

252. *The Infrared Absorption of ¹⁸O-Labelled Nitromethane.*

By M. HALMANN and S. PINCHAS.

The infrared absorption of normal and ¹⁸O(58 atoms %)-labelled nitromethane was measured both in the vapour phase and in a carbon tetrachloride solution. The labelled nitromethane showed its bands in solution at 3040, 2890, 2700, 2430, 1563, 1545, 1526, 1432, 1396, 1357, 1089, 914, 900, and 884 cm.⁻¹. The ultraviolet spectrum of this compound was also measured and found to be appreciably different from that of normal nitromethane.

THE effect of substituting ¹⁸O for ¹⁶O in various compounds on their infrared spectra has been studied in several cases.¹ As a continuation of this work the infrared absorption of nitromethane containing 58 atoms % of ¹⁸O was measured both in the vapour phase and in solution in carbon tetrachloride. For comparison, normal nitromethane was measured under the same conditions although its infrared spectrum has already been reported several times.²⁻⁴

The Table gives the frequencies of the observed bands. The vapour spectra were measured at the vapour pressure of the isotopic nitromethane samples at room temperature and unless otherwise stated are for a 100 mm. path length. The main frequencies reported by Smith, Pan, and Nielsen,³ who worked with the higher resolution obtained by a big prism and a low vapour pressure (2 mm.), are added for comparison.

Infrared absorption frequencies of normal and ¹⁸O-labelled nitromethane (cm.⁻¹).

		Vapour								
MeN ¹⁶ O ₂ *	2960b ^a	1591s ^a	1567b, vs ^a	1392 ^a	1378 ^a	1099 ^a	1093w, sh ^a	931	917	
						1075w ^a			912vw	
MeN ¹⁶ O ₂ ³	2990sh	2972	1592vs	1580vs	1397s	1377s	1100	1087b	931	918
	2955sh					1390sh				914
"MeN ¹⁸ O ₂ "	2920b		1570—1550b, vs		1366b, s		1082b			899b, w
		Solution in CCl ₄								
MeN ¹⁶ O ₂ ^b	2930	2770vw	1564b, vs ^e		1428s	1396s	1095	1077vw, sh	914 ^d	
	2475vw					1375s				
"MeN ¹⁸ O ₂ " ^a	3040w ^f	2890b	1563sh	1548vs ^g	1432	1396		1089b	914w ^h	900w ^h
	2700w ^f	2430w ^f	1525sh ^g			1357b, s			884w ^h	

b = Broad; s = strong; v = very; w = weak; sh = shoulder.

* Present work. ^a Measured in a 20 mm. cell. ^b Concentration: 0.05 g. + 1 ml.; cell thickness: 0.2 mm. ^c A solution of 0.03 g. + 1 ml. also showed the absorption maximum here. ^d A capillary liquid layer of nitromethane did not show any band in the 910—675 cm.⁻¹ region. ^e Unless stated to the contrary: a 0.04 g. + 1 ml. of solvent; cell thickness 0.2 mm. ^f Observed only with a 0.10 g. + 1 ml. of solvent. ^g When measured precisely in a 0.02 g. + 1 ml. solution these bands were found at 1545 and 1526 cm.⁻¹, respectively. ^h These bands merge together into a weak and obliterated band at 897 cm.⁻¹ in the 0.04 g. + 1 ml. solution.

The agreement between the various results for the normal compound is thus in general very good, the only real discrepancy being in the location of the 1567 cm.⁻¹ band (1580 according to Smith *et al.*³). Haszeldine,⁴ however, also reports the same value, and it can further be seen from the absorption curve of Smith *et al.* that the band is really at about 1570 cm.⁻¹ and not 1580 cm.⁻¹ as published. The last number seems thus to be a misprint. The medium band, observed by Haszeldine at 1422 cm.⁻¹, could not be detected by us in the vapour spectrum.

¹ Braude and Turner, *Chem. and Ind.*, 1955, 1223; Halmann and Pinchas, *J.*, 1958, 1703, 3264; Pinchas, Halmann, and Stoicheff, *J. Chem. Phys.*, in the press; Anbar, Halmann, and Pinchas, preceding paper.

² Wells and Wilson, *J. Chem. Phys.*, 1941, 314.

³ Smith, Pan, and Nielsen, *ibid.*, 1950, 18, 706.

⁴ Haszeldine, *J.*, 1953, 2525.

DISCUSSION

It can be calculated from the ¹⁸O content of the labelled sample (58%) that (the equilibrium constant of the reaction: $\text{RN}^{16}\text{O}_2 + \text{RN}^{18}\text{O}_2 \rightleftharpoons 2\text{RN}^{16}\text{O}^{18}\text{O}$ being assumed to be 1/4) it is composed of $\text{RN}^{16}\text{O}^{18}\text{O}$ 48.8%, RN^{18}O_2 33.6%, and RN^{16}O_2 17.6%. It could be expected therefore to produce three series of bands which would probably be merged together in many cases, and form split bands in others. The Table shows that this is really the case.

The broad band which appeared in the vapour spectrum of the normal molecule at about 2960 cm^{-1} appears in the spectrum of the labelled nitromethane at about 40 cm^{-1} lower, *i.e.*, approximately at 2920 cm^{-1} . Similarly, the solution frequency of this band also decreases by 40 cm^{-1} , *i.e.*, from 2930 cm^{-1} in the normal nitromethane to 2890 cm^{-1} in the labelled compound. This frequency shift, because of the isotopic substitution of the oxygen atoms, is much bigger than would be expected if this band is really due to the symmetrical stretching of the methyl group.³ Wilson,⁵ however, observed a strong CD_3NO_2 band at 2940 cm^{-1} and attributed it to the combination of the symmetrical and antisymmetrical NO_2 stretching frequencies. This band is considerably stronger than the C-D bands. If * the 2960 cm^{-1} band is analogously mainly due to such a combination of the 1579 + 1385 cm^{-1} frequencies (= 2964; these correspond to the centres of the *PR*-split NO_2 bands, see below), then its expected frequency in the labelled compound will be (according to the Table) near 1560 + 1366 = 2926 cm^{-1} , in good agreement with the observed value of 2920 cm^{-1} .

The two bands which appear in the vapour spectrum of the normal nitromethane at 1591 and 1567 cm^{-1} , respectively, being the *R* and the *P* branch, correspondingly, of the antisymmetrical stretching vibration of the nitro-group, appear in its solution spectrum merged together at 1564 cm^{-1} . In the labelled compound these bands formed a very broad band at 1570—1550 cm^{-1} in the case of the vapour spectrum; in the solution spectrum, however, one can detect a shoulder at about 1563 cm^{-1} (for the normal molecule), a very strong band at 1545 cm^{-1} (for $\text{RN}^{16}\text{O}^{18}\text{O}$), and a shoulder at about 1526 cm^{-1} (for RN^{18}O_2). The $\text{RN}^{16}\text{O}^{18}\text{O}$ frequency is thus half-way between those of RN^{16}O_2 and RN^{18}O_2 , as could be expected.

Since the precise symmetry of the nitromethane molecule is not known, and also some of the lower frequencies (below 675 cm^{-1}) of its labelled species have not been measured, it is impossible to apply here the Teller-Redlich product rule. One can, however, try to get an approximation of the ratio of the RNO_2 antisymmetrical stretching frequencies $\nu\text{RN}^{18}\text{O}_2/\nu\text{RN}^{16}\text{O}_2$ by considering the NO_2 group as an independent oscillator. The symmetry of the isolated NO_2 group being very probably that of the C_{2v} point group, and the ONO angle equal ³ to 127°, one gets here ⁶ $\omega_3^1/\omega_3 = 0.981$, in satisfactory agreement with the observed value of $\nu\text{RN}^{18}\text{O}_2/\nu\text{RN}^{16}\text{O}_2 = 1526/1564 = 0.976$. This agreement further supports the above assignments.

The solution spectrum band which appears at about 1428 cm^{-1} (in the vapour spectrum it is much weaker) is due to the methyl group antisymmetrical bending vibration.† It is therefore practically unaffected by the ¹⁸O substitution, appearing in the solution spectrum of the labelled compound at 1432 cm^{-1} . The methyl-group symmetrical bending frequency of 1396 cm^{-1} (in solution) is, as expected, also not affected by the isotopic change. The symmetrical stretching band of the nitro-group, at 1375 cm^{-1} (in solution), however, is shifted in the spectrum of the ¹⁸O sample to 1357 cm^{-1} , no other band being observed in its vicinity. This peak seems to be due to that isotopic species the concentration of which

* This point was kindly suggested by a Referee.

† In the spectrum of pure liquid nitromethane it is located ³ at 1429 cm^{-1} .

⁵ Wilson, *J. Chem. Phys.*, 1943, **11**, 361.

⁶ Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, 1945, p. 228.

is highest, *i.e.*, to RN¹⁶O¹⁸O. The corresponding bands due to the minor isotopic constituents are thus overlapped by its strong absorption.

That this band really belongs to RN¹⁶O¹⁸O can be verified by estimating the expected ratio of the symmetric isotopic frequencies $\nu_{\text{RN}^{16}\text{O}^{18}\text{O}}/\nu_{\text{RN}^{16}\text{O}_2}$ in this case and comparing it with the experimental result, 1357/1375 = 0.987. This can be done by assuming this ratio to be very near to the ratio of the isotopic frequencies of an oscillator A-B when A = ¹⁶O₂ = 32 or ¹⁶O¹⁸O = 34 and B = MeN = 29 atomic mass units. According to Hooke's law, this ratio is $\nu_1/\nu = 0.986$, in very good agreement with the observed value.

The bands observed with the normal nitromethane at 1095 and 1077 cm.⁻¹ (in solution) are rocking bands of the methyl group³ and are therefore practically unaffected by the ¹⁸O substitution.

The normal band at 914 cm.⁻¹ (in solution; in the vapour spectrum it is split into *PQR* branches) is due to a C-NO₂ stretching³ and is accordingly shifted to lower frequencies in the spectrum of RN¹⁶O¹⁸O and RN¹⁸O₂. Thus the labelled sample showed (in solution) bands at 914, 900, and 884 cm.⁻¹, with the middle one being, as expected, the strongest of the triplet. When the ratio ν_1/ν is calculated also in this case, by using again the A-B oscillator approximation where A = Me = 15 and B = N¹⁶O₂ = 46 or N¹⁸O₂ = 50, the value obtained is $\nu_1/\nu = 0.99$. This ratio is in poor agreement with the observed one equal to 884/914 = 0.967. This seems to suggest a weaker force constant for the C-N bond in the case of the labelled molecule than in the normal one. Such a weakening might be the result of a somewhat higher electronegativity* of ¹⁸O which would probably increase a contribution from a resonating structure such as (I) to the actual state of the molecule, thereby making the C-N bond weaker.

The Ultraviolet Spectrum.—The ultraviolet absorption of the labelled nitromethane was also found to be appreciably different from that of the normal compound; for, while the latter showed absorption maximum only at 2180 Å (ϵ 1500) the former showed in this region a very weak band at 2330 Å (ϵ 17), the spectrum of the normal species at this point showing only $\epsilon = 15$ l. mole⁻¹ cm.⁻¹. The second absorption maximum of normal nitromethane which was found at 2780 Å (ϵ 17) was, however, shared also by the labelled sample which showed it, albeit somewhat weaker, at the same place (ϵ 14). Haszeldine⁴ reports only the second maximum of the normal compound (2780 Å) and gives a little higher molecular extinction coefficient (20). A similar decrease in the intensity of an ultraviolet absorption band because of an ¹⁸O substitution was also observed for ¹⁸O-labelled benzophenone which absorbs at 2530 Å with a molecular extinction coefficient of 17,500 as compared with 18,400 (at 2530 Å) for the normal compound.⁷

EXPERIMENTAL

Normal Nitromethane.—A chemically pure commercial product was used.

¹⁸O-Nitromethane.—In a flask fitted with a magnetic stirrer and a reflux condenser, ¹⁸O-labelled silver nitrite⁸ (6.59 g.) was treated gradually with methyl iodide⁹ (10 ml.). The reaction was exothermic and cooling was at first required. The mixture was then heated on the water-bath for 3 hr. The excess of methyl iodide was recovered by distillation at 42–55°, and the nitromethane was collected at 98.0–98.3° (yield 0.917 g.). In accord with Meyer's observation,⁹ this material contained impurities. It was purified by vapour-phase chromatography, through a 110 cm. column of tritoyl phosphate on crushed firebrick, with a thermal conductivity detector and a recorder. Aliquot parts (0.02–0.1 ml.) were introduced for each run. At a column temperature of 118° and a helium flow-rate of 22 ml./min., the material was

* The electrical moment of [¹⁸O]benzophenone was found to be 3.04 ± 0.02 D, that of the normal being 2.96 D (Fischer, Halmann, and Pinchas, unpublished work).

⁷ Fischer and Halmann, personal communication.

⁸ See preceding paper.

⁹ Meyer, *Annalen*, 1873, **171**, 32.

easily resolved into three fractions appearing at 8 min. (methyl iodide, identified by a separate run of pure material), 12 min. (possibly water), and (the major peak: 13 times larger than the others) 26 min. (nitromethane, identified by a run of Merck's reagent-grade material). The pure nitromethane fraction from several runs was collected together in a trap cooled with liquid air. Its ^{18}O content was determined by introducing a vapour sample into a mass-spectrometer, and scanning masses 59—66. With normal nitromethane¹⁰ the main (parent) peak occurred at mass number 61, while with the labelled compound the peaks at masses 63 and 65 were more intense.

The atom % of ^{18}O was calculated from the peak heights p^x of the masses x : $^{18}\text{O}\% = 100(p^{63}/2 + p^{64}/2 + p^{65} + p^{66})/(p^{61} + p^{62} + p^{63} + p^{64} + p^{65} + p^{66})$. The sample contained 58 atoms % of ^{18}O .

The infrared measurements were carried out with a Perkin-Elmer Model 12C spectrophotometer equipped with a sodium chloride prism.

Measurements of ultraviolet absorption were made on iso-octane solutions with a Beckman DU spectrophotometer.

The authors are indebted to Dr. M. Anbar for a sample of ^{18}O -enriched silver nitrite, to Dr. J. Manassen for advice on vapour-phase chromatography, and to Mrs. P. Geron for the mass-spectra.

THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL.

[Received, July 2nd, 1959.]

¹⁰ American Petroleum Institute, Catalog of Mass Spectral Data, 1953, Serial No. 836.
