The Oscillation Frequencies of Nitrates

BY DUDLEY WILLIAMS AND LORAINE DECHERD

It has been of interest to determine the characteristic oscillation frequencies of various atomic groups occurring in inorganic compounds and numerous studies of this subject have been made.[1] The infrared frequencies of XO_3 groups have been determined by means of reflection and absorption measurements. In the case of the NO_3 group, the reflection measurements of Schaefer and Schubert[2] have revealed the presence of bands near 7.5, 12, and 15μ which arise from inner vibrations of the group in the crystal lattice. The frequencies of these vibrations decrease with increasing atomic weight of the cation.

The variation of frequency with the state of aggregation has been the subject of several investigations. Pfund,[3] the first to make a systematic study of this variation in the spectra of the nitrates, observed a reflection maximum between 7 and 7.5μ in the spectra of crystal and solution. In the case of every compound studied the reflection maximum of the solution appeared at longer wave lengths than that of the solid. Further studies of Gehrts[4] confirmed this result and also established the existence of similar shifts of high frequency fundamentals of the sulfates, carbonates, and chromates. The results obtained in this work led to the generalization that solution produces weaker binding forces and hence lower frequencies of vibration.[5] However, since the above-mentioned studies all concerned themselves with the high-frequency fundamentals, it would seem desirable to extend the studies to include the lower-frequency bands before drawing definite conclusions.

It was the purpose of the present investigation to determine the effect of solution on the nitrate bands between 6 and 15.5μ. The experimental difficulties involved were numerous. As Gehrts' studies indicated, the intensity of the reflection bands is low—only 10% for the intense 7.5μ band—and hence absorption measurements seemed

desirable. However, absorption measurements involve the use of transparent cell windows, and the sodium chloride windows ordinarily used in this region are unsuited for use with aqueous solutions. Mica, fluorite, and magnesia windows may be used with aqueous solutions, but these materials have intense absorption bands in the region under consideration. After several tests it was decided to use thin fluorite windows and to make suitable corrections for their absorption.

The absorption determinations were made in the following manner. The transmission of a cell containing a solution was compared with that of an empty cell. The ratio of these transmissions gives a value for the transmission of the solution but neglects the variations in the reflection of fluorite caused by the presence of the solution in the cell. Although these reflection variations cannot be removed entirely, their effects can be minimized by comparing the solution transmission with the transmission of a water cell. Probably the most desirable procedure would be to compare the transmission of cells of equal water content, but, since it is difficult to duplicate cell thicknesses of the order of 0.02 mm., it was decided to make a logarithmic comparison in the following way. If I_s and I_w represent the intensity of the energy transmitted by solution and water cell, respectively, and I_0 the intensity transmitted by an empty cell, Lambert's law may be written

$$I_s = I_0 e^{-k_s t_s} \qquad I_w = I_0 e^{-k_w t_w}$$

where k is the extinction coefficient and t the cell thickness. Then the ratio R of the absorption factors

$$R = \frac{k_s t_s}{k_w t_w} = \text{const.} \frac{k_s}{k_w}$$

is a measure of the solute absorption. As one may see readily R does not give the absolute value of the solute extinction coefficient, but indicates the ratio of the solution and solvent extinction coefficients multiplied by a constant. Other methods of representing the absorption of the solute could be employed, but in cases where the cell thicknesses are doubtful, the present method seems to be a safe and convenient one. Another effect not mentioned is the change in water ab-

(1) Early work on nitrates: W. W. Coblentz, *Phys. Rev.*, **17**, 51 (1903); Carnegie Institution Publication 35 and 65.

(2) C. Schaefer and M. Schubert, *Ann. Physik*, **55**, 577 (1918).

(3) A. H. Pfund, *Astrophys. J.*, **24**, 19 (1906).

(4) F. Gehrts, *Ann. Physik*, **47**, 1059 (1915).

(5) C. Schaefer and F. Matossi, "Das Ultrarote Spektrum," Verlag von Julius Springer, Berlin, 1930, p. 369; F. G. Rawlius and A. M. Taylor, "Infrared Analysis of Molecular Structure," Cambridge, 1929, p. 57.

sorption caused by the presence of the solute, but in the present case this effect is probably negligible since water has no major bands near the nitrate bands.

The spectra of the solutions were studied by means of the spectrometer described in previous papers,[6] the wave length calibration being checked by means of the bands listed by Plyler and Shearin.[7] On account of the low transmission of fluorite it was necessary to use rather broad slits, effective slit width of approximately 0.06μ over the whole range. In order to ensure sufficiently intense absorption and to maintain approximately equal numbers of absorbing units, 6 N solutions were used for all compounds except potassium nitrate; for this compound a saturated solution (approximately 2.3 N) was employed. The effects of concentration on the position of infrared bands were not studied exhaustively in the present work, although measurements on sodium nitrate solutions yielded results in accord with Gehrts' observations. Band shifts arising from variations in concentration are usually small as compared with the solid-to-solution transition, and it was felt that little information on the subject could be obtained with effective slit widths as large as those used.[8]

The results obtained are shown in Fig. 1. In this figure R, the "relative absorption factor," is plotted as a function of wave length. It will be seen that all the nitrates studied have absorption bands corresponding to the reflection bands observed in nitrate crystals. The intense high-frequency band appears at 7.30μ in lithium nitrate, at 7.40μ in sodium nitrate, and at 7.42μ in potassium nitrate. There is evidence of double absorption maxima in lithium nitrate and sodium nitrate, while the potassium nitrate band at 7.42μ is almost symmetrical and shows little indication of complexity. The bands appearing at 11.95μ in lithium nitrate, 12.05μ in sodium nitrate, and 12.08μ in potassium nitrate all have double maxima, the relative intensities of which vary with the compound. The low-frequency bands at 14.65μ in lithium nitrate, at 14.75μ in sodium nitrate and at 14.85μ in potassium nitrate show two well-re-

(6) D. Williams and R. Taschek, *J. Applied Phys.*, **8**, 497 (1937).

(7) E. K. Plyler and P. E. Shearin, *J. Optical Soc. Am.*, **28**, 61 (1938).

(8) D. Franklin and E. Laird, *Phys. Rev.*, **45**, 738 (1934). These authors report that a solid-to-solution transition in sodium nitrate produces a change of 20 cm.$^{-1}$ in sodium nitrate Raman lines, while the difference in frequency of the same line is only 1.5 cm.$^{-1}$ in 1.25 and 8 N solutions.

solved maxima, with indications of a third maximum in potassium nitrate. The relative intensities of the two low-frequency bands observed do not agree entirely with the intensity of the reflection bands observed by Schaefer and Schubert[2] in the case of the crystals; in the reflection measurements the intensities of the two bands were more nearly equal than in the present case.
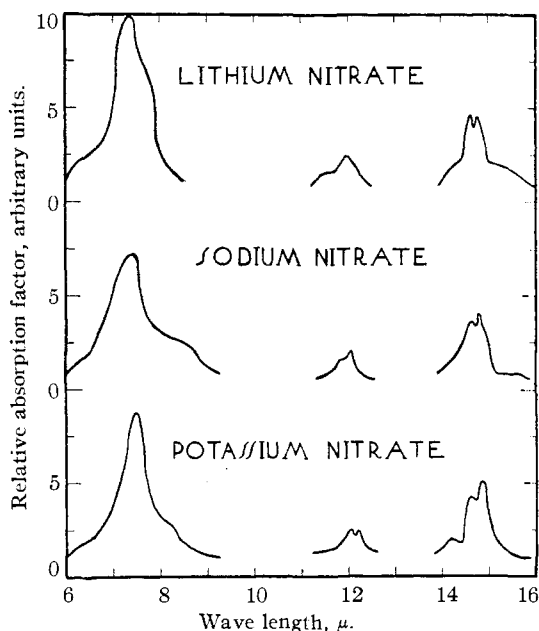

Fig. 1.—The absorption of nitrate solutions as a function of wave length.

In Table I, the infrared frequencies obtained in this study are compared with the frequencies observed by Schaefer and Schubert. It will be seen that in the case of sodium nitrate the solution frequencies are all lower than the corresponding frequencies in the crystal. However, in potassium nitrate the solution frequencies are higher in all cases except that of the vibration giving rise to the band at 7.42μ. The frequencies of the Raman lines for the three nitrates are recorded in Table I for comparison with the infrared frequencies; the data are taken from the tables in Kohlrausch's "Der Smekal-Raman Effekt." In the case of the Raman frequencies, it will also be noted that the solution frequencies are all lower than the crystal frequencies except in the case of potassium nitrate. Here the highest and lowest frequencies are greater in the case of the solution, while the intermediate frequency remains practically unchanged. Thus, it would appear that in the nitrates the rule of lower solution frequen-

cies is obeyed in the majority of cases but that there are some exceptions to the rule. A survey of the available Raman data reveals only two other cases in which frequencies are increased on

TABLE I

THE OSCILLATION FREQUENCIES OF NITRATES

Infrared, cm.$^{-1}$ Present study	Schaefer and Schubert[a]	Raman, cm.$^{-1}$ Solution	Crystal
	Lithium nitrate		
			1391
1370	..	..	1069
837	..	1050	1052
683	..	..	728
	Sodium nitrate		
1350	1405	1361	1389
830	831	1049	1071
678	693	721	726
	Potassium nitrate		
1350	1390	1357	1351
827	816	1049	1051
673	659	730	711

[a] The crystal frequencies observed by absorption would be slightly lower than those observed in reflection.

the crystal-to-solution transition; in ammonium nitrate and in hydrated calcium nitrate one finds such an increase in the lower frequencies.

Thus, the results of this study and also the existing Raman data for nitrates justify the generalization based on the early infrared measurements of the high-frequency bands that the frequencies of anions are usually decreased in solutions. However, there are a few exceptions to this rule, especially in the case of low frequencies.

Summary

Early infrared measurements on bands in the 7 to 9μ region arising from the NO_3 group showed that the frequencies were reduced when the salts were in solution. In the present work the spectra of several nitrate solutions were studied between 6 and 16μ. The results obtained are in agreement with previous results except in the case of potassium nitrate. The infrared data are compared with the existing Raman data.

The Magnetic Flux Distribution when a Cylinder of Constant Permeability Is Placed in a Homogeneous Field. The Magnetic Susceptibility of Gadolinium Oxide at Low Temperatures

BY W. F. GIAUQUE AND J. W. STOUT

The problem of the distribution of a magnetic field when a body of permeability μ is introduced into a homogeneous field has been solved accurately only for the real case of an ellipsoid and such hypothetical cases as a cylinder of infinite length or a plate of infinite extent. This well-known problem has not been solved, partly because of its mathematical complexity, and perhaps more because there has been no real incentive for obtaining an accurate solution since it would not apply to ferromagnetic substances. These substances have a variable permeability, hysteresis, and a lack of reproducibility that have made precise measurements of doubtful value. At very low temperatures many paramagnetic substances have a sufficient permeability so that Giauque and MacDougall[1] selected the convenient induction method for determining magnetic susceptibility at the very low temperatures

(1) Giauque and MacDougall, (a) *Phys. Rev.*, **43**, 768 (1933); (b) THIS JOURNAL, **57**, 1175 (1935).

obtained by the adiabatic demagnetization method. Some form of the induction method is now used by all experimenters engaged in this type of investigation. The exact application of this procedure requires a solution of the magnetic distribution problem within the sample and the space enclosed by the measuring coil.

For reasons of convenience most of the existing results have been obtained with cylindrical samples, although Professor F. Simon and his collaborators recently have made use of ellipsoidal forms. In the experiments performed in this Laboratory advantage has been taken of the fact that the absolute magnetic susceptibility was known at the higher temperatures for the substances investigated. Thus a factor due to the geometry of the arrangement could be determined experimentally. Further, since the range of permeability was small the assumption was made that the factor remained constant.

Although a uniform intensity of magnetization,