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Citation: *The Journal of Chemical Physics* **73**, 2773 (1980); doi: 10.1063/1.440445

View online: <http://dx.doi.org/10.1063/1.440445>

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# Vibrational energy transfer between HCN and DCN and hydrogen and deuterium halides<sup>a)</sup>

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(Received 7 May 1980; accepted 27 May 1980)

Using the technique of laser-induced infrared fluorescence, rate constants have been determined for the relaxation at room temperature,  $(297 \pm 3)$  K, of: (a)  $\text{HCl}(v=1)$  and  $\text{HBr}(v=1)$  by HCN and DCN, and (b)  $\text{HCN}(001)$  by  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{DCI}$ ,  $\text{DBr}$ , and  $\text{DCN}$ . Vibrational-to-vibrational ( $V-V$ ) energy exchange between the H-C (or D-C) stretching mode in HCN (or DCN) and the diatomic's vibrational mode is not the major channel by which energy is transferred. The results are examined in terms of the formation of hydrogen-bonded collision complexes in which there is only a restricted transfer of energy from the excited high frequency mode to other degrees of freedom in the complex.

## I. INTRODUCTION

Despite extensive studies in recent years of vibrational relaxation of hydrogen halides,<sup>1</sup> it is still not entirely clear to what extent, or by what mechanism, hydrogen bonds can facilitate the transfer of vibrational energy in molecular collisions. This paper deals with vibrational relaxation in systems containing HCN (or DCN), which is the simplest polyatomic molecule capable of forming strong hydrogen bonds.<sup>2</sup> Moreover, its  $\nu_3$  mode is highly localized, with the H atom vibrating against the CN group at a frequency ( $\approx 3311.5 \text{ cm}^{-1}$ ) similar to those of the fundamental modes of the hydrogen halides. In these properties, HCN can be regarded as a "pseudo hydrogen halide." On the other hand, it is polyatomic, and molecules excited in the  $\nu_3$  mode can be transferred to levels associated with the other modes. In addition, the moment of inertia of HCN is much larger than those of the hydrogen halides, making it less likely to absorb large amounts of energy as molecular rotation during collisional energy transfer.

The results of two series of experiments are reported here. In the first, we studied the relaxation of  $\text{HX}(v=1)$ — $\text{X}=\text{Cl}$ ,  $\text{Br}$ —by HCN and DCN; in the second, the relaxation of  $\text{HCN}(001)$  by DCN,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{DCI}$ , and  $\text{DBr}$ . In both, the rates of removal of the excited species were determined by observing their time-resolved infrared fluorescence following pulsed laser excitation. Conventional, discharge-initiated, chemical lasers could be used to prepare  $\text{HX}(v=1)$ . To excite HCN *directly*, a tunable infrared source is required. A powerful angle-tuned optical parametric oscillator (OPO) was employed, of a type<sup>3</sup> which has been previously used only rarely.<sup>4</sup>

In all the systems which have been investigated, relaxation is quite rapid [collisional probabilities vary from  $1.1 \times 10^{-2}$  for  $\text{HCl}(v=1) + \text{DCN}$  to  $6.9 \times 10^{-4}$  for  $\text{HCN}(001) + \text{DCI}$  and  $\text{HCN}(001) + \text{DBr}$ ] and near-resonant vibrational-to-vibrational ( $V-V$ ) energy exchange is not

a major channel. It therefore seems likely that energy transfer is promoted by the existence of hydrogen bonds between the collision partners. This possibility is examined by estimating the rates of association and dissociation of hydrogen-bonded complexes using the approximate models developed for such processes by Quack and Troe.<sup>5,6</sup>

## II. EXPERIMENTAL

The apparatus and experimental method for measuring the relaxation rates of  $\text{HX}(v=1)$  were similar to those previously used<sup>7,8</sup> in this laboratory. Mixtures of  $\text{HX}$  and HCN or DCN diluted in argon were admitted to a fluorescence cell which was 3 cm in diameter and 15 cm long. This cell was constructed of Pyrex with two  $\text{CaF}_2$  end-windows through which radiation from a pulsed-discharge hydrogen halide laser passed. Precautions, including the use of greaseless stopcocks, were taken to ensure that there was no significant adsorption of HCN. Infrared fluorescence was observed normal to the laser beam through a 2.5 cm diameter  $\text{CaF}_2$  window. A 1 cm long "cold gas" filter cell was mounted between the observation window and the liquid- $\text{N}_2$  cooled semiconductor detector (InSb, Mullard Ltd., ORP 13, or InAs, Barnes Engineering, Ltd.). Fluorescence signals were stored on a transient digitizer (Data Laboratories, DL905), and recorded either on punched paper tape or on a chart recorder.

The same general method was used to study the kinetics of  $\text{HCN}(001)$ . However, in these experiments, the source of radiation was a lithium niobate optical parametric oscillator pumped by the fundamental output of a Nd:YAG oscillator-amplifier laser. This system is based on the design of Wyatt *et al.*<sup>3</sup> and was constructed by JK Lasers, Ltd. The Nd:YAG oscillator consists of a 3 in.  $\times$  0.25 in. rod, with ends cut normal to the laser axis, mounted in a stable plano-concave resonator. It is Q-switched with a KD\*P Pockel cell. A mode-selecting aperture causes the laser to operate at  $\text{TEM}_{00}$ , while a temperature stabilized intracavity étalon limits the output linewidth to approximately  $0.1 \text{ cm}^{-1}$ . A two lens telescope expands the oscillator beam three times before it enters the 4 in.  $\times$  0.25 in. amplifier rod which has a gain of about 4. The system typically produces 85 mJ pulses of 10 ns duration at a repetition rate of 20 Hz.

<sup>a)</sup>Research supported by the U.S. AFOSR under Grant number 77-3240 and by the Science Research Council.

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The 1.06  $\mu\text{m}$  beam from the Nd:YAG laser is folded through two right angles and, after passing through a Faraday isolator, is coupled by means of a dichroic mirror into the OPO cavity. The  $1 \times 5$  cm cylindrical LiNbO<sub>3</sub> rod is mounted in a temperature stabilized oven (303 K) within a cavity formed by a gold-coated diffraction grating and a concave mirror, which is transparent to the pump beam. This mirror is backed by a second mirror which transmits the frequencies generated by the OPO, but reflects radiation at 1.06  $\mu\text{m}$ , thereby effecting double pass pumping of the LiNbO<sub>3</sub> crystal. The output frequencies are selected by adjusting the grating, the angle of the crystal, and the angle of an intracavity étalon. The OPO delivers 1–4 mJ per pulse at wavelengths between 1.5 and 3.5  $\mu\text{m}$ ,<sup>9</sup> with two narrow dips where idler photons are absorbed near 2.7  $\mu\text{m}$  by OH groups present in the crystal. The OPO was tuned into resonance with a line of the HCN(001, 000) band with the aid of a simple spectrophone.<sup>10</sup>

Radiation from the OPO passed through an iris and into the fluorescence cell without focusing. The cell was made from a 20 cm length of 2 cm diameter Pyrex tubing, with CaF<sub>2</sub> end-windows mounted at Brewster's angle, and a Pyrex jacket through which water was circulated to keep the temperature constant. Infrared fluorescence, viewed normal to the laser beam through a 2 cm CaF<sub>2</sub> window, was collected by a 25 mm diameter, 50 mm focal length, CaF<sub>2</sub> lens and was focused onto the liquid-N<sub>2</sub> cooled InAs detector with a second identical lens. The detector was equipped with a filter (Grubb-Parsons Ltd.) which only passes radiation of wavelengths  $> 2.4$   $\mu\text{m}$ . The collection system reduced any signal from scattered laser light to a negligible level and also allowed a cold gas filter cell to be used without changing the position of the detector.

Amplified fluorescence signals were digitized in a transient recorder (Data Laboratories, DL905) and accumulated in a signal averager (Data Laboratories, System 4000). Although the scattered laser radiation was negligible, noise generated by the Q-switch of the Nd:YAG laser was not. This unwanted background was subtracted out by averaging equal numbers of shots (typically, 2048 each way) with and without the OPO beam present in the fluorescence cell.

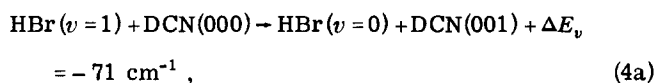
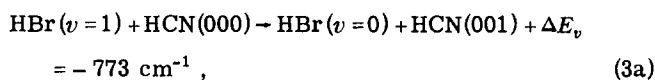
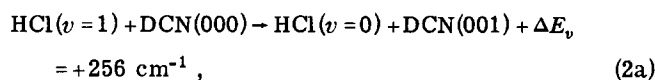
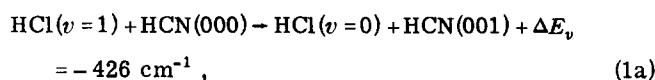
HCN and DCN were prepared by the reaction of NaCN with H<sub>2</sub>SO<sub>4</sub> and D<sub>2</sub>SO<sub>4</sub> (Merck, Sharpe and Dohme, Ltd.).<sup>11</sup> The product was purified by trap-to-trap distillation from 246 K to 77 K and thoroughly degassed at 77 K. Mass and infrared spectra of DCN indicated an isotopic purity of 90%. Since the rates of relaxation by HCN and DCN were found to be rather similar, higher isotopic purity was unnecessary. No other significant impurities were found. The preparation and handling of the other gases has been described previously.<sup>7,10</sup> Pressures were measured with a capacitance manometer.

### III. RESULTS

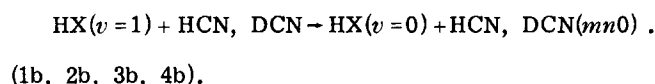
#### A. Deactivation of HCl( $v=1$ ) and HBr( $v=1$ ) by HCN and DCN

When considering the results of experiments on these four systems, it is convenient to distinguish between (a)

near-resonant  $V-V$  energy exchange causing excitation of the  $\nu_3$  mode in the triatomic molecule, i.e.,

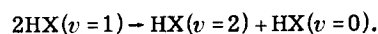


and (b) other processes, which may involve promotion of HCN or DCN to levels associated with their other modes, i.e.,



Only the fundamental (001, 000) emission from HCN or DCN has both the strength and the frequency to contribute to the overall fluorescence signals. In practice, several pieces of evidence show clearly that any pathway producing HCN(001) or DCN(001) is, at most, a minor channel in all the systems studied. [As well as Processes (1a)–(4a), other  $V-V$  energy exchange processes such as  $\text{HBr}(v=1) + \text{HCN}(010) \rightarrow \text{HBr}(v=0) + \text{HCN}(001) - 41 \text{ cm}^{-1}$  are excluded.] First, there is the observation that all the fluorescence signals decayed as *single* exponentials. There was no sign of the type of *double* exponential decay which is characteristic of systems which relax by near-resonant intermolecular  $V-V$  exchange followed by slower vibrational-to-rotational translational ( $V-R$ ,  $T$ ) energy transfer processes involving either or both of the excited species in the coupled system. Although quite rapid,<sup>10,12</sup> the self-relaxation of HCN(001) is not fast enough to explain the absence of double exponential kinetics. Furthermore, HCN(001) is relaxed less rapidly by HCl and HBr (see below) than  $\text{HCl}(v=1)$  and  $\text{HBr}(v=1)$  are relaxed by HCN. Straight-forward calculations based on the principle of detailed balance demonstrate unequivocally that the endothermic processes (1a) and (3a) must be of minor importance in the relaxations of  $\text{HCl}(v=1)$  and  $\text{HBr}(v=1)$  by HCN.

To confirm that the  $V-V$  pathways (1a) to (4a) make only slight contributions to the measured rates of relaxation, experiments were performed with cold gas filters in place. With 30 Torr of HCN or DCN in the filter cell, there was no change in the fluorescence signals. On the other hand, filling it with 30 Torr of the appropriate hydrogen halide reduced the signals to  $\sim 5\%$  of their original value. This small signal remained when HCN, as well as HX, was admitted to the filter cell, and when HX was excited in the absence of HCN or DCN. It corresponds to the fluorescence from  $\text{HX}(v=2)$  formed in the process



The intensity was quite consistent with earlier estimates<sup>7</sup> of the fraction of HX which is excited in our experiments.

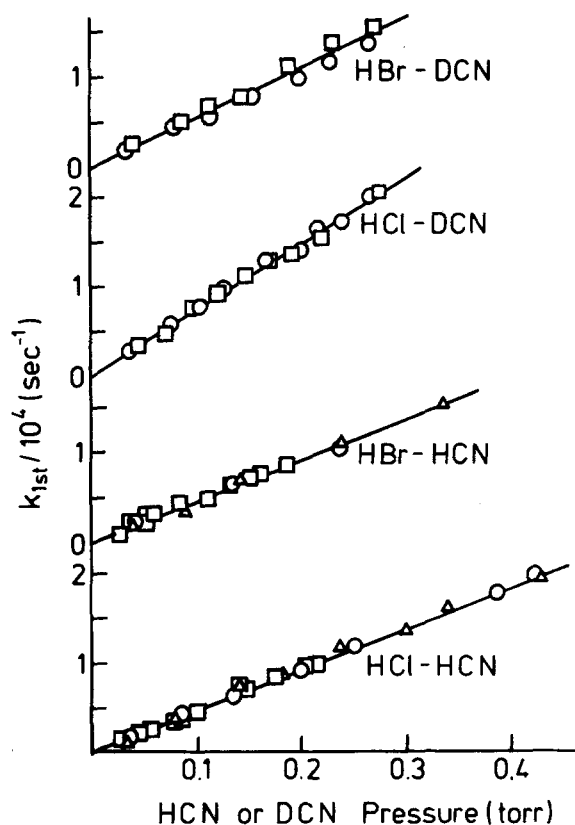


FIG. 1. Difference between first-order decay constants for  $\text{HCl}(v=1)$  and  $\text{HBr}(v=1)$  fluorescence with and without HCN or DCN present, plotted against HCN or DCN partial pressure. Experimental conditions: (i)  $\text{HCl-HCN}$ :  $\circ$ , 0.15 Torr HCl;  $\Delta$ , 0.24 Torr HCl;  $\square$ , 0.36 Torr HCl; (ii)  $\text{HBr-HCN}$ :  $\circ$ , 0.26 Torr HBr;  $\Delta$ , 0.35 Torr HBr;  $\square$ , 0.41 Torr HBr; (iii)  $\text{HCl-DCN}$ :  $\circ$ , 0.15 Torr HCl;  $\Delta$ , 0.24 Torr HCl; (iv)  $\text{HBr-DCN}$ :  $\circ$ , 0.25 Torr HBr;  $\square$ , 0.34 Torr HBr. Gas mixtures were diluted in Ar to a total pressure of between 4 and 12 Torr.

By replacing the InSb detector by the InAs detector, which is roughly 40 times more sensitive at  $3.05 \mu\text{m}$ , it was just possible to detect emission from  $\text{HCN}(001)$  in  $\text{HCl/HCN}$  mixtures. However, these signals were very weak and this observation in no way conflicts with the

conclusion that (1a) is only a minor pathway for relaxation of  $\text{HCl}(v=1)$  by HCN.

The results of our experiments are summarized in Fig. 1 and Table I. The actual measurements were carried out in pairs yielding first-order rate constants for decay of the fluorescence from an  $\text{HX/HCN}$ , DCN mixture ( $k_{1st}$ ) and from a mixture containing the same partial pressure of HX but no HCN or DCN ( $k_{1st}^0$ ). The dependence of the difference between these rate constants, i.e.,  $k'_{1st} = (k_{1st} - k_{1st}^0)$ , on the partial pressure of HCN or DCN is shown in Fig. 1. The second-order rate constants presented in Table I were obtained by linear least-squares-fits: the quoted errors correspond to two standard errors in the calculated slopes.<sup>13</sup>

#### B. Deactivation of $\text{HCN}(001)$ by $\text{HCl}$ , $\text{HBr}$ , $\text{DCI}$ , or $\text{DBr}$ and DCN

In these five systems, the  $\text{HCN}(001, 000)$  fluorescence was observed with the InAs detector. Its response falls steeply beyond  $\sim 3.3 \mu\text{m}$ , so it was insensitive to emissions from the hydrogen halides, DCN, or other levels of HCN. Decay of the  $\text{HCN}(001)$  fluorescence corresponded to a single exponential in every case. The measured decay rates are for deactivation by the following processes:

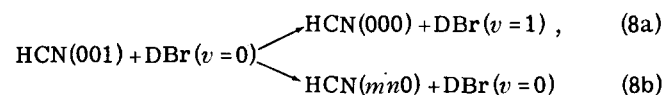
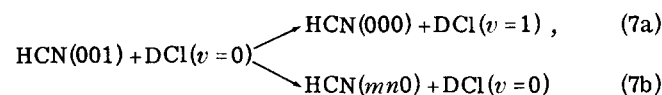
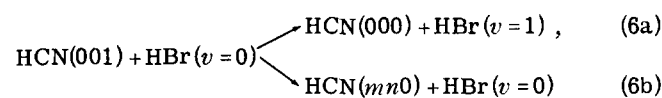
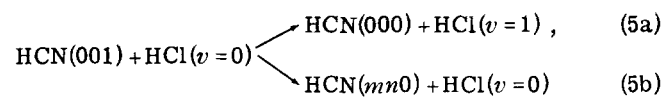
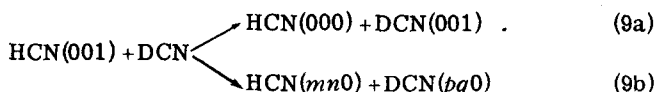


TABLE I. Rate constants for the deactivation of  $\text{HX}(1)$  at  $(296 \pm 2)$  K.

Process	$k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	Probability <sup>a</sup>	Reference
$\text{HF}(1) + \text{HCN}(000) \rightarrow \text{HF}(0) + \text{HCN}(001) \}$ $\rightarrow \text{HF}(0) + \text{HCN}(mn0) \}$	$(5.3 \pm 1.2) \times 10^{-12}$	$2.1 \times 10^{-2}$	12
$\text{DF}(1) + \text{HCN}(000) \rightarrow \text{DF}(0) + \text{HCN}(001) \}$ $\rightarrow \text{DF}(0) + \text{HCN}(mn0) \}$	$(3.3^{+0.4}_{-0.5}) \times 10^{-12}$	$1.6 \times 10^{-2}$	12
$\text{HCl}(1) + \text{HCN}(000) \rightarrow \text{HCl}(0) + \text{HCN}(001) \}$ $\rightarrow \text{HCl}(0) + \text{HCN}(mn0) \}$	$(1.43 \pm 0.04) \times 10^{-12}$	$7.0 \times 10^{-3}$	This work
$\text{HCl}(1) + \text{DCN}(000) \rightarrow \text{HCl}(0) + \text{DCN}(001) \}$ $\rightarrow \text{HCl}(0) + \text{DCN}(mn0) \}$	$(2.22 \pm 0.12) \times 10^{-12}$	$1.1 \times 10^{-2}$	This work
$\text{HBr}(1) + \text{HCN}(000) \rightarrow \text{HBr}(0) + \text{HCN}(001) \}$ $\rightarrow \text{HBr}(0) + \text{HCN}(mn0) \}$	$(1.40 \pm 0.06) \times 10^{-12}$	$7.6 \times 10^{-3}$	This work
$\text{HBr}(1) + \text{CCN}(000) \rightarrow \text{HBr}(0) + \text{DCN}(001) \}$ $\rightarrow \text{HBr}(0) + \text{DCN}(mn0) \}$	$(1.66 \pm 0.15) \times 10^{-12}$	$9.1 \times 10^{-3}$	This work

<sup>a</sup>Collision diameters HCN, DCN, HCl, HBr, HF, DF: 3.1, 3.1, 3.3, 3.4, 3.0, 3.0 Å.

<sup>b</sup>At 298 K.



Using the InSb detector and appropriate filtering, a search was made for fluorescence from HX, DX( $v=1$ ). Weak signals were detected from HCl( $v=1$ ) formed in Process (5a), which is the reverse of (1a). Because the effects of radiation imprisonment are difficult to estimate, it is impossible to assess quantitatively how much Process (5a) contributes to the overall relaxation of HCN(001) by HCl. However, the observation that the HCN(001, 010) emission at  $2600\text{ cm}^{-1}$  was stronger than that from HCl( $v=1$ ) indicates clearly that (5a)—and, by inference, (6a), (7a) and (8a)—are only minor channels. No attempt has been made to resolve the states resulting from relaxation of HCN(001) by DCN.

Figures 2 and 3 show plots of the increase in decay rate of HCN(001) with increasing HX, DX, or DCN pressure. Measurements were performed by adding mixtures of HX and argon to a fixed pressure of a solution of HCN in argon. Because the measurements were not carried out at the same argon pressure, it was necessary to correct the observed rates for the relaxation of HCN(001) by Ar, using the room-temperature rate constant of  $6.4 \times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  recently determined in this laboratory.<sup>9</sup> The background rate due to self-relaxation of HCN(001) was also not negligible. Although different concentrations of HCN were

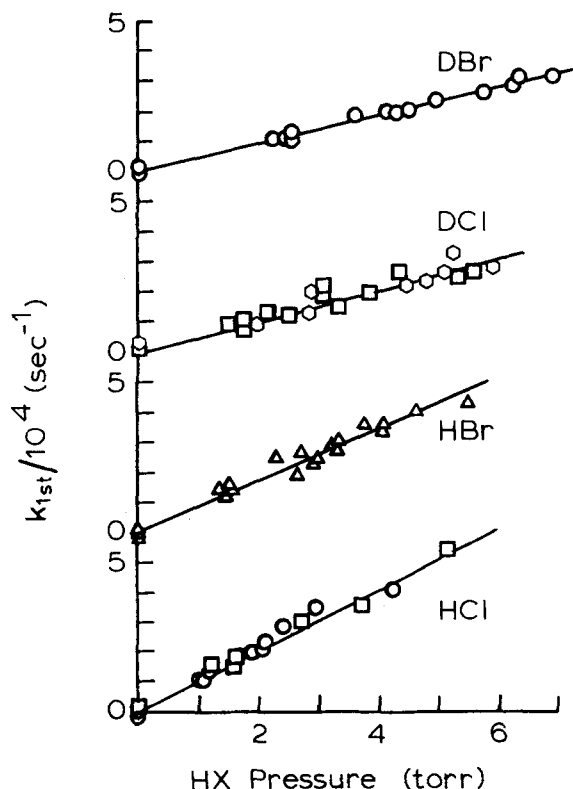


FIG. 2. First-order decay constants for HCN (001, 000) fluorescence, less the contribution to the relaxation by HCN and argon, plotted against the partial pressure of HX or DX. Different symbols identify the results from different series of experiments.

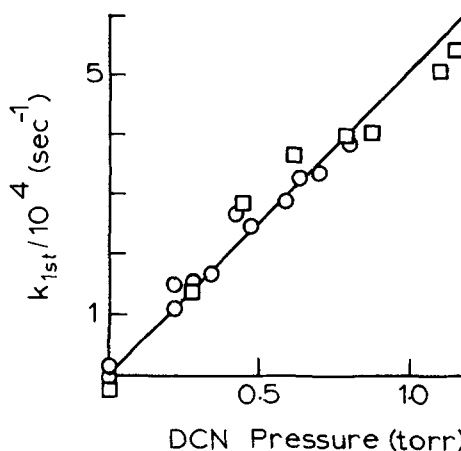


FIG. 3. First-order decay constants for HCN (001, 000) fluorescence, less the contribution to the relaxation of HCN and argon, plotted against the partial pressure of DCN. Different symbols identify the results from different series of experiments.

used in different series of experiments, there was insufficient dispersion on these concentrations to obtain a stable fit to all the data of the form

$$k_{1st}(i) = k_{HX}[HX]_i + k_{Ar}[Ar]_i + k_{HCN}[HCN]_i,$$

if  $k_{HX}$  and  $k_{HCN}$  were both allowed to "float." Consequently, each set of data (with [HCN] constant) was treated separately by finding a least-squares fit to the form

$$k_{1st}(i, j) - k_{Ar}[Ar]_{i,j} = k_{HX}[HX]_{i,j} + b(j).$$

The values of  $b(j)$  obtained in this manner were consistent with previous measurements<sup>10,12</sup> of the self-relaxation rate. In Figs. 2 and 3 all the data are gathered together by plotting  $k_{1st} = k_{1st}(i, j) - k_{Ar}[Ar]_{i,j} - b(j)$  against the partial pressure of HX, DX, or DCN. The gradients of these lines yield the second-order rate constants listed in Table II. As before, the quoted errors are twice the standard errors in the slopes. The rate constants for relaxation by deuterated species include a correction for hydrogenated impurity, and the errors also reflect the uncertainties in these corrections.

#### IV. DISCUSSION

There have been no previous determinations of the rate coefficients for Processes (1)–(9). In Tables I and II, rate constants for energy transfer between HF, DF, and HCN<sup>12</sup> and for self-relaxation of HCN(001)<sup>10,12</sup> are included for comparison with the present results. In the experiments of McGarvey *et al.*,<sup>12</sup> fluorescence from HCN(001) was excited by V–V energy transfer from HF( $v=1$ ) and DF( $v=1$ ) which were excited directly by absorption of radiation from the corresponding pulsed chemical lasers. Despite the observation of HCN(001, 000) emission, the contribution of V–V processes producing HCN(001) could not be determined. As in our work, the observed rate constants are for overall relaxation by either or both of the pathways distinguished earlier, i.e.,

Process	$k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	Probability <sup>a</sup>	Reference
$\text{HCN}(001) + \text{HCN} \rightarrow \text{HCN}(mn0) + \text{HCN}(pq0)$	$(1.94^{+0.4}_{-0.5}) \times 10^{-12}$	$1.3 \times 10^{-2}$	12 <sup>c</sup>
	$(1.4^{+0.15}_{-0.3}) \times 10^{-12}$	$9.4 \times 10^{-3}$	12 <sup>c</sup>
	$(2.4 \pm 0.6) \times 10^{-12}$	$1.6 \times 10^{-2}$	10
$\text{HCN}(001) + \text{DCN} \rightarrow \text{HCN}(mn0) + \text{DCN}$	$(14.8 \pm 1.4) \times 10^{-13}$	$7.3 \times 10^{-3}$	This work
$\text{HCN}(001) + \text{HF}(0) \rightarrow \text{HCN}(mn0) + \text{HF}(0) \}$ <sup>b</sup> $\rightarrow \text{HCN}(000) + \text{HF}(1) \}$	$(13^{+1.5}_{-2.1}) \times 10^{-13}$	$6.2 \times 10^{-3}$	12
$\text{HCN}(001) + \text{DF}(0) \rightarrow \text{HCN}(mn0) + \text{DF}(0) \}$ <sup>b</sup> $\rightarrow \text{HCN}(000) + \text{DF}(1) \}$	$(9.4^{+3.1}_{-2.1}) \times 10^{-13}$	$4.5 \times 10^{-3}$	12
$\text{HCN}(001) + \text{HCl}(0) \rightarrow \text{HCN}(mn0) + \text{HCl}(0) \}$ $\rightarrow \text{HCN}(0p0) + \text{HCl}(1) \}$	$(3.17 \pm 0.18) \times 10^{-13}$	$1.5 \times 10^{-3}$	This work
$\text{HCN}(001) + \text{DCl}(0) \rightarrow \text{HCN}(mn0) + \text{DCl}(0) \}$ $\rightarrow \text{HCN}(0p0) + \text{DCl}(1) \}$	$(1.5 \pm 0.3) \times 10^{-13}$	$6.9 \times 10^{-4}$	This work
$\text{HCN}(001) + \text{HBr}(0) \rightarrow \text{HCN}(mn0) + \text{HBr}(0) \}$ $\rightarrow \text{HCN}(0p0) + \text{HBr}(1) \}$	$(2.63 \pm 0.15) \times 10^{-13}$	$1.4 \times 10^{-3}$	This work
$\text{HCN}(001) + \text{DBr}(0) \rightarrow \text{HCN}(mn0) + \text{DBr}(0) \}$ $\rightarrow \text{HCN}(0p0) + \text{DBr}(1) \}$	$(1.3 \pm 0.3) \times 10^{-13}$	$6.9 \times 10^{-4}$	This work

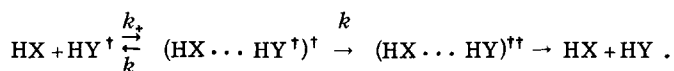
<sup>c</sup>The first value was derived from experiments in which HCN was excited via energy transfer from HF( $v=1$ ), and the second when DF( $v=1$ ) was used to excite HCN.

$$\rightarrow \text{HCN}(mn0) + \text{DF}(v=0) \quad (13b)$$

observations bearing in mind that these dimers are only weakly bound, so that their lifetimes with respect to re-dissociation are short, and that intramolecular energy transfer between modes of very different frequency will not be facile.<sup>23</sup>

That attractive forces play an important role in governing the dynamics of HX/HCN collisions is not really in question: the high collisional probabilities, despite the absence of dominant  $V-V$  channels, and the inverse temperature dependence of the rate constants  $k_{10}$  to  $k_{13}$ <sup>12</sup> confirm this. A reasonable hypothesis is that weakly bound collision complexes can form, with lifetimes which are largely determined by the statistical randomization of the potential energy released through formation of the hydrogen bond among the low frequency modes of the dimer. Such lifetimes would be long, compared with the vibrational period of any high frequency vibration. However, energy transfer from these modes to other degrees of freedom would be restricted, so that there is a finite—indeed, a high—probability that the complex would redissociate without vibrational relaxation having occurred.

The mechanism just proposed can be represented by the equations:



Here,  $\text{HY}^{\dagger}$  is the initially excited hydrogen halide or cyanide,  $(\text{HX} \cdots \text{HY}^{\dagger})^{\dagger}$  is the hydrogen bonded complex in which one quantum of vibrational excitation is retained in the HY stretching mode, and  $(\text{HX} \cdots \text{HY})^{\ddagger\dagger}$  is a complex in which the energy earlier present in the HY vibration has now been redistributed into other degrees of freedom. It is assumed that the dissociation of  $(\text{HX} \cdots \text{HY})^{\ddagger\dagger}$  is essentially “immediate” with HX and HY being produced in vibrational levels different from their original states.

According to this model, the rate of relaxation of  $\text{HY}^{\dagger}$  is

$$-\frac{d[\text{HY}^{\dagger}]}{dt} = \left\{ \frac{k k_{+}}{k + k_{-}} \right\} [\text{HY}^{\dagger}][\text{HX}]. \quad (\text{I})$$

The ratio  $(k_{+}/k_{-})$  can be calculated from statistical mechanics:

$$\left( \frac{k_{+}}{k_{-}} \right) = \frac{Q^{*}}{Q_{\text{HX}} Q_{\text{HY}^{\dagger}} Q_{\text{T}}} \quad (\text{II})$$

where  $Q_{\text{HX}}$ ,  $Q_{\text{HY}^{\dagger}}$ , and  $Q_{\text{T}}$  are the partition functions for the internal degrees of freedom of HX and  $\text{HY}^{\dagger}$  and for their relative translation, and  $Q^{*}$ , the internal partition function for  $(\text{HX} \cdots \text{HY}^{\dagger})^{\dagger}$ , is given by

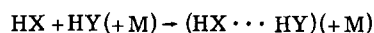
$$Q^{*} = \int_0^{\infty} \rho^{*}(E' + D) e^{-E'/kT} dE' \quad (\text{III})$$

with  $\rho^{*}(E)$  being the density of states in the complex at energy  $E$ , and  $D$  being the energy of the  $\text{HX} \cdots \text{HY}$  bond. In connection with calculations on the rates of unimolecular decompositions at low pressure, Troe<sup>5</sup> has presented approximate methods for estimating partition functions such as  $Q^{*}$  from spectroscopic data. Furthermore,  $k_{+}$  should correspond to the rate constant for the reaction

TABLE III. Vibrational frequencies and rotational constant of  $(\text{HF} \cdots \text{HCN})$ .

	$\omega/\text{cm}^{-1}$	Degeneracy	Reference
$\nu_1^a$	2097	1	24
$\nu_2^a$	713.5	2	24
$\nu_3^a$	3311.5	1	24
$\nu_{\beta}$	91	2	19
$\nu_{\beta}$	555	2	16
$\nu_{\sigma}$	197	1	19
$\nu_s$	3710	1	16
$B_0/\text{cm}^{-1}$	0.12	...	19

<sup>a</sup>Taken as being unchanged from the corresponding frequencies in the isolated HCN molecule.<sup>24</sup>



in the limit of high pressure, which, according to RRKM theory, is given by

$$k_{+} = (kT/h) (Q^{\ddagger}/Q_{\text{HX}} Q_{\text{HY}} Q_{\text{T}}). \quad (\text{IV})$$

Quack and Troe<sup>5</sup> have proposed a method of estimating  $Q^{\ddagger}$ , the transition state partition function, and hence  $k_{+}$ , based on a “maximum free energy” criterion and an interpolation procedure for finding the variation of partition function along the reaction coordinate. Given sufficient information about the  $(\text{HX} \cdots \text{HY})$  dimer, Eqs. (II) and (IV) can be used to find values of  $k_{+}$  and  $k_{-}$ . If the model is correct  $k$  can then be estimated by equating  $\{k k_{+}/(k + k_{-})\}$  to the observed rate constant for vibrational relaxation.

Only one hydrogen-bonded dimer involving HCN, that with HF, has been the subject of thorough spectroscopic<sup>15–17,19</sup> and theoretical<sup>2</sup> investigations. The studies have established that the more stable form of the dimer is linear with HF acting as a proton donor. The values of  $D_e$  and  $D_0$  are 6.2 kcal/mole and 4.5 kcal/mole.<sup>19</sup> Formation of this linear dimer creates five new vibrational modes, a stretching of the hydrogen bond, and two doubly degenerate bending vibrations. The frequency of the HF stretch is lowered by approximately 250  $\text{cm}^{-1}$  in the complex,<sup>18</sup> but that of the CH stretch is likely to be almost unaltered.<sup>14</sup>

Values of  $(k_{+}/k_{-})$  and of  $k_{+}$  have been estimated by the methods outlined earlier, using the spectroscopic data for the  $(\text{HF} \cdots \text{HCN})$  dimer given in Table III. These calculations yield:  $(k_{+}/k_{-}) = 5 \times 10^{23} \text{ cm}^3$ ;  $k_{+} \approx 5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$  so  $k_{-} \approx 10^{13} \text{ sec}^{-1}$ . When combined with the McGarvey *et al.* value of  $k_1$ , one obtains the result that  $k \approx (k_{-}/80) \sim 10^{11} \text{ sec}^{-1}$  in the relaxation of  $\text{HF}(v=1)$  by HCN, although this rate would be lowered by any contribution to the overall relaxation rate by  $V-V$  energy exchange by any mechanism not involving collision complexes. If it is presumed that  $\text{HCN}(001)$  is also relaxed by HF via  $(\text{HCN} \cdots \text{HF})$  complexes, one obtains  $k$  for  $(^1\text{HCN} \cdots \text{HF})^{\dagger} \rightarrow (\text{HCN} \cdots \text{HF})^{\ddagger\dagger}$  of  $(k_{-}/400) \sim 2.5 \times 10^{10} \text{ sec}^{-1}$ .

While we do not wish to imply that the above calcula-

tions are quantitatively correct, they indicate that a model of slow energy redistribution from high frequency modes within a transient weakly bound dimer is consistent with the observed rates of relaxation in HX/HCN systems. The variation of the relaxation rates with X is also consistent with the progressive weakening of the hydrogen bonding as X varies from F to Cl to Br, and the temperature dependences of  $k_{10}$  to  $k_{13}$  found by McGarvey *et al.*<sup>12</sup> could be explained by the decrease in  $(k_+/k_-)$  as the temperature is raised. Within the framework of the model, there are two reasons why hydrogen halides might relax HCN(001) more slowly than HCN relaxes HX( $v=1$ ). Firstly, the remoteness of the CH stretch from the hydrogen bond perturbation renders the intramolecular transfer of excitation less efficient. Secondly, the dimer with HX as the proton donor is less weakly bound, so  $(k_+/k_-)$  for formation of  $(^1\text{HX} \cdots \text{HCN})^\ddagger$  is less than for formation of  $(^1\text{HCN} \cdots \text{HX})^\ddagger$ .

Finally, we emphasize that the values of  $k$  required to bring the model calculations into agreement with the experimental relaxation data cannot be directly compared with theoretical estimates of the rates of vibrational predissociation in hydrogen-bonded dimers. The latter calculations<sup>23</sup> have been carried out—not only on simplified models—but also on species containing insufficient energy to dissociate until energy from the high frequency mode is transferred to other degrees of freedom.

#### ACKNOWLEDGMENTS

We are grateful to Professor G. E. Ewing and Professor D. J. Millen for giving us preprints of their papers<sup>19,23</sup> prior to publication.

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