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# Thermodynamic Properties of Hydrogen-bonded Dimers $B \cdots HF$ from Spectroscopy: $B = HCN, CH_3CN, HC_2CN, (CH_3)_3CCN$ and $H_2O$

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The rotational and vibrational spectra of several hydrogen-bonded dimers  $B \cdots HF$  have now been investigated in sufficient detail to allow the thermodynamic properties of  $B \cdots HF$  to be evaluated with useful accuracy. Dissociation energies  $D_0$  for dimers  $B \cdots HF$  are known from the measurement of absolute intensities of rotational transitions in equilibrium gas mixtures of  $B$ ,  $H$  and  $B \cdots HF$ . Together with vibrational separations and rotational constants, the  $D_0$  have been used to estimate  $\Delta H_m^\ominus(T)$  for the reaction



where  $B = HCN, CH_3CN, HC_2CN, (CH_3)_3CCN$  and  $H_2O$ . The standard spectroscopic entropies  $S^\ominus(T, M)$  have been evaluated for each participant  $M$  in the reaction and thence  $\Delta S_m^\ominus(T)$ ,  $\Delta G_m^\ominus(T)$  and  $K^\ominus(T)$ . Finally, standard functions for each  $B \cdots HF$  at 298.15 K are tabulated.

## 1. Introduction

Certain hydrogen-bonded dimers  $B \cdots HX$  have been investigated extensively through their rotational and vibrational spectra. In particular,  $HCN \cdots HF$  has been characterized in great detail. The rotational spectrum has provided the rotational constant  $B_0$ , the dissociation energy  $D_0$  (absolute intensity measurements) and some approximate values for the wavenumbers of the intermolecular vibrational modes (relative intensity measurements). The last of these have recently been superseded in accuracy by measurements of the high-resolution infrared spectrum. As long ago as 1982, during Faraday Discussion No. 73 'van der Waals Molecules', the late A. J. B. Cruickshank pointed out that for  $HCN \cdots HF$  it was possible even then to set up the rotation-vibration partition function for the dimer and thereby calculate standard thermodynamic functions for the hydrogen-bonded species as well as changes in the standard thermodynamic properties for formation of the dimer from its components according to the general association reaction:<sup>1</sup>



In this paper, we bring together a large number of observed spectroscopic properties for the components in eqn. (1) and use these to calculate  $\Delta S_m^\ominus$ ,  $\Delta H_m^\ominus$ ,  $\Delta G_m^\ominus$  and  $K^\ominus$  in the temperature range 150–298.15 K at 20 K intervals for  $B = HCN, CH_3CN, HC_2CN$  (cyanoacetylene),  $(CH_3)_3CCN$  and  $H_2O$ .

## 2. Experimental

Rotational spectra observed, for example, by Stark-modulation microwave spectroscopy of cooled equilibrium gas mixtures or Fourier-transform microwave spectroscopy of adiabatically expanded gas mixtures lead, *via* frequency measurements, to rotational constants and thence to rotational partition functions.<sup>2</sup> On the other hand, intensity measurements of vibrational satellites associated with the intermolecular modes yield, when using the former technique, vibrational separations for these modes. Such separations are difficult to determine by other techniques, although for  $HCN \cdots HF$  the vibrational wavenumbers of fundamentals

for *all* the vibrational modes have been determined with high accuracy from the exhaustive study of the infrared spectrum by Bevan *et al.*<sup>3</sup> If the absolute intensity of a rotational transition in each of the components,  $B$ ,  $HX$  and  $B \cdots HX$  in an equilibrium gas mixture is measured (either directly or indirectly), it is then possible to obtain the dissociation energy  $D_0$  of  $B \cdots HX$  to give  $B$  and  $HX$ . Such measurements have been made in a limited number of cases<sup>4–7</sup> and confine the present calculations to the dimers  $B \cdots HF$ , where  $B = HCN, HC_2CN, CH_3CN, (CH_3)_3CCN$  and  $H_2O$ .

The rotational constants of  $B$ ,  $HF$  and  $B \cdots HF$  for the series under discussion<sup>6,8–18</sup> are collected in Table 1. The corresponding vibrational wavenumbers<sup>17,19–23</sup> are given separately in Table 2, while the dissociation energies  $D_0$ <sup>30,34–36</sup> for  $B \cdots HF$  are recorded in Table 3.

## 3. Calculations

The first step is to calculate the standard entropy  $S^\ominus(T)$  for each of the components  $M = B, HX$  and  $B \cdots HX^\ddagger$  according

† We use  $M$  for the general chemical symbol, instead of the more usual  $B$ , because of the long-standing convention in which a general hydrogen-bonded dimer is written  $B \cdots HX$ . The general chemical reaction is then  $0 = \sum_M \nu_M M$ , where  $\nu_M$  is the stoichiometric number of  $M$ . Note that  $\nu_i$  is used here for the frequency of the  $i$ th vibrational mode of a general molecule  $M$ .

**Table 1** Rotational constants used in the calculation of thermodynamic properties

M	$A_0/\text{MHz}$	$B_0/\text{MHz}$	$C_0/\text{MHz}$
HCN	—	44 315.98 <sup>a</sup>	44 315.98 <sup>a</sup>
$CH_3CN$	158 095 <sup>b</sup>	9 198.898 <sup>c</sup>	9 198.898 <sup>c</sup>
$HC_2CN$	—	4 549.05 <sup>d</sup>	4 549.05 <sup>d</sup>
$(CH_3)_3CCN$	4 599 <sup>e</sup>	2 749.89 <sup>f</sup>	2 749.89 <sup>f</sup>
$H_2O$	835 840 <sup>g</sup>	435 352 <sup>g</sup>	278 139 <sup>g</sup>
HF	—	616 365.5 <sup>h</sup>	616 365.5 <sup>h</sup>
$HCN \cdots HF$	—	3 591.155 2 <sup>i</sup>	3 591.155 2 <sup>i</sup>
$CH_3CN \cdots HF$	158 095 <sup>b</sup>	1 853.333 <sup>j</sup>	1 853.333 <sup>j</sup>
$HC_2CN \cdots HF$	—	1 220.684 31 (9) <sup>k</sup>	1 220.684 31 (9) <sup>k</sup>
$(CH_3)_3CCN \cdots HF$	4 599 <sup>e</sup>	876.492 7 <sup>l</sup>	876.492 7 <sup>l</sup>
$H_2O \cdots HF$	391 100 <sup>m</sup>	7 263.5 (2) <sup>m</sup>	7 140.3 (2) <sup>m</sup>

<sup>a</sup> Ref. (8). <sup>b</sup> Ref. (9). <sup>c</sup> Ref. (10). <sup>d</sup> Ref. (11). <sup>e</sup> Calculated from structure in Ref. (12). <sup>f</sup> Ref. (12). <sup>g</sup> Ref. (13). <sup>h</sup> Ref. (14). <sup>i</sup> Ref. (15). <sup>j</sup> Ref. (16). <sup>k</sup> Ref. (17). <sup>l</sup> Ref. (6). <sup>m</sup> Ref. (18).

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**Table 2** Fundamental vibrational wavenumbers  $\bar{\nu}$  and degeneracies [ $g$ ] for B and B...HF where B = HCN, CH<sub>3</sub>CN, HC<sub>2</sub>CN (CH<sub>3</sub>)<sub>3</sub>CCN and H<sub>2</sub>O

$\bar{\nu}/\text{cm}^{-1}$ [ $g$ ]						
	HCN	CH <sub>3</sub> CN	HC <sub>2</sub> CN	(CH <sub>3</sub> ) <sub>3</sub> CCN	H <sub>2</sub> O	HF
monomers						
	711.98 [2] <sup>a</sup>	362 [2] <sup>b</sup>	222.4 [2] <sup>c</sup>	245 [1] <sup>d</sup>	181 [2]	1595.0 [1] <sup>e</sup>
	2096.85 [1]	920.2 [1]	498.5 [2]	361 [1]	300 [2]	3651.7 [1]
	3311.40 [1]	1040.8 [2]	663.2 [2]	684 [1]	376 [2]	3755.8 [1]
		1385 [1]	863.5 [1]	765 [1]	579 [2]	
		1447.9 [2]	2079.3 [1]	1209 [1]	869 [2]	
		2266.5 [1]	2274.0 [1]	1247 [1]	935 [2]	
		2954.1 [1]	3327.4 [1]	1390 [1]	1145 [2]	
		3009.2 [2]		1400 [1]	1370 [2]	
				2235 [1]	1477 [2]	
				2865 [1]	2934 [2]	
				2875 [1]	1461 [3]	
				2887 [1]	2968 [4]	
dimers						
B...HF	726.531 22 [2] <sup>g</sup>	except for HCN...HF, monomer modes of B assumed unchanged on dimer formation				
	2120.935 [1] <sup>g</sup>					
	3310.329 [1] <sup>g</sup>					
$\nu_S$	3716.20 [1] <sup>g</sup>	3631.1 [1] <sup>j</sup>	3733 [1] <sup>m</sup>	3601.5 [1] <sup>p</sup>	3608 [1] <sup>r</sup>	
$\nu_\sigma$	168.33 [1] <sup>h</sup>	168.8 [1] <sup>j</sup>	138 [1] <sup>n</sup>	159.2 [1] <sup>p</sup>	176 [1] <sup>r</sup>	
$\nu_{B(i)}$	550.028 5 [1] <sup>i</sup>	620 [1] <sup>k</sup>	555 [1] <sup>o</sup>	640 [1] <sup>p</sup>	696 [1] <sup>r</sup>	
$\nu_{B(o)}$	550.028 5 [1] <sup>i</sup>	620 [1] <sup>k</sup>	555 [1] <sup>o</sup>	640 [1] <sup>p</sup>	666 [1] <sup>r</sup>	
$\nu_{\beta(i)}$	73.58 [1] <sup>h</sup>	45 [1] <sup>l</sup>	30 [1] <sup>n</sup>	55 [1] <sup>q</sup>	157 [1] <sup>r</sup>	
$\nu_{\beta(o)}$	73.58 [1] <sup>h</sup>	45 [1] <sup>l</sup>	30 [1] <sup>n</sup>	55 [1] <sup>q</sup>	54 [1] <sup>r</sup>	

<sup>a</sup> Ref. (19). <sup>b</sup> Ref. (20). <sup>c</sup> Ref. (21). <sup>d</sup> Ref. (22). Degeneracies here also include accidental ones. <sup>e</sup> Ref. (23). <sup>f</sup> Ref. (24). <sup>g</sup> Ref. (25). <sup>h</sup> Ref. (26). <sup>i</sup> Ref. (27). <sup>j</sup> Ref. (28). <sup>k</sup> Ref. (29). <sup>l</sup> Ref. (30). <sup>m</sup> Ref. (17) as corrected in H. M. North, Ph.D. Thesis, University of London, 1986. <sup>n</sup> Ref. (17). <sup>o</sup> Value assumed unchanged from value for HCN...HF given in Ref. (29). <sup>p</sup> Ref. (31). <sup>q</sup> Ref. (32). <sup>r</sup> Ref. (33).

to

$$S^\ominus(T, M) = S_{\text{trans}}^\ominus(T, M) + S_{\text{rot}}^\ominus(T, M) + S_{\text{vib}}^\ominus(T, M) \quad (2)$$

where

$$S_{\text{trans}}^\ominus(T) = R \ln[(2\pi mk_B T/h^2)^{3/2} k_B T/p^\ominus] + \frac{5}{2}R \quad (3)$$

$$S_{\text{vib}}^\ominus(T) = R \sum_i g_i [(\theta_i/T) \exp(-\theta_i/T)] \times [1 - \exp(-\theta_i/T)]^{-1} - R \sum_i g_i \ln[1 - \exp(-\theta_i/T)] \quad (4)$$

$$\text{and} \quad S_{\text{rot}}^\ominus(T) = R \ln q_{\text{rot}} + nR \quad (5)$$

In eqn. (4)  $g_i$  is the degeneracy of the  $i$ th vibrational mode and  $\theta_i$  is the characteristic vibrational temperature  $h\nu_i/k_B$ . The rotational partition function  $q_{\text{rot}}$  in eqn. (5) has the well known standard forms for linear ( $n = 1$ ), symmetric-top ( $n = \frac{3}{2}$ ) and asymmetric-top molecules ( $n = \frac{3}{2}$ ).

The second step is to calculate the standard enthalpy

$\Delta H_m^\ominus(T)$  for reaction (1) according to eqn. (6)

$$\Delta H_m^\ominus(T) = -D_0 - \frac{7}{2}RT + \Delta H_{m, \text{vib}}^\ominus(T) \quad (6)$$

where

$$\Delta H_{m, \text{vib}}^\ominus(T) = \sum_M \nu_M H_{\text{vib}}^\ominus(T, M) \quad (7)$$

and

$$H_{\text{vib}}^\ominus(T, M) = R \sum_i g_i \theta_i \exp(-\theta_i/T) [1 - \exp(-\theta_i/T)]^{-1} \quad (8)$$

In the above, the rigid rotor-harmonic oscillator approximation is in use except in two cases. For  $q_{\text{rot}}$  in eqn. (5) the classical integrated expression is sufficient except in the case of HF where direct examination of summation over the rotational states shows a negligible effect in the calculation of  $S^\ominus(T, \text{HF})$  but contributes a just significant effect in the estimation of  $\Delta H_m^\ominus(T)$  [*i.e.* to the term approximated by  $\frac{7}{2}RT$  in eqn. (6)] and has been allowed for throughout. The harmonic approximation fails for the out-of-plane hydrogen-bond bending mode  $\nu_{\beta(o)}$  of H<sub>2</sub>O...HF since this mode is governed by a low-barrier, double-minimum potential-energy function. The contribution of this mode is considered explicitly in section 4. In all evaluations of  $D_0$  and  $S^\ominus(T)$ , the perfect-gas approximation is used.

**Table 3** Observed dissociation energies  $D_0$  for dimers B...HF, where B = HCN, CH<sub>3</sub>CN, HC<sub>2</sub>CN, (CH<sub>3</sub>)<sub>3</sub>CCN and H<sub>2</sub>O

B...F	$D_0/\text{kJ mol}^{-1}$
HCN	18.9 (11) <sup>a</sup>
CH <sub>3</sub> CN	26.1 (6) <sup>b</sup>
HC <sub>2</sub> CN	20.4 (7) <sup>b</sup>
(CH <sub>3</sub> ) <sub>3</sub> CCN	28.5 (7) <sup>c</sup>
H <sub>2</sub> O	34.3 (3) <sup>d</sup>

<sup>a</sup> Ref. (30). <sup>b</sup> Ref. (34). <sup>c</sup> Ref. (35). <sup>d</sup> Ref. (36).

## 4. Results

The detailed results of calculations for HCN...HF are set out below as an example while those for CH<sub>3</sub>CN...HF, HC<sub>2</sub>CN...HF, (CH<sub>3</sub>)<sub>3</sub>CCN...HF and H<sub>2</sub>O...HF are briefly summarized in separate sections.

**Table 4** Contribution from the various degrees of freedom to the individual entropies ( $\text{J K}^{-1} \text{mol}^{-1}$ ) and to the standard molar entropy change for reaction (1) at different temperatures

calculated entropy	M			$\sum_{\mathbf{M}} \nu_{\mathbf{M}} S^{\ominus}(T, \mathbf{M})$
	HCN	HF	HCN $\cdots$ HF	
T = 150 K				
$S_{\text{trans}}^{\ominus}(T, \mathbf{M})$	135.57	131.83	142.49	− 124.92
$S_{\text{rot}}^{\ominus}(T, \mathbf{M})$	43.70	21.81	64.59	− 0.70
$S_{\text{vib}}^{\ominus}(T, \mathbf{M})$	0.14	$< 10^{-14}$	28.60	28.46
$S^{\ominus}(T, \mathbf{M})$	179.41	153.64	235.68	− 97.37
T = 230 K				
$S_{\text{trans}}^{\ominus}(T, \mathbf{M})$	144.46	140.71	151.37	− 133.80
$S_{\text{rot}}^{\ominus}(T, \mathbf{M})$	47.25	25.37	68.15	− 4.25
$S_{\text{vib}}^{\ominus}(T, \mathbf{M})$	1.07	$< 10^{-8}$	41.36	40.29
$S^{\ominus}(T, \mathbf{M})$	192.78	166.08	260.88	− 97.98
T = 298.15 K				
$S_{\text{trans}}^{\ominus}(T, \mathbf{M})$	149.85	146.11	156.76	− 139.20
$S_{\text{rot}}^{\ominus}(T, \mathbf{M})$	49.41	27.52	70.30	− 6.41
$S_{\text{vib}}^{\ominus}(T, \mathbf{M})$	2.45	$< 10^{-6}$	51.07	48.62
$S^{\ominus}(T, \mathbf{M})$	201.71	173.63	278.14	− 97.21

#### 4.1 HCN...HF

We begin by considering the translational, rotational and vibrational contributions to the entropy change  $\Delta S_m^\ominus$  for reaction (1) when  $B = \text{HCN}$ . These contributions have been calculated using eqn. (3)–(5) and the spectroscopic quantities in Table 1 and 2. The results are set out in Table 4. It is clear that  $\Delta S_m^\ominus$  is almost independent of temperature in the range  $T = 150$ – $298.15 \text{ K}$ . The major contribution is seen to arise

**Table 5** Values of  $\Delta H_m^\ominus(T)$ ,  $\Delta S_m^\ominus(T)$ ,  $\Delta G_m^\ominus(T)$  and  $K^\ominus(T)$  for reaction (1) when  $B = \text{HCN}$ 

$T/\text{K}$	$\Delta H_m^\ominus(T)$ /kJ mol $^{-1}$	$\Delta S_m^\ominus(T)$ /J K $^{-1}$ mol $^{-1}$	$\Delta G_m^\ominus(T)$ /kJ mol $^{-1}$	$K^\ominus(T)^a$
150	-20.90	-97.37	-6.29	160 (130)
170	-20.97	-97.79	-4.34	22 (16)
190	-21.00	-98.00	-2.38	4.5 (29)
210	-21.01	-98.05	-0.42	1.3 (7)
230	-21.00	-97.98	1.54	0.45 (23)
250	-20.96	-97.82	3.50	0.19 (9)
273.15	-20.89	-97.56	5.76	0.08 (4)
298.15	-20.79	-97.21	8.19	0.037 (15)

<sup>a</sup> The error in  $K^\ominus(T)$  has been obtained from  $dK^\ominus/d(\Delta H^\ominus) \approx -K^\ominus/RT$ . The error in  $\Delta H^\ominus$  follows from the error in  $D_0$  in Table 3 and is a little too large to be allowed for precisely by the linear term in the differentiation but nevertheless gives a satisfactory approximation for the error transmitted to  $K^\ominus$ . Although  $K^\ominus(T)$  is not well determined its order of magnitude is established.

**Table 6** Values of  $\Delta H_m^\ominus(T)$ ,  $\Delta S_m^\ominus(T)$ ,  $\Delta G_m^\ominus(T)$  and  $K^\ominus(T)$  at  $T = 298.15 \text{ K}$  for reaction (1) when  $B = \text{HCN}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{HC}_2\text{CN}$ ,  $(\text{CH}_3)_3\text{CCN}$  and  $\text{H}_2\text{O}$ 

B	$\Delta H_m^\ominus(T)$ /kJ mol $^{-1}$	$\Delta S_m^\ominus(T)$ /mol $^{-1}$	$\Delta G_m^\ominus(T)$ /kJ mol $^{-1}$	$K^\ominus(T)$
HCN	-20.8 (11)	-97.21	8.2 (10)	0.04 (2)
$\text{CH}_3\text{CN}$	-28.8 (6)	-99.57	0.9 (5)	0.7 (1)
$\text{HC}_2\text{CN}$	-21.7 (7)	-93.44	6.2 (5)	0.08 (2)
$(\text{CH}_3)_3\text{CCN}$	-30.4 (7)	-108.76	2.1 (5)	0.4 (1)
$\text{H}_2\text{O}$	-39.1 (3)	-94.42	-11.0 (5)	84 (18)

from the loss of three degrees of translational freedom on formation of  $\text{HCN} \cdots \text{HF}$  from HCN and HF. The loss of rotational degrees of freedom, on the other hand, contributes relatively little. The concomitant increase in the number of vibrational degrees of freedom provides some compensation but leaves the value of  $\Delta S_m^\ominus$  at  $97.5 \pm 0.5 \text{ J K}^{-1} \text{mol}^{-1}$ . The reason for the effective lack of dependence of  $\Delta S_m^\ominus$  on  $T$  lies in a cancellation between the sum of the temperature coefficients of the contributions from translation and rotation on the one hand and the equal and opposite value of the coefficient of the vibrational contribution on the other. Thus we find  $d\Delta S_{\text{trans}}^\ominus/d \ln T = -20.84 \text{ J K}^{-1} \text{mol}^{-1}$  which is close to  $-\frac{5}{2}R$  [as expected from eqn. (3)] and  $d\Delta S_{\text{rot}}^\ominus/d \ln T = -8.35 \text{ J K}^{-1} \text{mol}^{-1} \approx -R$ , as required by eqn. (5) while  $d\Delta S_{\text{vib}}^\ominus/d \ln T = 19.03 \text{ J K}^{-1} \text{mol}^{-1}$ , which is noted to be almost  $\frac{7}{2}R$ . Although the temperature dependences of both  $\Delta S_{\text{trans}}^\ominus$  and  $\Delta S_{\text{rot}}^\ominus$  can be obtained in a reasonably direct manner from eqn. (3) and (5) the temperature dependence of  $\Delta S_{\text{vib}}^\ominus$  requires a more detailed examination of the relevant equations. We begin by recognising from eqn. (4) that to a good approximation we may write

$$\Delta S_{\text{vib}}^\ominus = \sum_j S_j^\ominus = R \sum_j g_j \{ \theta_j/T \exp(-\theta_j/T) \times [1 - \exp(-\theta_j/T)]^{-1} - \ln[1 - \exp(-\theta_j/T)] \} \quad (9)$$

where the sum over  $j$  indicates the sum over the intermolecular modes  $\nu_\beta$ ,  $\nu_\sigma$  and  $\nu_B$ . This equation would be exact if the vibrational wavenumbers of the modes of the monomers B and HF remained unchanged on dimer formation. A check on  $\text{HCN} \cdots \text{HF}$ , for which the wavenumbers of all the dimer modes are known from infrared spectroscopy, shows that the wavenumbers of the HCN monomer modes change by the following percentages:  $\bar{\nu}_1 = 3311.5$  (0.03%),  $\bar{\nu}_2 = 2096.9$  (1.2%),  $\bar{\nu}_3 = 712.0$  (2%). Although for HF the wavenumber of the stretching mode changes by 10% on dimer formation ( $\bar{\nu} = 3716 \text{ cm}^{-1}$  for the dimer), this mode makes a contribution to the entropy for both monomer and dimer which is entirely negligible. Thus eqn. (9) is seen to be a good approximation and it seems likely that this will be the case for dimer formation generally.

As the next step we note that it is readily shown from eqn. (4) that the contribution  $S_j^\ominus$  of the  $j$ th mode to  $\Delta S_{\text{vib}}^\ominus$  in eqn. (9) has a temperature dependence given by

$$dS_j^\ominus/d \ln T = R g_j \{ (\theta_j/T)^2 \exp(\theta_j/T) [\exp(\theta_j/T) - 1]^{-2} \} \quad (10)$$

With some simplification, the required temperature dependence of  $\Delta S_{\text{vib}}^\ominus$  is given by

$$d\Delta S_{\text{vib}}^\ominus/d \ln T = \frac{1}{2}R \sum_j g_j \{ (\theta_j/T)^2 [\cosh(\theta_j/T) - 1]^{-1} \} \quad (11)$$

For  $\text{HCN} \cdots \text{HF}$  the contributions of  $\nu_\beta$ ,  $\nu_\sigma$  and  $\nu_B$  are calculated at the mid-temperature point of  $210 \text{ K}$  to be  $1.956R$ ,  $0.897R$  and  $0.688R$ , respectively, leading to  $3.54R$ , which approximately cancels the effect of translation and rotation, namely  $-\frac{7}{2}R$ . It seems likely that this will generally be the case.

Values of  $\Delta H_m^\ominus(T)$  for reaction (1) with  $B = \text{HCN}$  have been calculated according to eqn. (6) for temperatures in the range  $150$ – $298.15 \text{ K}$  by using the spectroscopic quantities in Tables 1–3. The results are given in Table 5 in which  $\Delta S_m^\ominus(T)$  is also included for convenience. The calculated values of  $\Delta G_m^\ominus(T)$  and  $K^\ominus(T)$  in columns 4 and 5 of Table 5 then follow immediately. It is at once evident from Table 5 that  $\Delta H_m^\ominus$ , as well as  $\Delta S_m^\ominus$ , for reaction (1) ( $B = \text{HCN}$ ) is to a high

**Table 7** Contributions of individual vibrational energy levels associated with the mode  $\nu_{\beta(o)}$  to the vibrational partition function of  $\text{H}_2\text{O} \cdots \text{HF}$ 

$\nu_{\beta(o)}$	$(E_v - E)/\text{cm}^{-1}$	$\exp\{-(E_v - E_0)/k_B T\}$
0	0.00	1.0000
1	70.00	0.71330
2	260.90	0.28376
3	470.00	0.10309
4	716.83	0.03140
5	989.48	0.008419
6	1190.17	0.00320
7	1540.17	0.00059
8	1940.17	0.00009

degree of approximation independent of temperature. Thus we can write  $\ln K^\ominus \approx a/T + b$ , where  $a$  and  $b$  are constants.

#### 4.2 $\text{CH}_3\text{CN} \cdots \text{HF}$ , $\text{HC}_2\text{CN} \cdots \text{HF}$ and $(\text{CH}_3)_3\text{CCN} \cdots \text{HF}$

Similar calculations have been carried out for  $\text{CH}_3\text{CN} \cdots \text{HF}$ ,  $\text{HC}_2\text{CN} \cdots \text{HF}$  and  $(\text{CH}_3)_3\text{CCN} \cdots \text{HF}$ , but we quote here only the results for  $T = 298.15$  K. Values for  $\Delta H_m^\ominus(298.15 \text{ K})$ ,  $\Delta S_m^\ominus(298.15 \text{ K})$ ,  $\Delta G_m^\ominus(298.15 \text{ K})$  and  $K^\ominus(298.15 \text{ K})$  for reaction 1 when  $B = \text{CH}_3\text{CN}$ ,  $\text{HC}_2\text{CN}$  and  $(\text{CH}_3)_3\text{CCN}$  are therefore shown in Table 6. The required spectroscopic quantities are those in Tables 1–3. When using eqn. (5) for  $B = \text{CH}_3\text{CN}$  and  $(\text{CH}_3)_3\text{CCN}$  the rotational partition function includes nuclear spin statistical weight factors  $g_{I,J}$ , which are conveniently allowed for in the usual way by employing a symmetry number  $\sigma$ . For  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CN} \cdots \text{HF}$  the appropriate value is  $\sigma = 3$ , but for  $(\text{CH}_3)_3\text{CCN}$  and  $(\text{CH}_3)_3\text{CCN} \cdots \text{HF}$  the value  $\sigma = 81$  was used.<sup>37</sup>

#### 4.3 $\text{H}_2\text{O} \cdots \text{HF}$

The calculations for reaction (1) in the case  $B = \text{H}_2\text{O}$  were similar to those described above except in two details. First, the rotational partition function  $q_{\text{rot}}$  appropriate to an asymmetric-rotor molecule was used and, secondly, the serious anharmonicity of the low-frequency, out-of-plane bending mode  $\nu_{\beta(o)}$  in  $\text{H}_2\text{O} \cdots \text{HF}$  required a separate treatment. Thus, the contribution of this mode to the vibrational partition function was evaluated numerically. The first step in the procedure was to evaluate the eigenvalues<sup>38</sup> for a one-dimensional oscillator governed by the potential-energy function  $V(z)/\text{cm}^{-1} = 64.31(z^4 - 2.80z^2)$  determined experiment-

ally<sup>39</sup> for  $\text{H}_2\text{O} \cdots \text{HF}$ . The sum  $\sum_v \exp\{-(E_v - E_0)/k_B T\}$  for the first eight levels was evaluated as 2.1438 at  $T = 298.15$  K, with contributions from the individual levels as shown in Table 7. Similar summations were carried out over a range of temperatures and the quantity  $d \ln q^N/dT = 4.497 \text{ K}^{-1}$  obtained at  $T = 298.15$  K by numerical differentiation. The contribution of the mode in question to the vibrational entropy is then just  $k_B \ln q^N + k_B T d \ln q^N/dT$ .

### 5. Discussion

In this paper we have presented various thermodynamic quantities for the components  $B$ ,  $\text{HX}$  and  $B \cdots \text{HX}$  and for the reaction (1). The standard molar entropies  $S^\ominus(T, M)$  for  $M = B$ ,  $\text{HX}$  and  $B \cdots \text{HX}$  are well determined. The values in Table 4 for  $\text{HCN} \cdots \text{HF}$  show that the major contributions to  $S^\ominus(T, B \cdots \text{HX})$  arise from translation and rotation, with that from vibration being significantly smaller. This means that fortunately the wavenumbers of the fundamental vibrations of  $B \cdots \text{HF}$  do not need to be known with high accuracy. In fact, for  $\text{HCN} \cdots \text{HF}$  all such wavenumbers have been measured with high precision<sup>25–27</sup> and in this case  $S_{\text{vib}}^\ominus(T, B \cdots \text{HX})$  is established as well as for any molecule with low wavenumber vibrations. Indeed, it has also been shown<sup>40</sup> that the use of the harmonic oscillator approximation does not affect significantly the values of the thermodynamic function of  $\text{HCN} \cdots \text{HF}$ . For the other dimers discussed here, the lower wavenumber fundamentals  $\nu_\beta$  have been determined from vibrational satellites in the rotational spectrum by relative intensity measurements and the wavenumbers of  $\nu_\alpha$  from centrifugal distortion constants, but the larger errors thereby incurred do not affect seriously the  $S_{\text{vib}}^\ominus(T, B \cdots \text{HX})$  values. Even in the most serious case of  $(\text{CH}_3)_3\text{CCN} \cdots \text{HF}$  an assumed error as large as  $10 \text{ cm}^{-1}$  in the lowest-wavenumber mode  $\bar{\nu}_\beta$  leads to a change of  $< 1\%$  in  $S^\ominus(T, B \cdots \text{HF})$ . The value of  $\Delta S_m^\ominus(298.15 \text{ K})$  that we obtain for reaction (1) when  $B = \text{HCN}$  is consistent with an earlier estimate<sup>41</sup> of  $-95 \text{ J K}^{-1} \text{ mol}^{-1}$ .

The standard molar enthalpy  $\Delta H_m^\ominus(T)$  for reaction (1) is in general less well known than  $\Delta S_m^\ominus(T)$  as a result of the error in the experimental measurement of  $D_0$  which relies on absolute intensity measurements of rotational transitions. The effects of the errors in  $D_0$  lead to those in  $\Delta H_m^\ominus(T)$ ,  $\Delta G_m^\ominus(T)$  and  $K^\ominus(T)$  shown in Table 6 for reaction (1) when  $B = \text{HCN}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{HC}_2\text{CN}$ ,  $(\text{CH}_3)_3\text{CCN}$  and  $\text{H}_2\text{O}$  but fortunately even  $K^\ominus(T)$  is still usefully determined. We note that at room temperature (298.15 K)  $\Delta G_m^\ominus(T)$  is positive (and therefore  $K^\ominus < 1$ ) in all cases except for  $B = \text{H}_2\text{O}$ . This is consistent with our experience that the only dimer we have been able to observe through its rotational spectrum in an equilibrium gas mixture at room temperature is  $\text{H}_2\text{O} \cdots \text{HF}$ . We estimate, for example, that when  $T = 298.15$  K and with initial partial pressures  $p_{\text{H}_2\text{O}} = p_{\text{HF}} \approx 1$  Torr there is a 10% conversion to

**Table 8** Standard thermodynamic functions at  $T = 298.15$  K and  $p^\ominus = 101325$  Pa for  $B \cdots \text{HF}$  in the perfect-gas approximation, where  $B = \text{HCN}$ ,  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$ 

B	$\Delta H_m^\ominus/\text{kJ mol}^{-1}$	$\Delta_f H_m^\ominus(B)/\text{kJ mol}^{-1}$ <sup>a</sup>	$\Delta_f H_m^\ominus(B \cdots \text{HF})/\text{kJ mol}^{-1}$ <sup>b</sup>	$S_m^\ominus(B \cdots \text{HF})/\text{J K}^{-1} \text{ mol}^{-1}$
HCN	-20.8 (11)	135.14	-158.2 (11)	278.1
$\text{CH}_3\text{CN}$	-28.8 (6)	74.04	-227.3 (6)	317.4
$\text{H}_2\text{O}$	-39.1 (3)	-241.82	-553.5 (3)	267.6

<sup>a</sup> T. E. Daubert and R. P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*, Taylor and Francis, London, 1990. <sup>b</sup> In the calculation of  $\Delta_f H_m^\ominus(B \cdots \text{HF})$  the value  $\Delta_f H_m^\ominus(\text{HF}) = -272.55 \text{ kJ mol}^{-1}$  has been taken from M. W. Chase, J. L. Curnutt, J. R. Downey, R. A. McDonald, A. N. Syverud and E. A. Valenzuela, *JANAF Thermochemical Tables*, 1982 Suppl., *J. Phys. Chem. Ref. Data*, 1982, **11**, 695.

$\text{H}_2\text{O} \cdots \text{HF}$ . When  $p_{\text{H}_2\text{O}} = p_{\text{HF}} = 100$  mTorr (as is typical in experiments on  $\text{B} \cdots \text{HF}$  using rotational spectroscopy) the extent of conversion is still 1% while under the same conditions for  $\text{B} = \text{HCN}$  only  $5 \times 10^{-4}\%$  of dimer is present at equilibrium. Even when  $T$  is reduced to 170 K for the same initial partial pressures this figure increases only to 0.3%. Nevertheless the systems having  $\text{B} = \text{HCN}$  and  $\text{CH}_3\text{CN}$  have an inherent spectral simplicity and intensity which gives them distinct advantages from the standpoint of detection.<sup>42</sup>

Finally, we tabulate standard thermodynamic functions for the dimer  $\text{B} \cdots \text{HF}$  at  $T = 298.15$  K for  $\text{B} = \text{HCN}$ ,  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  (Table 8).

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