Microwave Spectrum of 2-Pyridinecarbaldehyde

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The microwave spectrum of 2-pyridinecarbaldehyde has been observed in the region 8—22 GHz. The rotational constants of the ground state are $A=5362.52\pm2.19$ MHz, $B=1620.07\pm0.03$ MHz, and $C=1244.42\pm0.03$ MHz and the inertia defect is -0.075 amu·Å^2. This value demonstrates that the molecule is planar in its equilibrium position. The total dipole moment is 3.56 ± 0.07 D, the components of which are $\mu_a=3.48\pm0.05$ D and $\mu_b=0.76\pm0.08$ D. From these facts it is concluded that the conformation of the molecule is of the O–N *s-trans* form. The rotational constants of the five vibrationally-excited states have also been determined.

Several studies of the microwave spectra have been done to determine the structural isomerism of conjugated aldehyde compounds. While two isomers, *i.e.*, the *s-trans* and the *s-cis* isomer, have been observed for furfural,[1,2] only the *s-trans* isomer has been found for 2-thiophenecarbaldehyde,[1] acrolein,[3] and crotonaldehyde.[4,5] By means of the microwave spectrum it is also known that only one isomer exists in the vapor of methacrolein and the structure of this isomer is quite similar to that of crotonaldehyde, except for the methyl group.[6]

By measuring the NMR spectrum of 2-pyridinecarbaldehyde in solution it has been suggested that the molecules are of the O–N *s-trans* form to the extent of 70—80 per cent.[7] However, in the study of the far infrared spectrum only one torsional frequency has been observed.[8] In order to know whether or not the two isomers exsist for this compound and to ascertain the stable conformation, this investigation was carried out.

Experimental

The sample of 2-pyridinecarbaldehyde, obtained from a commercial source, was purified by distillation at 53 °C/7 Torr before use. The microwave spectrum was measured over the frequency range from 8- to 22-GHz with a conventional 100-kHz square-wave Stark modulation spectrometer. The measurements were made by using a 6-m absorption cell cooled by ice.

Results and Discussion

TABLE 1. ASSIGNED TRANSITION FREQUENCIES OF 2-PYRIDINECARBALDEHYDE IN THE VIBRATIONALLY-GROUND STATE (in MHz)

Transition	ν_{obsd} a)	$\Delta\nu$ b)	Transition	ν_{obsd} a)	$\Delta\nu$ b)
$3_{13}\leftarrow2_{12}$	8013.92	0.14	$5_{14}\leftarrow4_{13}$	15130.92	0.01
$3_{03}\leftarrow2_{02}$	8487.09	0.22	$6_{16}\leftarrow5_{15}$	15876.29	−0.04
$3_{22}\leftarrow2_{21}$	8593.60	0.11	$6_{06}\leftarrow5_{05}$	16367.69	−0.09
$3_{21}\leftarrow2_{20}$	8699.90	−0.22	$6_{25}\leftarrow5_{24}$	17066.21	−0.24
$3_{12}\leftarrow2_{11}$	9139.48	−0.04	$6_{52}\leftarrow5_{51}$	17254.42	0.07
$4_{14}\leftarrow3_{13}$	10656.16	−0.20	$6_{51}\leftarrow5_{50}$	17254.42	0.06
$4_{04}\leftarrow3_{03}$	11197.18	0.10	$6_{34}\leftarrow5_{33}$	17303.64	0.31
$4_{23}\leftarrow3_{22}$	11437.38	0.32	$6_{33}\leftarrow5_{32}$	17369.06	−0.24
$4_{32}\leftarrow3_{31}$	11508.70	0.38	$6_{24}\leftarrow5_{23}$	17883.92	−0.14
$4_{31}\leftarrow3_{30}$	11515.50	−0.03	$6_{15}\leftarrow5_{14}$	18064.18	−0.07
$4_{22}\leftarrow3_{21}$	11697.93	0.01	$7_{17}\leftarrow6_{16}$	18452.54	0.02
$4_{13}\leftarrow3_{12}$	12151.68	−0.07	$7_{07}\leftarrow6_{06}$	18856.56	0.14
$5_{15}\leftarrow4_{14}$	13277.70	−0.02	$7_{26}\leftarrow6_{25}$	19844.40	0.16
$5_{05}\leftarrow4_{04}$	13822.00	0.03	$7_{35}\leftarrow6_{34}$	20206.18	0.18
$5_{24}\leftarrow4_{23}$	14262.81	0.03	$7_{34}\leftarrow6_{33}$	20351.12	−0.06
$5_{42}\leftarrow4_{41}$	14382.45	0.25	$7_{16}\leftarrow6_{15}$	20936.70	−0.12
$5_{41}\leftarrow4_{40}$	14382.45	−0.11	$7_{25}\leftarrow6_{24}$	21033.96	−0.02
$5_{33}\leftarrow4_{32}$	14403.00	0.13	$8_{18}\leftarrow7_{17}$	21008.22	0.07
$5_{32}\leftarrow4_{31}$	14427.60	−0.34	$8_{08}\leftarrow7_{07}$	21314.90	−0.25
$5_{23}\leftarrow4_{22}$	14763.04	0.10			

a) Maximum experimental uncertainty in frequency measurements is ±0.1 MHz. b) $\Delta\nu=\nu_{obsd}-\nu_{calcd}$.

TABLE 2. ROTATIONAL CONSTANTS AND INERTIA DEFECT OF 2-PYRIDINECARBALDEHYDE IN THE VIBRATIONALLY-GROUND STATE

Rotational constants	Moments of inertia a)
$A=5362.52\pm2.19$ MHz	$I_a=94.243$ amu·Å^2
$B=1620.07\pm0.03$	$I_b=311.947$
$C=1244.42\pm0.03$	$I_c=406.113$
asymmetric parameter $\kappa=-0.81756$	
inertia defect $\Delta=I_c-I_a-I_b=-0.075\pm0.038$ amu·Å	

a) Conversion factor: 5.05377×10^5 MHz·amu·Å^2

Microwave Spectrum and its Assignments. By assuming that the stable conformation is of the O–N *s-trans* form and the form is planar in its equilibrium configuration and by using the normal values of the structural parameters, the rotational constants were roughly calculated. The low-*J* R-branch transitions of the a-type for the vibrationally-ground state could be found near the frequencies calculated from the preliminary rotational constants by using the rigid rotor approximation. The splittings caused by the nuclear quadrupole of the nitrogen atom were not observed. The $J=4\leftarrow3$ transitions were ascertained by their characteristic features in the Stark effect. By using the least-squares method the rotational constants were determined so as to get the best fit between the observed and the calculated frequencies. The transition frequencies thus assigned are listed in Table 1, together with the differences between the observed and the calculated frequencies. A search was made for b-type transitions at the expected frequencies, but none could be detected unambiguously. As can be seen from Table 1, the agreement is such that the effect of centrifugal distortion can be said to be negligible in the range studied. The rotational constants determined are shown in

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Table 2. The small negative value of the inertia defect demonstrates that the molecule is planar in its equilibrium configuration.

By assuming the molecular parameters of the r_s structure of pyridine[9] for the ring and the parameters of furfural[1] for the aldehyde group, the distance, C_2–C, between the C_2 atom and the carbon atom of the CHO group and the angle of $\angle$N–C_2–C were determined so as to get a good fit between the observed and the calculated rotational constants, where the ring carbons are numbered from the nitrogen starting with C_2. The results obtained for the *s-trans* isomer are shown in Table 3, where the hydrogen atom attached to C_n is designated as H_n. The rotational constants thus calculated from these parameters were A=5362.5 MHz, B=1620.1 MHz, and C=1244.2 MHz, in good agreement with the observed values. By using these parameters the molecular configurations calculated for the *s-trans* and the *s-cis* isomer are schematically shown in Fig. 1. When the *s-cis* form is assumed for this compound, it seems hard to adjust the parameters to fit the calculated rotational constants with those observed, unless the parameters of the CHO group, for instance, are varied beyond the reasonable values. Therefore, it is probable that the molecule is of the O–N *s-trans* isomer. Some evidence for this is given by the data of the dipole moments.

TABLE 3. MOLECULAR PARAMETERS OF 2-PYRIDINECARBALDEHYDE

Assumed structural parameters[a]	
Distances	Angles
N–C_2: 1.340 Å	$\angle C_6$–N–C_2: 116°50′
C_2–C_3: 1.395	$\angle$N–C_2–C_3: 123°53′
C_3–C_4: 1.394	$\angle C_2$–C_3–C_4: 118°32′
C_2–H_2: 1.081	$\angle C_3$–C_4–C_5: 118°20′
C_4–H_4: 1.077	$\angle$N–C_6–H_6: 115°53′
C_6–H_6: 1.084	$\angle C_4$–C_3–H_3: 121°18′
C=O: 1.250*	$\angle C_2$–C=O: 121°36′*
C–H: 1.088*	$\angle C_2$–C–H: 116°55′*
Fitted structural parameters	
C_2–C: 1.477	$\angle$N–C_2–C: 112°0′

a) Parameters are quoted from Ref. 9 and, for those with asterisk, from (1).

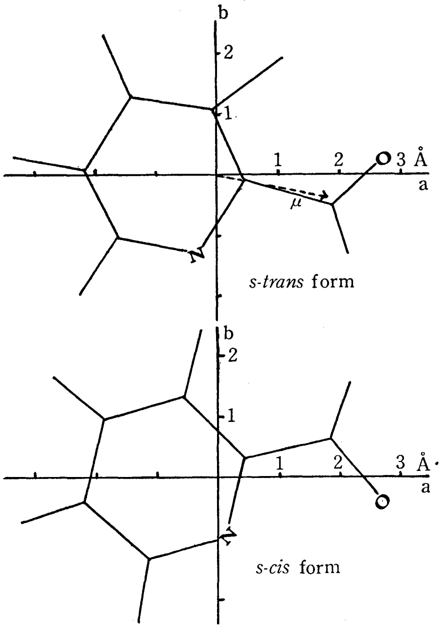

Fig. 1. Two isomers of 2-pyridinecarbaldehyde.

Dipole Moment. In order to determine the electric dipole moment, the Stark displacements of the six transitions, shown in Table 4 were measured. These lines fit the quadratic Stark displacements nicely. The absorption cell was calibrated using the J=1←0 transition of OCS, taking the dipole moment of OCS as 0.7152 D.[10] The observed and calculated Stark coefficients are given in Table 4, together with the value of the total dipole moment, μ, and those of its components along the a and b principal axes, μ_a and μ_b.

TABLE 4. (a) STARK EFFECT AND OBSERVED VALUES OF DIPOLE MOMEMNTS OF 2-PYRIDINECARBALDEHYDE

Transition		$\Delta\nu/E^2$[MHz/(kV/cm)^2] observed	calculated
$4_{04}\leftarrow 3_{03}$	M=1	−6.03±0.87	−6.12
	M=2	7.72±0.41	7.71
$4_{14}\leftarrow 3_{13}$	M=0	−7.15±0.67	−6.99
	M=1	4.08±0.41	4.01
$4_{13}\leftarrow 3_{12}$	M=1	−6.64±0.32	−6.59
	M=2	−22.41±0.67	−22.47

μ_a=3.48±0.05; μ_b=0.76±0.08 D

μ=3.56±0.07 D; $\tan^{-1}(\mu_b/\mu_a)$=12.3°

(b) Calculated values of dipole moments.

	μ_a	μ_b	$\tan^{-1}(\mu_a/\mu_b)$
s-trans form	3.83 D	0.78 D	11.5°
s-cis form	4.47	2.84	32.4°

It is reasonable to consider that the dipole moment of this compound is approximately given by the vector sum of the moment of benzaldehyde and that of pyridine.

Our recent study of the microwave spectrum of benzaldehyde has elucidated that the value of the component of the dipole moment parallel to the C=O bond is 2.95 D, pointing the negative end toward the oxygen atom, and that perpendicular to the C=O bond is 1.28 D, pointing the negative end toward the hydrogen atom of the aldehyde group.[11] By using the microwave spectrum the value of the dipole moment of pyridine is found to be 2.15 D.[12] There is no doubt that the C_2 axis of the pyridine molecule coincides with the orientation of the moment vector, the negative end of which points to the nitrogen atom. By considering that the molecular parameters of the *s-cis* form are not so different from those of the *s-trans* form, it can be calculated from the parameters that for the *s-trans* or the *s-cis* form the C_2 axis of the pyridine ring makes an angle of 66.7 ° or 43.5 ° with the a principal axis, and the C=O bond makes an angle of 43.3 ° or 48.5 ° with the same axis, respectively.

By adding the vectors mentioned above, the a and b components of the moment were calculated for the *s-trans* and the *s-cis* isomer. The results obtained are shown in Table 4(b). From the table it can be concluded that the compound in the vapor exists mainly as the O-N *s-trans* isomer, in agreement with the preliminary result described above. Of the four possible directions of the dipole moment, the direction supported by the calculation is shown by an arrow in Fig. 1.

From the dielectric constant measurements, the value of the dipole moment has been reported as 3.35 D in the benzene solution at 25 °C,[13,14] and the values of the moments for the *s-trans* and the *s-cis* form have been estimated as 3.51 D and 5.05 D, respectively.[13] These values estimated in the benzene solution seem almost to agree with the values of 3.91 D and 5.30 D estimated in the vapor, respectively, as can be calculated from the values shown in Table 4(b).

In the case where two isomers of a compound exist in equilibrium, it is well known that the abundance ratio of the molecules of the more polar isomer to those of the less polar isomer generally increases when the state changes from vapor to a benzene solution. Therefore, as the barrier to internal rotation of the CHO group of this molecule is considered to be comparable to that of benzaldehyde,[15] from the fact that the value of the moment obtained in the vapor is larger than that obtained in the benzene solution it can be said that no considerable amount of the molecules of the *s-cis* isomer exists even in the benzene solution.

Vibrationally-excited states. As the spectrum is very rich, an attempt should be made to find the lines due to the *s-cis* form. Therefore, the measurements were carefully made near the frequencies estimated by using the rotational constants of the *s-cis* form, which were tentatively calculated from the molecular parameters listed in Table 3. However, we could not observe

TABLE 5. ASSIGNED TRANSITION FREQUENCIES OF 2-PYRIDINECARBALDEHYDE IN THE VIBRATIONALLY-EXCITED STATES (in MHz)

Transition	v_1		v_2		v_3	
	ν_{obsd} a)	$\Delta\nu$ b)	ν_{obsd} a)	$\Delta\nu$ b)	ν_{obsd} a)	$\Delta\nu$ b)
$3_{03}\leftarrow 2_{02}$	8494.30	−0.10	8477.45	0.23	8500.20	−0.32
$3_{22}\leftarrow 2_{21}$	8600.60	−0.26	—		—	
$3_{21}\leftarrow 2_{20}$	8707.30	−0.02	—		8709.40	−0.11
$3_{12}\leftarrow 2_{11}$	9144.88	−0.07	9121.87	0.39	9150.31	−0.13
$4_{14}\leftarrow 3_{13}$	10668.68	−0.20	10654.67	0.49	10673.93	−0.05
$4_{04}\leftarrow 3_{03}$	11207.56	0.24	11184.93	0.28	11217.15	−0.31
$4_{23}\leftarrow 3_{22}$	11446.93	0.02	11424.35	0.47	11452.65	−0.19
$4_{32}\leftarrow 3_{31}$	11518.10	0.04	11495.10	0.16	—	
$4_{22}\leftarrow 3_{21}$	11707.57	0.21	11684.30	0.35	—	
$4_{13}\leftarrow 3_{12}$	12158.93	−0.10	12127.96	0.23	12166.95	−0.10
$5_{15}\leftarrow 4_{14}$	13293.66	0.21	13275.52	0.34	13300.28	−0.19
$5_{05}\leftarrow 4_{04}$	13835.02	−0.10	13807.73	0.31	13849.88	−0.24
$5_{24}\leftarrow 4_{23}$	14275.20	0.06	14246.42	0.03	14283.01	−0.18
$5_{42}\leftarrow 4_{41}$	14394.40	0.01	14365.70	0.17	—	
$5_{33}\leftarrow 4_{32}$	14415.00	−0.01	14386.20	0.18	—	
$5_{32}\leftarrow 4_{31}$	14439.60	−0.48	14411.60	0.27	—	
$5_{23}\leftarrow 4_{22}$	14774.27	−0.16	14745.00	0.44	14774.30	0.12
$5_{14}\leftarrow 4_{13}$	15140.06	−0.02	15100.79	−0.13	15151.68	0.30
$6_{16}\leftarrow 5_{15}$	15895.14	−0.18	15873.67	0.07	15904.61	0.10
$6_{06}\leftarrow 5_{05}$	16383.72	−0.40	16352.02	−0.24	16404.06	0.18
$6_{25}\leftarrow 5_{24}$	17081.49	0.13	17045.95	−0.96	17092.30	0.38
$6_{52}\leftarrow 5_{51}$	{ 17268.92	−0.06	{ 17233.77	−0.59	—	
$6_{51}\leftarrow 5_{50}$	{ 17268.92	−0.07	{ 17233.77	−0.60	—	
$6_{42}\leftarrow 5_{41}$	17294.14	0.05	17259.00	−0.47	—	
$6_{43}\leftarrow 5_{42}$	—		—		17298.70	−0.40
$6_{34}\leftarrow 5_{33}$	17318.12	0.29	17282.73	−0.14	—	
$6_{33}\leftarrow 5_{32}$	17383.74	−0.08	17348.74	−0.72	17388.33	0.31
$6_{24}\leftarrow 5_{23}$	17896.96	−0.40	17860.30	0.14	17897.00	0.44
$6_{15}\leftarrow 5_{14}$	—		—		18091.30	0.25
$7_{17}\leftarrow 6_{16}$	18474.74	−0.09	18449.68	−0.15	18486.48	0.15
$7_{07}\leftarrow 6_{06}$	18876.54	0.29	18841.00	−0.39	18899.50	−0.13
$7_{26}\leftarrow 6_{25}$	19861.74	0.00	19821.30	−0.32	—	
$7_{35}\leftarrow 6_{34}$	20222.70	−0.14	—		20230.30	0.56
$7_{34}\leftarrow 6_{33}$	20368.10	0.04	20327.74	−0.47	20371.00	0.32
$7_{16}\leftarrow 6_{15}$	20949.90	−0.02	20895.00	0.25	20971.80	0.34
$7_{25}\leftarrow 6_{24}$	21049.12	0.29	21003.32	0.18	21049.12	0.15
$8_{18}\leftarrow 7_{17}$	21034.00	0.16	21006.00	0.23	—	
$8_{08}\leftarrow 7_{07}$	21338.04	−0.68	21301.76	−0.18	—	

a) Maximum experimental uncertainty in frequency measurements is ±0.1 MHz. b) $\Delta\nu=\nu_{\text{obsd}}-\nu_{\text{calcd}}$.

Table 5. (Continued)

Transition	v_4		v_5	
	ν_{obsd}[a)]	$\Delta\nu$[c)]	ν_{obsd}[b)]	$\Delta\nu$[c)]
$3_{03}\leftarrow 2_{02}$	8496.30	0.01	—	
$3_{12}\leftarrow 2_{11}$	9150.31	0.17	9157.0	0.08
$4_{14}\leftarrow 3_{13}$	10667.60	0.02	10682.8	0.18
$4_{04}\leftarrow 3_{03}$	11209.65	0.16	11221.2	−0.25
$4_{23}\leftarrow 3_{22}$	11449.70	−0.06	11461.8	−0.01
$4_{31}\leftarrow 3_{30}$	11528.50	0.17	—	
$4_{22}\leftarrow 3_{21}$	11710.88	−0.07	11723.0	−0.09
$4_{13}\leftarrow 3_{12}$	—		12175.3	0.43
$5_{15}\leftarrow 4_{14}$	13291.95	0.27	13310.6	0.10
$5_{05}\leftarrow 4_{04}$	13837.16	−0.07	—	
$5_{24}\leftarrow 4_{23}$	14278.58	−0.04	14293.7	0.05
$5_{42}\leftarrow 4_{41}$	14398.30	−0.12	—	
$5_{41}\leftarrow 4_{40}$	14398.30	0.24	—	
$5_{33}\leftarrow 4_{32}$	14419.30	0.41	—	
$5_{32}\leftarrow 4_{31}$	14443.80	−0.16	14458.8	−0.37
$5_{23}\leftarrow 4_{22}$	14779.46	0.03	14794.5	0.03
$5_{14}\leftarrow 4_{13}$	15148.57	0.08	15159.3	−0.36
$6_{16}\leftarrow 5_{15}$	15892.86	−0.15	15915.5	−0.12
$6_{06}\leftarrow 5_{05}$	16385.40	−0.35	16404.1	−0.17
$6_{25}\leftarrow 5_{24}$	17085.53	0.13	17103.5	0.08
$6_{52}\leftarrow 5_{51}$	17273.51	−0.01	—	
$6_{51}\leftarrow 5_{50}$	17273.51	−0.02	—	
$6_{42}\leftarrow 5_{41}$	17298.70	0.01	—	
$6_{34}\leftarrow 5_{33}$	17323.00	0.41	17341.0	0.39
$6_{33}\leftarrow 5_{32}$	17388.33	−0.25	17406.5	−0.45
$6_{24}\leftarrow 5_{23}$	17904.30	0.18	17921.9	0.16
$6_{15}\leftarrow 5_{14}$	18085.40	0.15	18098.4	−0.12
$7_{17}\leftarrow 6_{16}$	18471.92	0.04	18498.3	−0.03
$7_{07}\leftarrow 6_{06}$	18876.54	−0.41	18899.5	0.19
$7_{26}\leftarrow 6_{25}$	19866.10	−0.16	19887.5	0.25
$7_{34}\leftarrow 6_{33}$	20373.92	0.16	20395.5	0.12
$7_{16}\leftarrow 6_{15}$	20961.00	−0.18	20976.0	−0.42
$7_{25}\leftarrow 6_{24}$	21057.80	0.05	21077.5	0.07
$8_{18}\leftarrow 7_{17}$	21029.80	−0.34	21060.2	−0.32
$8_{08}\leftarrow 7_{07}$	21338.04	−0.10	—	

a) Maxmium experimental uncertainty in frequency measurements is ±0.1 MHz. b) The uncertainty is ±0.2 MHz. c) $\Delta\nu=\nu_{\text{obsd}}-\nu_{\text{calcd}}$.

any lines which might be assigned to the *s-cis* form, while we could find the five sets of the spectra due to the vibrationally-excited states near the spectrum of the ground state. The excited states will be designated hereafter by the symbol of v_i, the suffix, i, being numbered from one upward in the order of decreasing intensity. By using the least-squares procedure, the five sets of the rotational constants were determined so as to get the best fit between the observed and the calculated frequencies. Of the observed frequencies for each set, several values, which do not seem to be precise, were omitted in this calculations. The assigned transition frequencies for the excited states are listed in Table 5, together with the differences between the observed and the calculated frequencies. The rotational constants thus obtained are shown in Table 6.

From the values of the inertia defects shown in Table 6, it is concluded that the v_1, v_2, and v_5 states are the excited ones for the out-of-plane deformation vibrations.

TABLE 6. ROTATIONAL CONSTANTS AND INERTIA DEFECTS OF 2-PYRIDINECARBALDEHYDE IN VIBRATIONALLY-EXCITED STATES

	Rotational constants (MHz)			Inertia defect (amu·Å²)
	A	*B*	*C*	
v_1	5342.21 ±2.71	1620.65 ±0.04	1246.31 ±0.04	−0.937 ±0.048
v_2	5256.60 ±4.22	1615.70 ±0.07	1245.49 ±0.05	−3.167 ±0.077
v_3	5432.22 ±4.66	1621.67 ±0.06	1246.67 ±0.04	0.709 ±0.076
v_4	5374.64 ±2.94	1622.03 ±0.03	1245.65 ±0.03	0.112 ±0.051
v_5	5342.23 ±2.92	1622.79 ±0.04	1247.91 ±0.04	−1.047 ±0.051

It should be noted that the values of the inertia defects for the v_1 and v_2 states are almost the same as those of the $v=1$ and $v=2$ states of benzaldehyde obtained by Kakar *et al.*,[15)] respectively.

Table 7. LOW-FREQUENCY VIBRATIONS OF 2-PYRIDINECARBALDEHYDE

	Microwave spectrum	Far-infrared spectrum	Raman spectrum
v_1	127±20 cm⁻¹	111[a)] cm⁻¹	117 cm⁻¹
v_2	187±15	—	—
v_3	219±19	225	230
v_4	239±13	(broad)	
v_5	312±35	—	—

a) This value is quoted from Ref. 8.

By measureing the relative intensities of the satellite lines with respect to the ground state transitions, the vibrational energy separations were estimated from the Boltzmann factor. The results are shown in Table 7, together with the corresponding wave numbers obtained from the far-infrared and the laser Raman spectrum of the liquid state for comparison. The broad infrared band near 225 cm⁻¹ may be a doublet.

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