band exhibits its maximum absorption at very nearly the same wave length (11.48 μ) as does pure calcium carbonate (11.46 μ). Also shown in Fig. 2 is the spectrum of a sample of the same apatite after equilibration with a bicarbonate solution at *p*H 7.5 followed by centrifugation at high speed according to a procedure reported elsewhere.[14] It is apparent from the spectrum that during the equilibration bicarbonate was transformed into carbonate before assuming its final state in the apatite.

It appears reasonable to postulate the over-all reaction to account for the appearance of carbonate

$$\underset{\text{(soln.)}}{HCO_3^-} + \underset{\text{(solid)}}{PO_4^{\equiv}} = \underset{\text{(solid)}}{CO_3^{=}} + \underset{\text{(soln.)}}{HPO_4^{=}}$$

in the apatite treated with bicarbonate solution. As shown by the pK_a values for bicarbonate (*ca.* 10.2) and monohydrogen phosphate (*ca.* 12.4), bicarbonate is a stronger acid than monohydrogen phosphate; thus the reaction would be expected to proceed toward the right as written provided the exchange between solid and solution can occur. Such an exchange appears reasonable on the basis of other studies.[5] It is necessary that the apatite be suspended in an aqueous phase to effect this transformation of bicarbonate to carbonate: a mixture of dry apatite and potassium bicarbonate yielded a spectrum in which the apatite carbonate absorption band was not enhanced and the bicarbonate peak was also present; but when the mixture was moistened and allowed to stand overnight, the bicarbonate band disappeared and the carbonate absorption was enhanced.

Calcified Tissues.—Spectra have been obtained with a large number of samples of bone, dentine and enamel, ranging from the fresh materials through variously treated preparations. In Fig. 3 a few of the curves are reproduced as examples of the fact that the calcium carbonate absorption band is prominent in all the specimens except those which had been treated at high temperatures and where, accordingly, no carbonate is anticipated. The glycol-ashed samples exhibit the largest absorption bands, since, in this treatment, carbon dioxide of organic origin is converted into carbonate.

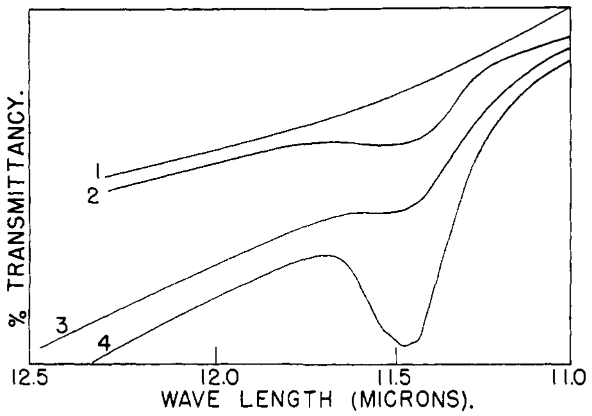

Fig. 3.—Spectra of calcified tissues: 1, enamel, ashed above 750°; 2, fresh enamel; 3, veal shaft, unashed, fat-extracted; 4, glycol-ashed rabbit bone.

The results summarized above clearly indicate that the carbon dioxide of bone and related materials is present entirely as carbonate. While this is reasonable, and, indeed, has been tacitly assumed by many workers, the infrared evidence appears to be the first direct verification of the idea. Preliminary studies indicate that an infrared method for the quantitative determination of bone carbonate will prove feasible.

ROCHESTER, NEW YORK

---

[14] W. F. Neuman, T. Y. Toribara and B. J. Mulryan, THIS JOURNAL, **75**, 4239 (1953).

[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

The Vibrational Spectrum of Methyl Nitrate[1]

BY J. C. D. BRAND AND T. M. CAWTHON[2]

RECEIVED AUGUST 23, 1954

The infrared absorption of methyl nitrate in the vapor and liquid phase has been measured in the range 2–15μ and frequencies have been assigned to all the fundamental vibrations except the two torsional modes. The characteristic frequencies of the $-ONO_2$ group are at 1672 (vs), 1287 (s), 854 (s), 759 (m), 657 (m), and 578 (m) cm.$^{-1}$. Comparison of the statistical and thermal entropies indicates that the barriers hindering internal rotation are small, and the infrared band contours and Raman depolarization factors are interpreted assuming free rotation about the O–N bond.

Introduction

The Raman spectrum of methyl nitrate has been recorded by several observers.[3] Apart from a small number of weak or doubtful bands the measurements of frequency and depolarization factors[3b,c] are in good agreement and the main aspects of the spectrum are firmly established. The infrared absorption has been investigated for both the liquid[3c,4] and vapor[5] phase, but the resolving power was less than is now available and band contours of the vapor spectrum were not determined.

The structural evidence is not complete. The only nitrate ester examined by X-ray methods is pentaerythritol tetranitrate,[6] wherein each nitrate

---

[1] This research was supported by the United States Air Force under Contract No. AF33(038)-23976 monitored by the Office of Scientific Research.

[2] Allied Chemical and Dye Fellow, 1953–1954.

[3] (a) A. Dadieu, F. Jele and K. W. F. Kohlrausch, *Wien. Ber.*, **140**, 293 (1934); L. Medard and F. Alquier, *J. chim. phys.*, **31**, 281 (1934); J. Chedin, *J. Physik*, **10**, 445 (1939). (b) H. Wittek, *Z. physik. Chem.*, **B52**, 153 (1942). (c) J. Lecomte and J. P. Mathieu, *J. chim. phys.*, **39**, 57 (1942).

[4] E. K. Plyler and P. J. Steele, *Phys. Rev.*, **34**, 599 (1929); H. Lenormant and P. L. Clement, *Bull. soc. chim.*, **13**, 565 (1946).

[5] L. F. Kettering and W. W. Sleator, *Physics*, **4**, 39 (1933).

[6] A. D. Booth and F. J. Llewellyn, *J. Chem. Soc.*, 837 (1947).

group is planar and the adjacent carbon atom lies slightly off the same plane. The coplanarity of the ONO_2 nuclei would have been anticipated on general theoretical grounds, and from the fact that the nitric acid molecule is itself planar.[7] Electron diffraction measurements have been reported for methyl nitrate vapor but the interpretation is not final. Pauling and Brockway[8] considered that the configuration with the methyl group in a plane of symmetry perpendicular to the plane of the ONO_2 nuclei was probable, although an alternative model in which all heavy nuclei were coplanar was not ruled out. Rogowski[9] subsequently proposed a strange model in which the nitrogen valences were directed pyramidally, but this suggestion is opposed by a great weight of evidence and will not be considered further.

In the present work the infrared absorption of methyl nitrate in the liquid and vapor phase has been re-measured (2–15 μ) and the results, together with Raman data[3] and recent thermal measurements,[10] are used to interpret the vibrational spectrum as fully as possible. Frequencies are assigned to all the harmonic vibrational modes: torsional frequencies are uncertain, but the thermal evidence shows that they lie very low and that the internal rotations are practically free at room temperature.

Experimental

Methyl nitrate was prepared by esterification of methanol with mixed nitric–sulfuric acids. It was purified by extraction with 85% phosphoric acid, aqueous sodium carbonate and water, and was dried with calcium chloride.

Spectra were recorded with a Perkin–Elmer instrument (Model 21) using NaCl optics. The path was 0.05–2 cm. atm. for the vapor (10-cm. cell) and 0.008–0.1 mm. for the liquid, and a solution in CCl_4 was also used to observe some of the strong bands. Frequencies of the absorption maxima (and shoulders) are in Table I, where Raman frequencies and depolarization factors recorded by Wittek[3b] are reproduced for comparison.

Table I

Infrared and Raman Frequencies of Methyl Nitrate

Infrared				Raman		De-pol. factor
Vapor		Liquid		Liquid[a]		
ν, cm.$^{-1}$	Description[d]	ν, cm.$^{-1}$	Description[c]	ν, cm.$^{-1}$	Description[d]	
				351	0.5	0.52
		577[b]		578	7, b	0.37
ca. 647	m, vb					
655	m, s	662	ms, b	664	3	0.88
658	m, s	(657	ms, s)			
665	m, b					
670	w, s					
758	m. s	759	ms			
760	m, s					
ca. 775	mw, vb					
844	s					
853	s, s	859	s	860	10	0.12
855	s, s					
862	s					
913	w, s	*ca.* 926	vw, sh			
ca. 921	vw, sh					
1007	ms, b					
ca. 1013	w, sh					
1017	s, s	993	s	993	0.5, b	0.50
1025	ms, b					
ca. 1126	w, sh					
1132	w, b	(1140	w, b)			
1136	mw, s	1150	w	1152	0	dp[b]
ca. 1144	w, b					
1153	w, s					
ca. 1164	vw, vb					
1176	vw, s	1174	mw	1175	0.5	0.60
1186	vw, b	(1174	w, s)			
ca. 1211	vw, sh					
1225	w, s	*ca.* 1220	vw. sh			
1232	w, b					
1278	s. b	1282	vs, s	1283	10	0.16
1287	s, s	(1282	vs)			
1296	s, b					
1430	m	1429	m. b	1425	2, d	
1442	m	(1430	s)			
1455	mw			1435	3, d	0.85
1468	mw, s	*ca.* 1458	mw, sh	1456	2, d	
1477	mw	(1460	s)			
ca. 1495	w, sh					
1507	w, s					
1516	w	1521	mw, b	1522	0.5	p
ca. 1532	vw, sh					
1538	vw					
1556	vw, s					
1576	vw					
1661	vs, b	1634	vs	1634	3, vb	0.82
1678	vs	(1647	vs)			
1776	vvw, sh					
1789	vw					
1859	w	1862	w			
1934	vw					
1951	vw	1953	w			
2012	vw					
		2037	vvw			
		2096	vvw			
2186	vw	2162	vw			
2294	vw	2294	vw			
2519	vw	2500	vw			
2575	w	2570	w			
2681	vvw	*ca.* 2675	vvw, sh			
2837	vw	*ca.* 2841	vw, sh	2833	2	
ca. 2917	mw, sh	2907	m, s	2900	0	p
2941	m, s	2963	m, s	2962	10, b	p
ca. 2959	mw, sh					
3008	mw, s	3040	mw, s	3041	1, vb	dp[b]
3330	w	3268	vw			
4024	vvw	4032	vvw			
4175	vvw	4184	vw			
4395	w	4420	w			

[a] Wittek, ref. 3b. [b] Lecomte and Mathieu, ref. 3c. [c] Frequencies in parentheses are for a 0.054 *M* solution in CCl_4 (1-mm. cell). [d] Under the heading Description a qualitative estimate of intensity is given in the first column (s = strong, m = medium, w = weak, etc.) and an indication of the shape of the band in the second column (s = sharp, sh = shoulder, b = broad and d = diffuse Raman line).

Discussion

By internal rotation about the O–N bond methylnitrate can be twisted into two planosymmetric configurations (C_s) and an infinite number of intermediate configurations having no symmetry element (C_1). The C_s structures correspond to the

---

(7) L. R. Maxwell and V. M. Moseley, *J. Chem. Phys.*, **8**, 742 (1940) (vapor); V. Luzzati, *Acta Cryst.*, **4**, 120 (1951) (crystal).

(8) L. Pauling and L. O. Brockway, This Journal, **59**, 13 (1937).

(9) F. Rogowski, *Ber.*, **75**, 244 (1942).

(10) P. Gray and P. L. Smith, *J. Chem. Soc.*, 2380 (1953).

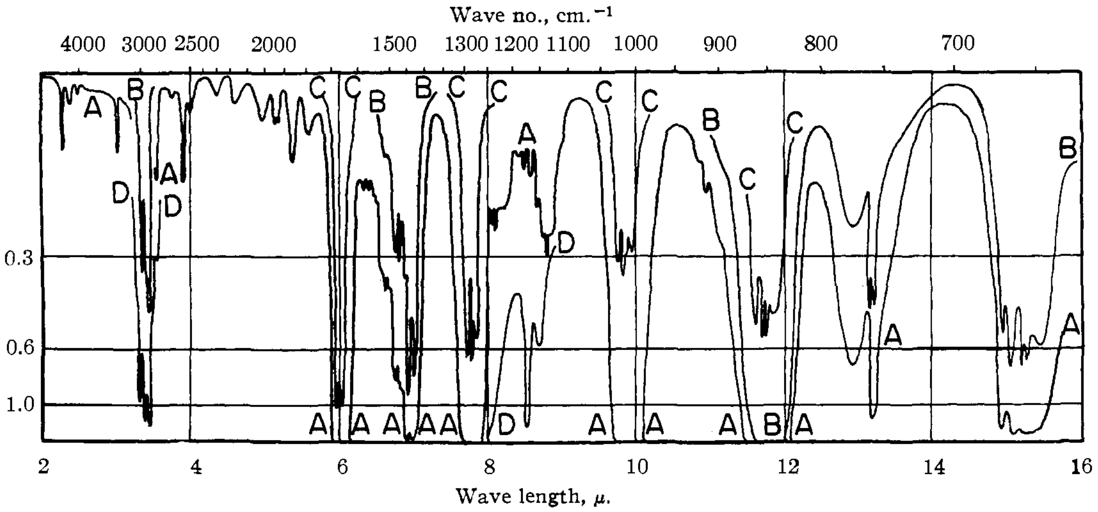

Fig. 1.—Infrared absorption spectrum of methyl nitrate: A, 150 mm.; B, 40 mm.; C, 5 mm. vapor, 10-cm. cell; D, liquid, 0.1-mm. cell.

two models considered by Pauling and Brockway[8] to which reference was made in the Introduction. For either the C_s or the C_1 structures all fundamentals are formally allowed in the infrared and Raman spectrum.

The Skeletal Vibrations.—Methyl nitrate has eighteen normal modes of which two are torsional. Of this total nine fundamentals are essentially skeletal and comprise the stretching deformational and torsional modes of the set of heavy nuclei. It is convenient to consider this class of vibrations first, for on grounds of intensity and location they are easily distinguished from the second class of nine fundamentals composing the vibrations of the methyl group.

The skeletal internal rotation introduces the possibility of rotational isomerism, but only one set of fundamentals appear in the spectrum and a statistical calculation of the entropy indicates that the barrier to internal rotation is small. As a working hypothesis it is assumed, therefore, that the internal rotation is essentially free; this is not inconsistent with the fact that the spectral bands are of normal width, and the assumption of higher barriers runs into severe difficulties in the course of analysis. In the limiting case of unrestricted internal rotation the molecule has no symmetry element common to all possible orientations (and therefore no rigorous selection rules based on group-theoretical considerations) but the plane defined by the C–O–N nuclei is a symmetry plane of the whole molecule in four special orientations during a complete revolution of the methoxyl group about the axis of the O–N bond. Vibrations antisymmetric to this plane under the internal rotation may be expected to show a high depolarization factor in the Raman spectrum. The approximate description of the skeletal fundamentals and their classification on this basis into polarized and depolarized Raman lines is in Table II.

The infrared band contours depend on the orientation of the principal axes of inertia and their behavior under the internal rotation. The orientation of axes for the configuration in which all the heavy nuclei are coplanar is shown in Fig. 1. Owing to the relatively small mass of the off-center methyl group, the internal rotation does not alter this picture significantly: the *a*-axis always lies in the plane of the three nuclei C–O–N, and the *b*- and *c*-axes make small angles with the plane of the ONO_2 nuclei and the normal to this plane, respectively. As there is no differentiation on symmetry grounds between the principal axes the fundamentals are, in general, all hybrid bands, but where the description of the vibration is a sufficiently good approximation it is possible by inspection to write down the dominant character of a vibration and this has been entered in Table II. The theoretical envelopes of pure type A, B and C bands are well known.[11]

TABLE II

CLASSIFICATION OF SKELETAL FUNDAMENTALS (FREE ROTATION MODEL)

Mode	Infrared	Raman	Mode	Infrared	Raman
N:O stretching (as)	B	dp	NO_2 non-planar rocking	C	dp
N:O stretching (s)	A	p	NO_2 planar rocking	A or B	dp
C–O stretching	A	p	NO_2 deformation	A	p
N–O stretching	A	p	Skeletal bending		p

The vibrational analysis presents no serious difficulty. The four outstandingly strong infrared bands (1672, 1287, 1017 and 854 cm.$^{-1}$) are assigned to the skeletal stretching vibrations, in agreement with Wittek's interpretation[3b] of the Raman spectrum. Other nitrate esters have strong infrared bands in the region of the upper two (N:O as and s stretching modes) and the lowest (N–O stretching) frequencies.[3c] The band at 1672 cm.$^{-1}$ has a central minimum (type B) and a high depolarization factor, but the remaining three bands of this group are (mainly) type A and are polarized in the Raman spectrum. These contours and depolarization factors are in agreement with the freely rotating model (Table II).

Of the skeletal deformation modes, the NO_2 def-

---

[11] R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938).

ormation, planar and non-planar rocking vibrations must correlate with the deformation frequencies of the nitrate ion at 720 (e', infrared, Raman) and 830 (a_2'', infrared) cm.$^{-1}$. The type C infrared band at 759 cm.$^{-1}$ is clearly the non-planar rocking mode: the fact that this vibration is unobservably weak in the Raman spectrum is explained by its relation to the Raman-forbidden a_2'' non-planar fundamental of the nitrate ion. (The corresponding vibration of nitric acid is also missing in the Raman spectrum.[12]) The NO_2 deformation and planar rocking modes, both of which correlate with the e' nitrate ion vibration, are assigned to the Raman and infrared bands at 578 (p) and 657 (dp) cm.$^{-1}$, respectively. The remaining skeletal mode, ideally a deformation of the valence angle of the central oxygen atom, is identified with the polarized Raman line at 351 cm.$^{-1}$.

The infrared contour of the NO_2 planar rocking mode requires comment. This vibration (657 cm.$^{-1}$) is perpendicular to the non-planar rocking mode, and as the latter is (mainly) type C the planar mode should be type A or B. On the simple argument used in drawing up Table II, the contour would be expected to have more type B than type A character. Experimentally the absorption curve has in this region a series of maxima that can be explained as a type A fundamental partly overlapping the overtone of a low-lying vibration. If this is correct, the vibration in question is represented by a type A band, and it must be admitted therefore that the dipole moment change makes a smaller angle with the *a*-axis than would be anticipated from the description as a planar rocking mode. An effect of this kind may be explained by interaction between vibrations, which is unrestricted in a molecule without symmetry but is neglected in the intuitive description of the normal modes.

TABLE III

FUNDAMENTAL FREQUENCIES

	Vibration	Infrared vapor frequency, cm.$^{-1}$	Apparent contour	$(\nu - \nu_0)$,[c] cm.$^{-1}$	Infrared liquid frequency, cm.$^{-1}$	Raman liquid frequency,[a] cm.$^{-1}$
1	CH stretching	3008			3040	3041
2	CH stretching	2940			2963	2962
3	CH stretching				2907	2900
4	N:O stretching (as)	1672	B	8	1634	1634
5	CH_3 deformation	1468	A	11	1458	1456
6	CH_3 deformation	. .			. .	1435
7	CH_3 deformation	1434	B	6	1429	1425
8	N:O stretching (s)	1287	A	9	1282	1283
9	CH_3 rocking	1176	A	11	1174	1175
10	CH_3 rocking	1136	A or C	10	1150	1152
11	C–O stretching	1017	A	9	993	993
12	N–O stretching	854	A	9	859	860
13	NO_2 non-planar rocking	759	C	16	759	. .
14	NO_2 planar rocking	657	A	9	662	664
15	NO_2 deformation ∼	578[b]			577	578
16	Skeletal bending ∼	340[b]	Calcd.			351
			A, 9–10 cm.$^{-1}$			
			B, 6–7			
			C, 5–15			

[a] Wittek, ref. 3b. [b] From overtone and combination bands. [c] $(\nu - \nu_0)$ is the separation in cm.$^{-1}$ of the apparent band origin from the maxima in the P and R branches. Theoretical values (calcd.) were obtained by interpolation from the ideal asymmetric top band envelopes calculated by Badger and Zumwalt.[11]

The assignment of the fundamental frequencies is in Table III. Two low-frequency vapor assignments are from overtone and combination bands (Table IV). It is noteworthy that the combination band at (657 + 1287) cm.$^{-1}$ is type B whereas each of the fundamentals is type A: this could not occur if the *a*- and *b*-axes of inertia belonged to different symmetry species.

TABLE IV

OVERTONE AND COMBINATION BANDS

ν, cm.$^{-1}$	Assignment
670	2 × 340 = 680
913	340 + 578 = 918
1153	2 × 578 = 1156
1225	578 + 657 = 1235
1507	657 + 854 = 1511
and 1532	and 2 × 759 = 1518
1566	340 + 578 + 657 = 1575
1776	759 + 1017 = 1776
1859	578 + 1287 = 1865
1942	657 + 1287 = 1944
2012	2 × 1017 = 2034
	or 1672 + 340 = 2012
2037 (L)[a]	759 + 1282 = 2041
2096 (L)	662 + 1429 = 2091
2162 (L)	993 + 1174 = 2167
2186	759 + 1434 = 2193
2294 (L)	2 × 1150 = 2300
2294	1017 + 1287 = 2304
2519	854 + 1672 = 2526
2575	2 × 1287 = 2574
2625 (L)	993 + 1634 = 2627
2681	1017 + 1672 = 2689
2833	2 × 1434 = 2868
3268 (L)	2 × 1634 = 3268
3330	2 × 1672 = 3344
4024	1017 + 3008 = 4025
4032 (L)	993 + 3040 = 4033
4184 (L)	1282 + 2907 = 4189
4395	1468 + 2941 = 4409
4420 (L)	1458 + 2963 = 4421

[a] Liquid.

The C–H Vibrations.—This group of vibrations comprises the methyl stretching, deformational and rocking modes. One vibration in each subgroup should give rise to a depolarized Raman line, and in the region of the stretching and rocking modes this expectation is fulfilled. The deformational modes, however, appear as a group of three closely spaced lines which collectively are reported as depolarized.[3b]

Near 3000 cm.$^{-1}$, three peaks occur in the infrared absorption of the liquid but only two peaks are observed in the vapor spectrum. The contours of the vapor bands were not resolved in this region. The liquid bands coincide with Raman lines and from their intensity appear to be fundamentals, although the lowest frequency (2907 cm.$^{-1}$) might be interpreted as the overtone of the 1458 cm.$^{-1}$ fundamental intensified by resonance. One of the methyl deformation modes is missing or hidden in the infrared spectrum.

Standard Entropy of Methyl Nitrate.—Bond lengths and angles adopted for the statistical calculation are: C–H = 1.08, C–O = 1.45, N–O =

---

[12] O. Redlich, THIS JOURNAL, **69**, 2240 (1947).

1.40, N:O = 1.22 Å., ∠CON = 105° and ∠O:N:O = 135°[13]; tetrahedral angles were assumed within the methyl group. With these parameters the principal moments of inertia of the configuration in which the C, N and O nuclei are coplanar (Fig. 2) are 41.9, 103.8 and 142.1 a.w. – Å.^{2}, and the reduced moments of inertia for internal rotation are 2.8 (methyl rotation) and 10.5 (skeletal rotation).[14] The rotational entropy is calculated for the limiting case of free internal rotation and is corrected for the change of the moments of inertia with the angle of the internal skeletal rotation (Table V).

TABLE V

STANDARD ENTROPY OF METHYL NITRATE VAPOR (298.2°, 1 ATM.)

	$S^0_{298.2}$		$S^0_{298.2}$
Translation	38.92	Liquid (0–298°)[10]	51.81
Rotation	24.88	Vaporization	27.20
Vibration (ν_{1-16})	2.79	Compression	−3.15
Free internal rotation(2)	9.38	Vapor imperfection	0.03
	75.97		75.89

The entropy of methyl nitrate has been measured by Gray and Smith,[10] but the heat and entropy of vaporization are available only from vapor pressure data over a limited temperature range.[15] The published vapor pressure equation corresponds to $\Delta S^{298.2}_{\mathrm{evap}} = 27.40$ e.u. and $\Delta C_p = -12.6$ cal. mole^{-1}. When, as a precaution, C_p (vapor) is calculated from the spectroscopic data and subtracted from the observed heat capacity of the liquid[10] it is found that ΔC_p should lie between −18.0 and −21.4 cal. mole^{-1} (at 298°), the second value being for the case of free internal rotation. Either of these values can be used in a vapor pressure equation without seriously disturbing the agreement with the experimental data. For consistency we have chosen the value corresponding to free rotation and fitted an equation to the experimental points in the mid and upper section of the pressure range where the measurements are presumably most accurate: This treatment yields $\Delta H^{298}_{\mathrm{evap}} = 8110$ cal. (Berthelot correction of 54 cal.[16]) and $\Delta S^{298}_{\mathrm{evap}} = 27.20$ e.u. The entropy of compression to the standard state is corrected for vapor imperfection using the modified Berthelot equation.[16]

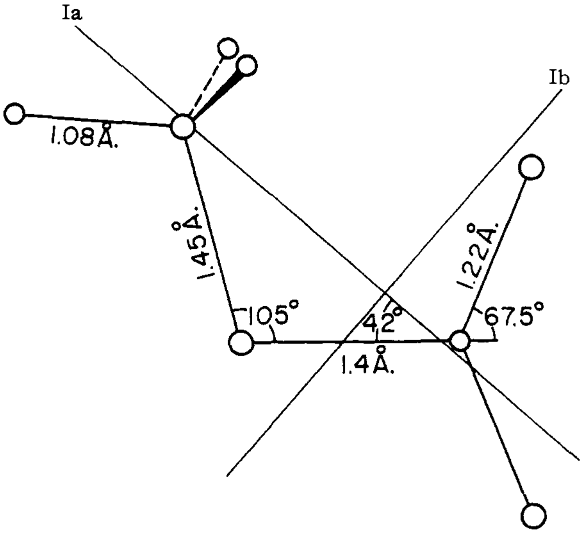

Fig. 2.—Methyl nitrate in the planar configuration and the principal axes of inertia.

---

(13) The value of ∠O:N:O = 135° is adopted by analogy with nitric acid (vapor): *cf.* the discussion by H. Cohn, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, 2284 (1952).

(14) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

(15) J. S. McKinley-McKee and E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, **48**, 247 (1952).

(16) Based on T_c = 520°K. and P_c = 65 at (estimated).

PRINCETON, N. J.

NOTES

Complexes of Histamine with Co^{II}, Ni^{II} and Cu^{II}[1]

BY B. L. MICKEL AND A. C. ANDREWS

RECEIVED SEPTEMBER 16, 1954

Metal complexes of histamine, 4(5)-(2-aminoethyl)-imidazole, have been reported,[2-5] but this information has been largely qualitative. It might be expected that histamine forms chelate complexes through the aminoethyl nitrogen and the basic 3-nitrogen of the imidazole nucleus, and that the 1-nitrogen makes no contribution to bond formation. In its reactions with the ions Co^{II}, Ni^{II} and Cu^{II}, histamine has been here considered, mathematically, to behave as an aliphatic diamine. The apparent fulfillment of ordinary coördination numbers permits the calculation of formation constants in terms of this complexing mechanism.

Experimental

The potentiometric technique of Bjerrum,[6] as applied to ethylenediamine, was used. The average number of histamine molecules bound per central ion, $\bar{n}$, was calculated conventionally in terms of total reactant concentrations and

---

(1) Portion of a dissertation presented by B. L. Mickel as partial fulfillment of the requirement for the degree Doctor of Philosophy in chemistry at Kansas State College, 1955. This investigation was supported by a research grant G 3920 from the National Institutes of Health, Public Health Service.

(2) W. Zimmermann, *Z. physiol. Chem.*, **186**, 260 (1930).

(3) F. Axmacher, *Biochem. Z.*, **284**, 339 (1936).

(4) O. Eichler and G. Meyer, *Naturwissenschaften*, **35**, 934 (1948).

(5) R. W. Cowgill and W. M. Clark, *J. Biol. Chem.*, **198**, 33 (1952).

(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, pp. 198–219.