Rotational Isomerism as a General Property of Alkyl Nitrites

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The infrared and ultraviolet spectra of 15 alkyl nitrites were studied in the gaseous state. In the infrared, the $O-N=O$ group is characterized by very strong absorption in the three regions 600, 800, and 1650 cm^{-1}, corresponding to $O-N=O$ bending, $N-O$ stretching, and $N=O$ stretching frequencies, respectively. The doubling of the characteristic frequencies and the temperature dependence of the bands of methyl nitrite are explained by rotational isomerism, which appears to be a general property of alkyl nitrites. The influence of the length, shape, and kind of the carbon chain on the frequencies and intensities of the characteristic bands has been studied. The intensity variation of the $\nu_{N=O}$ bands strongly suggests that the relative abundances of the two isomers vary widely from primary to secondary and tertiary nitrites, but depend only to a small extent upon the length and shape of the carbon chain. Application of this property to the diagnosis of primary, secondary, or tertiary alcohols is suggested.

The uv spectra consist essentially of two systems of diffuse bands (and not of one, as stated by previous workers), whose relative intensities vary in the same manner as the relative abundances of the two rotational isomers. The two systems of bands are accordingly assigned to these rotational isomers. This hypothesis has been checked by a study of the temperature dependence of the intensity of the bands.

INTRODUCTION

THE vibration spectra of alkyl nitrites have not yet been extensively studied: only the Raman spectra of a few alkyl nitrites,[1] without frequency assignment, and very incomplete infrared data (between 5 and 8μ only)[2] are to be found in the literature.

The electronic spectra, however, were carefully investigated by Kuhn and co-workers,[3–5] who discovered a characteristic system of diffuse bands between 3000 and 4000A, and by Purkis and Thompson,[6–8] who found a frequency interval of ∼1100 cm^{-1} between the bands. A number of facts, however, remained unexplained: the abnormally high frequency interval between the first and the second band of the system,[7] the peculiar intensity distribution in the bands,[6–8] and the abnormal fluctuations of the circular dichroism in the case of optically active nitrites.[5]

This paper deals with the results of the investigation of the infrared and ultraviolet spectra of 15 alkyl nitrites.

Technique

All the nitrites were prepared by the following general method: action of cold diluted H_2SO_4 on the aqueous solution of very pure alcohol and sodium nitrite. The crude product was dessicated and purified by repeated low temperature distillation in vacuum.

The infrared spectra were taken with a Perkin-Elmer spectrometer equipped with KBr and NaCl prisms (length of the cell: 90 mm) and with a Beckman spectrometer with NaCl and LiF prisms (length of the cell: 1 meter). The ultraviolet spectra were taken with a Hilger E1 quartz spectrograph, having a dispersion of about 8A/mm at 3500A and with a one-meter cell. High contrast plates (Ilford Process P 40) were used. All the nitrites were studied in the gaseous state.

RESULTS AND INTERPRETATION

A. Infrared Spectra

(1) General Characteristics

All the nitrites studied are characterized by very strong absorption in the three regions 600, 800, and 1650 cm^{-1}. These bands are attributed to the funda-
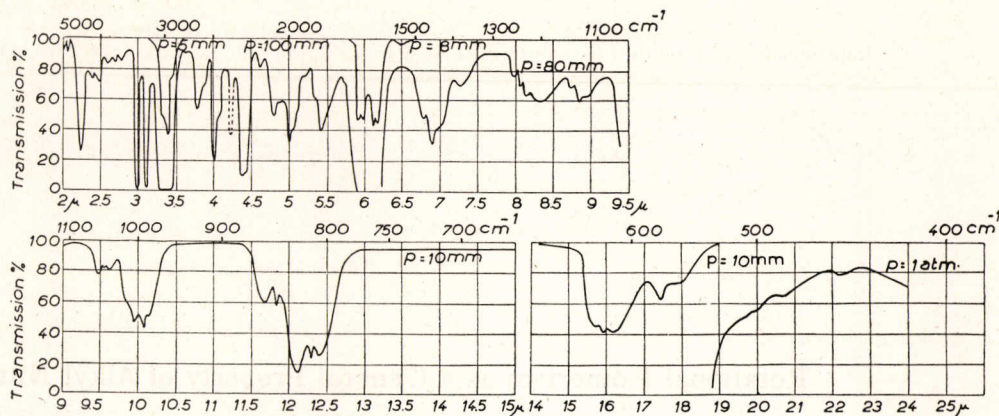
[1] K. W. F. Kohlrausch, *Ramanspektren* (Akademische Verlagsgesellshaft, Leipzig, 1943), p. 286.

[2] H. Lenormant and P. Clément, Bull. Soc. Chim. France 1946, pp. 559, 566.

[3] W. Kuhn and H. Lehmann, Z. Elektrochem. **37**, 549, 552 (1931); Z. physik. Chem. **B18**, 32–48 (1932).

[4] W. Kuhn and H. Biller, Z. physik. Chem. **B29**, 1–41 (1935).

[5] H. Elkins and W. Kuhn, J. Am. Chem. Soc. **57**, 296–299 (1935).

[6] H. W. Thompson and C. Purkis, Trans. Faraday Soc. **32**, 674–680 (1936).

[7] C. Purkis and H. W. Thompson, Trans. Faraday Soc. **32**, 1466–1474 (1936).

[8] H. W. Thompson and F. Dainton, Trans. Faraday Soc. **33**, 1546–1555 (1937).

FIG. 1. Infrared spectrum of methyl nitrite. 2–6μ Beckman LiF $d=1$ meter. 6–15μ Perkin Elmer NaCl $d=9$ cm. 14–25μ Perkin Elmer KBr $d=9$ cm.

mental frequencies of the $-O-N=O$ group, namely, the $O-N=O$ bending, $N-O$ stretching, and $N=O$ stretching frequencies, respectively. One of the most important features of these spectra is the doubling of the $O-N=O$ bending and the $N=O$ stretching frequencies in most of the nitrites studied. The $N-O$ stretching frequency appears also to be double, but this can be ascertained only in methyl and ethyl nitrites (in more complex molecules, this spectral region is obscured by bands arising from the carbon chain).

Such a doubling cannot be ascribed to intermolecular association, because the nitrites were studied in the gaseous state at low pressures (intermolecular associations are weak, even in the liquid state, as indicated by the relatively low boiling point of the nitrites). Moreover, the relative intensities of the bands have been found to be independent of pressure.

A much more attractive explanation of the frequency doubling seems to be rotational isomerism. This will be fully demonstrated by the study of the methyl nitrite spectrum.

(2) The Infrared Spectrum of Methyl Nitrite and the Temperature Dependence of the Intensity of the Bands

The infrared spectrum of gaseous methyl nitrite is given by Fig. 1, which clearly shows the doubling of the $\delta_{O-N=O}(\sim 600 \text{ cm}^{-1})$, $\nu_{N-O}(800 \text{ cm}^{-1})$, $\nu_{C-O}(1000 \text{ cm}^{-1})$, and $\nu_{N=O}(1650 \text{ cm}^{-1})$ frequencies.

The temperature dependence of the bands was studied between 3 and 15μ, using the Beckman spectrometer in conjunction with a one meter cell. The cell was surrounded over a 80 cm length by a nearly thermally insulated jacket. This design is very simple and quite sufficient for qualitative measurements.

The spectra were taken, first at room temperature, and then with the jacket filled with dry ice (taking spectra at too high temperatures must be avoided, the alkyl nitrites being thermally unstable).[9]

A temperature dependence has been found for all the pairs of bands between 6 and 15μ (Fig. 2), and also for a number of overtone and combination bands.

[9] E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, 1946), pp. 141–143.

These results strongly support the hypothesis of rotational isomerism. However, no evidence is found about the structure of the isomers: They are possibly *cis*- and *trans*-isomers, which can also be described as chelated and nonchelated form, such as
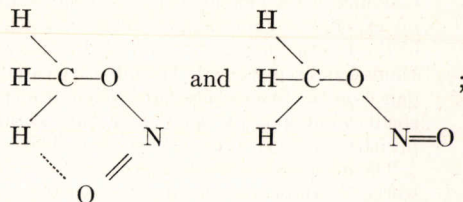
but the existence of *trans*- and *gauche*-isomers cannot be excluded.

In this paper, they will be simply referred to as *cis*- and *trans*-isomers.

Table I gives the observed fundamental frequencies, with their assignment to *cis*- and *trans*-isomers, the *cis*- or chelated form being supposed to be the more stable and therefore of decreasing abundance with increasing temperature.

The temperature dependence of the δ_{ONO} fundamental (617–565 cm^{-1}) has not been studied (the frequency of these bands is too low for study with a NaCl spectrometer), and the assignment to *cis*- and *trans*-forms is deduced from the temperature dependence of their first harmonics, at 1234 and 1130 cm^{-1}, respectively. The most important harmonic and combination bands are collected in Table II.

(3) Rotational Isomerism in Other Alkyl Nitrites

It is not possible to study the temperature dependence of the bands in all alkyl nitrites in the gaseous state, owing to their low vapor pressure at low temperatures, but the interpretation of the frequency doubling by rotational isomerism is almost obvious. The influence of length, shape, and kind of the carbon chain on the frequencies and intensities of the characteristic bands has been studied. The most important data are collected in Table III.

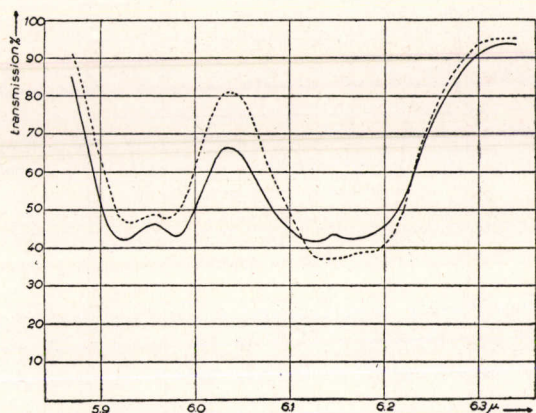The $\nu_{N=O}$ pair of bands is by far the most characteristic one. The frequency of these bands undergoes a

FIG. 2a. Influence of $t°$ on the $\nu_{N=O}$ pair of bands. Beckman LiF $d=1$ meter $p \simeq 0.7$ mm Hg. Curve ———: room temperature (23°C). Curve -----: dry ice.

small, but systematic shift towards low frequencies when going from methyl nitrite to the nitrites of other primary alcohols, then to nitrites of secondary alcohols, and last to nitrites of tertiary alcohols. But the most important and characteristic feature is the change in the band intensities, which appears clearly in the fifth column of Table III; this column gives the ratio of the extinction $D=\log \cdot I_0/I$ for the trans- and the cis-forms. The value of this ratio, which is nearly one in methyl nitrite at ordinary temperature, becomes roughly 3 in the other nitrites of primary alcohols, 6 to 10 in the nitrites of secondary alcohols, and finally 35 to 50 in the nitrites of tertiary alcohols; in these last nitrites, the band of the cis-form has almost completely disappeared.

In fact, it must be noted that not only the intensity ratio but also the absolute intensity of the bands varies from one class (primary, secondary, or tertiary) nitrites to another, the trans-band becoming more and more intense, the cis-band, more and more weak. This result is illustrated by Fig. 3, in which the two $\nu_{N=O}$ bands of four characteristic nitrites have been plotted, the spectra
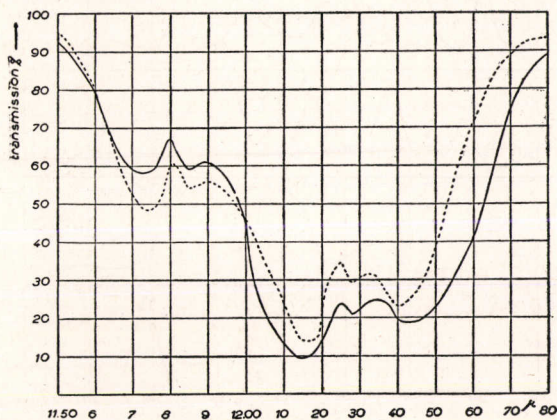

FIG. 2b. Influence of $t°$ on the $\nu_{N=O}$ pair of bands. Beckman NaCl $d=1$ meter $p \simeq 1$ mm Hg. Curve ———: room temperature (23°C). Curve -----: dry ice.

having been taken under the same conditions of temperature and pressure.

Such changes in the band intensities are most probably the result of a variation of the relative abundances of the two rotational isomers, the trans-isomer becoming more and more abundant when going from primary to tertiary nitrites.

It is remarkable indeed that the relative abundance of the isomers depends essentially on the nature (primary, secondary, or tertiary) of the carbon adjacent to the $-O-N=O$ group, and to a much smaller extent on the length and shape of the carbon chain. The study of additional nitrites is necessary for checking the generality of this rule, but if these results are confirmed, their most immediate application would be a new method of identifying primary, secondary, or tertiary alcohols.

The first harmonic of the $\nu_{N=O}$ frequency has also been studied, the bands of the cis- and trans-forms being near 3200 and 3300 cm^{-1}, respectively. The variations of the frequencies and intensities of these bands are in all respects similar to those of the corresponding fundamentals. The observed frequencies are about 40 cm^{-1}

TABLE I. Fundamental frequencies of methyl nitrite.

Vibration	Frequency	
	cis	trans
δ_{ONO}	617	565
δ_{CH_3}	1445	1375
ν_{N-O}	844	814
ν_{C-O}	993	1045
$\nu_{N=O}$	1625	1681

lower than the calculated ones; this lowering is attributed to anharmonicity.

The ν_{N-O} fundamental is characterized by the very high intensity of the band of the trans-form; in most of the nitrites, this band is by far the strongest of the spectrum. As already stated, the corresponding band of the cis-form has been identified with certainty in methyl and ethyl nitrites only, it is much weaker than the band of the trans-form, and, in all the other nitrites, superimposed bands of the carbon chain make the assignments quite arbitrary.

The observed frequencies of the ν_{N-O} trans-band are reported in Table III. There is a significant shift towards lower frequencies from primary to tertiary nitrites. The frequency values for the third fundamental, δ_{ONO}, are also reported in Table III. Neither the frequencies, nor the intensities exhibit any regularity; this result is not surprising, as the deformation vibration must be affected by the length and shape of the adjacent carbon chain.

In a few cases, the occurrence of other bands in the same spectral region makes assignments uncertain.

B. Ultraviolet Spectra

As previously stated, much experimental work has already been performed on the ultraviolet spectrum of

alkyl nitrites, but the following difficulties still remain:

(1) No attempt has been made to assign the ultraviolet frequency interval to a fundamental frequency in the ground state.

(2) In previous studies, Kuhn[10,11] pointed out, and this was substantiated by many workers,[12,13] that the anisotropy factor remains constant throughout a given electronic transition, being independent of the vibrations and rotations superimposed on the electronic transition. But alkyl nitrites apparently do not follow this rule,[5] and Kuhn postulated the occurrence, in alkyl nitrites, of two superimposed systems of bands, whose detection was quite difficult, owing to their very diffuse nature.

TABLE II. Harmonic and combination bands of methyl nitrite.

ν_{obs} (cm^{-1})	Assignment
1130	$2\delta_{ONO}$ trans $= 1130$ cm^{-1}
1234	$2\delta_{ONO}$ cis $= 1234$ cm^{-1}
1980	$2\nu_{C-O}$ cis $= 1986$
2083	$2\nu_{C-O}$ trans $= 2090$
2252	$\delta_{ONO} + \nu_{N=O}$ $= 2245$
2451	$\nu_{N-O} + \nu_{N=O}$ cis $= 2469$
2494	$\nu_{N-O} + \nu_{N=O}$ trans $= 2494$
3225	$2\nu_{N=O}$ cis $= 3250$
3333	$2\nu_{N=O}$ trans $= 3360$

(3) The frequency interval of 1100 cm^{-1}, which is characteristic of organic nitrites, was obtained by neglecting the first band of the system.

(1) Assignment of the Ultraviolet Frequency Interval

The difficulties arising from this assignment have already been pointed out.[14] The ultraviolet frequency interval can be assigned either to the $\nu_{N=O}$ or to the ν_{N-O} vibration. The latter assignment implies an in-

TABLE III. Characteristic bands of alkyl nitrites.

Nitrite	cis (cm^{-1})	$\nu_{N=O}$ trans (cm^{-1})	ν trans $-\nu$ cis (cm^{-1})	$\dfrac{D \text{ trans}}{D \text{ cis}}$ ($t°=23°C$)	ν_{N-O} trans (cm^{-1})	$\delta_{O-N=O}$ cis (cm^{-1})	trans (cm^{-1})
CH$_3$ONO	1625	1681	56	0.95 ±0.05	814	617	565
C$_2$H$_5$	1621	1675	54	2.3 ±0.1	~800	691	581
C$_3$H$_7$	1621	1672	51	3.0 ±0.2	802	687	602
n-C$_4$H$_9$	1618	1669	51	3.3 ±0.2	790	689	610
iso-C$_4$H$_9$	1618	1669	51	3.5 ±0.2	794	680	625
iso-C$_5$H$_{11}$	1618	1669	51	3.5 ±0.2	800	687	617
allyle	1623	1681	58	2.8 ±0.2	796	680?	598
benzyle	1621	1678	57	3.1 ±0.2	793		
sec-C$_3$H$_7$	1615	1667	52	6.0 ±0.4	783	688	605
sec-C$_4$H$_9$	1615	1665	50	7.2 ±0.4	776	678	600?
sec-C$_5$H$_{11}$	1618	1664	46	10 ±0.7	775	678	594?
cyclo-C$_5$H$_9$	1613	1664	51	4.7 ±0.3	780	682	604
cyclo-C$_6$H$_{11}$	1615	1664	49	9.3 ±0.6	775		
tert-C$_4$H$_9$	1610	1655	45	~35	764		621?
tert-C$_5$H$_{11}$	~1613	1653	40	~50	751		613?

crease of the frequency from 800 cm^{-1} in the ground state to 1100 cm^{-1} in the excited state. Although unexpected, this is not impossible; such an increase has

[10] W. Kuhn and E. Braum, Z. physik. Chem. **B8**, 445–454 (1930).
[11] W. Kuhn and H. Gore, Z. physik. Chem. **B12**, 389–397 (1931).
[12] S. Mitchell and S. Cormack, J. Chem. Soc. London, 415–419 (1932).
[13] T. Lowry and H. Hudson, Trans. Roy. Soc. (London) **232A**, 117 (1933).
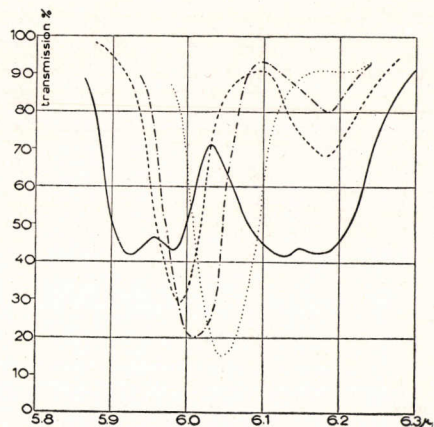[14] L. D'Or and P. Tarte, Bull. Soc. Roy. Sci. Liège, 685–692 (1951).

FIG. 3. $\nu_{N=O}$ pair of bands, for 4 characteristic nitrites. ———— methyl nitrite. ------------ n-butyl nitrite. -·-·-·-·-·-. sec. butyl nitrite. ········ tert. butyl nitrite. Beckman LiF $d=1$ meter $p\simeq0.6$ mm Hg $T°=23°C$.

already been found in the fluorine molecule, whose vibration frequency increases from 891.8 cm^{-1} in the electronic ground state to 1139.8 cm^{-1} in one of the excited states.[15]

An alternative explanation would be the occurrence of fractional valences, with the formation of an $O \dddot{} N \dddot{} O$ group in the excited state. This would explain the fact that the uv band system seems to be characteristic, not of an NO single or double bond, but of the $O-N=O$ group as a whole, as it is missing in the spectra of other substances with $N-O$ or $N=O$ bonds (inorganic and organic nitrates, inorganic nitrites, nitro- and nitroso-compounds).

(2) Occurrence of Two Bands Systems

As the infrared spectra, the ultraviolet spectra are characteristic (but to a lesser extent) of primary, secondary, and tertiary nitrites: all these spectra exhibit diffuse bands, but these bands are much broader in
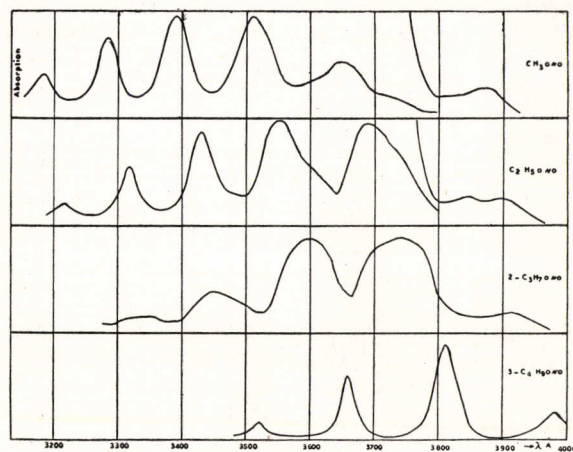

FIG. 4. Microphotometer tracings of the uv spectra of four alkyl nitrites (absorption in arbitrary units).

[15] D. Andrychuk, Can. J. Phys. **29**, 151–158 (1951).

TABLE IV. Ultraviolet spectrum of tert-butyl nitrite.

Wavelength measurements (A)	(cm⁻¹)	Frequency interval (cm⁻¹)
3982	25106	
		1126
3811	26232	
		1097
3658	27329	
		1088
3518	28417	
		1073
3390	29490	

secondary nitrites than in the primary ones; in tertiary nitrites, however, they are surprisingly much narrower.

Microphotometer tracings of the uv spectra of methyl, ethyl, sec-propyl, and tert-butyl nitrites are reproduced in Fig. 4. If we first consider the spectrum of tert-butyl nitrite, we find a very regular frequency interval (Table IV); the bands although diffuse, are not broad and their contour is very symmetrical. It is quite obvious that one, and only one, band system is present here. This is not the case with methyl nitrite, and the following facts must be pointed out:

(1) The first band is extremely broad, with an irregular contour. Moreover, the frequency interval between this first band and the following one is abnormally high according to Thompson:[7] 1700 cm⁻¹ (Table V, A).
(2) A faint band appears near 3740A. This band cannot be fitted into the main band system.
(3) A small hump on the high frequency side of the 3651A band seems to show the existence of another band, which also cannot be fitted into the main band system.

All these irregularities are well explained by the existence of a second, weak band system, occurring on the low frequency side of the main band system. This leads to the new band classification of Table V, B.

In ethyl nitrite, the first four bands are obviously asymmetric, a fact which can be interpreted by an increase of the intensity of the second band system. This new band classification is reported in Table VI.

In sec-propyl nitrite, the bands are extremely broad,

TABLE V. Ultraviolet spectrum of methyl nitrite.

A.—Thompson's classification		B.—New classification			
ν (cm⁻¹)	Δν (cm⁻¹)	1st system		2nd system	
25674		26240		25770	
	1708		1142		960
27382		27382		26730	
	1116		1116		1040
28498		28498		27770	
	990		990		
29488		29488			
	953		953		
30441		30441			
	926		926		
31367		31367			
⋮					
⋮					
⋮					

and the contour asymmetry is now at the top of the bands. This is explained by the increased intensity of the second band system, which is now strong as the first one. Frequency measurements are quite fallacious, owing to the broad and diffuse nature of the bands. In tert-butyl nitrite, the only band system to be found is the second one, as shown by the low frequency of the bands.

Summarizing, the ultraviolet spectra of alkyl nitrites seem to consist essentially of two bands systems with approximately the same frequency interval, the relative intensities of the two systems varying strongly from one class of nitrites to another, but remaining roughly constant within a given class.

This is to be compared with the results, obtained in the infrared, on the existence and relative abundance of rotational isomers. This comparison, summarized in Table VII, strongly suggests that the two rotational isomers are responsible for the appearance of two band systems in the ultraviolet, the first system (on the high

TABLE VI. Ultraviolet spectrum of ethyl nitrite.

A.—Thompson's classification		B.—New classification			
		1st system		2nd system	
ν (cm⁻¹)	Δν (cm⁻¹)	ν	Δν	ν	Δν
25582		~26000		~25630	
	1518		1100		1030
27100		27100		~26660	
	1060		1060		900
28169		28169		~27650	
	985		985		1040
29154		29154		~28690	
	994		994		
30148		30148			
	956		956		
31104		31104			

frequency side) being related to the cis-isomers. This hypothesis is confirmed by the fact that the relative intensities of the two systems depend on temperature, the first system being more intense at lower temperatures. (The experiments were made with gaseous methyl and ethyl nitrites, spectra being taken at −78°, +20°, and +70°C. The pressure was about 1 mm Hg, with an optical path of 3 meters.)

Two objections can however be put forward: (1) The frequency difference between the two rotational isomers is of the order of 50 cm⁻¹ or less in the ground state; it becomes 400 or 500 cm⁻¹ in the excited state. Although the rotational isomers should possess different electronic transition energies, such a difference is unexpected. (2) The relative intensities of the bands of cis- and trans-isomers are very different in the infrared and in the ultraviolet.

This objection is not serious because the cis- and trans-isomers should have different electronic transition probabilities, but the effect is much greater than expected.

It is worth while to remark that a very close analogy exists between alkyl nitrites and nitrous acid itself:

(1) The ir spectrum of the latter in the gaseous state[16,17] has shown that (a) The three characteristic frequencies of the $O-N=O$ group are found also in nitrous acid. (b) The six fundamental frequencies of nitrous acid appear to be double;[16] this doubling is explained, as in alkyl nitrites, by rotational isomerism.

(2) The uv spectrum of nitrous acid[14,18,19] is essentially composed of three systems of diffuse bands, which exhibit a frequency interval of ~ 1100 cm^{-1}.

ACKNOWLEDGMENTS

[16] L. D'or and P. Tarte, J. Chem. Phys. **19**, 1064 (1951); Bull. Soc. Roy. Sc. Liège, 1951, 478–496.
[17] Jones, Badger, and Moore, J. Chem. Phys. **19**, 1599–1604 (1951).
[18] P. Tarte, Bull. Soc. Chim. Belges **59**, 365–376 (1950).
[19] G. Porter, J. Chem. Phys. **19**, 1278–1281 (1951).

TABLE VII.

Nitrite	Infrared	Ultraviolet
CH$_3$ONO	Two rotational isomers *cis* and *trans*.	Two band systems 1 and 2.
Primary nitrites	The relative abundance of the *trans*-isomer is greater than in CH$_3$ONO. It remains approximately constant in all the primary nitrites.	The relative intensity of the second system is greater than in CH$_3$ONO. It remains roughly constant in all the primary nitrites.
Secondary nitrites	The relative abundance of the *trans*-isomer is much greater.	The relative intensity of the 2nd system is also much greater.
Tertiary nitrites	The *trans*-isomer is by far the most abundant one. The *cis*-isomer has almost completely disappeared.	The second band system only is present.