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The Oscillation Frequencies of Nitrites

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In a recent article Penney and Sutherland¹ have surveyed the existing data on the vibrational frequencies of triatomic molecules and triatomic groups occurring in more complex molecules and have determined force constants and angles by the valence-force-field and central-force-field approximations. A comparison of results obtained through these approximations with the results obtained in cases where more detailed analyses were possible, showed that in the majority of cases the valence-force-field is more satisfactory than the older approximation involving central forces. Values for the angles as obtained by the valence-force method agreed with the accepted values to within 10%, while the discrepancies in the values obtained by the central-force method were sometimes larger.

However, in the case of the nitrite ion neither approximation gave satisfactory values for the force constants. It was found that the valence-force-field equation for the angle had no real solution. Although the central-force-field equations gave a reasonable value for the angle, they yielded improbable values for the force constants, the oxygen-oxygen force constant appearing larger than the nitrogen-oxygen force constants. Since the valence-force approximation gave satisfactory results for other triatomic systems with the same number of valence electrons, Penney and Sutherland suggested that further experimental work on the nitrites might be desirable.

(1) W. G. Penney and G. B. B. M. Sutherland, *Proc. Roy. Soc. (London)*, **156**, 654 (1936).

It was the object of the present investigation to obtain additional data on the oscillation frequencies of the nitrites through a study of their infrared spectra in the region of the fundamentals. Previous studies of the infrared absorption of nitrites have been made by Maslakowez² and by Bailey and Thompson,³ while Raman studies of nitrites have been reported by Langseth and Welles,⁴ by Carrelli, Pringsheim and Rosen,⁵ by Bar,⁶ and by Dadiou, Jele, and Kohlrausch.⁷ The results obtained by these authors are summarized in Table I.

The experimental methods employed in the present study are essentially the same as those reported previously.⁸ Solutions of sodium nitrite and potassium nitrite (3 *N*) were studied and the results obtained are shown in Fig. 1. In this figure the "relative absorption factors" as defined in the previous article⁸ are plotted as a function of wave length.

As one may see from the figure, three absorption maxima were observed in the spectrum of each nitrite. In the spectrum of sodium nitrite the positions of the maxima are 7.6, 8.2, and 13.3 μ , while the potassium nitrite bands appear at 7.7, 8.2, and 13.4 μ . The shapes of the absorption

- (2) I. Maslakowez, *Z. Physik*, **51**, 696 (1928).
- (3) C. R. Bailey and J. W. Thompson, *Nature*, **135**, 915 (1935).
- (4) A. Langseth and E. Welles, *Z. physik. Chem.*, **B27**, 209 (1934).
- (5) A. Carrelli, P. Pringsheim and B. Rosen, *Z. Physik*, **51**, 511 (1928).
- (6) R. Bar, *Nature*, **124**, 692 (1929).
- (7) A. Dadiou, F. Jele and K. W. F. Kohlrausch, *Wien. Ber.*, **140**, 293 (1931).
- (8) D. Williams and L. Decherd, *THIS JOURNAL*, **61**, 1382 (1939).

TABLE I
PREVIOUS STUDIES OF THE NITRITE GROUP

Observed frequencies, cm. ⁻¹	Compounds	Method	Observer
1380 1240	Potassium nitrite crystal	Infrared	Maslakowez
1330 1392 1127 and 1220 707 834	Sodium nitrite crystal	Infrared	Bailey and Thompson
1331 1240 813	Sodium nitrite solution	Raman	Langseth and Welles
2151 1303 785 696	Sodium nitrite solution	Raman	Carrelli, Pringsheim, and Rosen
1333	Powdered sodium nitrite	Raman	Bar
1324 1220 814 715 655 588	Sodium nitrite solution	Raman	Dadieu, Jele, and Kohlrausch

bands of the two solutions are similar except in the case of the low-frequency band. The sodium nitrite band at 13.3 μ has an asymmetry not observed in the corresponding potassium nitrite band; the reason for this difference is not clear. As the three bands shown are the only ones

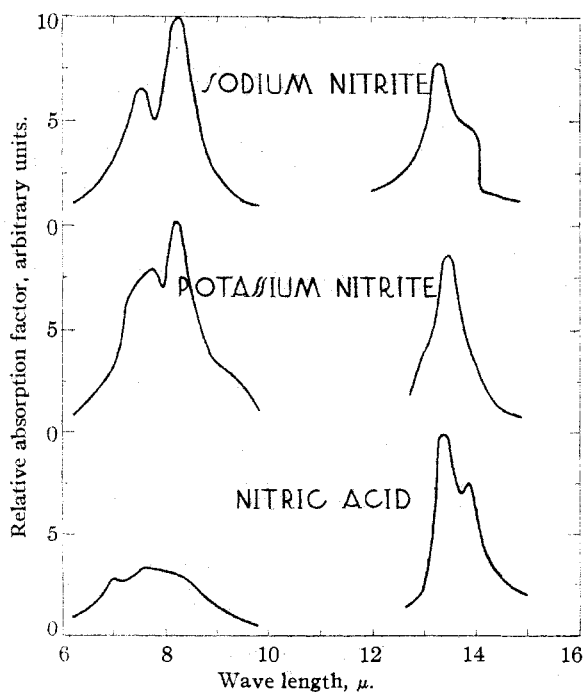


Fig. 1.

observed between 5 and 16 μ , it is assumed that they arise from fundamental vibrations of the nitrite group. The two sets of fundamentals arising in the crystal reported by Bailey and Thompson³ apparently are replaced by a single set when the nitrite ion is in solution. The agreement between the present data and the infrared data of Bailey and Thompson seems better than the agreement between independent Raman investigations. Two Raman lines for solutions (814 and 655 cm.⁻¹) apparently have no counterparts in the infrared spectrum.

In assigning the observed frequencies to the normal vibrations of the nitrite ion there are essentially only two possible choices as it is probable that the lowest frequency arises from the "bending" vibration ν_2 . Since the other frequencies are so nearly equal, there is no obvious choice for ν_1 , the "central" vibration, and ν_3 , the "non-symmetrical" vibration. Therefore, it was decided to test both the assignments given below in the equations arising from the valence-force and central-force fields.

	ν_1	ν_2	ν_3
Assignment I	1320	750	1220
Assignment II	1220	750	1320

Frequencies are given in cm.⁻¹

The valence-force-field relations in the form used in the present work are

$$k_{NO} = m M \nu_3^2 / (M + 2m \sin^2 \alpha/2) \quad (1)$$

$$k_\alpha = m \nu_1^2 \nu_2^2 d_{NO}^2 (M + 2m \sin^2 \alpha/2) / \nu_3^2 (M + 2m) \quad (2)$$

$$m(\nu_1^2 + \nu_2^2) = [k_{NO}(M + 2m \cos^2 \alpha/2)/M] + [K\alpha(M + 2m \sin^2 \alpha/2)/M d_{NO}^2] \quad (3)$$

where m is the mass of the oxygen atom, M is the mass of the nitrogen atom, α is the angle at the nitrogen, d_{NO} is the nitrogen-oxygen internuclear distance, and the k 's are the indicated force constants. From these equations α can be determined by means of a cubic equation in the square of the sine of the half angle. When the observed frequencies are introduced, it is found that neither I nor II gives a real solution for the angle, a result indicating that the valence-force-field is an unsatisfactory approximation for the nitrite group. However, it was decided to assume angles of reasonable magnitude and use these in determining k_{NO} and k_α from (1) and (2). Since other similar groups were found by Penney and Sutherland¹ to have angles between 90 and 130°, these limiting angles were used. The value of 1.13 Å. for d_{NO} is taken from the X-ray data of Zeigler,⁹

(9) G. E. Zeigler, *Phys. Rev.* **38** 1040 (1931).

who gives 130° as the value for α in sodium nitrite crystals. The results obtained with the valence-force-field are shown below:

	Assumed angle	k_{NO} dynes/cm.	k_α dyne-cm./radian
Assign- ment I	90°	6.6×10^6	5.3×10^{-11}
	130°	4.8	7.4
Assign- ment II	90°	7.9	3.6
	130°	5.8	5.0

The values for k_{NO} are all considerably lower than the corresponding values for other comparable groups, while the values for k_α are all considerably higher. The use of Assignment II and 90° seems to give results more nearly similar to the values obtained for the other groups studied by Penney and Sutherland. However, since the equations yield no real values for α , little emphasis can be placed on this choice.

The central-force-field relations used in the present study are

$$k_{NO} = m\nu_3^2/[1 + (2m/M) \sin^2 \alpha/2] \quad (4)$$

$$k_{OO} = mM\nu_1^2\nu_2^2[1 + (2m/M) \sin^2 \alpha/2]/2\nu_3^2(M + 2m) \cos^2 \alpha/2 \quad (5)$$

$$m(\nu_1^2 + \nu_2^2) = 2k_{OO} + k_{NO}[1 + (2m/M) \cos^2 \alpha/2] \quad (6)$$

where the symbols have the same significance as in the first set of equations. When the Assignments I and II are introduced, it is found that I yields two real solutions for α , 86 and 100° , while II leads to no real solutions. Use of Assignment I with the two values for α leads to the following values for the force constants:

	Angle	k_{NO} , dynes/cm.	k_{OO} , dynes/cm.
Assignment I	86°	6.9×10^6	4.3×10^6
	100°	5.9	5.5

Since it is to be expected that k_{NO} is considerably greater than k_{OO} , the α value 86° seems to be the better choice.

Although 86 and 100° are the angles obtained from the central-force-field equations, the angle as determined from X-ray measurements⁹ is 130° . Therefore a computation of force constants was made with this angle substituted in (4) and (5). The results are as follows:

	Assumed angle	k_{NO} dynes/cm.	k_{OO} dynes/cm.
Assignment I	130°	4.9×10^6	16.2×10^6
Assignment II ^a	130°	5.8	10.8

^a When an angle of 90° is assumed, Assignment II gives the force constants: $k_{NO} = 8.0 \times 10^6$, $k_{OO} = 2.8 \times 10^6$ dynes/cm.

Since k_{OO} in each case is much larger than k_{NO} , it is believed that 130° is too large an angle, if

the actual force field of the nitrite group at all resembles the central-force approximation. As stated above, Zeigler's X-ray studies were made with sodium nitrite crystals, and it is possible that the angle undergoes a considerable change when the salt is dissolved.

Summarizing the above results, one finds that neither assignment of frequencies is wholly satisfactory on the basis of a valence-force approximation, but that the assumption of an angle of 90° leads to more satisfactory values than the 130° angle obtained from X-ray measurements. With the central-force approximation, Assignment I gives 86° as the value of the angle. Force constants computed for this angle are satisfactory, whereas those based on an angle of 130° are unsatisfactory. Comparison of the force constant k_{NO} with the corresponding force constant of comparable molecules shows that it is relatively smaller, while the constant k_{OO} is relatively greater. Table II gives a comparison of nitrogen dioxide, the nitro group, and the nitrite ion.

TABLE II
CHARACTERISTIC FREQUENCIES, FORCE-CONSTANTS, AND VALENCE ANGLES IN NO_2 GROUPS

Group	ν_1 cm. ⁻¹	ν_2 cm. ⁻¹	ν_3 cm. ⁻¹	α	k_{NO} 10 ⁶ dynes/cm.	k_{OO} 10 ⁶ dynes/cm.
Nitrogen dioxide	1370	640	1620	109°	9.78	3.15
The nitro group	1380	480	1560	106°	9.50	1.56
The nitrite ion	1320	750	1220	86°	6.87	4.31

The last curve in Fig. 1 represents the absorption spectrum of a 65% solution of nitric acid. One might expect the spectrum of this solution to show a marked similarity to the spectra of the nitrates reported previously.⁸ Actually, the observed spectrum shows more similarity to the nitrite spectra than to those of other nitrates. Concentrated nitric acid solutions have a region of absorption extending from 6 to 9 μ , and there is evidence of several unresolved bands in this region. It is probable that a part of this absorption may arise from vibrations of the undissociated nitric acid molecule. Raman data which are in agreement with this hypothesis have been reported by Dadieu, Jele, and Kohlrausch,⁷ who suggest that the nitric acid molecule has the form $HO \cdot NO_2$, where the NO_2 group has inner vibrational frequencies of 454, 1300, and 1625 $cm.^{-1}$, the corresponding frequencies of nitro groups in ali-

phatic compounds being 480, 1380, and 1560 cm^{-1} . If this interpretation is correct, the complex absorption bands observed near 13.4 μ may arise from an outer vibration involving OH and NO_2 groups. Although the spectrum of nitric acid has no direct connection with the nitrites, it was included in the present paper, since it can possibly be interpreted in terms of a related NO_2 group.

Summary

The infrared absorption spectra of sodium ni-

trite and potassium nitrite have been studied between 6 and 16 μ and absorption bands have been observed at 7.6, 8.2, and 13.3 μ . These bands are interpreted as arising from fundamental vibrations of the nitrite group. Force constants and valence angles of the nitrite group are computed by means of the central-force-field approximation. The valence-force-field proves to be an unsatisfactory approximation for the nitrites. The spectrum of nitric acid is discussed.

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Viscosity Relationships of Aqueous Solutions of Sodium Oleate and Various Phenols

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Weichherz and Saechtling^{2,3} in a viscometric investigation of the system sodium oleate-phenol-water observed the occurrence of viscosity maxima at certain ratios of sodium oleate to phenol, indicating the formation of complexes between these substances. The authors did not consider them to be definite chemical compounds, but rather a loose association of the soap micelle with the phenol. The present paper presents a more extended study of this phenomenon, with the object of ascertaining how far it is characteristic of phenolic substances.

Attempted verification of some of Weichherz and Saechtling's results showed general qualitative agreement but considerable quantitative discrepancy, the present values for viscosities, especially in the region of lower water content, being without exception higher, sometimes of another order altogether. Comparison of the viscosities of solutions of sodium oleate prepared from oleic acid of varying degrees of purity (*cf.* Table II, expts. 1, 2, 3, 4) indicates that the cause of this lack of agreement lies in the relative degree of purity of the two specimens of sodium oleate in question, since Weichherz and Saechtling used Kahlbaum "reinst" (I), while the present author used samples (II) prepared from oleic acid which had been purified rigorously by a method analogous to that later described by Brown and Shinowara.⁴

Illustrative of these discrepancies are the following examples.

Solutions of a concentration of 10% or higher in sodium oleate II were found to be metastable at 20°, slowly increasing in viscosity and finally crystallizing, in striking contrast to the reported investigations of Weichherz and Saechtling on solutions containing up to 30% sodium oleate. In a similar manner the viscosities obtained in the present investigation for the ternary system containing phenol were higher than the corresponding values of Weichherz and Saechtling, the former showing, for 90% water content, a maximum of over 1000 cp. at 20°, while in the case of the latter the value was about 17. For the system with 95% water the latter investigators could find no maximum, whereas in the present work the maximum at this concentration was well marked. In addition, the acid soap separation reported by the earlier investigators for this system was not observed, even after keeping the solution for several days. This heterogeneity was only observed (together with the absence of maxima in the viscosity isotherms) when the solutions containing 97% water were examined.

In order to determine whether the ability to cause maxima in the viscosity-concentration isotherms of sodium oleate solutions is a property common to all phenols, the following carefully purified materials have been examined: guaiacol, *p*-cresol, creosol, catechol, resorcinol, *p*-hydroxybenzyl alcohol, vanillyl alcohol, *o*-bromophenol.

(1) Rayonier Pulp and Paper Company Post-Doctorate Research Fellow, 1936-37. Present address: Arthur D. Little, Inc., Cambridge, Mass.

(2) Weichherz and Saechtling, *Kolloid Z.*, **60**, 192 (1932).

(3) *Ibid.*, pp. 298-306.

(4) Brown and Shinowara, *THIS JOURNAL*, **59**, 6 (1937).