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R. L. Williams

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Infrared Spectrum of Methyl Isocyanide

R. L. WILLIAMS*

Department of Chemistry and Chemical Engineering, University of California, Berkeley, California

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The infrared spectrum of methyl isocyanide vapor has been remeasured with medium resolving power from 1.7–10 μ and in the far infrared region around 38 μ . From these observations it has been possible to obtain unequivocally the three degenerate fundamental vibration frequencies ν_6 , ν_7 , and ν_8 , and the symmetric frequency ν_3 . Thermodynamic properties are calculated for the molecule. In addition the spectrum of acetonitrile vapor has been remeasured around 6 μ with slightly increased resolving power and the ν_3 and ν_6 fundamental frequencies obtained.

THE infrared spectrum of methyl isocyanide has been measured only in the liquid state,¹ except for some recent high-dispersion work by Thompson and Williams,² in which the fine structure of some of the fundamental vibration bands was recorded for methyl isocyanide and also for acetonitrile. However, this work did not yield accurate values for the three degenerate (*E*) fundamentals ν_6 , ν_7 , and ν_8 and it was not possible to locate symmetric (*A*₁) fundamental, ν_3 , because of atmospheric absorption. The present investigation yields more precise values for these quantities and gives an assignment of the spectrum of the molecule from 1.7–14 μ . In addition, an examination of the 6 μ region of the spectrum of acetonitrile vapor provides some evidence that the ν_6 fundamental lies at 1454.9 cm⁻¹ compared with a value of 1412.6 cm⁻¹ suggested by Venkateswarlu.³

EXPERIMENTAL

The sample of methyl isocyanide was prepared by the method described by Hartley,⁴ in which methyl iodide was heated under pressure with cuprous cyanide in the presence of acetonitrile. The solid complex thus formed was decomposed with aqueous potassium cyanide solution and the methyl isocyanide was distilled off. Traces of ammonia were eliminated by treatment with anhydrous calcium chloride and the methyl isocyanide was then carefully fractionated, b.p. 59–60°C, to separate a small amount of contaminating acetonitrile. Successful removal of this substance was shown by the absence from the spectrum of methyl isocyanide of the 1041 cm⁻¹ band and certain strong *Q* branches in the 1455 cm⁻¹ band of acetonitrile.

Reagent grade acetonitrile, dried with phosphorus pentoxide, was used without further purification.

The spectra were measured with a Perkin-Elmer 12C spectrometer, using a lithium fluoride prism

(6000–2050 cm⁻¹) and with a Perkin-Elmer 21 double beam spectrometer, using prisms of fluorite (1700–1300 cm⁻¹) and rocksalt (4000–800 cm⁻¹). In order to obtain highest possible accuracy in measurement of the perpendicular bands at 6 μ and 9 μ , calibration spectra of water vapor and ammonia were superimposed directly on the recorded spectra. A half-meter absorption cell was used.

The far infrared measurements were made with the Berkeley spectrometer⁵ equipped with a 500-lines per inch grating, thin rocksalt chopper and 70 cm absorption cell. False energy was reduced by means of a fluorite reststrahlen and by filters of polythene thoroughly scratched with 180 mesh sandpaper. Calibration was effected with the pure rotation spectrum of water.⁶

It is estimated that sharp lines were measured with an accuracy of ± 10 cm⁻¹ from 6000–4000 cm⁻¹, ± 5 cm⁻¹ from 4000–3200 cm⁻¹, ± 1 cm⁻¹ from 3200–1000 cm⁻¹ and ± 0.5 cm⁻¹ in the far infrared.

RESULTS

The spectrum from 6000–1600 cm⁻¹ is shown in Fig. 1, while band positions are given in Table I, together with their assignment and frequencies calculated from the fundamentals of the molecule.

Methyl isocyanide belongs to symmetry point group

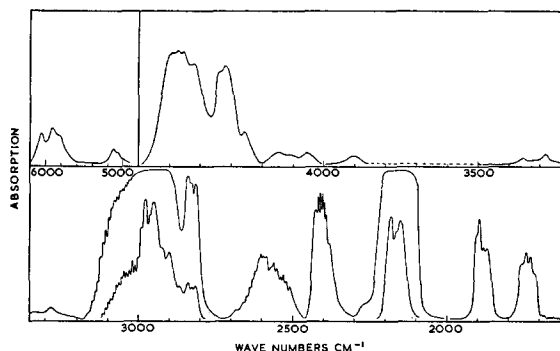


FIG. 1. The spectrum of methyl isocyanide from 6000–1600 cm⁻¹. 50 cm cell, pressures 70 mm and 10 mm.

* Present address: Ministry of Supply, E.R.D.E., Waltham Abbey, Essex, England.

¹ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 332.

² H. W. Thompson and R. L. Williams, *Trans. Faraday Soc.* **48**, 502 (1952).

³ P. Venkateswarlu, *J. Chem. Phys.* **19**, 293 (1951).

⁴ E. J. Hartley, *J. Chem. Soc.* **1928**, 781.

⁵ Bohn, Freeman, Gwinn, Hollenberg, and Pitzer, *J. Chem. Phys.* **21**, 719 (1953).

⁶ Randall, Dennison, Ginsberg, and Weber, *Phys. Rev.* **52**, 160 (1937).

C_{3v} and has four symmetric fundamental vibrations of the A_1 class and four doubly degenerate E class vibrations. All eight vibrations are active in both the Raman effect and in infrared absorption. Of these two species of vibration, those of A_1 symmetry give rise to parallel bands, but because of the smallness of the rotation constant, B_v , no fine structure is observed under prism resolution, and they appear as a weak central Q branch bordered by stronger unresolved P and R branches. The separation of the P and R maxima can be calculated from the Gerhard and Dennison formula⁷ to be 24.8 cm^{-1} , using the microwave values⁸ for the moments of inertia, *viz.* $I_A = 5.360 \times 10^{-40}$, $I_B = 83.469 \times 10^{-40} \text{ gm cm}^2$. The degenerate vibrations, on the other hand, give rise to perpendicular bands which generally show fine structure consisting of a number of Q branches, the position of whose maxima is given by the equation⁹

TABLE I. The spectrum of methyl isocyanide.

Frequency cm^{-1} vac. ^a	Assignment	Species	Calculated
6050	$2\nu_6$	$A_1 + E$	6029
5910	$\nu_1 + \nu_6$	E	5980
5840s	$2\nu_1$	A_1	5932
5129	$\nu_2 + \nu_5$	E	5180
5097s	$\nu_1 + \nu_2$	A_1	5133
4483	$\nu_5 + \nu_6$	$A_1 + A_2 + E$	4481
4468	$\nu_3 + \nu_5$	E	4443
4455	$\nu_1 + \nu_6$	E	4433
4420	$\nu_1 + \nu_3$	A_1	4395
4340R	$2\nu_2$	A_1	4332
4320P			
4259	$\nu_4 + \nu_5 + \nu_8$	$A_1 + A_2 + E$	4222
4150	$\nu_3 + \nu_7$	$A_1 + A_2 + E$	4144
4060	$\nu_1 + \nu_7$	E	4095
3900	$\nu_1 + \nu_4$	A_1	3911
3322	$\nu_5 + \nu_8$	$A_1 + A_2 + E$	3295
3282	$\nu_2 + \nu_7$	E	3277
3014r	ν_5	E	...
2966	ν_1	A_1	...
2910	$2\nu_6$	$A_1 + E$	2933
2829	$2\nu_3$	A_1	2858
2590r	$\nu_6 + \nu_7$	$A_1 + A_2 + E$	2595
2550r	$\nu_3 + \nu_7$	E	2558
2426r	$\nu_2 + \nu_8$	E	2429
2405r	$\nu_4 + \nu_6$	E	2411
2270	$2\nu_7$	$A_1 + E$	2258
2166	ν_2	A_1	...
1896	$2\nu_4$	A_1	1903
1879	$\nu_2 - \nu_8$	E	1889
1867			
1742	$\nu_6 + \nu_8$	$A_1 + A_2 + E$	1730
1728	$\nu_3 + \nu_8$	E	1692
1467	ν_6	E	...
1429	ν_3	A_1	...
1214	$\nu_4 + \nu_8$	E	1208
1129r	ν_7	E	...
945	ν_4	A_1	...
263	ν_8	E	...

^a s shoulder. R R-branch maxima. P P-branch maxima. r partially resolved.

⁷ S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).

⁸ Kessler, Ring, Trambarulo, and Gordy, Phys. Rev. **79**, 54 (1950).

⁹ D. R. J. Boyd and H. W. Thompson, Trans. Faraday Soc. **48**, 493 (1952).

TABLE II. The 3μ region of methyl isocyanide.

RQK	Observed $\nu_{\text{vac. cm}^{-1}}$	Calculated $\nu_{\text{vac. cm}^{-1}}$
8	3087	3088.6
9	3096	3097.3
10	3106	3105.9
11	3114	3114.4
12	3122	3123.0
13	3132	3131.6
14	3140	3140.1
15	3148	3148.5
16	3159	3157.0

$$\nu = \nu_0 + [A'(1 - \xi_i)^2 - B'] \pm 2[A'(1 - \xi_i) - B']K - [(A' - A'') - (B' - B'')]K^2,$$

where A' , B' , and A'' , B'' are the rotational constants of the excited and ground states, respectively, ξ_i , the Coriolis coupling coefficient, ν_0 , the band origin, and K the quantum number of momentum about the symmetry axis. On account of the nuclear spins of the off-axis hydrogen atoms, the statistical weight of every third K level is enhanced, so that the Q branches show an intensity sequence; strong, weak, weak, strong.

FUNDAMENTAL BANDS

The spectrum of methyl isocyanide from 3–4 μ has already been studied in detail by Thompson and Williams,² who found $\nu_1 = 2965.8$, $\nu_5 = 3014.3 \text{ cm}^{-1}$ and $\xi_5 = 0.08$. However, the use of longer absorbing paths has enabled eight more Q branches on the high frequency side of ν_5 to be observed. The line positions are given in Table II, together with the values calculated from the formula given by Thompson and Williams.

$$\nu = 3018.34 \pm 8.901K - 0.0148K^2.$$

Very satisfactory agreement is obtained.

The ν_2 parallel band at 2166 cm^{-1} shows the expected contour with a PR maxima separation 24 cm^{-1} . The spectrum in the 6 μ region is shown in Fig. 2; line positions and their assignment are given in Table III. Raman measurements¹ show that there are two lines in this region, corresponding to the $\nu_3(A)$ and $\nu_6(E)$ fundamentals. In the infrared spectrum, ν_3 is weak compared with ν_6 and it is therefore partly masked by the overlapping fine structure of the latter band. However, its Q branch can be seen to lie at 1428 cm^{-1} , and the abnormal shapes of the PQ_3 and PQ_4 lines of ν_6 are due to the R and P maxima of ν_3 , the approximate contour of

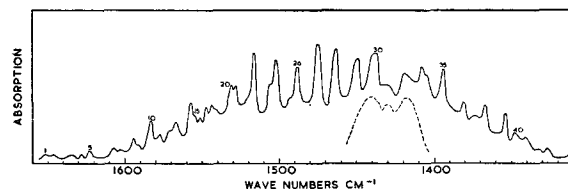


FIG. 2. The spectrum of methyl isocyanide in the 6 μ region. 50 cm cell, pressure 70 mm.

TABLE III. The 6μ region of methyl isocyanide.

Line number	$\nu_{\text{vac. cm}^{-1}}$	Assignment	Line number	$\nu_{\text{vac. cm}^{-1}}$	Assignment
1	1651.8		23	1504.8	
2	1645.7		24	1502.3	RQ_2
3	1634.6		25	1493.2	
4	1627.8		26	1488.4	RQ_1
5	1623.8		27	1475.1	RQ_0
6	1607.0	RQ_{10}	28	1462.7	PQ_1
7	1603.1		29	1449.8	PQ_2
8	1594.5	RQ_9	30	1436.3	PQ_3
9	1590.6		31	1429	ν_3
10	1582.9	RQ_8	32	1421.3	PQ_4
11	1576.9		33	1407.5	PQ_5
12	1570.5	RQ_7	34	1405.1	
13	1567.1		35	1394.1	PQ_6
14	1557.6	RQ_6	36	1380.7	PQ_7
15	1555.1		37	1374.2	
16	1551.5		38	1367.3	PQ_8
17	1547.1		39	1353.8	PQ_9
18	1543.5	RQ_5	40	1347.7	
19	1540.5		41	1340.6	PQ_{10}
20	1530.2	RQ_4	42	1332.1	
21	1527.7		43	1326.5	PQ_{11}
22	1515.8	RQ_3	44	1312.5	PQ_{12}

which is shown as a broken line in the diagram. The assignment of the Q branches in the perpendicular band follows at once from the fact that the strongest line in such a band is RQ_0 which in this case is the line at 1475.1 cm^{-1} . The positions of the lines can be fitted by the method of least squares to the following formula:

$$\nu = 1476.15 \pm 13.42_5 K - 0.02_1 K^2$$

with a standard deviation of 0.85 cm^{-1} . From this it follows that

$$\nu_0 + [A'(1-\zeta_6)^2 - B'] = 1476.15 \text{ cm}^{-1}$$

$$[A'(1-\zeta_6) - B'] = 6.71 \text{ cm}^{-1}$$

$$(A' - A'') - (B' - B'') = -0.02 \text{ cm}^{-1}.$$

By using the microwave values of $B'' = 0.3354 \text{ cm}^{-1}$ and $A'' = 5.221 \text{ cm}^{-1}$ and assuming that $A'\zeta_6 = A''\zeta_6$, the following constants are obtained: $\nu_0 = 1466.9_1 \text{ cm}^{-1}$, $\zeta_6 = -0.35_6$, and $A' - B' = 4.86_5 \text{ cm}^{-1}$. Apart from the Q branches of the main band, there remain a number of lines still unassigned, especially at the high frequency end of the band, where series can be picked out having approximately the same spacing as the fundamental. Similar series appear in the 3μ -perpendicular bands of both methyl isocyanide and acetonitrile and are probably due to transitions $\nu_i + \nu_8 - \nu_8$ and $\nu_i + 2\nu_8 - 2\nu_8$,

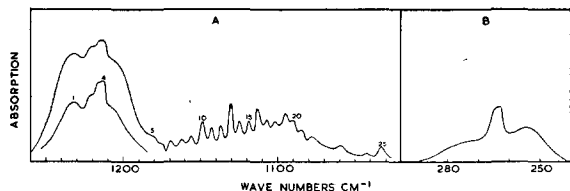


FIG. 3. The spectrum of methyl isocyanide: A. In the 9μ region. 50 cm cell, pressures 70 mm and 10 mm. B. Around 38μ . 70 cm cell, pressure 70 mm.

which should have roughly the same spacing of Q branches as ν_i . At the low frequency side of the band, there is the possibility that some of the structure of $\nu_7 + \nu_8$ (calc = 1392 cm^{-1}) has been resolved; the spacing for this band can be shown to be approximately 23.5 cm^{-1} .

The spectrum of the ν_7 perpendicular band is shown in Fig. 3a, line positions in Table IV. The Q branches show a well-defined alternation of intensity, that at 1131 cm^{-1} being RQ_0 , the most intense one in the band. The line positions are well represented by the equation

$$\nu = 1131.0_9 \pm 6.06_8 K + 0.02_5 K^2,$$

the standard deviation being 0.20 cm^{-1} . The constants for the ν_7 fundamental are therefore

$$\nu_0 + [A'(1-\zeta_7)^2 - B'] = 1131.0_9 \text{ cm}^{-1}$$

$$[A'(1-\zeta_7) - B'] = 3.03_4 \text{ cm}^{-1}$$

$$(A' - A'') - (B' - B'') = 0.02_5 \text{ cm}^{-1}$$

TABLE IV. The 9μ region of methyl isocyanide.

Line number	$\nu_{\text{vac. cm}^{-1}}$	Assignment	Line number	$\nu_{\text{vac. cm}^{-1}}$	Assignment
1	1232		14	1125.0	PQ_1
2	1221.1	$\nu_4 + 2\nu_8 - \nu_8$	15	1118.8	PQ_2
3	1215.9	$\nu_4 + \nu_8$	16	1113.0	PQ_3
4	1214.0		17	1107.0	PQ_4
5	1181.2	RQ_5	18	1101.7	PQ_5
6	1174.5	RQ_7	19	1095.4	PQ_6
7	1168.5	RQ_8	20	1090.2	PQ_7
8	1162.2	RQ_5	21	1084.2	PQ_8
9	1156.1	RQ_4	22	1078.3	PQ_9
10	1149.4	RQ_3	23	1059.1	
11	1143.2	RQ_2	24	1042.7	
12	1137.2	RQ_1	25	1033.4	
13	1131.2	RQ_0			

from which it follows that

$$\nu_0 = 1129.2_9 \text{ cm}^{-1}, \quad \zeta_7 = 0.37 \quad \text{and} \quad A' - B' = 4.91 \text{ cm}^{-1}.$$

The ν_4 fundamental was not examined in this investigation but its value has been shown to be 944.6 cm^{-1} .

It is now possible to deduce a value for ζ_8 from the sum rule for Coriolis coefficients:¹⁰

$$\Sigma \zeta_i = B/2A + 1 = 1.032.$$

Using the values for ζ_5 , ζ_6 , and ζ_7 given above, it is found that $\zeta_8 = 0.94$. The spacing of the Q branches in the ν_8 band will therefore be roughly 0.04 cm^{-1} and the band should appear as a strong central maximum with wings corresponding to unresolved P and R substructure. The observed contour is shown in Fig. 3b. The band center lies at 263 cm^{-1} .

COMBINATION BANDS

Table I lists the positions of the combination bands of methyl isocyanide. Several of the bands show fine structure especially in the region from 2700 – 2300 cm^{-1} ,

¹⁰ R. D. Cowan, J. Chem. Phys. **18**, 1101 (1950).

where there are two absorptions. The first, centered around 2590 cm^{-1} shows great similarity to a band in acetonitrile observed by Venkateswarlu³ at 2430 cm^{-1} and assigned by him to two overlapping perpendicular bands, $\nu_3 + \nu_7$ and $\nu_6 + \nu_7$. With methyl isocyanide, these two bands lie closer together at 2558 cm^{-1} and 2595 cm^{-1} and it is not possible to disentangle the overlapping Q branches, which should have separations of about 6.1 and 9.8 cm^{-1} , respectively. The observed spacings in the band system vary from 7 to 15 cm^{-1} (Table V).

The interpretation of the structure around 2400 cm^{-1} is uncertain. Two bands, $\nu_4 + \nu_6$ and $\nu_2 + \nu_8$, lie at 2411 and 2429 cm^{-1} , respectively, but the spacing of the first

TABLE V. Line positions in the region of 4μ .

Region	$\nu_{\text{vac. cm}^{-1}}$	Region	$\nu_{\text{vac. cm}^{-1}}$
2680–2500	2679	2680–2500	2536
	2659		2528
	2647		2521
	2640		2510
	2629		
	2618	2400	2426
	2601		2418
	2593		2411
	2584		2404
	2569		2398
	2561		2392
	2548		2386

TABLE VI. The fundamentals of methyl isocyanide.

Vibration	Infrared (vap.) $\nu_{\text{vac. cm}^{-1}}$	Raman (liq.) ^a $\nu_{\text{vac. cm}^{-1}}$
ν_1 sym. CH stretch	2965.8	2951
ν_2 N=C stretch	2166.0	2161
ν_3 CH ₃ deform.	1429	1414
ν_4 C–N stretch	944.6	928
ν_5 asym. CH stretch	3014.3	3002
ν_6 CH ₃ deform.	1466.9	1456
ν_7 CH ₃ rock.	1129.3	1041(?)
ν_8 C–N=C bend.	263	290

^a From reference 1.

of these should be around 13 cm^{-1} and of the second, very small, neither of which corresponds to the observed spacing of 6.5 cm^{-1} (Table V). Since the levels lie very close together and are of the right species, it is possible that there is a very strong Coriolis interaction between them which would be sufficient to alter the Q -branch spacings.

The remaining assignments are quite straightforward, though the contour of $\nu_4 + \nu_8$ at 1214 cm^{-1} is of interest since it should be the same as that of ν_8 itself. The observed similarity is very marked; it is probable that the shoulder on the side of the Q branch of $\nu_4 + \nu_8$ is due to $\nu_4 + 2\nu_8 - \nu_8$.

THERMODYNAMIC PROPERTIES

The observed infrared fundamentals together with the Raman data are given in Table VI. These have been

TABLE VII. Thermodynamic properties of methyl isocyanide.^a

$^{\circ}\text{K}$	C_p^0	$(H^0 - E_0^0)/T$	$-(F^0 - E_0^0)/T$	S^0
100	9.304	8.299	37.394	45.692
200	11.123	9.310	43.466	52.776
273.16	12.227	9.939	46.463	56.402
298.16	12.655	10.149	47.342	57.491
300	12.688	10.164	47.405	57.568
400	14.577	11.028	50.445	61.474
500	16.483	11.930	53.004	64.934
600	18.238	12.838	55.260	68.098
700	19.802	13.724	57.306	71.030
800	21.178	14.570	59.194	73.764
900	22.387	15.374	60.956	76.332
1000	23.443	16.129	62.617	78.746

^a All functions are measured in cal/deg mole.

used to calculate the thermodynamic properties listed in Table VII, using the microwave dimensions of the molecule.

ν_3 AND ν_6 FUNDAMENTALS OF ACETONITRILE

The spectrum of acetonitrile in the 6μ region is shown in Fig. 4; line positions being shown in Table VIII. There is a marked similarity to that of methyl

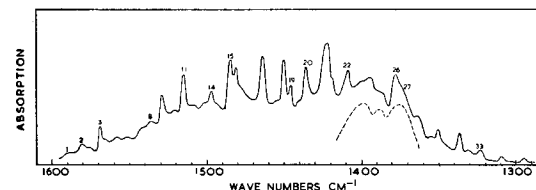


FIG. 4. The spectrum of acetonitrile in the 6μ region. 50 cm cell, pressure 50 mm.

isocyanide, the ν_3 band again being masked by the structure of the ν_6 perpendicular band. The Q branch of ν_3 lies at 1387 cm^{-1} , agreeing closely with the value measured by Venkateswarlu. The choice of the strongest Q line in the ν_6 band lies between that at 1421.7 cm^{-1} and the one at 1464.2 cm^{-1} . However, the former is

TABLE VIII. The 6μ region of acetonitrile.

Line number	$\nu_{\text{vac. cm}^{-1}}$	Assignment	Line number	$\nu_{\text{vac. cm}^{-1}}$	Assignment
1	1591.8		19	1444.9	
2	1578.9	$RQ_7(?)$	20	1435.7	PQ_2
3	1568.6		21	1421.7	PQ_3
4	1566.3		22	1408.9	PQ_4
5	1558.1	RQ_6	23	1399.2	R branch ν_3
6	1548.6		24	1393.0	PQ_5
7	1541.2	RQ_5	25	1386.9	Q branch ν_3
8	1535.9		26	1378.2	PQ_6
9	1529.2	RQ_4	27	1372.6	P branch ν_3
10	1520.8		28	1363.7	PQ_7
11	1515.2	RQ_3	29	1354.6	
12	1508		30	1350.2	PQ_8
13	1499.9		31	1336.5	PQ_9
14	1496.2	RQ_2	32	1331.4	
15	1483.6		33	1322.9	PQ_{10}
16	1480.8	RQ_1	34	1308.6	PQ_{11}
17	1464.2	RQ_0	35	1294.5	PQ_{12}
18	1449.8	PQ_1			

TABLE IX. Vapor and liquid phase frequencies for methyl isocyanide and acetonitrile.

Vibration	Methyl isocyanide	Acetonitrile
ν_8	-27	-19
ν_4	+16	+2
ν_7^a
ν_3	+15	+11
ν_6	+11	(+14)
ν_2	+5	+18
ν_1	+14	+10
ν_5	+12	+10

^a Raman values are not known with accuracy. The values in the columns are infrared frequency (vapor phase) minus Raman frequency (liquid).

anomalously wide, 7 cm⁻¹, compared with an average value of about 3 cm⁻¹ for most of the other Q branches of the band. This suggests that its intensity is fortuitously increased both by the R branch of ν_3 and also by the presence of $\nu_7 + \nu_8$ which lies near 1400 cm⁻¹. If the higher line is taken as RQ_0 , then line positions are represented by

$$\nu = 1466.3_4 \pm 15.2_9 K + 0.08_2 K^2.$$

This equation gives a value for ν_0 of 1454.9 cm⁻¹ and ζ_6 of -0.51. Confirmatory evidence for this figure for ν_6 comes from the values of the fundamental in the liquid state of 1440 cm⁻¹ and 1443 cm⁻¹ for Raman and infrared spectra. A comparison of the difference between infrared vapor and Raman liquid values for the fundamentals in Table IX, shows that methyl isocyanide and acetonitrile run closely parallel and that ν_6 for acetonitrile should be about 15 cm⁻¹ higher in the vapor phase. The higher value for ν_6 also gives in every case better agreement between calculated and observed values for the overtone and combination frequencies of the molecule.

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General Formulas for Kinetic Energy Matrix Elements of In-Plane Vibration in Planar Molecules

TAKEHIKO SHIMANOCHI

Chemical Laboratory, Faculty of Science, Tokyo University, Tokyo, Japan

(Received December 14, 1955)

General formulas for kinetic energy matrix elements are given in terms of internal coordinates of the bond stretching and bending type for in-plane vibration in planar molecules. The definition for the sign of bond angle makes those formulas independent of the mutual positions of atoms. An example is given.

THE kinetic energy of vibration for polyatomic molecules, T , can be written in terms of internal coordinates, R , as:

$$2T = \sum_{k,h} (G^{-1})_{kh} \dot{R}_k \dot{R}_h.$$

For the calculation of vibration frequencies and vibrational modes we need the elements of the G -matrix^{1,2} which have been obtained and tabulated.^{3,4,5} However, when the vibrations of compounds with aromatic rings or peptide bonds are dealt with, we often need the expression for the G -matrix for various types of planar molecules. The present paper gives the tabulation of the elements for such molecules.

In the present table special care has been paid to the expression of bond angle. As shown in Fig. 1, ϕ_{ijk}

denotes such an angle as is traced from the bond (ij) to the bond (jk) in the counterclockwise sense. In this case we have

$$\begin{aligned}\phi_{ijk} &= 2\pi - \phi_{kji} \\ \Delta\phi_{ijk} &= -\Delta\phi_{kji} \\ \sin\phi_{ijk} &= -\sin\phi_{kji} \\ \cos\phi_{ijk} &= \cos\phi_{kji}.\end{aligned}$$

TABLE I. Elements of in-plane G matrix for planar molecules.

$g(\Delta r_{ij}, \Delta r_{ij}) = \mu_i + \mu_j$
$g(\Delta r_{ij}, \Delta r_{jk}) = \mu_{ijk}$
$g(\Delta r_{ij}, \Delta\phi_{ijk}) = -x_{ijk}$
$g(\Delta r_{ij}, \Delta\phi_{jkl}) = x_{ijk}$
$g(\Delta r_{ij}, \Delta\phi_{ikm}) = x_{ijk} - x_{ijm}$
$g(\Delta\phi_{ijk}, \Delta\phi_{ijk}) = z_{ij} + z_{jk} - 2y_{ijk}$
$g(\Delta\phi_{ijk}, \Delta\phi_{jkl}) = -z_{jk} + y_{ijk} + y_{jkl}$
$g(\Delta\phi_{ijk}, \Delta\phi_{ikm}) = -y_{jkl}$
$g(\Delta\phi_{ijk}, \Delta\phi_{ikm}) = -z_{jk} + y_{ijk} - y_{ijm} + y_{ikm}$
$g(\Delta\phi_{ijk}, \Delta\phi_{ikn}) = -y_{jkl} + y_{ikn}$

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