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Vibrational Spectra and Normal Coordinate Calculations of $HgNH_2Cl$ and $HgNH_2Br$*

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Infrared spectra of $HgNH_2Cl$ and $HgNH_2Br$ and the Raman spectrum of $HgNH_2Cl$ have been measured in the region from 4000 cm^{-1} to 30 cm^{-1}. Effects of changing the X(X=Cl,Br) ion were observed mainly in N–H stretching bands and in lattice vibrations. Calculations of normal frequencies were carried out using a force field which includes inter-molecular forces. An assignment of the lattice vibrations was proposed and the force constants were also calculated. The force constants of the inter-molecular hydrogen bonds N–H···Cl and N–H··· Br were obtained as 0.212 mdyn/Å and 0.142 mdyn/Å, respectively.

The structure of orthorhombic crystal of mercuric amidohalide $HgNH_2X$ (X=Cl, Br) consists of halogen ions and infinite chains of alternating Hg and NH_2 with linear bonds about Hg and tetrahedral bonds about N.[1–3] The vibrational assignment of the infrared bands observed between 4000 to 400 cm^{-1} has already been given for the infinite chain of $(HgNH_2^+)_n$ by Nakagawa *et al.*[4,5] And the force constants associated with the $(HgNH_2^+)_n$ chain have also been computed.[4]

However, the lattice vibrations of these compounds have not been studied. It is considered interesting to examine the effects of changing the halogen ion on the vibrational frequencies. The effects are expected to appear mainly in the lattice vibrations and also in the N–H stretching vibrations because of the possible N–H ···X type hydrogen bonds.

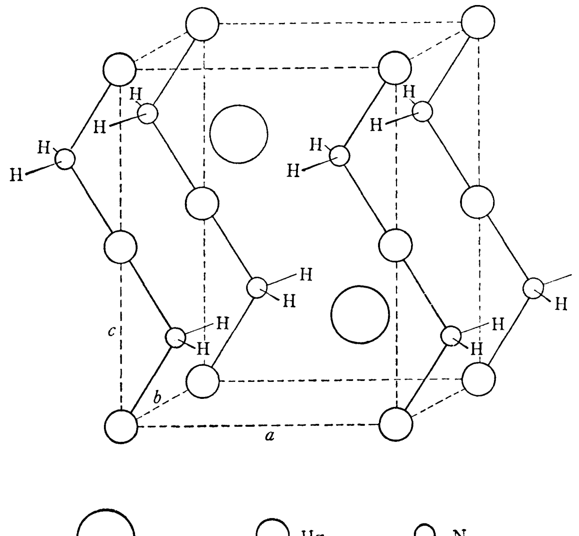

Fig. 1. Crystal structure of $HgNH_2X$ (X=Cl, Br).

We have measured the infrared spectra of $HgNH_2X$ (X=Cl, Br) and the Raman spectrum of $HgNH_2Cl$ in the region from 4000 to 30 cm^{-1}. The calculation of the normal frequencies was carried out including Cl^- and Br^- ions, and hence both the intra-molecular force constants and the inter-molecular ones were obtained. It then becomes possible to discuss quantitatively about the hydrogen bond N–H···X (X=Cl, Br) and its effects on the N–H stretching force constant.

Experimental

Mercuric amidochloride $HgNH_2Cl$ of special grade (Sanko Seiyaku Kogyo Co. Ltd.) was used without further purification. Although mercuric amidobromide $HgNH_2Br$ has two types of modifications, namely orthorhombic and cubic, only the orthorhombic one was prepared by the reaction of 150 m*l* of 14 N aqueous ammonia with 2 g of mercury bromide Hg_2Br_2.[2,6] The infrared spectrum of the prepared $HgNH_2Br$ coincided with that of the orthorhombic modification reported by Nakagawa et al.[5]

The infrared spectra of these substances dispersed in Nujol and in KBr disks were recorded by a Hitachi EPI G3 spectrometer (4000—400 cm^{-1}) and these in Nujol by a Hitachi FIS 3 spectrometer (400—30 cm^{-1}). However, the KBr disk method was not adequate for $HgNH_2Cl$ because it was found that a part of chlorine ions in the sample were exchanged by bromine ions in KBr. The Raman spectrum of $HgNH_2Cl$ crystal powder pressed to a disk was obtained by a laser Raman spectrometer (Japan Electron Optics Laboratory Co. Ltd.). The 5145 Å line of argon ion was used as the light source for excitation.

Observed spectra

The infrared spectra of $HgNH_2Cl$ and $HgNH_2Br$ observed from 4000 to 400 cm^{-1} are shown in Figs. 2 and 3, respectively. The far-infrared spectra from 400 to 30 cm^{-1} are given in Figs. 4 and 5. In Fig. 6, the Raman spectrum of $HgNH_2Cl$ is reproduced.

Vibrations of $HgNH_2$. Nakagawa *et al.*[4,5] have

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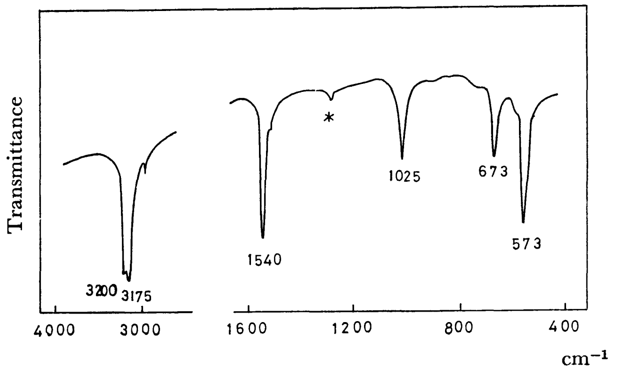

Fig. 2. Infrared spectrum of $HgNH_2Cl$ in nujol mull (nujol bands eliminated). * is due to $Hg(NH_3)_2Cl_2$.[4]

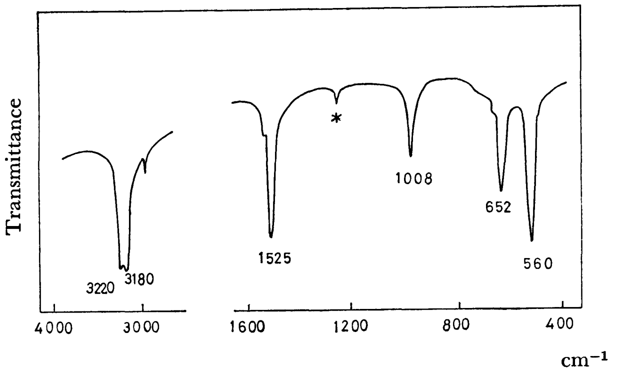

Fig. 3. Infrared spectrum of $HgNH_2Br$ in nujol mull (nujol bands eliminated). * is due to $Hg(NH_3)_2Br_2$.[5]

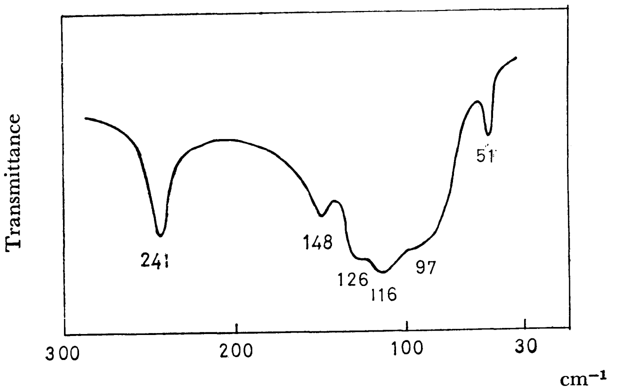

Fig. 4. Far-infrared spectrum of $HgNH_2Cl$ in nujol mull.

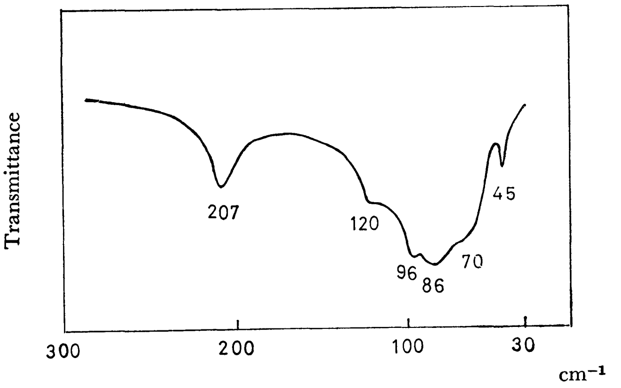

Fig. 5. Far-infrared spectrum of $HgNH_2Br$ in nujol mull.

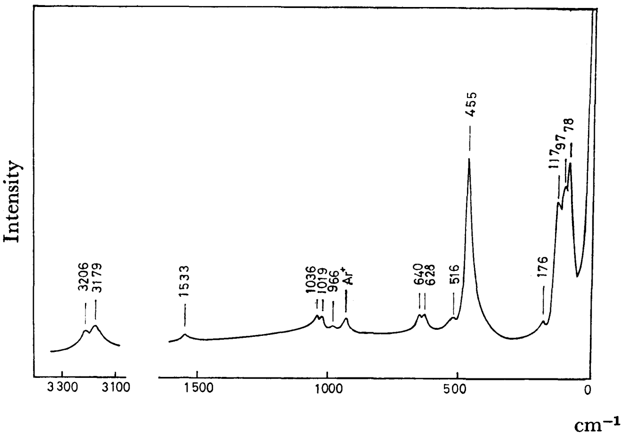

Fig. 6. Raman spectrum of $HgNH_2Cl$ powders (pressed disk).

already measured the infrared spectra of $HgNH_2Cl$ and $HgNH_2Br$ from 4000 to 400 cm^{-1} and have given the assignment of the infrared active vibrations (B_{1u}, B_{2u} and B_{3u} symmetry species) of $HgNH_2^+$. The frequencies which we observed and the assignment which we have made are in substantial agreement with theirs, hence the complete list is not reproduced here. Our contribution is to measure Raman spectrum which was not reported previously and to present the assignment of the Raman active vibrations (A_g, B_{1g}, B_{2g}, and B_{3g} symmetry species).

One interesting feature in the infrared spectra, however, should be pointed out. The NH_2 anti-symmetric stretching vibration is observed at 3200 cm^{-1} in $HgNH_2Cl$ while it is observed at 3220 cm^{-1} in $HgNH_2Br$. The same phenomenon is observed in the NH_2 symmetric stretching also: 3175 cm^{-1} for $HgNH_2Cl$ and 3180 cm^{-1} for $HgNH_2Br$. These high-frequency shifts in N–H stretching vibrations when Cl^- is substituted by Br^- are explained by the existence of the $N–H\cdots X$ (X=Cl, Br) hydrogen bond. All the other vibrations shift to the side of lower frequencies when Cl^- is exchanged by Br^-.

In the Raman spectrum of $HgNH_2Cl$, ten bands are observed above 400 cm^{-1}. The assignment of these Raman bands presented in Table 2 was made by analogy with that of the infrared bands. However, the observed two doublets of NH_2 wagging and of NH_2 rocking vibrations are not explained unambiguously at present. They may be either due to combination bands or to impurities in the sample.

Chain bending and lattice vibrations. There has been no work of the far-infrared spectra below 400 cm^{-1} of these compounds. We have observed the bands due to chain bending vibrations and lattice vibrations of $HgNH_2Cl$ and $HgNH_2Br$ for the first time. They are shown in Figs. 4 and 5, respectively. In the spectrum of $HgNH_2Cl$, six bands are observed at 241, 148, 126, 116, 97, and 51 cm^{-1}. The corresponding bands in $HgNH_2Br$ spectrum are 207, 120, 96, 86, 70, and 45 cm^{-1}. These bands are considered to be due to chain bending vibrations and lattice vibrations or the mixture of these.

In the low frequency region of the Raman spectrum of $HgNH_2Cl$, four bands are observed at 176, 117, 97, and 78 cm^{-1}. The assignment of these low frequency bands observed in the infrared and Raman spectra are made according to the results of the normal frequency calculations.

Normal coordinate treatment

The crystal structure of $HgNH_2X$ (X=Cl, Br) is orthorhombic with two $HgNH_2X$ units in a Bravis unit cell as shown in Fig. 1. The lattice parameters and the bond-lengths are summarized in Table 1.[1,2]

TABLE 1. LATTICE PARAMETERS AND BOND LENGTHS[1,2]

	$HgNH_2Cl$	$HgNH_2Br$
Lattice parameter	a=5.167 Å	a=5.439 Å
	b=4.357	b=4.487
	c=6.690	c=6.761
Bond length		
N—H	1.04 Å	1.04 Å
Hg—N	2.05	2.07
H···H	1.70	1.70
H···Hg	2.59	2.61
Hg···Hg	3.35	3.38
H···X	2.18	2.36
Hg···X	3.21	3.30
X···X	3.83	3.91

The calculation of the normal frequencies[7] was made assuming a modified Urey-Bradly type force field[8] and a few coordinates corresponding to inter-molecular forces were also taken into account. These coordinates are given below.

	X=Cl	X=Br
q (H···X)	2.18 Å	2.36 Å
q (Hg···X)	3.21 Å	3.30 Å
h (N-H···X)		

The coordinate q(X···X) was omitted because of the large X···X distance: 3.83 Å for X=Cl and 3.91 Å for X=Br.

The potential function was expressed as

$$U = U_i + U_l$$

$$\begin{aligned} U_i = 1/2\{ & \textstyle\sum K_{\mathrm{N-H}}(\Delta r_{\mathrm{N-H}})^2 + \sum K_{\mathrm{Hg-N}}(\Delta r_{\mathrm{Hg-N}})^2 \\ & + \textstyle\sum F_{\mathrm{H\cdots H}}(\Delta q_{\mathrm{H\cdots H}})^2 + \sum F_{\mathrm{H\cdots Hg}}(\Delta q_{\mathrm{H\cdots Hg}})^2 \\ & + \textstyle\sum H_{\mathrm{H-N-H}}(\Delta\alpha_{\mathrm{H-N-H}})^2 + \sum H_{\mathrm{H-N-Hg}}(\Delta\alpha_{\mathrm{H-N-Hg}})^2 \\ & + \textstyle\sum H_{\mathrm{Hg-N-Hg}}(\Delta\alpha_{\mathrm{Hg-N-Hg}})^2 + \sum H^{\perp}_{\mathrm{N-Hg-N}}(\Delta\alpha^{\perp}_{\mathrm{N-Hg-N}})^2 \\ & + \textstyle\sum H^{//}_{\mathrm{N-Hg-N}}(\Delta\alpha^{//}_{\mathrm{N-Hg-N}})^2 + \sum Y_{\mathrm{N-Hg-N}}(\Delta\tau_{\mathrm{N-Hg-N}})^2\} \\ & + \textstyle\sum \text{angle interaction constant } l_{ij} \text{ term[9]} \end{aligned}$$

$$\begin{aligned} U_l = 1/2\{ & \textstyle\sum f_{\mathrm{H\cdots X}}(\Delta q_{\mathrm{H\cdots X}})^2 + \sum f_{\mathrm{Hg\cdots X}}(\Delta q_{\mathrm{Hg\cdots X}})^2 \\ & + \textstyle\sum h_{\mathrm{N-H\cdots X}}(\Delta\phi_{\mathrm{N-H\cdots X}})^2\} \end{aligned}$$

where

U_i is the potential function associated with the $(HgNH_2^+)_n$ chain.

U_l is that of the lattice vibration.

K, F, H, and Y denote bond-stretching, repulsive, angle-bending and torsional force constants, respectively. f and h are, respectively, stretching and angle-bending force constants associated with the lattice vibrations.

The calculation of the normal frequencies was carried out by the Cartesian coordinate method.[7] The coordinates, with which the potential function is expressed, are transformed into Cartesian displacement coordinates X. And then the optically active potential energy matrix F_{op} is set up in terms of the optically active Cartesian displacement coordinates. The secular equation

$$|M^{-1}F_{op} - E\lambda| = 0$$

gives the eigenvalues and eigenvectors which correspond to the frequencies and the vibrational modes respectively, where M is a diagonal mass matrix and E is a unit matrix.

Results and Discussions

Normal frequency calculation. Lipscomb *et al.* have reported from X-ray studies that the space groups of both $HgNH_2Cl$[1] and $HgNH_2Br$[2] belong to C^1_{2v}-P2mm. However, as can be seen in Table 2, there are very few infrared frequencies which correspond to Raman fre-

TABLE 2. OBSERVED AND CALCULATED FREQUENCIES IN cm^{-1}

Species	$HgNH_2Cl$		$HgNH_2Br$		Assignment
	Obsd.	Calcd.	Obsd.	Calcd.	
A_g	3179	3176		3185	NH_2 sym. str.
	1533	1539		1535	NH_2 scis.
	455	459		449	Hg-N sym. str. +Hg-N-Hg def.
	117	130		77	lattice
B_{1g}	3206	3204		3215	NH_2 anti. str.
	640 628	642		615	NH_2 rock.
	176	165		119	lattice
	97	93		66	lattice
B_{2g}	1036 1019	1018		1004	NH_2 wag.
	516	524		525	Hg-N anti. str.
	78	76		47	lattice
B_{3g}	966	960		921	NH_2 twist.
A_u	inact.	967	inact.	928	NH_2 twist.
		68		66	N-Hg-N bend.(⊥)
B_{1u}	1025	1019	1008	1006	NH_2 wag.
	573	564	560	565	Hg-N anti. str.
	97	93	70	76	N-Hg-N bend. (//)
	51	53	45	44	lattice
B_{2u}	3200	3204	3220	3215	NH_2 anti. str.
	673	675	652	649	NH_2 rock.
	241	234	207	216	N-Hg-N bend.(⊥)
	126	135	96	90	lattice
B_{3u}	3175	3176	3180	3185	NH_2 sym. str.
	1540	1540	1525	1535	NH_2 scis.
	—	508	—	499	Hg-N sym. str.
	148	141	120	116	lattice
	116	117	86	91	N-Hg-N bend.(//) +Hg-N-Hg def.

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[7] T. Shimanouchi, M. Tsuboi, and T. Miyazawa, *J. Chem. Phys.*, **35**, 1597 (1961).

[8] T. Shimanouchi, *Pure Appl. Chem.*, **7**, 131 (1963).

[9] T. Shimanouchi and I. Suzuki, *J. Mol. Spectrosc.*, **6**, 277 (1961); **8**, 222 (1962).

quencies. This fact would suggest that the vibrational spectra of $HgNH_2Cl$ (and also $HgNH_2Br$) are explained more adequately by a D_{2h} symmetry than a C_{2v}. Therefore we have carried out normal frequency calculations assuming a D_{2h} symmetry instead.

The calculated frequencies listed in Table 2 are in good agreement with the observed values. As the Bravis unit cell contains one $(HgNH_2^+)_n$ chain and two X atoms, one rotational and six translational lattice vibrations are expected to appear. The assignment of lattice vibrations and also of chain bending vibrations are given in the same table. The L_x matrices of lattice vibrational modes and chain bending modes are shown schematically in Figs. 7, 8, and 9. L_x is the transformation matrix between the Cartesian coordinates X and the normal coordinates Q. These figures demonstrate that the low frequency bands cannot be distinctly classified into either lattice vibrations or chain bending vibrations; rather, they are more or less coupled with each other. The low-frequency shifts in the chain bending vibrations, when Cl^- is substituted by Br^-, are well understood from this viewpoint. The chain bending vibrations in the A_u species of $HgNH_2Cl$ and $HgNH_2Br$, however, are both calculated to be almost of the same value: 68 cm^{-1} for $HgNH_2Cl$ and 66 cm^{-1} for $HgNH_2Br$. As can be seen in Table 2 and in Fig. 9, this mode is a pure chain bending vibration so that the effect of changing the halogen ion is negligible. Low-frequency shifts in the lattice vibrations when Cl^- is exchanged by Br^- are explained mainly both by the difference of atomic weight of halogen and by the difference of inter-molecular force constants which will be discussed below.

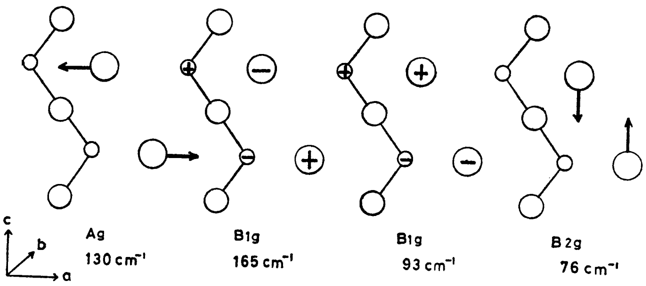

Fig. 7. Displacements of atoms for the Raman active lattice vibrational modes, with calculated frequencies of $HgNH_2Cl$.

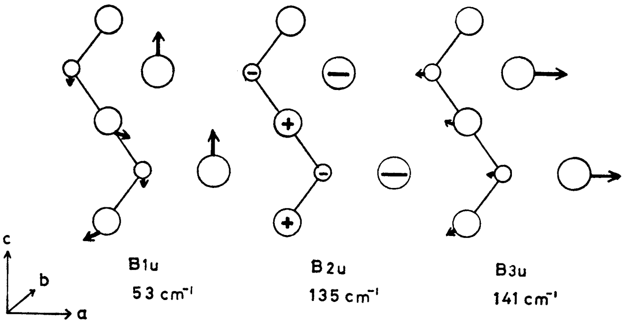

Fig. 8. Displacements of atoms for the infrared active lattice vibrational modes, with calculated frequencies of $HgNH_2Cl$.

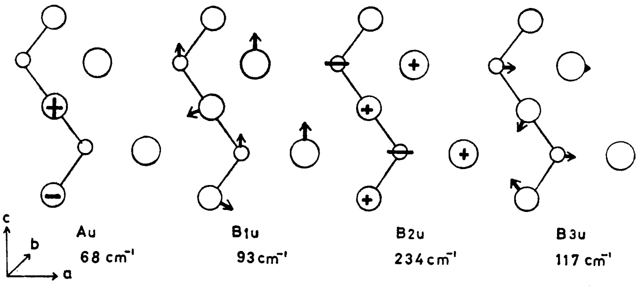

Fig. 9. Displacements of atoms for the chain bending modes, with calculated frequencies of $HgNH_2Cl$.

Table 3. Force constants in mdyn/Å

	$HgNH_2Cl$	$HgNH_2Br$
K(N-H)	5.276	5.371
K(Hg-N)	1.775	1.775
F(H···H)	0.100	0.100
F(H···Hg)	0.160	0.160
f(H···X)	0.212	0.142
f(Hg···X)	0.111	0.101
H(H-N-H)	0.555	0.555
H(H-N-Hg)	0.105	0.105
H(Hg-N-Hg)	0.081	0.081
h(N-H···X)	0.016	0.011
$H^{\perp}$(N-Hg-N)	0.083	0.083
$H^{//}$(N-Hg-N)	0.077	0.077
Y(N-Hg-N)	0.030	0.030[a]
l(Hg, H, H)	−0.003	0.002[a]
l(H, H, Hg)	0.009	0.009[a]
l(H, Hg, Hg)	−0.035	−0.024[a]

a) mdyn·Å

N-H···X (X=Cl, Br) hydrogen bond. The values of the force constants obtained by the least squares method are shown in Table 3. In the course of the calculation, all the force constants except for K (N-H), f (H···X), f (Hg···X), h (N-H···X) and four kinds of angle interaction constant l[9] were set to be equal for $HgNH_2Cl$ and $HgNH_2Br$ in spite of the slight difference of the bond lengths summarized in Table 1. Nakagawa *et al.* determined F (H···H) to be 0.06 mdyn/Å[4], however, in this calculation it was fixed to 0.10 mdyn/Å according to Harada and Shimanouchi.[10]

The force constants K(N-H) are calculated as 5.276 mdyn/Å for $HgNH_2Cl$ and 5.371 mdyn/Å for $HgNH_2Br$. High-frequency shifts in the N-H stretching vibrations when Cl^- is substituted by Br^- are explained by the fact that K (N-H) of $HgNH_2Br$ is larger than that of $HgNH_2Cl$. This difference in K (N-H) between $HgNH_2Cl$ and $HgNH_2Br$ may suggest that the hydrogen bond of H···Cl is stronger than that of H···Br. And actually, the calculated values of the force constant f (H···Cl) and h (N-H···Cl) become larger than those of f (H···Br) and h (N-H···Br), respectively, as shown in Table 3. Therefore, low-frequency shifts in the lattice vibrations when Cl^- is exchanged by Br^- are understandable. All the other force constants obtained are considered reasonable.

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[10] I. Harada and T. Shimanouchi, *J. Chem. Phys.*, **44**, 2016 (1966)