over the temperature ranges which are typically used for the Classius–Clapeyron equation (30–50 K) the variation of these parameters is within experimental error. Under the temperature conditions of this experiment (233 K) the standard enthalpy change for complex formation is essentially equal to the dissociation energy. Other investigations which have assumed that their low temperature evaluations of the enthalpy of bond formation yield the D_0 are supported with this experimental determination of D_0.

ACKNOWLEDGMENTS

[1] S. N. Vinogradov and R. H. Linnell, *Hydrogen-Bonding* (Van Nostrand Reinhold, New York, 1971).

[2] C. Sandorfy, Topics Current Chem. 120, 41 (1984).

[3] *The Hydrogen Bond*, edited by P. Schuster, G. Zundel, and C. Sandorfy (North-Holland, Amsterdam, 1976).

[4] G. D. Pimental and A. L. McClellan, *The Hydrogen Bond* (W. H. Freeman, San Francisco, 1960).

[5] (a) M. D. Joesten and L. J. Schaad, *Hydrogen-Bonding* (Dekker, New York, 1974); (b) cf. Ref. 7.

[6] J. C. Lassegue and J. Lascombe, in *Vibrational Spectra and Structure*, edited by J. R. Durig (Elsevier, Amsterdam, 1982), Vol. II, Chap. 2, p. 51.

[7] A. C. Legon, D. J. Millen, D. J. Mjoberg, and S. C. Rogers, Chem. Phys. Lett. 55, 157 (1978).

[8] A. C. Legon, D. J. Millen, and H. M. North, J. Chem. Phys. 86, 2530 (1987).

[9] A. C. Legon, D. J. Millen, and H. M. North, Chem. Phys. Lett. 135, 303 (1987).

[10] A. S. Pine and B. J. Howard, J. Chem. Phys. 84, 590 (1986).

[11] (a) M. A. Benzel and C. E. Dykstra, J. Chem. Phys. 78, 4052 (1983); (b) Y. Bouteiller, M. Allavena, and J. M. Leclercq, Chem. Phys. Lett. 84, 91 (1981); (c) R. D. Amos, J. F. Gaw, N. C. Handy, E. D. Simandiras, K. Somasundram, Theor. Chem. Acta 71, 41 (1987); (d) P. Botschwina, Proceedings NATO Advanced Research Workshop, Structure and Dynamics of Weakly Bound Complexes, Maratea, Italy, Sept. 22–26 (1986), pp. 181–190.

[12] (a) B. A. Wofford, J. W. Bevan, W. B. Olson, and W. J. Lafferty, J. Chem. Phys. 83, 6188 (1985); (b) B. A. Wofford, M. W. Jackson, J. W. Bevan, W. B. Olson, and W. J. Lafferty, *ibid.* 84, 6115 (1986); (c) M. W. Jackson, B. A. Wofford, J. W. Bevan, W. B. Olson, and W. J. Lafferty, *ibid.* 2401 (1986).

[13] J. W. Bevan, Proceedings NATO Advanced Research Workshop, Struc-

ture and Dynamics of Weakly Bound Complexes, Maratea, Italy, Sept. 22–26 (1986), pp. 149–170.

[14]B. A. Wofford, J. W. Bevan, W. B. Olson, and W. J. Lafferty, Chem. Phys. Lett. **124**, 579 (1986).

[15]J. F. Lee, F. W. Sears, and D. L. Turcotte, *Statistical Thermodynamics* (Addison–Wesley, Reading, MA, 1973).

[16]M. C. Allen and P. C. Cross, *Molecular Vib-Rotors* (Wiley, New York, 1963).

[17]D. W. Michael, C. E. Dykstra, and J. M. Lisy, J. Chem. Phys. **81**, 5998 (1984).

[18]R. A. Toth, J. Mol. Spectrosc. **53**, 1 (1974).

[19]A. M. Gallegos and J. W. Bevan (submitted).

[20]D. U. Webb and K. N. Rao, J. Mol. Spectrosc. **28**, 121 (1968).

[21]D. H. Rank, D. P. Eastman, B. S. Rao, and T. A. Wiggins, J. Opt. Soc. Am. **51**, 929 (1961).

[22]J. W. Johns (private communication).

[23]G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, 1959).

[24]B. A. Wofford, S. G. Lieb, and J. W. Bevan, J. Chem. Phys. **87**, 4478 (1987).

[25]B. A. Wofford, M. W. Jackson, and J. W. Bevan, J. Chem. Phys. **86**, 2518 (1987).

[26]A. C. Legon, D. J. Millen, and S. C. Rodgers, Proc. R. Soc. London Ser. A **370**, 213 (1980).

[27]*JANAF Thermochemical Tables*, Natl. Stand. Ref. Data Series, Natl. Bur. Stand. 37 (U.S. GPO, Washington, D.C., 1971).