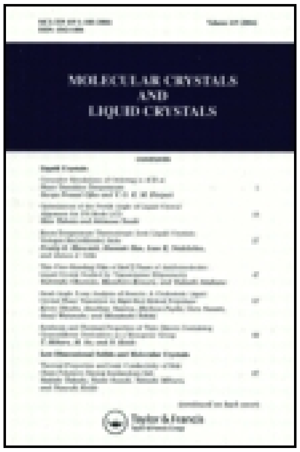

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The Lattice Vibrations of Molecular Crystals III. The Spectrum, Dynamics and Lattice Energy of the Methylamine System

F. G. Baglin [a] [b], S. F. Bush [a] [c] & J. R. Durig [a]

[a] Department of Chemistry, University of South Carolina Columbia, South Carolina, 29208
[b] Department of Chemistry, University of Nevada, Reno, Nevada
[c] Department of Chemistry, Erskine College, Due West, South Carolina

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The Lattice Vibrations of Molecular Crystals III.‡ The Spectrum, Dynamics and Lattice Energy of the Methylamine System

F. G. BAGLIN,§ S. F. BUSH‖ and J. R. DURIG

Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208

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Abstract—The infrared spectra of crystalline methylamine and methylamine-d_5 have been recorded from 33 to 500 cm^{-1}. Spectral band assignments were made according to whether they arose primarily from translational or librational motions. A model is proposed so that the principal features of the spectrum can be interpreted. Some quantitative results are offered in support of the model and the modes of motion arising from it. The " center law of lattice vibrational spectra " is interpreted and used to calculate the lattice energies of methylamine and a previously studied system, cyanamide. The agreement achieved for both the dynamics and the energy calculations are in good agreement with observed frequencies and other molecular crystal energies.

Introduction

We have previously investigated two other rather strongly hydrogen bonded systems[1,2] without proposing any model by which the dynamics and energy of molecular crystal systems could be evaluated. In this paper we propose to calculate some of the intermolecular vibrations and also to determine the lattic energy

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‡ For part II, see *J. Chem. Phys.* **49**, 4695 (1968).

§ Present address: Department of Chemistry, University of Nevada, Reno, Nevada.

‖ Present address: Department of Chemistry, Erskine College, Due West, South Carolina.

of the methylamine and cyanamide systems. Methylamine was chosen because it had the same crystal (factor group) symmetry as the cyanamide molecule studied earlier, and because of the comparatively large frequency shift this molecule should exhibit upon deuteration. The mass changes from 31 to 36 amu for methylamine with deuteration which should prove valuable for differentiating between librational and translational motions in the crystal. We were anxious to compare the far infrared transmission spectrum of cyanamide (NH_2CN) to that of the methylamine (CH_3NH_2) molecule for two reasons. First, there is a large difference in the melting points of the two solids (NH_2CN at 45 °C and CH_3NH_2 at − 92 °C), and second, their factor groups are isomorphic (D_{2h}^{15} for CH_3NH_2 and D_{2h}^{16} for NH_2CN both with 8 molecules per unit cell). Thus, we have recorded the far infrared spectra of methylamine and methylamine-d_5 and compared them to those previously published for the cyanamide molecule.

In the past, the calculation of intermolecular crystal frequencies has been accomplished by two different procedures. These have been discussed elsewhere.[2] To state them briefly they are the method given by Pople and Walmsley[3] and the other given by Shimanouchi which uses the Urey-Bradley force field.[4] Since we feel the Pople-Walmsley approach to be more theoretically sound, we have constructed our potential functions in basically the same way they have. However, because we have no single crystal polarization data we could not assign the various translational and librational frequencies according to symmetry species. This led us to use a frequency evaluation procedure given by Hirschfelder, Curtiss and Bird.[5] This method was satisfactory for the translational type of crystal vibration, but could not be used for the librational crystal modes. To calculate some of the librational modes it was necessary to use experimental data, i.e. the root mean square average librational frequency and then apply the coupled oscillator procedure of Lennard-Jones.[6]

The calculation of molecular lattice energies from infrared active crystal frequencies has, to our knowledge, not been previously undertaken. We have adopted the approach taken by

Plendl for ionic systems to molecular crystal systems. In a series of earlier publications, he proposes a particularly simple method for the calculation of crystal energies.[7,8] Indeed, the results obtained from his method are in excellent agreement with those found by other means even though his method is strictly empirical. We were particularly interested to see what kind of agreement Plendl's procedure would yield for methylamine in comparison to cyanamide. Although it is qualitatively accepted that cyanamide should have a greater lattice energy than methylamine, the external lattice frequencies of the two compounds do not outwardly appear to reflect this result.

EXPERIMENTAL

The far infrared spectra were recorded from 33 to 500 cm^{-1} by using a Beckman IR-11 spectrophotometer. The instrument was calibrated by using atmospheric water vapor. The single beam energy was kept between 10–15% at all times. Various gain settings and scanning speeds were used to obtain the best resolution and presentation of spectral data. A low temperature cell identical to one described earlier[1] was used to examine the samples which were evaporated onto silicon sample support plates described elsewhere.[9] The sample of CH_3NH_2 was purchased from Matheson Chemical Company, while the CD_3ND_2 compound was purchased from Merck, Sharpe and Dohme of Canada. The spectra of both the " light " and " heavy " compounds were examined in the mid-infrared region and were found to be free of ammonia, water or other contaminates. As a result, the samples were used without further purification.

DISCUSSION OF EXPERIMENTAL RESULTS

The number and species of the intermolecular vibrations to be expected from solid methylamine can be predicted in a straightforward manner by using the group theoretical treatment for solids proposed by Halford and Hornig.[10] The results for a D_{2h}^{15}-Pcab system with eight molecules per unit cell are given below. The total irreducible external vibrational representation is,

$$\Gamma(vib) = 6A_g + 6B_{1g} + 6B_{2g} + 6B_{3g} + 6A_u + 6B_{1u} + 6B_{2u} + 6B_{3u} \quad (1)$$

The acoustic modes are given by,

$$\Gamma(AT) = B_{1u} + B_{2u} + B_{3u}. \quad (2)$$

The optic translational modes are then

$$\Gamma(OT) = 3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g} + 3A_u + 2B_{1u} + 2B_{2u} + 2B_{3u} \quad (3)$$

while the optic librational modes are found to be

$$\Gamma(OL) = 3A_g + 3\mathrm{B}_{1g} + 3B_{2g} + 3B_{3g} + 3A_{B1u} + 3B_{2u} + 3B_{3u}. \quad (4)$$

The Raman active modes are the gerade species whereas the infrared active ones are all the ungerade species with the exception of the A_u species. Therefore, the far infrared spectrum of methylamine could contain nine frequencies arising from librational motions and six frequencies arising from the translational motions of the molecules in the unit cell.

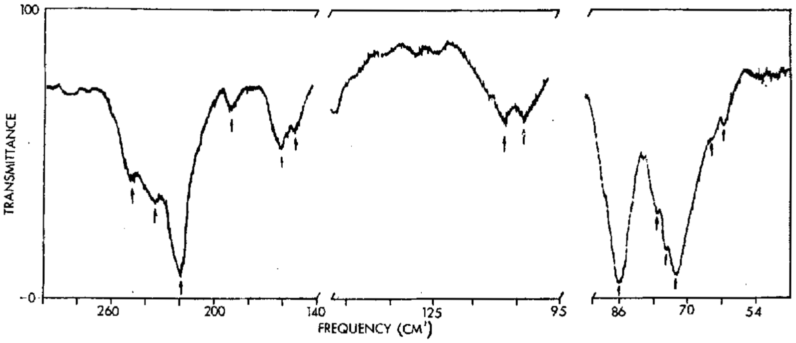

Figure 1. An original far infrared spectrum of crystalline methylamine. The arrows indicated spectral features which became quite pronounced with increased sample thickness. It was necessary to record the spectrum many times with several different sample thickness in order to differentiate between weak background absorption and the real lattice modes.

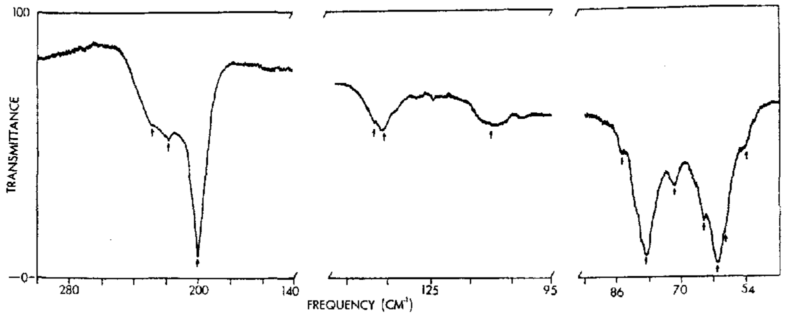

Figure 2. An original far infrared spectrum of crystalline methylamine-d$_5$. See caption for Fig. 1 for explanation of arrows.

Figures 1 and 2 show the infrared spectra of CH$_3$NH$_2$ and CD$_3$ND$_2$, respectively. For the light compound, 14 of the predicted 15 bands are clearly distinguishable, whereas 13 of the bands can be readily identified for the " heavy " molecule. The observed frequencies for CH$_3$NH$_2$ and CD$_3$ND$_2$ are shown in Table 1. The band at 104 cm^{-1} in the CH$_3$NH$_2$ spectrum has very

Table 1 Observed and Calculated Far Infrared Bands for Methylamine and Methylamine-d$_5$

CH$_3$NH$_2$ freqs. cm^{-1}		CD$_3$ND$_2$ freqs. cm^{-1}	Calc. Shift	Obs. Shift
obs.	calc.	obs.	Parameter	Parameter
62	56	53	0.855	0.854
65	61	57	0.855	0.877
73	—	64	0.845	0.808
75	—	59	0.845	0.787
78‡	76	71	0.928	0.910
86‡	—	79	0.928	0.919
104	—	77	0.707	0.740§
107	—	85	0.855	0.794
151	154	108	0.707	0.715
160	158	133	0.845	0.821
188	—	135	0.707	0.718
220‡	—	200	0.928	0.909
235‡	236	218	0.928	0.928
247‡	244	235	0.928	0.978§

‡ Translational modes; all others are librational modes.

§ Band peak could not be accurately measured in either isotope.

likely been shifted under the strong 79 cm^{-1} absorption found in the CD_3ND_2 spectrum. In fact, one can faintly discern a low frequency asymmetry to the 79 cm^{-1} band near 77 cm^{-1}. We have very tentatively assigned this asymmetric shoulder to the same mode found in the light compound at 104 cm^{-1}. The one band which was not found in either spectra is of translatory origin. Of the 5 observed absorptions assigned as translations, four are quite strong (247, 235, 220, and 86 cm^{-1}), whereas the band at 78 cm^{-1} arising from the remaining translation is quite weak. It is possible the unobserved translational mode may be of the same low intensity as that observed for the 78 cm^{-1} band or it may be hidden under the 86 cm^{-1} band or one of the high frequency translations. If this were the case, it would very likely not be observed in the spectrum for either isotope.

The calculated and observed isotopic shift parameters are given in Table 1 along with a summary of the observed absorption bands for CH_3NH_2 and CD_3ND_2 with their respective assignments. The calculated isotopic shift parameters were found in the usual way,[1] and frequency assignments were made principally on the basis of these parameters. However, the band intensity was also considered, since we assumed that the intensities of the bands arising from the corresponding modes for the two isotopes should be quite similar. Variations between the observed and calculated isotopic shift parameters are explained on the basis of mixing of translational and librational modes. Since the mixing appears to be weak on the basis of the results given in Table 1, we have neglected it in the calculation of intermolecular frequencies given later in this paper. The center of inversion which the D_{2h}^{15} space group possesses is not occupied by a molecule; therefore *g–g* or *u–u* mixing of the vibrational modes is allowed whereas the *g–u* type mixing is not allowed.

From the crystal structure data taken by Atoji and Lipscomb,[11] one can visualize a model to qualitatively, and in the next section of the paper quantitatively, interpret some of the motions of the system. Figure 3 (taken from Atoji and Lipscomb's paper—the number N_5, N_6 and N_5' were added for aid in discussion) shows this model. The high frequency translations can be described as intermolecular motions along the hydrogen bonds (dotted Lines), whereas the low frequency translations can be considered as motions arising from non-hydrogen bonded neighbors. Thus, the 247 and 235 cm^{-1} absorption bands arise from translational motions of the N_6 and N_1 atoms along the dotted (hydrogen bonds) lines toward the N_2 atom, and N_4' and N_4 atoms along the dotted lines toward the N_2 atom, respectively. The 78 cm^{-1} absorption band corresponds to a mode of motion in which the N_5' and N_3 atoms move along a line passing through the N_5', N_2 and N_3 atoms and in the same mode the N_3' and N_5 atoms move along a line passing through the N_3', N_2 and N_5 atoms. Thus, the

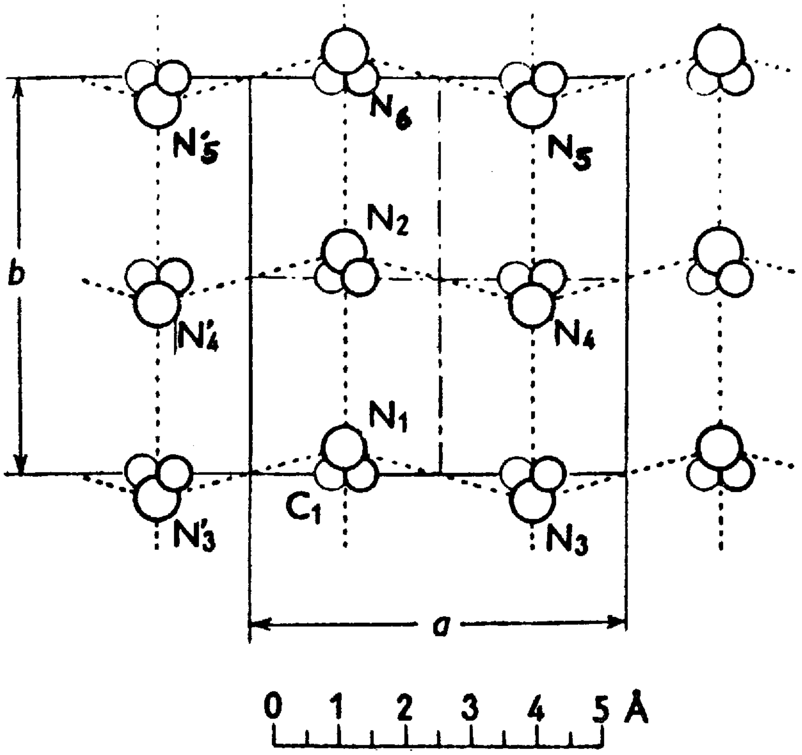

Figure 3. The crystal structure of methylamine, view is parallel to the c axis (figure is from Atoji and Lipscomb's work, see reference 11).

latter motion involves the displacements of four molecules (N_5', N_5, N_3' and N_3), where the former modes (the 247 and 235 cm^{-1} absorption bands) involve only motions of pairs of molecules, (N_1, N_6 and N_4', N_4).

The librations between molecules along the hydrogen bonds were examined only in a pairwise fashion. Thus, when pairs oscillate out of phase the high frequency transitions are observed whereas if they oscillate in phase the low frequency transitions are observed. Only two pairs of molecular oscillators were considered, they were N_6 or N_1 coupled in an in-phase or out-of-phase motion with N_2, and N_4 or N_4' coupled in an in-phase or out-of-phase motion with N_2. The modes could be described in terms of either N_6 or N_1 and N_4 or N_4' since the following distances are equal: $N_6 - N_2 = N_1 - N_2$ and $N_4 - N_2 = N_4' - N_2$. The model disregards any interactions with next nearest neighbors or the next layer in the structure. Some quantitative results will be offered in the following section to support this model.

Calculation of the External Lattice Vibrations of Methylamine

INTRODUCTION

It would seem appropriate to discuss briefly our reasons for using the method proposed by Hirschfelder *et al.* for evaluation of translational crystal frequencies and the adaptation of Lennard-Jones' early work to the librational modes of this crystal. All intermolecular vibrations are considered to be occurring at or very close to the center of the Brillouin zone ($k \approx 0$). In the D_{2h} system there are seven symmetry directions in the Brillouin zone. Since there will be $3N$ branches for each symmetry direction (where N is the number of molecules per unit cell), there would be a total of 168 separate dispersion relations in the methylamine crystal. If a potential function is correct for an ordered system then one should be able to evaluate the dispersion relations along each symmetry direction. In order to decide if such an evaluational procedure is accurate one must also gather experimental data on these dispersion curves. It is clear that such calculations and experiments are literally impossible at the present time due to the extremely complex nature of the methylamine system. There are, of course, computer programs now available[12,13,14] which allow one to calculate the intermolecular vibrations at $k \approx 0$. However, except for one of the procedures,[14] they have been used on systems to which they are not strictly applicable. The programs are based upon harmonic restoring forces and when the intermolecular crystal system's force constants vary as $1/r^3$, $1/r^5$, $1/r^n$ they are not harmonic. Furthermore, the intermolecular restoring forces are not, in general, the induced dipole-induced dipole type included in the Lennard-Jones $-b/r^6$ terms. These $-b/r^6$ terms are usually included in a Urey-Bradley force field treatment in order to take into account the non-bonded interactions. By including specific types of interactions, i.e. charge-dipole, dipole-dipole, dipole-induced dipole, we avoided having to give values to the a and b parameters in the Lennard-Jones potential. Such a procedure would be justified if we had an independent check on the magnitudes of the parameters; unfortunately this is not the case. Therefore, we have constructed a potential which might be called an extended Stockmayer potential. It will be fully discussed in detail in the next section. Thus, we wish to examine the intermolecular forces from a point of view different from that taken by previous workers. The analysis presented here is carried out in terms of displacements of the molecules along the hydrogen bonds and other nearest neighbor modes of motion which are governed by restoring forces of the specific type mentioned above for the model shown in Fig. 3. The use of a simple lattice model made up of idealized diatomic molecules interacting through well understood terms allows evaluation of some of the external lattice frequencies. The method used for the translational frequency calculation was first proposed by O. K. Rice[15] for evaluating Debye frequencies and Debye temperatures of rare gas crystal lattices; however, it readily lent itself to the evaluation of nearest neighbor translational frequencies for the

CH_3NH_2 crystal. Within the limitations of the model, it shows a possible origin for the translational frequency distribution observed in the far infrared spectra of the system (these motions have been qualitatively discussed in the previous section). Furthermore, it has good flexibility, since the kinds of terms which make up the potential function can be readily added to, subtracted from, and tested quickly. Finally, it makes use of the model's symmetry through introduction of the n_i term, as will be seen momentarily.

The librational frequency evaluation procedure was not as satisfactory as that used for the translational modes for the reasons previously mentioned, i.e., the need to use experimental frequency data. All librations were simply evaluated as pairwise interactions. As a result, this method produced symmetric and asymmetric coupling for each of the two nearest neighbor distances along the hydrogen bonds shown in Fig. 3.

METHOD

The frequencies arising from the translational modes were calculated without the use of *any* experimental vibrational data. However, the calculated librational frequencies were obtained by using the root mean square average ($\langle \nu_{\text{lib}} \rangle = 118\ \text{cm}^{-1}$) of all experimentally assigned librational frequencies. The potential functions for both libration and translation were comprised of a principal and a minor interaction term. The translational potential function terms were as follows: (1) principal–hydrogen bond interaction and (2) minor–Φ_{m1} (defined below). In a like manner, the librational potential function terms were the following: (1) principal–$\langle \nu_{\text{lib}} \rangle = 118\ \text{cm}^{-1}$ and (2) minor–Φ_{m2} (defined below). Thus we may write,

$$\Phi_{\text{total}} = \Phi_{\text{trans}} + \Phi_{\text{lib}} \tag{5}$$

where we neglect cross terms between libration and translation. Furthermore,

$$\Phi_{\text{trans}} = \Phi_{\text{H-bond}} + \Phi_{m1} \tag{6}$$

$$\Phi_{\text{lib}} = \Phi\langle \bar{\nu}_{\text{lib}} \rangle + \Phi_{m2} \tag{7}$$

The principal interaction terms are further defined as follows:

$$\Phi_{\text{H-bond}} = \frac{[(-\langle Z^*_{\text{dir}}\rangle)(+\langle Z^*_{\text{dir}}\rangle)]}{r_i} - \frac{(\langle Z^*_{\text{dir}}\rangle)\mu\cos\theta}{r_i^{2}} \tag{8}$$

$$\overset{\ddagger}{\Phi}\langle\bar{\nu}_{\text{lib}}\rangle = -\oint\left\{\frac{I\pi^{2}\langle\bar{\nu}_{\text{lib}}\rangle}{\sum_i r_i^{2}}\right\}\cdot d\mathbf{r} \tag{9}$$

All terms in these and other equations are defined in the appendix at the end of the paper.

We have two force constants, one for the complete translational force constants k^i_{ct},

$$k^i_{ct} = 1/3\sum_i n_i[1/r_i\underset{\text{trans}}{\Phi'(r_i)} + 1/2\underset{\text{trans}}{\Phi''(r_i)}] \tag{10}$$

and the other for minor librational force constant k^i_{mL},

$$k^i_{mL} = \sum_i[1/r_i\Phi'_{m1}(r_i) + 1/2\Phi''_{m1}(r_i)] = 1/3n_ik^i_{mt} \tag{11}$$

The individual terms which are to be placed in Eq. (11) for the evaluation of k^i_{mL} are given in the discussion section below.

The translational and librational frequencies are evaluated, respectively, by the following:

$$\nu_i = 1/2\pi[k^i_{ct}/m_a]^{1/2} \tag{12}$$

$$\nu_i = 1/\pi\{\sum_i r_i^{2}/I(k^i_{pL} \pm k^i_{mL})\}^{1/2} \tag{13}$$

DISCUSSION

The hydrogen bonding term, $\Phi_{(\text{H-bond})}$, is approximated by modified classical electrostatic methods. This procedure is suggested by other workers.[16] The values used for $(+\langle Z^*_{\text{dir}}\rangle)$ and $(-\langle Z^*_{\text{dir}}\rangle)$ were simply the fraction of an electronic

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‡ We define $\mathbf{F}$ as the line integral of the force along a curve. If $\mathbf{F}$ is well-behaved and irrotational, $\nabla \times \mathbf{F} = 0$, then there exists a potential function Φ such that $\mathbf{F} = -\nabla\cdot\Phi$. It then follows that Φ is a single valued function. This equation is included so as to be consistent with the form Φ (H-Bond) and for purposes of definition.

charge which the proton " sees " under the approximation of Slater 1*S* electronic shielding parameters applied to the nitrogen's lone pair electrons. Here we assume that the hydrogen's electron will have no probability of shielding its proton from one of the neighboring nitrogen's lone pair electrons, i.e., it is completely involved in the *N–H* intramolecular bond. It should be noted that this procedure encompasses the entire $[\Phi'_{\text{H-bond}}/r_i + \Phi''_{\text{H-bond}}/2]$ term. That is, the anharmonic correction brought about by the implicit use of the first derivative term in the *i*th complete translational force constant k^i_{ct} was deleted in place of the repulsion correction introduced by the Slater shielding parameter. Alternatively one could simply evaluate the Φ' and Φ'' hydrogen bond terms by using a " best fit " for the charges $\langle Z^*_{\text{dir}}\rangle$ developed along the various hydrogen bonds during the mode of motion under consideration. However, one should still use the Slater shielding parameter values as guides for such calculations. In the definition of $\langle Z^*_{\text{dir}}\rangle$, it is worth noting that this type of interaction has been included by other workers. Pitzer[17] has designated the interaction between part of one molecule and part of a second molecule as the acentric term. Thus, the effective charge used here i.e. $\pm \langle Z^*_{\text{dir}}\rangle$ is the acentric term between two particular parts of two different molecules, i.e., the *N–H– – –N* hydrogen bond. Later, another effective charge will be introduced which is derived from the overall or concentric interactions and will be denoted simply $\langle Z^*\rangle$. The use of the term k^i_{pL} has been discussed in a recent publication.[1] The k^i_{ct} term of Eq. (10) is from Hirschfelder *et al.*[18] (Eq. (13.9–9). We wish to focus our attention then on the terms used in constructing k^i_{mL} (since k^i_{mt} is simple related to k^i_{mL} by Eq. (11), we shall not explicitly discuss it). From the work of Margenau,[19] the important interactions necessary to describe a molecular crystal system made up of a collection of ideal dipoles are apparent. In the case of methylamine we assume it to be a diatomic system with geometrically similar ends, i.e. volume of $CH_3 \approx$ volume of NH_2, but with different electrical environments caused by the dipole moment in methylamine (1.25D). In as much as there is a dipole moment present, we have found, by calculation of nearest neighbor interactions, that quadrupole and induced dipole contributions are negligible. Indeed, it is possible that if enough next nearest neighbors contribute to these $1/r^7$, $1/r^8$ etc. terms, absorptions due to such interactions might be predicted below $\sim 100\ \text{cm}^{-1}$. However, our purpose is to analyze the nearest neighbor interactions rather that those neighbors beyond this point. These latter terms are undoubtedly important, but it is possible to find many different combinations of these weak interaction terms without any way of distinguishing one type of effect from another. Since the results we obtained lacked the correct number of frequencies below $110\ \text{cm}^{-1}$ (8 observed 3 calculated), it would seem that some type of long range interactions might be present. Correction was made for the deformable nature of the electronic cloud by allowing the dipole moment to interact with the polarizability $\alpha = 40.81 \times 10^{-25}\ \text{cm}^3 \pm 4.08 \times 10^{-25}\ \text{cm}^3$). The following terms were included in k^i_{mL}: (1) a modified repulsion term from the Buckingham potential for crystalline argon,[15] (2) a London resonance interaction (for systems interacting at less than 7Å), (3) a London induction interaction term, mentioned above, and (4) an angular orientation or first order Keesom interaction term. It is worth pointing out that *only* the modified repulsion term was adjusted in the calculation of *both* the librational and translational frequencies and its constants once determined, were not changed. These terms are given below for k^i_{mL} in explicit form and are shown in the order mentioned in the previous sentence

$$k^i_{mL} = \left\{(0.92 \times 10^2)(-2.90)\exp(-2.90 r_i)\left[1/r_i \frac{-2.90}{2}\right]\right\} + \left\{\frac{-3\mu^2}{r_i^5}\right\} + \left\{\frac{-15\alpha\mu^2}{r_i^8}\right\} + \left\{\frac{-3\mu^2}{r_i^5}(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi)\right\} \tag{14}$$

As was noted earlier, all terms are defined in the appendix. In regard to the last term in Eq. (14), it can be shown that given the proper geometry ($\cos\phi \simeq 1, \theta_1 \simeq \theta_2$) it reduces to a term containing $(2 - 3\sin^2\theta)$. All geometric data necessary for this and other terms were evaluated by a simple symmetry transformation computer program. In the evaluation of the frequency for all the librations and the high frequency translations the interacting molecules were taken to be (from Fig. 3) N_2 interacting with N_4, N_4', N_1 and N_6 in the same manner discussed in the previous section. For the evaluation of the low frequency translational modes N_3, N_3', N_5 and N_5' interact with N_2, also discussed in the previous section. From Fig. 3 it is clear that these latter modes are " non-hydrogen bond " interactions and as a result neither a principal translational interaction term $k^i_{pt}(\Phi''_{\text{H-bond}})$ or a repulsion term, like the first term in equation fourteen, were included. We should like to briefly comment on the relation between k^i_{mL} and k^i_{mt} in Eq. (11). The 1/3 factor which appears here is due to the orientational averaging procedure used by O. K. Rice and Hirschfelder *et al.*[18] and was excluded from the librational results. We have, however, adopted the form of the force constants taken, i.e. $(\Phi'/r_i + \Phi''/2)$ so as to include the very important anharmoric features of an intermolecular system. We also have set $n_i = 1$ for a pairwise librational interaction.

Finally, Table 1 shows a summary of the calculated frequencies. Whereas the overall calculated frequency distribution is good, the distribution below 110 cm^{-1} is rather poor as was noted above. The higher multipole terms might be important to include when considering first, the next nearest neighbor intralayer interactions with N_2, or second, those interlayer interactions which would be found at distances corresponsing to intralayer next nearest neighbor distances. It is worth noting that there is another high frequency (220 cm^{-1}) absorption which is not accounted for by the interactions corresponding to $n_i = 2$ (the motions along the hydrogen bonds) or to $n_i = 4$ (the motions not associated with the hydrogen bonds). Whereas the interlayer N–H– –N interaction may not be strong, compared to the interactions occurring along the a and b directions, it may be that there is indeed an important C component which has been neglected in our simplification of the layer to a plane. Since the structure of methylamine shows a " zig-zag " arrangement of molecules along both *ac* and *bc* planes (here we can visualize the planes as intersecting at only N_2 for simplicity), the " *ab* plane " lies between N_2 and N_1, N_4' and N_6. Thus, if N_2 is displaced in the $-C$ direction and the other molecules are displaced in the $+C$ direction the mid points of all the C–N bonds would become coplanar. As a result, we could consider our layer to be a plane with thickness. This would certainly be a mode which could give rise to the 220 cm^{-1} absorption band. However, the above mathematical treatment cannot be used to consider such a mode. We believe that the method described here should be applicable to other molecular crystal systems which have similar structural properties and interactions both stronger and weaker than the methylamine system.

Calculation of the Lattice Energy of Methylamine and Cyanamide

In several recent publications Plendl[7,8] has shown a rather interesting correlation between what he calls ν_{ctr} frequency and the Debye frequency ν_D. Plendl showed that ν_{ctr} is easily evaluated by tracing the infrared active spectrum of an alkali halide, alkaline earth halide, or other system on to a piece of cardboard and then finding the balance point of the " cut-out ". This is then the spectral center of gravity. In the first of the afore mentioned publications he outlines his results and states the " Center Law of Lattice Vibration Spectra " to wit, $\nu_{\text{ctr}} = (k/h)\theta = \nu_D$. This law is slightly modified in the later publication to take into account certain deviations from the absolute one to one correlation between ν_{ctr} and ν_D. The concept is offered on an empirical premise, but from the amount of data Plendl has gathered it seems clear that he has established a relationship between ν_{ctr} and ν_D through the infrared spectra of various solids. He has also established this relationship in 34 different metals, e.g. K, Na, Fe, Mo, Bi, etc.[20]

In this section of the paper, we wish to determine if this empirical law will also hold for molecular crystals. One finds that there is a correlation between the temperature at which the lattice ceases to exist (the melting point) and the lattice cohesive potential energy U_0 [simply defined by the following process: $M(s) \rightarrow M(g) + U_0$]. This can be seen by referring to Fig. 4 and in particular by referring to the data illustrated by the circular dots. These data were gathered from an independent source[21] and clearly illustrate the above relationship for systems whose molecular mass and intermolecular attraction are nearly equal. It may be argued that since Plendl's equation does not possess a theoretical basis one should not use it. However, it should be borne in mind that the

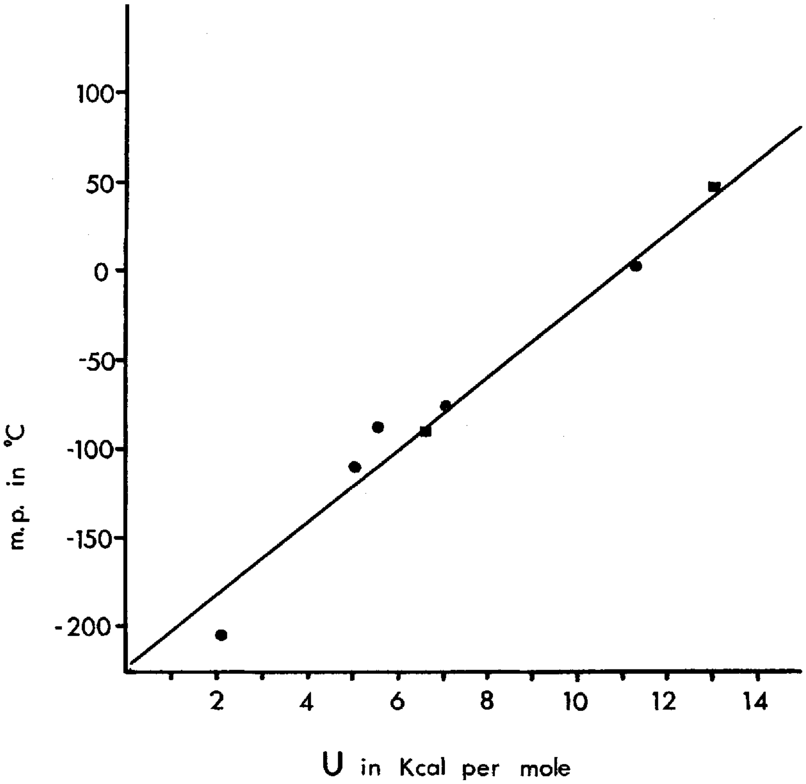

Figure 4. The lattice cohesive potential energy vs. the melting point of, from lower left to upper right, CO, HCl, HBr, CH_3NH_2, NH_3, H_2O and NH_2CN.

heat of sublimation is calculated *empirically* from log P versus T data; furthermore, it is tacitly assumed that the surface interaction between molecules in a crystal is equal to the internal interaction and as a result $U_0 = \Delta H_{\text{sublimation}}$. Notice in particular that the zero point energy (kinetic) must not be neglected; as is well known this term is of great importance in hydrogen bonded molecular crystals.

In ionic dielectric solids, or any solid in which the terms inter- and intra-molecular vibrations are meaningless (e.g., SiO_2, diamond, SiC, etc.), the observed infrared spectrum is used to determine ν_{ctr}. Of course, in molecular solids we find molecules substituted for the ions or atoms of the " hard " dielectric solids (i.e., systems with a very low compressibility). Thus, in " soft " dielectric solids, i.e. molecular solids, it is clear that we must include those frequencies which arise from intermolecular forces as opposed to those arising from intramolecular vibrations. As will be seen below it is possible to calculate ν_D with an error of $\sim 5\%$. This measurement is sufficiently accurate to determine whether or not a particular absorption is inter or intramolecular in origin. Making this distinction, of course, depends on the assumption that the coupling between inter and intramolecular frequencies is small.

As mentioned earlier, one must be cautious about using some of the terms usually associated with ionic solids and also some of the terms Plendl presents in his second paper,[8] when working with soft dielectric materials. The fact that molecular crystals have librational degrees of freedom and that this additional freedom manifests itself in rather high frequency absorptions (at least in hydrogen bonded solids), tends to render the concept of a Debye temperature useless, e.g. methylamine's calculated Debye temperature is nearly 100 degrees above the melting point (in fact, it is very close to the boiling point)! At the same time, cyanamide's calculated θ_D is about 60 degrees below the melting point. Therefore, one might generally infer that systems which depend upon directed interaction as their chief means of cohesion are likely to suffer from such inconsistencies (see also the publication by O. K. Rice[15]). Plendl also discusses the concepts of hard and soft force characteristics and compressibility in his second paper. While we have not taken data on enough systems to warrant a completely accurate evaluation, it seems likely that the anisotropy of intermolecular forces in soft dielectrics may render the afore mentioned concepts much more difficult to interpret in comparison to the results on hard dielectrics. However, none of the above comments should detract from the method's applicability to the estimation of lattice energies (both total and kinetic as well as potential).

Plendl gives the following expression for the relation of ω_D to U, the lattice potential energy in ergs per formula weight.

$$2\pi\nu_D = \omega_0 = F(A)(1/r_0)(2U/Zm_r)^{1/2} \tag{15}$$

$$F(A) = X_m^{1/p} = \omega_{\mathrm{ctr}}/\omega_D = \log n \tag{16}$$

In Eq. (17) the zero point correction is given as

$$E_0 = \frac{3Nhc}{2}\tilde{\nu}_{\mathrm{ctr}} \tag{17}$$

In Eq. (15) r_0 is the nearest neighbor distance, or the average of the nearest neighbor distances in cm., U was defined above, Z the valency within the molecule and m_r is the reduced molecular mass in grams. The quantity $F(A)$ is called the anharmonicity factor and is equal to the ratio of $(m_r/m_{\mathrm{KCl}})^{1/P}$. KCl is chosen because Plendl defines the anharmonicity in terms of the KCl spectral line shape and other properties of this compound. The term P in Eq. (16) is found by Plendl to be equal to 23 for systems whose reduced mass is equal to or less than 12×10^{-24} g and equal to 9 for other systems. The n term is the familiar electrostatic repulsion coefficient. The properties of n are the same as those of the exponent in the repulsion term of Eq. (14). Thus, the repulsive energy is inversely proportional to n or to the exponent of the repulsion term, $(-2.90\, r_i)$, found in Eq. (14). In fact, it was found that if n, taken from Eq. (16), was set equal to $(-br_i)$ and if the average nearest neighbor value of r_i was used, the value of the b was found to be 3.00 compared to 2.90 previously determined from the repulsive term in Eq. (14). Finally, we are left to discuss Z. In Plendl's paper he defines it as the valency within the molecule and it is clearly a non-directional quantity for ionic systems. This means that $\langle Z^*_{\text{dir}}\rangle$ cannot be used in Eq. (15) because this charge is acentric, i.e. only involves parts of the interacting systems and does not, in this case, truly reflect the forces binding the molecules together in the crystal. We have interpreted Z as an effective charge and denoted it $\langle Z^*\rangle$. To evaluate $\langle Z^*\rangle$ for Eq. (15), we have used the method given by Kurosawa.[22] This method is strictly true only for cubic systems where the high frequency dielectric constant K_0 is isotropic, but it has given excellent results in both systems we have studied. As a result, the value of $\langle Z^*\rangle$ is an average to the extent that K_0 is anisotropic. The details of its evaluation for molecular crystals are given elsewhere.[2] It has been calculated for cyanamide (NH_2CN) and methylamine, both of which are D_{2h} systems i.e. *Pbca* and *Pcab*, respectively. From previous work we had enough information to calculate U for the cyanamide system. In this way we were able to compare the results obtained for CH_3NH_2 with those of NH_2CN and also the results obtained from other sources[21] on other molecular crystal systems.

In Fig. 4 the lattice potential energies of various systems are plotted against their respective melting points. The points represent, from lower left to upper right, carbon monoxide, hydrogen chloride, hydrogen bromide, methylamine (in square), ammonia, water and cyanamide (in square). It is quite evident that the correlations between the lattice potential energies and melting points for cyanamide and methylamine are as good as the correlations obtained on other systems by previous workers. The values for the total lattice energies found for methylamine and cyanamide are 8.21 ± 0.82 kcal/mole and 15.0 ± 1.5 kcal/mole, respectively. These values include a 2.61 kcal/mole and 1.95 kcal/mole zero correction for CH_3NH_2 and NH_2CN, respectively. While it is too soon to definitely state that Plendl's method will be generally applicable to molecular crystals, it certainly shows good promise of competing with and possibly surpassing heat of sublimation data [frequently, heat of sublimation data is not available for molecular crystal systems] for estimating the lattice cohesive energy of molecular crystal systems.

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Appendix

The terms in Eqs. (1)–(4) and (15)–(17) are either well known or adequately discussed in the text. However, for the sake of clarity, there is some overlap. The terms are defined in the order of their appearance in the text.

Φ	The potential energy.
Φ_{m1}	The minor translational energy component.
Φ_{m2}	The minor librational energy component.
Φ''	Force constants, i.e. the second derivative of Φ with respect to distance.
$\langle Z^{*}_{\mathrm{dir}} \rangle$	The acentric effective charge in fractions of e.
θ	The angle between a point charge and the dipole mid-point.
I	Moment of inertia.
k^{i}_{pL}	The principal librational force constant at the ith intermolecular distance, $= \Phi''\langle \bar{\nu}_{\mathrm{lib}} \rangle$.
k^{i}_{ct}	The complete translational force constant at the ith intermolecular distance, $= \Phi''_{\mathrm{trans}}$.
n_i	An integer identifying the number of molecules at the ith intermolecular distance.

k^i_{mL}	The minor librational force constant at the ith intermolecular distance, $= \Phi''_{m1}$.
k^i_{mt}	The minor translational force constant at the ith intermolecular distance, $= \Phi''_{mt}$.
r_i	The ith intermolecular distance.
ν_i	The frequency in cm^{-1} corresponding to the ith intermolecular distance.
$\Phi'_{(\text{H-bond})}$	The first derivative or force of the hydrogen bond.
α	The polarizability.
μ	The dipole moment.
m_a	The mass of an individual molecule.
θ_1 θ_2 and ϕ	Well defined on P. 211 of Hirschfelder, Curtiss and Bird.
$\langle Z^* \rangle$	The effective charge based upon Kurosawa's method of fractions of e.
U	The lattice energy.
ω	Angular frequency.
n	The repulsion coefficient.

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