The Journal of Chemical Physics

Far-Infrared Spectra and Hydrogen-Bond Frequencies of Imidazole

Cite as: J. Chem. Phys. **48**, 3079 (1968); https://doi.org/10.1063/1.1669576
Submitted: 14 November 1967 . Published Online: 05 September 2003

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A previous calculation of the author can be modified to show this is not the case.[7] The corrections are all magnetic-field dependent.

In Eqs. (22), (23) the "+···" indicates there are higher-order terms which have not been calculated but which would give rise to an additional magnetic-field dependence of the second moment[8] of the absorption. From the independence of the linewidth on the sense of the magnetic-field direction, the form of the broadening must be

$$\langle\text{second moment about absorption line}\rangle = [\Delta\nu^2/\mathrm{Tr}(S^z)^2] + (B/\Delta\nu_0^2) + (C/\Delta\nu_0^4) + \cdots .$$

[8] K. Brog and W. H. Jones, Jr. (private communication).

"B" will be a complicated expression and not subject to the same simple interpretation as can be given for "A" [Eq. (26)].

COMMENT

The method developed in this paper can also be used to calculate the shift of the resonance lines of a single spin type when $S>\frac{1}{2}$ and crystal-field effects cause two resonance lines to be near each other. One will again obtain a resonance shift of the form given in Eq. (2).

ACKNOWLEDGMENTS

I wish to thank W. H. Jones, Jr., and K. C. Brog for bringing the problem of the magnetic interaction of two resonance lines to my attention.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 48, NUMBER 7 1 APRIL 1968

Far-Infrared Spectra and Hydrogen-Bond Frequencies of Imidazole

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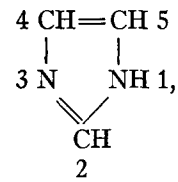
(Received 14 November 1967)

Far-infrared spectra of imidazole, imidazole-d_4, 1-methyl imidazole, and 1-methyl-d_3 imidazole have been examined in the 300–33-cm^{-1} range. Six of the nine infrared-active lattice modes of crystalline imidazole have been observed and assigned. A tentative assignment of these frequencies in terms of hydrogen-bond motion is given. Far-infrared spectra of solid and liquid imidazole and its methyl derivatives are compared and discussed. There is no obvious relationship between the hydrogen-bond frequencies and the structure of the νNH absorption band of crystalline imidazole.

INTRODUCTION

Most of the far-infrared studies of intermolecular hydrogen-bonded systems have been concerned only with the identification of the hydrogen-bond stretching frequencies,[1–5] although an unambiguous assignment of these vibrations is usually not straightforward. However, more thorough work has been done on formic and acetic acids.[6–11] In the spectrum of the formic acid dimer, for example, four of the six hydrogen-bond frequencies have been observed and assigned.[11]

In the present study we report the far-infrared spectrum of imidazole, a five-membered heterocyclic ring,



out to 33 cm^{-1}. The crystal spectra are assigned in terms of lattice vibrations as well as in terms of hydrogen-bond frequencies. An analysis of the internal vibrations of this compound was published along with some preliminary low-frequency spectral data in our previous papers.[12,13] No other far-infrared investigations of NH···N hydrogen-bonded systems appear to have been reported.

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[8] A. E. Stanevich, Opt. Spectrosk. **16**, 446 (1964) [Opt. Spectrosc. **16**, 243 (1964)].
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[10] G. L. Carlson, R. E. Witkowski, and W. G. Fateley, Spectrochim. Acta **22**, 117 (1966).
[11] R. J. Jakobsen, Y. Mikawa, and J. W. Brasch, Spectrochim. Acta **23A**, 2199 (1967).
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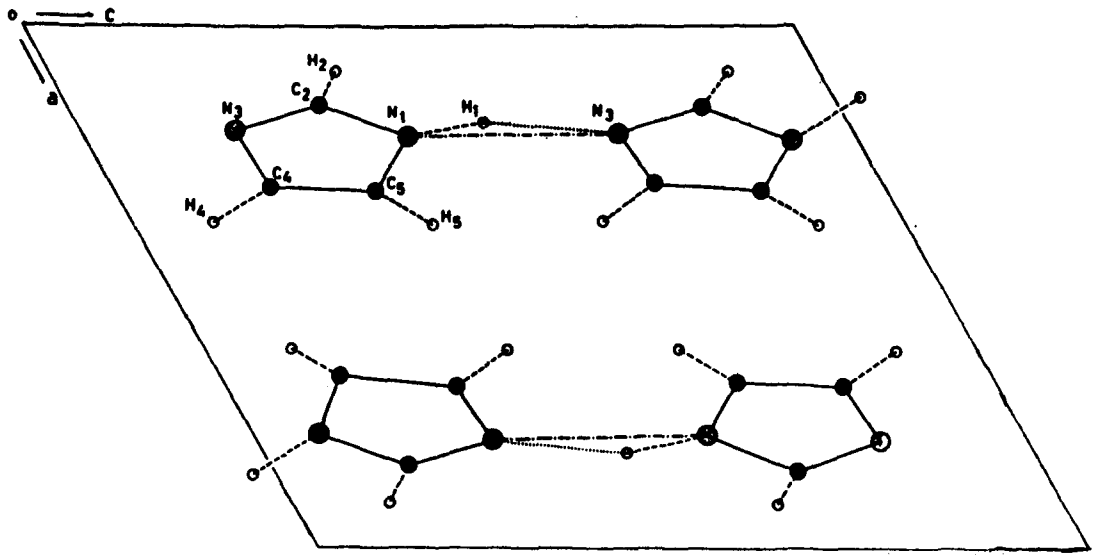

FIG. 1. Crystal structure of imidazole at −150°C. Projection of the structure along the b axis (Ref. 15).

EXPERIMENTAL

Samples

Imidazole was purchased from Eastman Organic Chemicals. Imidazole-d_4 was prepared in the manner described previously.[12] Both compounds were purified by vacuum sublimation.

1-Methyl imidazole was a commercial product (K and K), while the 1-methyl-d_3 imidazole was prepared by the method of Jocelyn.[14] These liquids were vacuum distilled before use.

Spectra

The far-infrared spectra were recorded in the range 300–33 cm^{-1} using a Beckman IR-11 spectrophotometer. The spectra of some samples were also recorded in the 4000–2000-cm^{-1} region using Perkin–Elmer 421 and 225 instruments. Silicon, quartz, polyethylene, or Teflon cell windows were used for the far-infrared work. Solid samples were investigated at room temperature in polyethylene or Teflon pellets, as emulsions in Nujol, and as crystalline films grown from the melt on quartz or silicon windows; these samples gave practically the same spectra. Crystalline films of imidazole and its derivatives were examined at liquid-nitrogen temperature in a conventional low-temperature cell. Polarized far-infrared spectra of an oriented crystal of imidazole with the 100 face developed were obtained using a transmission polarizer consisting of six thin polyethylene films. The crystal orientation was determined by x-ray analysis and by examining the crystal between crossed polarizers using visible light. Liquid films of imidazole were studied in a Perkin–Elmer hot cell. Spectra of imidazole and 1-methyl imidazole solutions in chloroform (0.5 to 2.0 moles/liter) were obtained at path lengths between 0.22 and 1.0 mm. The accuracy of frequencies is approximately ±1 cm^{-1} for sharp bands.

[14] P. C. Jocelyn, J. Chem. Soc. 1957, 3305.

RESULTS AND DISCUSSION

In the imidazole crystal there are infinite chains of NH···N hydrogen-bonded molecules.[15] In order to identify the hydrogen-bond frequencies, an analysis of the lattice vibrations is first required.

Crystal Structure and Lattice Vibrations

The symmetry of crystalline imidazole is monoclinic and belongs to the space group $P2_1/C(C_{2h}^5)$. There are four molecules per unit cell.[15] The arrangement of the molecules in the crystal is shown in Fig. 1. In Table I the results of factor-group analysis are shown. There are 21 lattice vibrations, which can be represented by $6A_g+6B_g+5A_u+4B_u$. Thus only nine lattice vibrations are infrared active. The transition moments of the A_u species vibrations will be directed along the b axis, while those of the B_u species vibrations will be

TABLE I. Symmetry species, characters, and selection rules for factor group C_{2h}, and the number of lattice vibrations of the imidazole crystal.[a]

C_{2h}^5	E	C_2^b	i	σ_c	T	T'	R'	ir	R
Ag	1	1	1	1	0	3	3	f	a
Bg	1	−1	1	−1	0	3	3	f	a
Au	1	1	−1	−1	1	2	3	**M**(b)	f
Bu	1	−1	−1	1	2	1	3	**M**(ac)	f

[a] C_2^b, screw axis; σ_c, glide plane; T, number of lattice translations; T', number of translational vibrations; R', number of rotational vibrations; ir, infrared; R, Raman, f, forbidden, a, active.

[15] S. Martinez-Carrera, Acta Cryst. 20, 783 (1966).

TABLE II. Far-infrared frequencies of crystalline imidazole and imidazole-d_4.

Imidazole		Imidazole-d_4				Assignment			
−180°C	25°C	−180°C	25°C	Polarization[a]	ν/ν' [b]	Crystal C_{2h}^5	Chain C_s	Approximate type of motion	
188 m	179	181	172	σ	1.04	Au	A''	T'	Stretching[c]
151 s	142	137	133	σ	1.10	Au	A''	R'	Stretching[c]
128 m	114	118	102	π	1.08	Bu	A'	R'	Bending
113 m	103	109	102	σ	1.04	Au	A''	T'	Bending
97 m	89	93	83	π	1.04	Bu	A'	T'	Bending
70 w	62	65	60	π	1.08	Bu	A'	R'	Torsion

[a] Parallel (π) bands are stronger when the electric vector is parallel to the c axis; perpendicular (σ) bands are stronger when the electric vector is perpendicular to c axis.

[b] ν/ν': Frequency ratio of a lattice vibration of imidazole and of the corresponding imidazole-d_4 vibration at −180°C.

[c] Hydrogen-bond motion.

situated in the a, c plane. The lattice vibrations can be further divided into rotational and translational motions. Among the infrared-active modes, three translational $T'(2A_u$ and $1B_u)$ and six rotational $R'(3A_u$ and $3B_u)$ vibrations are expected.

Crystal Spectra

In the observed spectrum of crystalline imidazole at room temperature (Fig. 2) there are six absorption bands: 179, 142, 114, 103, 89, and 62 cm^{-1}. At liquid-nitrogen temperature these bands become sharper and their frequencies increase. They must be due to lattice vibrations, since the lowest internal mode frequency is found at 622 cm^{-1}.[13]

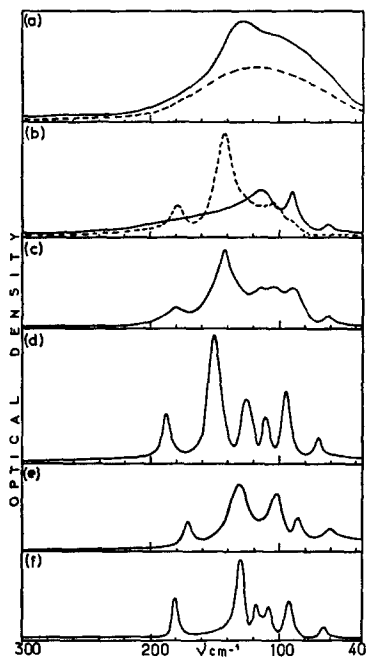

FIG. 2. Far-infrared spectra of: (a) solid line, imidazole in chloroform solution (0.5 mole/liter); dotted line, liquid imidazole at 100°C; (b) oriented crystal of imidazole (100); solid line, electric vector parallel to the c axis; dotted line, electric vector perpendicular to the c axis; (c) crystalline film of imidazole at room temperature; (d) crystalline film of imidazole at liquid-nitrogen temperature; (e) crystalline film of imidazole-d_4 at room temperature; (f) crystalline film of imidazole-d_4 at liquid-nitrogen temperature.

The assignments of the observed bands to corresponding symmetry species are made using the infrared dichroism. If the electric vector of the polarized radiation is parallel to the c axis of an oriented crystal with the 100 face developed, the resulting absorption spectrum will show strong parallel (π) bands corresponding to the B_u species. If, on the other hand, the electric vector is perpendicular to the c axis, the perpendicular (σ) bands will be stronger and will correspond to the A_u species. Three σ and the three π bands are observed (Fig. 2) and are assigned in Table II.

The identification of the translational and rotational vibrations is more difficult, although measurements of the shifts of imidazole lattice frequencies upon deuteration may help. As a first approximation, the ratio ν/ν' of a lattice frequency ν of imidazole and the corresponding frequency ν' of its isotopic species will be roughly proportional to $(M'/M)^{1/2}$ for a translational mode and to $(I_k'/I_k)^{1/2}$ for a rotational mode, where M' and M are the masses and I_k' and I_k the moments of inertia ($k=a, b, c$) of the heavy and light molecules, respectively. For the isotopic pair imidazole and imidazole-d_4 the square root of the mass ratio is equal to 1.03 and those of the three moments of inertia are approximately 1.08.[16] The difference between $(M'/M)^{1/2}$ and $(I_k'/I_k)^{1/2}$ is thus large enough to make possible an experimental distinction between translational and rotational vibrations.

The far-infrared spectral data of imidazole and imidazole-d_4 crystals at liquid-nitrogen temperature are used to determine the frequency ratios, as there is greater accuracy in frequency measurement and the

[16] Values of interatomic distances and angles of Ref. 15 have been used here to calculate the moments of inertia.

bands are well resolved at −180°C. This is not the case for the spectra of crystals at room temperature.

All six bands shift to lower frequencies upon deuteration. Three of them at 188, 113, and 97 cm^{-1}, give a frequency ratio of 1.04 and can thus be assigned to the translational vibrations (Table II). This result is consistent with assignments based on symmetry, as two of the vibrations are of A_u and one is of B_u species, as expected (Table I). The three remaining bands, which yield frequency ratios of 1.10, 1.08, and 1.08, are assigned to the rotational vibrations ($1A_u$ and $2B_u$).

The separation of rotational and translational motions cannot be derived from symmetry considerations. Nevertheless, the experimental results support the above assignments in terms of rotational and translational modes, which should be considered as approximate descriptions.

Six of the nine infrared-active lattice modes have thus been observed and assigned. All three translational ($2A_u$ and $1B_u$) and three of the six rotational vibrations ($1A_u$ and $2B_u$) have been identified.

Hydrogen-Bond Frequencies

The lattice modes necessarily include the hydrogen-bond motions. In order to distinguish them it seems useful to consider an isolated single chain of imidazole molecules which are linked by short hydrogen bonds, the distance N···N being equal to 2.86 Å.[15] This treatment can be justified, as the forces between neighboring molecules in a chain are much stronger than the interchain forces. Furthermore, the isolated-chain approximation has already been used for some other hydrogen-bonded chain systems,[17,18] and even for low-frequency vibrations such as in formic acid.[7]

The only symmetry element of an imidazole chain is a glide plane σ_c parallel to c axis. The corresponding factor group is C_s. The chain repeat unit contains two molecules. There are then eight intrachain vibrations, all infrared active. Four of them are symmetrical, $A'(1T'$ and $3R')$ and four are antisymmetrical, $A''(2T'$ and $2R')$, with respect to the glide plane.

Comparison with the unit-cell factor-group analysis (Table I) shows that the A' and the A'' vibrations can be derived from B_u and A_u crystal species, respectively. On the other hand, it is easily shown that of nine infrared-active modes of the crystal there are eight intrachain vibrations involving the hydrogen bond. The ninth vibration (species A_u) which is a rotation about the chain axis, is neglected in the single-chain approximation. This analysis implies that the six observed infrared bands correspond essentially to the hydrogen-bond frequencies.[19,20]

The eight intrachain vibrations can be described in terms of hydrogen-bond motions in a manner similar to that for the infinite chain in the formic acid crystal.[7] Two modes contain predominantly hydrogen-bond stretching vibrations. The first may be derived from the translational motion which is out of phase with respect to the glide plane and thus of species A''; the second, also an A'' vibration, is of rotational origin. The other translational motions ($1A'$ and $1A''$), as well as three rotational motions ($1A''$ and $2A'$), may give rise to hydrogen-bond bending frequencies while one rotational mode of A' species (rotation about the chain axis) can be described more specifically as a torsional mode.

The order of hydrogen-bond frequencies of imidazole is expected to be similar to that of an acetic acid crystal.[11] In fact, the strength of NH···N and OH···O hydrogen bonds in imidazole and acetic acid, respectively, are quite similar, as evidenced by their O···O and N···N distances, and by the observation that the relative shifts of the OH and NH stretching frequencies are both close to 20%.[12,21] Furthermore, the masses and the moments of inertia of the acetic acid and imidazole molecules are also similar. We suggest, therefore, the assignment of the two highest frequencies, at 188 and 151 cm^{-1}, of imidazole to predominantly hydrogen-bond stretching vibrations and the other four to predominantly bending modes, the 70-cm^{-1} band being a suitable candidate for the torsional vibration (Table II). This assignment is consistent with the band polarizations and deuteration shifts.

Comparison of Spectra of the Solid and Liquid Phase of Imidazole

The six well-resolved and sharp bands in the far-infrared spectrum of crystalline imidazole at −180°C shift to lower frequencies and become broader at room temperature (Fig. 2). The frequency ratios $\nu(-180°C)/\nu(25°C)$ vary between 1.13 and 1.05, the highest values being observed for the rotational modes of vibration.

There is a broad band at 134 cm^{-1} and an ill-defined shoulder near 104 cm^{-1} in the chloroform solution spectrum of imidazole at room temperature (Fig. 2). Existence of chains of NH···N hydrogen-bonded molecules can be assumed by analogy with solutions of imidazole[22] and of its 4(5)-methyl derivative.[23] It is likely that increased disorder of such a system contributes to further band broadening. It appears difficult to assign the resulting absorption to specific intermolecular vibrations.

A single broad band near 120 cm^{-1} is observed for liquid imidazole at about 100°C. The liquid is examined at higher temperature than the solution; thus there may be more hot bands which shift the band maxima

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[19] It may be of interest to note that five similar frequencies, at 149, 114, 105, 88, and 78 cm^{-1}, are observed in the Raman spectra of a single crystal of imidazole.[20]

[20] L. Colombo, "Low-Frequency Raman Spectrum of Imidazole Single Crystal," J. Chem. Phys. (to be published).

[21] M. Haurie and A. Novak, Spectrochim. Acta **21**, 1217 (1965).

[22] D. M. W. Anderson, J. L. Duncan, and F. J. C. Rossotti, J. Chem. Soc. **1961**, 2165.

[23] H. Zimmermann, Z. Elektrochem. **63**, 601 (1959).

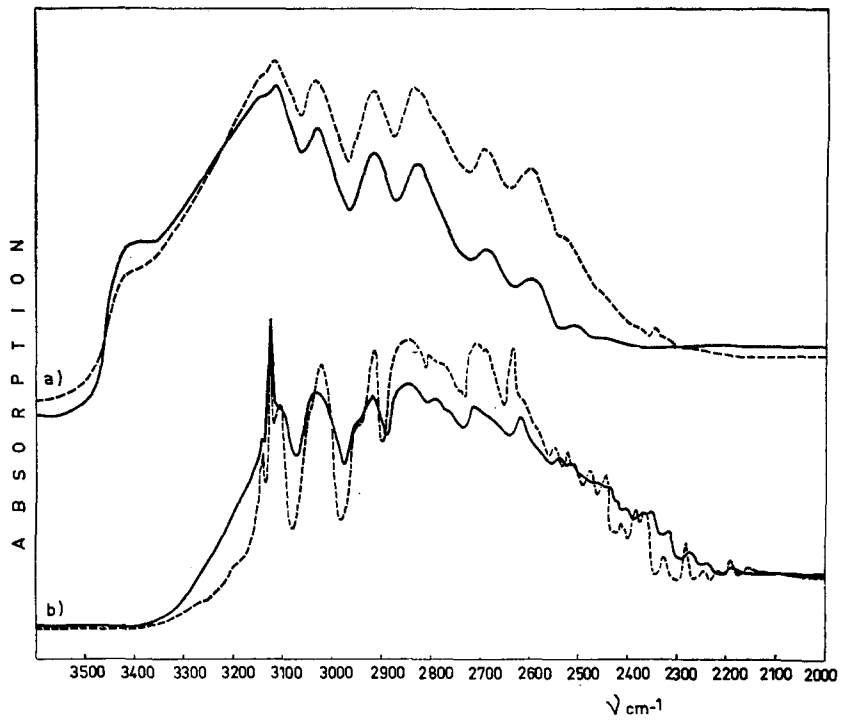

FIG. 3. Infrared spectra of imidazole (3600–2000-cm^{-1} region): (a) solid line, liquid at 200°C; dotted line, liquid at 100°C; (b) solid line, crystal at room temperature; dotted line, crystal at liquid-nitrogen temperature.

towards lower frequencies. On the other hand, in the liquid there can be another type of association besides the formation NH···N hydrogen-bonded chains. In order to check this point, we investigated the 4000–2000-cm^{-1} region of liquid imidazole. As shown in Fig. 3, the complex νNH band has a shoulder near 3410 cm^{-1} which is observed in neither crystal nor solution spectra. The relative intensity of this shoulder increases when the liquid is heated from 100° to 200°C, i.e., when chain breaking is increased. The 3410-cm^{-1} absorption is thus believed to be due to the NH group which are hydrogen bonded to the π-electron system of imidazole. In fact, its frequency can be favorably, compared to the νNH frequencies of imidazole in aromatic hydrocarbon solutions.[24] This NH···π type of interaction is of course much weaker than the NH···N hydrogen bonds. This difference may contribute to the shift of the far-infrared bands to lower frequencies.

Structure of the ν NH Stretching Band and Hydrogen-Bond Frequencies

The AH stretching band of a strongly hydrogen-bonded system AH···B is usually very broad and presents a more or less complicated structure. This is the case of the νNH absorption band near 2800 cm^{-1} of imidazole which contains numerous submaxima (Fig. 3). In our previous paper[12] we suggested that these subbands can be explained in terms of a Fermi resonance of the νNH fundamental with various combinations and overtones of the internal vibrations. Another explanation, invoking the role of the low hydrogen-bond frequencies as a possible cause of the νAH band structure, has been proposed for imidazole.[25] According to this frequency modulation theory[26,27] the subbands may obey a simple relationship $\nu_n = \nu\text{AH} \pm n\nu(\text{AH})\cdots\text{B}$ where $n=0, 1, 2, \cdots$ and $\nu(\text{AH})\cdots\text{B}$ can be any hydrogen-bond frequency.[28]

In order to check the above relationship we wanted therefore to compare the (NH)···N hydrogen-bond frequencies and their temperature and isotope shifts (Table II) with the behavior of the νNH and νND band submaxima.

If the imidazole crystal is cooled from the room to the liquid-nitrogen temperature, the hydrogen-bond frequencies increase. A corresponding trend is then expected at least for some submaxima; the summation bands should shift towards higher- and the difference bands towards the lower-frequency side of the νNH band center. Furthermore, the difference bands, at least those with hydrogen-bond stretching modes would be expected to show a marked intensity decrease upon cooling the crystal. These results are not observed (Fig. 3). In fact, the submaxima temperature shifts are quite irregular.

The hydrogen-bond frequencies decrease upon deuteration of imidazole (Table II). The structure of the νND band of imidazole-d_4,[12] however, is entirely different from that of the νNH band and the submaxima of

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[25] H. Zimmermann, Z. Elektrochem. **65**, 821 (1961).

[26] N. Sheppard, in *Hydrogen Bonding*, D. Hadzi, Ed. (Pergamon Press, Ltd., London, 1959), p. 85.

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[28] V. M. Chulanovski and S. D. Simova, Dokl. Akad. Nauk SSSR **68**, 1033 (1949).

TABLE III. Far-infrared frequencies of imidazole (liquid phase) and its 1-methyl derivative.

Imidazole		1-Methyl imidazole		1-Methyl-d_3 imidazole	
Liquid 100°C	Solution[a] 25°C	Solution[a] 25°C	Solid −180°C	Solid −180°C	Assignment
		223	255 247	237 227	$\gamma(CH_3)$–N
	134				
120			129	130	
	104		115	112	
		80	89	84	Lattice vibrations
			61	65	
			55	52	

[a] Chloroform solution, 0.5*M*.

these two bands do not appear to be related in any way.

Finally, the far-infrared spectra of crystalline imidazole and of its chloroform solution differ considerably (Fig. 2) while their νNH absorption patterns are very similar.

We are thus not able to find any obvious relationship between the submaxima of the νNH band and hydrogen-bond frequencies of imidazole.

Far-Infrared Spectra of 1-Methyl Imidazole(MI)

This imidazole derivative, whose crystal structure is not known, does not offer the possibility of intermolecular hydrogen-bond formation except for rather weak CH···N interactions.[29] The far-infrared spectrum of MI crystal is shown in Fig. 4. Two internal vibrations are expected in the 300–33-cm^{-1} region. One is a predominantly out-of-plane skeletal (γCH_3–N) mode; the doublet with components at 255 and 247 cm^{-1} due to intermolecular coupling can be assigned to this vibration.[29] The other one, a CH_3 torsional mode, has not been identified. In fact, none of the five remaining bands at 129, 115, 89, 61, and 55 cm^{-1}, shift appreciably upon deuteration of the methyl group (Table III). These bands are thus due to lattice vibrations.

Comparison of the spectra of imidazole and MI crystals at −180°C shows that the two hydrogen-bond stretching frequencies of imidazole are higher than any of the MI lattice frequencies. On the other hand, the half-bandwidths (between 6 and 10 cm^{-1}), are similar in both spectra.

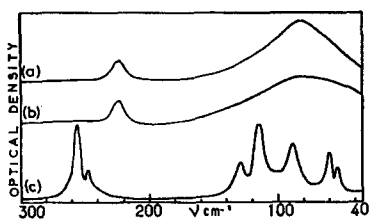

FIG. 4. Far-infrared spectra of 1-methyl imidazole: (a) liquid; (b) chloroform solution (0.5 mole/liter); (c) crystalline film at liquid-nitrogen temperature.

In the spectrum of liquid MI (Fig. 4) there is a strong band at 80 cm^{-1}, which is much lower than that in liquid imidazole. Such an absorption is characteristic of many polar liquids without hydrogen bonding.[30] The integrated intensities of the liquid imidazole and MI absorptions, however, are estimated to be of the same order of magnitude and close to 1600 liter mole^{-1}·cm^{-2}, which is about 100 times less than the integrated intensity of the νNH band measured under the same conditions ($A \simeq 200\,000$ liter mole^{-1}·cm^{-2}).

It thus appears that the hydrogen-bonding influences the far-infrared frequencies much more than band intensities or band shapes as far as the investigated systems are concerned.

CONCLUSIONS

Six of the eight intrachain, hydrogen-bond frequencies of the imidazole crystal have been assigned. The deuteration shifts indicate that these hydrogen-bond vibrations are not localized in the NH···N group, but must be considered as rotational and translational lattice vibrations like those of any molecular crystal. The widths of these low-frequency bands, at least at −180°C, are similar to those observed in molecular crystals without hydrogen bonds. The only unusual feature of the spectrum of crystalline imidazole is the very broad νNH band consisting of many submaxima. The hydrogen-bond frequencies do not seem to play an important part in this structure.

ACKNOWLEDGMENTS

The authors are grateful to Professor Josien and Professor Turrell for helpful suggestions, to Dr. Jakobsen and Dr. Brasch for providing them with a preprint of their paper, and to Professor Balkanski for supplying them with a far-infrared polarizer.

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