Mutual polarization of monomer charge distribution in (HCN)$_2$, (HCN)$_3$, and (HCN)$_\infty$

R. S. Ruoff

IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

A simple classical mutual polarization model accurately predicts the induced dipole moments of linear HCN dimer and trimer. The model employs the first four nonzero electrical molecular moments of each HCN, and both the molecular polarizability and the C–H and C–N bond dipole polarizabilities. The model is extended to linear H-bonded oligomers up to the pentamer, and also to an infinite linear H-bonded chain, appropriate for comparison with the H-bonded chains present in the HCN crystal. For the dimer and trimer, a relation is seen between the change in the electric field gradient at the N of HCN and the calculated induced C–N bond dipole moment. A semiquantitative proportionality constant, derived based on this relation, is used to enhance understanding of the underlying cause of the large increase in the ^{14}N quadrupole coupling constant in the HCN crystal relative to the free HCN monomer. This increase results from the strong polarization of the C–N bond by the local field at each HCN caused by the rest of the HCN crystal lattice.

INTRODUCTION

The induced dipole moment $\Delta\mu$ of molecular dimers provides information about charge rearrangement resulting from dimer formation.[1(a),2] The value of $\Delta\mu$ depends on the extent of charge rearrangement within monomers and between monomers comprising the dimer. In this paper we refer to these rearrangements as polarization and charge transfer, respectively.

Previous work suggests that charge transfer is not important for many dimers whose intermolecular bond energy does not exceed about 1000 cm^{-1}.[2,3] For example, Campbell *et al.* show charge transfer is less than 0.003 electrons in dimers of the type A–HX where A is a krypton or xenon atom and HX is HCl, HF, or HCN.[3] Intermolecular bonding energies for these dimers are roughly 250 cm^{-1},[4] similar to that of Xe$_2$.[5]

If charge transfer is negligible then $\Delta\mu$ should depend only on charge polarization within monomers. A classical mutual polarization model has been previously used for calculating $\Delta\mu$ for various dimers, using either molecular polarizabilities and experimentally determined electrical multipole moments,[1(a)] or *ab initio* generated point polarizabilities and point multipoles.[2] Comparison can be made with the experimentally determined induced dipole moment $\Delta\mu_{\text{exp}}$ which for a linear X–Y dimer is

$$\Delta\mu_{\text{exp}} = \mu_{\text{X-Y}} - \mu_{\text{X}} \langle \cos\theta_1 \rangle - \mu_{\text{Y}} \langle \cos\theta_2 \rangle. \tag{1}$$

In Eq. (1) $\mu_{\text{X-Y}}$ is the measured dipole moment of the dimer, μ_{x} and μ_{Y} the free monomer dimer moments, and $\langle \cos\theta_n \rangle$ the expectation value of $\cos\theta_n$ resulting from zero point vibrational averaging. θ_1 is the angle between the monomer X and the a inertial axis of the dimer.

The classical mutual polarization model estimates $\Delta\mu$ as

$$\Delta\mu = \sum E_n \alpha_n, \tag{2}$$

where E_n is the electric field at point n and α_n the appropriate dipole polarizability at point n. Higher-order terms in E_n can be added to Eq. (2) if the dipole hyperpolarizabilities at

n are known. The relevance of these higher-order terms for linear (HCN)$_n$ oligomers is discussed later.

There are several reasons why perfect agreement between $\Delta\mu$ and $\Delta\mu_{\text{exp}}$ may not occur, among them: (1) Mutual polarization of monomer charge distributions, alone, is not a realistic model for $\Delta\mu$. (2) The electric fields E_n are inadequately determined at the relevant points, or the polarizabilities are an inadequate representation of the polarizable charge, or both. (3) $\Delta\mu_{\text{exp}}$ is inaccurate because the $\langle \cos\theta_n \rangle$ of Eq. (1) are not well determined.

Relevant to number 2 is that, for a point n outside a given static charge distribution, E_n should be exactly that obtained from a complete multipole expansion of the charge distribution.[6] The complete expansion is not available for molecules, and for HCN the available molecular multipoles are the dipole, quadrupole, octupole, and hexadecapole moments. The available experimental dipole polarizabilities for HCN are either molecular or bond polarizabilities. In consideration of such factors, Buckingham *et al.* have suggested better representations of the charge density of a molecule can give better values for E_n at points close to the molecule, and also a better picture for the polarizable charge α_n.[2] Stone, for instance, places point multipoles, polarizabilities and hyperpolarizabilities derived from *ab initio* wave functions at chosen points along the molecule.[7]

Buckingham *et al.* find $\Delta\mu$ values in agreement with $\Delta\mu_{\text{exp}}$ for six linear dimers using distributed multipole, distributed polarizability analysis, in contrast to $\Delta\mu$ values obtained from experimental multipole moments and molecular polarizabilities, which were roughly 35% too low.[2] The agreement obtained shows that the mutual polarization of monomer charge distribution accounts for $\Delta\mu_{\text{exp}}$ for the dimers studied and that charge transfer is therefore likely to be small or negligible. The binding energies of these dimers range from about 570 cm^{-1} for OC–HCl[8] to 1000 cm^{-1} for OC–HF.[9]

Recent measurement of $\Delta\mu_{\text{exp}}$ for (HCN)$_3$[10] means that two test cases are available for any mutual polarization

model used for HCN, that is $\Delta\mu_{\text{exp}}^{(d)}$ and $\Delta\mu_{\text{exp}}^{(t)}$, where d means dimer and t trimer. In this respect, a fair number of linear or symmetric top trimers involving $(HCN)_2$ as a subunit have had their rotational spectra assigned,[11,12] as well as the ternary trimer $NH_3-HCN-HF$.[13] Such mixed trimers can be thought of as composed of two dimers, and one therefore has extra information, beyond the induced dipole moments of the dimers, with which to test mutual polarization models. It is hoped that something about the effect of three-body interactions can be obtained from data gathered on such trimers.

As will be shown, $\Delta\mu_{\text{exp}}^{(d)}$ and $\Delta\mu_{\text{exp}}^{(t)}$ of $(HCN)_2$ and $(HCN)_3$ are very well accounted for by mutual polarization of monomer charge distributions. Given an approximate H-bond energy of 1700 cm^{-1} for $(HCN)_2$[14] and higher still (per H bond) for $(HCN)_3$, this extends considerably the intermolecular bond energy range for which charge transfer need not be invoked to explain measured induced dipole moments. It has been suggested that the electrical multipoles of monomers within an intermolecular cluster can define their relative orientations, this statement more likely being true when charge transfer is negligible.[15]

Consideration is also given to calculation of the induced dipole moment per monomer in an infinite linear chain of HCN monomers. The crystal structure of HCN consists of parallel, linear chains of hydrogen-bonded HCN's, with one HCN per unit cell.[16] If the value of $\Delta\mu$/monomer obtained for HCN crystal is realistic,[17] it is shown that off-chain HCN's contribute about half the local field at a given site. This shows that neighboring chains separated by distances comparable to the sum of van der Waals radii have a tremendous effect on each other with regard to crystal energetics and $\Delta\mu$ at each site.

Independent information concerning charge rearrangement is available from the ^{14}N quadrupole coupling constants in $(HCN)_2$[18] and $(HCN)_3$,[10] from which the change in the electric field gradient from that of the free monomer value is obtainable. It is shown that the magnitude of the measured ^{14}N quadrupole coupling constant in the HCN crystal[19] is consistent with polarization of charge within each HCN.

RESULTS AND DISCUSSION

Calculation of induced dipole moments in $(HCN)_n$.

Given HCN as in Fig. 1, the E_n along the a axis resulting from the cylindrically symmetric HCN charge distribution at points 1 and 2 are

$$\text{at 1} \quad E_1 = \sum_{n=1}^{\infty} (n+1)(-1)^{(n+3)}$$
$$\times \psi^{(n)} r^{-(n+2)} \langle P_n (\cos\theta) \rangle, \quad (3)$$

$$\text{at 2} \quad E_2 = \sum_{n=1}^{\infty} (n+1) \psi^{(n)} r^{-(n+2)} \langle P_n (\cos\theta) \rangle. \quad (4)$$

In Eqs. (3) and (4), r is the distance from the center of mass (c.m.) of HCN to point 1 or 2, $\langle P_n (\cos\theta) \rangle$ is the expectation value of the nth Legendre polynomial of $\cos\theta$, θ the angle between the a axis and HCN, and $\psi^{(n)}$ designates the nth molecular electric multipole moment, located at the c.m.
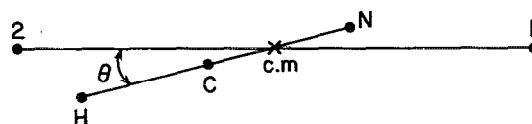

FIG. 1. Points 1 and 2 are each distance r from the c.m. of HCN.

of HCN. For example $\psi^{(1)}$ is the dipole moment μ, $\psi^{(2)}$ the quadrupole moment θ, $\psi^{(3)}$ the octupole moment Ω, and $\psi^{(4)}$ the hexadecapole moment Φ. $\Delta\mu_{\text{exp}}$ is a zero-point averaged quantity, dependent on the vibrational zero point motion of HCN's in both $(HCN)_2$ and $(HCN)_3$, Eq. (1).

Only the magnitude of the first nonzero electrical multipole moment of a charge distribution is independent of the choice of origin.[15] The dipole moment is the first nonzero moment for HCN. Therefore the quadrupole, octupole, and hexadecapole moments are dependent on origin choice. The quadrupole moment used here was determined for HC^{15}N by Allen et al.,[28] who defined the c.m. of HC^{15}N as the origin. The octupole and hexadecapole moments used here are ab initio values located at the c.m. of HC^{14}N.[25,29] Because the dipole and quadrupole terms are much more important than the higher order moments in determining the induced dipole moment, as demonstrated below, the reader should keep in mind that the model employed is essentially that for the homodimer and homotrimer of HC^{15}N. It will be seen that Ω and Φ can vary substantially about the values used here to determine the magnitudes of $\Delta\mu^{(d)}$ and $\Delta\mu^{(t)}$, with little effect on the magnitudes of the calculated induced moments. A shift in the values of Ω and Φ due to the small shift in the c.m. of HC^{14}N is not a serious limitation to using the available literature values for Ω and Φ in the calculation of induced moments discussed here.

In the same sense that $\langle \cos\theta \rangle$ is used in Eq. (1), it is appropriate to use $\langle P_n (\cos\theta) \rangle$ for determination of E_n at each relevant point n. From experimental data, $\langle \cos\theta_n \rangle$ is known for $(HCN)_2$ for θ_1 and θ_2, and for $(HCN)_3$ for θ_1 and θ_3.[10,18] An approximate value for θ_2 of 5° in $(HCN)_3$ can, however, be used as will be discussed below. We use the convention HCN(1)HCN(2) and HCN(1)HCN(2)HCN(3), for the dimer and trimer, respectively.

To obtain the $\langle P_n (\cos\theta) \rangle$, the librational motion of each HCN is assumed to be harmonic, with each HCN bending about its own c.m. For a ground state harmonic oscillator

$$\langle P_n (\cos\theta) \rangle = N \int_{-\pi}^{\pi} P_n (\cos\theta)$$
$$\times \exp[-\beta^2 (\theta - \theta_{\text{eq}})^2] d\theta, \quad (5)$$

in which N is a normalizing constant, β an inverse torsional amplitude, and θ_{eq} the equilibrium angle, which is assumed to be 0°. Values for β were determined from $\langle \cos\theta_n \rangle$ for the previously determined values of θ_n.[18] For example, for $\theta_n = 13.60$ and 9.00° amplitudes for β of 19.30 and 12.85° are obtained. For the same θ_n, the $\langle P_n (\cos\theta) \rangle$ as obtained from Eq. (5) differ little from $P_n (\langle \cos\theta \rangle)$ obtained from the usual algebraic recursion formula which generates higher order

TABLE I. Experimentally determined properties of HCN dimer and trimer.

Species	c.m. separation (Å)			Vibrational ampl. (deg.)			Dipole moment (D)	
	r	r_1	r_2	θ_1	θ_2	θ_3	μ	$\Delta\mu$
$(HCN)_2$ [a]	4.448	⋯	⋯	13.6	9.0	⋯	6.553(3)[b]	0.703
$(HCN)_3$ [c]	⋯	4.389	4.401	12.6	(5.0)[d]	8.6	10.6(1)[c]	1.75(10)

[a] Reference 18.
[b] Reference 1.
[c] Reference 10.
[d] Assumed value as discussed in text.
[e] Reference 10.

Legendre polynomials from lower order ones,[21] for $n < 7$. With $n = 8$ and $\theta = 13.6°$ the difference is only 25% from $P_n(\langle\cos\theta\rangle)$ calculated with the recursion formula. We have used $\langle P_n(\cos\theta)\rangle$ as calculated from Eq. (5) for obtaining E_n due to HCN at point n.

$\Delta\mu^{(d)}$ and $\Delta\mu^{(t)}$ were calculated using two different representations of polarizable charge present at each HCN. One involved placing the known molecular dipole polarizability, α_{HCN}, at the c.m. of each HCN. The second involved placing bond polarizabilities α_{HC} and α_{CN} at the bond midpoint of each bond in HCN. Denbeigh has shown that α_{HC} and α_{CN} sum to α_{HCN} for both the parallel ($\parallel$) and perpendicular ($\perp$) polarizabilities.[22] The correct polarizability along the a axis is[20]

$$\alpha = \alpha_\parallel\langle\cos^2\theta\rangle + \alpha_\perp\langle\sin^2\theta\rangle. \qquad (6)$$

Input geometries and relevant properties of $(HCN)_2$ and $(HCN)_3$ are included in Table I. Table II includes molecular properties of HCN monomer. The $\Delta\mu^{(d)}$ and $\Delta\mu^{(t)}$ were calculated from Eqs. (2)–(6), and the calculation involves obtaining $\Delta\mu_1$ and $\Delta\mu_2$ in $(HCN)_2$, adding them to μ_0 of HCN (2.985D, Table I), and recalculating $\Delta\mu_1$, $\Delta\mu_2$ until they no longer change, this involving about five or six computational cycles. One can also solve the coupled simultaneous equations in that $\Delta\mu_1$ is a function of $\Delta\mu_2$ and $\Delta\mu_2$ a function of $\Delta\mu_1$, the two approaches giving identical results.

The reason that the c.m. to c.m. distance is used is straightforward. We calculate $\Delta\mu^{(d)}$ and $\Delta\mu^{(t)}$ for homodimers and homotrimers, and the multipole moments are located at the c.m. of each HCN (with the limitations of Ω and Φ as discussed above). The molecular dipole polariza-

bility is also located, within this model, at the c.m. of each HCN.

Results are summarized in Table III for several different cases. $E(\mu,\theta,\Omega,\Phi)$ means that the first four nonzero electrical moments were used to calculate E, and $E(\mu,\theta)$ is E from only the first two electrical moments. Table II shows that use of α_{HCN} results in slightly lower values for $\Delta\mu$ than α_{HC} and α_{CN}, for $E(\mu,\theta,\Omega,\Phi)$. Values for $\Delta\mu_{exp}^{(d)}$ and $\Delta\mu_{exp}^{(t)}$ have been obtained from the measured dipole moments of $(HCN)_2$[1(b)] and $(HCN)_3$,[10] the known values for $\langle\cos\theta_n\rangle$, and Eq. (1). They are 0.703(4)D and 1.75(10)D, for $\Delta\mu_{exp}^{(d)}$ and $\Delta\mu_{exp}^{(t)}$, respectively. Comparison of $\Delta\mu$ with $\Delta\mu_{exp}$ shows that the first four electrical multipole moments of Table II predict $\Delta\mu_{exp}^{(d)}$ and $\Delta\mu_{exp}^{(t)}$ very well. Inclusion of only μ and θ in Eqs. (3) and (4) underestimates $\Delta\mu^{(d)}$ and $\Delta\mu^{(t)}$. Bond polarizabilities α_{HC} and α_{CN} yield a better value for $\Delta\mu^{(d)}$ than α_{HCN} with $E(\mu,\theta,\Omega,\Phi)$. One might expect bond polarizabilities to provide a better estimate of the induced dipole moment.

Is the agreement fortuitous when $E(\mu,\theta,\Omega,\Phi)$ is used? A useful approach for testing the convergence of the multipole expansion of E at the relevant distance is to calculate the functional dependences of $\Delta\mu^{(d)}$ on $\psi^{(n)}$ with $\psi^{(1)}$ set equal to μ_0, 2.985 D. Table IV summarizes changes in parameters which cause a change in $\Delta\mu^{(d)}$ of 0.01 D.

Although multipole moments beyond $\psi^{(4)}$ (i.e., Φ) are not available, it is clear from Table IV that $\psi^{(n)}$ for n greater than or equal to 6 are unlikely to contribute at all to $\Delta\mu^{(d)}$.

TABLE II. Molecular properties of HCN monomer.

r_0 bond lengths (Å)[a]		Electrical moments		Dipole polarizabilities (Å³)[b]	
H–C	1.0624	μ	2.985[c] D	$\alpha_\parallel^{HCN},\alpha_\perp^{HCN}$	3.92,1.92
C–N	1.1568	Q	3.1(6)[d] DÅ	$\alpha_\parallel^{CH},\alpha_\perp^{CH}$	0.79,0.58
		Ω	6.47[e] DÅ²	$\alpha_\parallel^{CN},\alpha_\perp^{CN}$	3.13,1.34
		Φ	6.422[f] DÅ³		

[a] Reference 26.
[b] Reference 22.
[c] Reference 27.
[d] Reference 28.
[e] Average of values from Ref. 25 (6.37) and Ref. 29 (6.56).
[f] Reference 25.

TABLE III. Induced dipole moments (D) calculated for HCN dimer and trimer with four combinations of electrical moments and polarizabilities.[a]

Induced moment	$E(\mu,Q)$		$E(\mu,Q,\Omega,\Phi)$	
	α_{HCN}	α_{HC},α_{CN}	α_{HCN}	α_{HC},α_{CN}
	Dimer			
$\Delta\mu_1$	0.360	0.339	0.430	0.405
$\Delta\mu_2$	0.202	0.236	0.249	0.298
$\Delta\mu^d$	0.562	0.575	0.674	0.703
	Trimer			
$\Delta\mu_1$	0.461	0.432	0.552	0.517
$\Delta\mu_2$	0.611	0.623	0.739	0.769
$\Delta\mu_3$	0.267	0.310	0.320	0.393
$\Delta\mu^t$	1.339	1.366	1.611	1.679

[a] Based on properties of monomer, dimer, and trimer given in Tables I and II.

TABLE IV. Changes in parameters that cause a 0.01 D change in calculated $\Delta\mu$ for $(HCN)_2$ and $(HCN)_3$.[a]

Change in property	Units	$(HCN)_2$	$(HCN)_3$
ΔQ	D Å	− 0.82	− 0.33
$\Delta\Omega$	D Å^2	0.47	0.20
$\Delta\Phi$	D Å^3	− 6.54	− 2.27
$\Delta\Psi^{(5)}$	D Å^4	6.33	...[b]
$\Delta\Psi^{(6)}$	D Å^5	− 88.5	...
$\Delta\Psi^{(7)}$	D Å^6	101.0	...
$\Delta\theta_1$	deg	− 3.5	− 3.2
$\Delta\theta_2$	deg	− 3.3	− 4.0[c]
$\Delta\theta_3$	deg	...	− 2.2

[a] $(HCN)_n$ geometries from Table I. μ_0 fixed at 2.985 D. $\Delta\mu^{(d)}$, $\Delta\mu^{(t)}$ calculated with bond polarizabilities α_{CH}, α_{CN}.
[b] Dependence on $\Delta\Psi^{(n)}$, $n = 5,6,7$ calculated only for $(HCN)_2$.
[c] Functional dependence calculated at $\theta_2 = 5.0°$.

Given the magnitudes of μ, θ, Ω and Φ there is no reason to expect values of magnitude 100 for $\psi^{(6)}$ or $\psi^{(7)}$. Table IV does suggest that $\psi^{(5)}$ may be contributing to $\Delta\mu^{(d)}$. If it's absolute magnitude were equal to Φ it would add about 0.01 D to $\Delta\mu^{(d)}$. Thus that $\Delta\mu_{exp}^{(d)}$ and $\Delta\mu_{exp}^{(t)}$ are well calculated by a mutual polarization model using only μ, θ, Ω, and Φ is not due to fortuitous cancellation of higher order terms. Table IV demonstrates that the functional dependence of $\Delta\mu^{(t)}$ on $\psi^{(n)}$ is stronger than that of $\Delta\mu^{(d)}$ for each $\psi^{(n)}$, and also that the functional dependence on θ_1 and θ_2 for the dimer, and on θ_1, θ_2, and θ_3 for the trimer, is weak. All angles except θ_2 (trimer) are known to better than a degree, while θ_2 (trimer) is likely about 5° (discussed below). Uncertainty in θ_2 contributes no more than 0.02 D to $\Delta\mu^{(t)}$.

Table V summarizes the functional dependence of $\Delta\mu_{exp}$ on $\langle\cos\theta_n\rangle$ as obtained from Eq. (1). Previous estimates of the uncertainties on θ_1 and θ_2 in $(HCN)_2$ were $\pm 0.5°$.[18] Even uncertainties of $\pm 1°$ in θ_1 and θ_2 would have a small effect on $\Delta\mu_{exp}^{(d)}$ and $\Delta\mu_{exp}^{(t)}$. It is important that at $\theta_2 = 5°$ a relatively large $\Delta\theta_2$ is needed to cause a 0.01 D change in $\Delta\mu_{exp}^{(t)}$, lack of a more precise value for θ_2 not being critical in testing the mutual polarization model.

Besides the measured $\Delta\mu_{exp}^{(t)}$ and $\Delta\mu_{exp}^{(d)}$, ab initio calculations are available for $\Delta\mu$ for linear $(HCN)_n$, $n = 2$ to 5 [23] and $(HCN)_\infty$,[24] a linear infinite chain. The ab initio value for μ_0 is high,[23] but a useful quantity to compare is the ratio $\Delta\mu/\mu_0$. The calculated ratio for $(HCN)_\infty$ is 0.15.[24] Use of the same ab initio basis set for $(HCN)_5$ gives a value for $\Delta\mu/\mu_0$ of 0.28 for $(HCN)_5$. Table VI shows comparison of $\Delta\mu/$

TABLE V. Changes in θ_n causing changes in $\Delta\mu_{exp}$ of 0.01 D.[a]

$\Delta\theta_n$	$(HCN)_2^{(deg)}$	$(HCN)_3$
$\Delta\theta_1$	− 0.67[b]	− 1.0[c]
$\Delta\theta_2$	− 0.87[b]	− 2.4[c]
$\Delta\theta_3$	...	...

[a] Equation (1).
[b] About $\theta_1 = 13.6°$, $\theta_2 = 9.0°$.
[c] About $\theta_1 = 12.6$, $\theta_2 = 5.0°$, $\theta_3 = 8.6°$.

TABLE VI. A comparison of $\Delta\mu/\mu_0$ for linear $(HCN)_n$ from experiment, from ab initio results, and from the mutual polarization model.

Source	$(HCN)_2$	$(HCN)_3$	$(HCN)_4$	$(HCN)_5$
Expt.[a]	0.117	0.198	...	...
Ab initio[b] (I)	0.139	0.211	0.256	0.285
Polarization[c] (II)	0.120	0.186	0.225	0.250
Ratio (I/II)	1.16	1.13	1.13	1.12

[a] From Table I.
[b] Calculated from Table VIII, Ref. 23.
[c] Based on α_{HCN} as described in text. Intermolecular distances for $(HCN)_2$ and $(HCN)_3$ from Table I, and those for $(HCN)_4$ and $(HCN)_5$ are scaled from Ref. 23 by Eq. (7) of this paper.

μ_0 per monomer from experiment and ab initio calculation as well as calculated from the mutual polarization model presented here.

Use of α_{HCN} with $E(\mu,\theta,\Omega,\Phi)$ gave $\Delta\mu^{(d)}$ and $\Delta\mu^{(t)}$ only slightly smaller than the same quantities calculated with α_{CN} and α_{HC} (Table III), and we have used α_{HCN} for simplicity to calculate $\Delta\mu$ for $(HCN)_n$, $n = 2$ to 5. Known intermolecular distances were used for $(HCN)_2$ [18] and $(HCN)_3$,[10] whereas for $(HCN)_4$ and $(HCN)_5$ the ab initio distances were scaled as

$$R = (r_{N\cdots H} - 2.2325) + 4.4475, \qquad (7)$$

where 2.2325 Å is the N---H H-bond length calculated for $(HCN)_2$,[23] 4.4475 Å the experimental c.m.–c.m. separation in $(HCN)_2$,[18] and $r_{N\cdots H}$ the ab initio calculated H-bond lengths.[23] All θ_n were set to 0° to correspond to the angles used in the ab initio study.

Table VI demonstrates an essentially constant value for the ratio of $\Delta\mu/\mu_0$ calculated ab initio to $\Delta\mu/\mu_0$ obtained with the mutual polarization model.

The internal consistency of the mutual polarization model as discussed above encourages its use for calculation of $\Delta\mu/\mu_0$ per monomer for $(HCN)_\infty$. The crystal structure determination of HCN showed two phases at normal pressure, with the phase transition at 170 K. Both phases consist of parallel, linear H-bonded chains with one HCN per unit cell. The H-bond length is, within experimental error, the same for both phases. Expressed as a c.m. to c.m. separation, this H-bond length is 4.34(2) Å.[16]

It is instructive to use the same H-bond distance for $(HCN)_\infty$. Using α_{HCN} rather than bond polarizabilities and setting all θ's equal to 0° simplifies determination of closed form expressions for $\Delta\mu(\mu)$ and $\Delta\mu(\mu,\theta,\Omega,\Phi)$ which are

$$\Delta\mu(\mu) = \mu_0\eta/(1 - \eta);$$

$$\eta = (4\alpha_{HCN}/r_a^3) \sum_{n=1}^{\infty} n^{-3}, \qquad (8)$$

$$\Delta\mu(\mu,\theta,\Omega,\Phi) = (\mu_0 + \tau)\eta/(1 - \eta) + \tau;$$

$$\tau = (8\alpha_{HCN}\Omega/r_a^5) \sum_{n=1}^{\infty} n^{-5}. \qquad (9)$$

With the multipole moments and α_{HCN} (Table II), Eqs. (8) and (9) yield $\Delta\mu(\mu_0) = 0.27 \mu_0$ and $\Delta\mu(\mu_0,\theta,\Omega,\Phi) = 0.33$ μ_0 for $(HCN)_\infty$. Note that multiplying 0.33 by the average

scaling factor 1.13 (Table VI) gives 0.37; if this type of extrapolation is valid, this would be the expected value for $\Delta\mu/\mu_0$ from *ab initio* calculation (using the same basis set) for $(HCN)_\infty$.

Up to now we have neglected higher-order dipole hyperpolarizabilities and their possible contribution to $\Delta\mu$ as calculated for linear HCN oligomers and $(HCN)_\infty$, at the electric fields present from monomer charge distributions. *Ab initio* work suggests that these terms contribute negligibly.[17] Bounds *et al.* obtain $\Delta\mu = 0.60\ \mu_0$ at each HCN in HCN crystal by local field treatment based on Lorentz values. The same authors calculated *ab initio* $\Delta\mu$ as a function of applied electric field strength at HCN. They note that for electric fields where $\Delta\mu = \mu_0$ terms up to the third dipole hyperpolarizability need to be included in correctly obtaining $\Delta\mu$.[17] However, at the local field of the crystal as quoted in Ref. 17, and with inclusion of only the dipole polarizability, Eq. (2), we obtain $0.59\ \mu_0 = \Delta\mu$ rather than $0.60\ \mu_0$, a small difference.[17] This suggests that higher-order terms contribute negligibly to $\Delta\mu$ in $(HCN)_\infty$, where the electric field at each HCN is about half the local field in the crystal.

Given the local field treatment as valid,[17] it obtains the same-chain HCN's contribute about half the local field at a given HCN, with the remainder of the field caused by off-chain HCN sites. Although chains are separated by van der Waals type distances, crystal energetics and $\Delta\mu$ per HCN are not well predicted by consideration of $(HCN)_\infty$ alone with only van der Waals interactions between chains.

Changes in electric field gradient at N

Additional information on charge rearrangement is available from the ^{14}N quadrupole coupling constants χ_a, measured for $(HCN)_2$[14,18] and $(HCN)_3$.[9] For $(HCN)_2$ χ_a is given by

$$\chi_a(n) = \chi_0(n)(1/2)\langle 3\cos^2\theta_n - 1\rangle, \qquad (10)$$

where $n = 1$ corresponds to $N(1)$. In Eq. (10) $\chi_0(n)$ refers to the quadrupole coupling constant at $\theta_n = 0°$, and differs from χ_0 of free HCN due to H-bond formation. Measurement of $\chi_a(n)$ and $(1/2)\langle 3\cos^2\theta_n - 1\rangle$ allows determination of $\Delta\chi_0(n)$ as previously shown for $(HCN)_2$.[18]

It has been suggested that the calculated induced dipole moment of the nitrile group $\Delta\mu_{CN}(n)$, is directly proportional to $\Delta\chi_0(n)$.[14] Table VII summarizes the $\Delta\chi_0(n)$ and calculated $\Delta\mu_{CN}(n)$ for both $(HCN)_2$ and $(HCN)_3$. The $\Delta\mu_{CN}$ are calculated with $E(\mu,\theta,\Omega,\Phi)$ and α_{HC},α_{CN}. The electric fields for dimer and trimer at the CN bond midpoints are multiplied by α_{CN} to obtain $\Delta\mu_{CN}(n)$. The $\Delta\chi_0(2)$ in $(HCN)_3$ is not precisely known because $\langle\cos^2\theta_2\rangle$ is not precisely known.

Table VII shows that for $(HCN)_2$ the ratio of $\Delta\mu_{CN}(1)/\Delta\mu_{CN}(2) = 1.96$ while $\Delta\chi_0(1)/\Delta\chi_0(2) = 2.16$; for $(HCN)_3$, $\Delta\mu_{CN}(1)/\Delta\mu_{CN}(3) = 1.88$ while $\Delta\chi_0(1)/\Delta\chi_0(3) = 1.88$. This suggests a relation between polarization of the CN group and the experimentally derived $\Delta\chi_0$. One might expect a nearly constant proportionality factor between the calculated $\Delta\mu_{CN}$ and $\Delta\chi_0$. In brackets, the ratios are for $(HCN)_2$: $\Delta\mu_{CN}(1)/\Delta\chi_0[1.59]$, $\Delta\mu_{CN}(2)/$

TABLE VII. Calculated induced C–N bond dipoles and experimental $\Delta\chi_0$ for $(HCN)_2$ and $(HCN)_3$.

Property	Units	$(HCN)_2$		$(HCN)_3$		
		(1)	(2)	(1)	(2)	(3)
$\Delta\chi(n)$[a]	MHz	0.229	0.106	0.349	(0.4)[b]	0.183
$\Delta\mu_{CN}(n)$[c]	D	0.364	0.185	0.463	0.599	0.247

[a]See Ref. 18, dimer; Ref. 10, trimer.
[b]Derived from $\Delta\mu_{CN}(2)$ and χ_a of $N(2)$ for $(HCN)_3$, as further discussed in text.
[c]Calculated from the electric fields present in $(HCN)_2$ and $(HCN)_3$ at each C–N bond midpoint and α_{CN}, as further discussed in the text.

$\Delta\chi_0(2)[1.75]$; for $(HCN)_3$: $\Delta\mu_{CN}(1)/\Delta\chi_0(1)[1.35]$; $\Delta\mu_{CN}(3)/\Delta\chi_0(3)[1.36]$.

These four ratios can be brought into agreement by small changes in θ_1, θ_2 of $(HCN)_2$ and θ_1, θ_3 of $(HCN)_3$. For example with $\Delta\mu_{CN}(n)/\Delta\chi_0(n)$ equal to 1.46 θ_1 and θ_2 equal 13.30 and 8.50° for $(HCN)_2$; θ_1 and θ_3 equal to 13.00 and 8.96° for $(HCN)_3$. These can be compared with the experimentally derived angles, Table I, the largest change being 0.5° for θ_2 of $(HCN)_2$. Use of 1.46 to scale $\Delta\mu_{CN}(2)$ in $(HCN)_3$ gives a calculated $\Delta\chi_0(2)$ of 0.411 MHz, which translates to $\theta_2 = 4.9°$.

Such a rough proportionality can be used to understand the measured ^{14}N quadrupole coupling constant of HCN crystal, -3.8904 MHz.[19] The value for the free monomer is -4.7091 MHz.[30] The calculated $\Delta\mu = 1.80$ D[17] can be partitioned between the C–N and C–H bonds by using the bond polarizabilities listed in Table II, the C–N bond being about 4 times as polarizable. This suggests an approximate induced C–N bond dipole of 1.44 D in HCN crystal. Using 1.46 to scale, one obtains 0.98 MHz for $\Delta\chi_0$. The experimentally determined 0.819 MHz difference is largely due to polarization of the C–N bond. One would expect the rms librationally averaged angle for HCN to be small, as suggested for HCN(2) of the linear HCN trimer. The above treatment demonstrates this. Obviously the predicted change is only semiquantitative, in that the experimentally determined change is smaller than the calculated change resulting from changes in the electric field gradient. The magnitude of the calculated value suggests that the rms librationally averaged angle for each HCN in the H-bonded chains in HCN crystal is small.

CONCLUSIONS

Mutual polarization of monomer charge distributions, as calculated with either molecular or bond polarizabilities and available molecular electrical moments located at the c.m. of each HCN, account for measured induced dipole moments in $(HCN)_2$ and $(HCN)_3$. The functional dependence of the calculated induced dipole moment of $(HCN)_2$ demonstrates that sixth and higher order electrical moments contribute negligibly to either $\Delta\mu^{(d)}$ or $\Delta\mu^{(t)}$, i.e., that the relevant electric fields are adequately represented by the dipole, quadrupole, octupole, hexadecapole, and $\psi^{(5)}$ electrical moments.

The $\Delta\mu$ per monomer for rigid linear $(HCN)_n$ ($n = 2$ to

5), calculated using the molecular polarizability α_{HCN} and first four nonzero electrical moments, are similar to *ab initio* calculated $\Delta\mu$ per monomer values. This is suggested as further supporting evidence for the validity of the mutual polarization model.

Extension of the model to $(HCN)_\infty$ for different representations of the electric field are given. Using the molecular polarizability and c.m.–c.m. nearest neighbor separation as in the infinite linear chains present in HCN crystals yields a 33% enhancement in dipole moment per HCN with electric fields calculated from μ, θ, Ω, and Φ (the first four nonzero electrical moments). Given the 60% enhancement calculated from local field theory for HCN crystal,[17] nonchain sites contribute about equally as same-chain sites to the local field at a given site in HCN crystal.

Experimentally derived values for the change in χ_0, $\Delta\chi_0(n)$ (caused by change in the electric field gradient), for ^{14}N in $(HCN)_2$ and $(HCN)_3$ show ratios essentially equal to the ratios of calculated induced C–N bond moments, $\Delta\mu_{CN}(n)$.

There has been a recent suggestion that the large 0.819 MHz increase in the ^{14}N nuclear quadrupole coupling constant in HCN crystal, relative to HCN monomer, is due largely to a combination of Sternheimer shielding and zero-point vibrational averaging effects.[31] The authors of this paper[31] have also suggested that the crystal structure of HCN likely consists of antiparallel H-bonded chains of HCN's, not parallel chains as Dulmage and Lipscomb reported from an analysis of x-ray diffraction data.[16] It is, however, shown here that the 0.819 MHz increase in the ^{14}N nuclear quadrupole coupling constant can be rationalized by a simple relation between the calculated induced C–N bond dipole moment and the change in the electric field gradient at N. The model presented here, therefore, suggests the 0.819 MHz increase is primarily due to polarization of the C–N bond.

It is satisfying that the linear HCN dimer[18] and trimer[10] data obtained from rotational spectroscopy can be employed to further understanding of HCN crystal, in that both can be looked upon as elements of the series of linear, H-bonded oligomers which contains as its end element the infinite, linear, H-bonded chain $(HCN)_\infty$. Such long, linear H-bonded chains are, as discussed, present in the HCN crystal.

Success of the mutual polarization model outlined here for H-bonded $(HCN)_2$ and $(HCN)_3$ suggests that there is not significant charge transfer between monomers. This is relevant because of the strength of the H bonds in $(HCN)_2$ and $(HCN)_3$, with the binding energy of $(HCN)_2$ about 1700 cm^{-1},[14] and the binding energy per H bond in $(HCN)_3$ greater than 1700 cm^{-1}. In this regard, future measurements of $\Delta\mu$ in other dimers and trimers should provide useful benchmarks against which to test mutual polarization models.

ACKNOWLEDGMENTS

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