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compound most of the exothermicity is converted into internal energy of the products, i.e., that the reactions on the molecular level are essentially thermoneutral $(Q \approx 0)$.

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APPENDIX

The confirmatory experiments (II in Table I) at $v_{\rm K} = 1007$ m/sec (E = 3.36 kcal/mole) were carried out primarily as a check on the kinematic procedures under quite different experimental conditions. For example, at $\theta_a = 22.5^\circ$, $v'_{\rm KBr}$ is expected (for Q = 0.5kcal/mole) to be approximately one-third greater than for the experiment at $v_{\rm K} = 732$ m/sec, at the same angle. The observed $v'_{\rm KBr}$ is within 3% of the expected value (and within 2% of the velocity corresponding to Q=0). In general, results at higher collision energy are less reliable as a measure of Q because of the relatively lower sensitivity of v'_{KBr} to Q, viz., $v'_{\text{KBr}} \propto (E+Q)^{\frac{1}{2}}$. Nevertheless, the value of Q inferred from the experiments at high E, namely $Q=0\pm 2$ kcal/mole, is in accord with the more reliable value at E=1.85kcal/mole quoted earlier.

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Far-Infrared Spectra of Anhydrous Metallic Nitrates*

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The far-infrared spectra from 350 to 70 cm⁻¹ of the anhydrous nitrates of Li, Na, K, Ca, Sr, Ba, Ag, Pb, Cu, Zn, Co, Mn, Nd, and Cd are reported. The possible nature of these absorptions is discussed.

THE infrared spectra of metallic nitrates (anhydrous **L** and hydrated) in the sodium chloride region have been published.¹⁻⁷ Two types of nitrate spectra have been observed. One is a simple spectrum of the ionic nitrate ion possessing D_{3h} symmetry. The other is a complex spectrum, and has been interpreted as being due to a coordinated nitrate of lowered symmetry (C_{2v}) .¹⁻⁷ Electron-diffraction and x-ray data,⁸⁻¹⁰ although meager, have shown that in those nitrates of lowered symmetry, metal-to-oxygen distances are shorter than those found in ionic nitrates.

- 1958, 464.
 ⁴ J. R. Ferraro, J. Mol. Spectry. 4, 99 (1960).
 ⁵ F. Vratny, J. Appl. Spectry. 13, 59 (1959).
 ⁶ C. C. Addison and B. M. Gatehouse, J. Chem. Soc. 1960, 613.
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- ⁸ S. C. Wallwork, Proc. Chem. Soc. 1959, 311.
 ⁹ S. M. Bauer and C. C. Addison, Proc. Chem. Soc. 1960, 251. ¹⁰ R. E. La Villa and S. M. Bauer, J. Am. Chem. Soc. 85, 2597 (1963).

In view of the fact that strong interactions occur in those nitrates of lowered symmetry, it should be possible to find internal modes of vibration involving the metal and oxygen atoms. These vibrations would be found in the region of the infrared spectrum beyond the KBr region (lower than 400 cm⁻¹). Metal nitrates have not been investigated beyond 300 cm^{-1,11} To avoid complications involving internal modes of vibration of coordinated water, anhydrous nitrates were investigated in the region of 350-70 cm⁻¹. Several anhydrous carbonates were also studied for comparison. The results of this investigation are reported in this paper.

EXPERIMENTAL

Synthesis of Anhydrous Nitrates

Dinitrogen tetroxide was obtained from the standard Matheson cylinder. The nitrates of copper,12 zinc,13 manganese, cobalt, and cadmium⁶ were prepared as previously described. Neodymium nitrate was prepared by reaction of the metal with a dinitrogen tetroxide-

^{*} Based on work performed under the auspices of the U.S. Atomic Energy Commission; paper presented at 3rd National Meeting, Society for Applied Spectroscopy, Cleveland, Ohio, September 1964. †Post-Doctoral Fellow from the University of Nottingham,

Great Britain.

¹B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, J. Chem. Soc. 1957, 4222.

² J. V. Quagliano, private communication and paper presented at American Chemical Society, 132nd meeting, April 1957, Miami, Florida. ³ C. C. Addison and B. M. Gatehouse, Chem. and Ind. (London)

¹¹ F. Miller, G. L. Carlson, F. F. Bentley, and W. H. Jones, Spectrochim. Acta **16**, 135 (1960). ¹² C. C. Addison and B. J. Hathaway, Proc. Chem. Soc. **1957**,

J. Chem. Soc. 1958, 3099.
 ¹³ C. C. Addison, J. Lewis, and R. Thompson, J. Chem. Soc.

^{1951, 2829}

ethyl acetate mixture followed by heating under vacuum to remove solvated dinitrogen tetroxide. Analysis for Nd and N were made by EDTA titration and Kjeldahl, respectively. (Found: Nd, 43.58%; N, 12.62%. Calc: Nd, 43.68%; N, 12.71%). The alkalimetal nitrates were dried under vacuum at 300°C. Silver and lead nitrates were dried in the oven at 110°C. Copper nitrate trihydrate was used from a fresh bottle opened and stored in the dry box. The anhydrous strontium and barium nitrates were used as obtained from the bottle. Anhydrous $Ca(NO_3)_2$ was prepared by heating $Ca(NO_3)_2 \cdot 4H_2O$ at 150°C.

Infrared Measurements

The region from 350 to 70 cm⁻¹ was investigated using the Perkin-Elmer No. 301 double-beam grating spectrometer with a dry-nitrogen-gas purge. This region was calibrated with the mercury orders and water lines.¹⁴ From 700 to 300 cm⁻¹ the Beckman IR-7, equipped with a CsI prism, was used. Spectra in the 4000-700 cm⁻¹ region were determined by means of a Perkin-Elmer No. 421 spectrometer. Results below 700 cm⁻¹ were obtained using Nujol mulls, between polyethylene sheets (1 mm thick), which were prepared in a dry box. Sample cells were transferred from the dry box to the instrument room in a desiccator. Measurements in the NaCl region were made using Nujol and halocarbon oil mulls on BaF2 windows. The lowtemperature studies were obtained using an evacuated, Dewar-type cell with polyethylene windows. Liquid nitrogen served as the coolant.

Raman Measurements

The Raman spectra where possible were determined with a Cary No. 81 spectrophotometer using solid sampling techniques recently published.^{15,16}

RESULTS AND DISCUSSION

The far infrared of the solid state gives rise to a complex spectrum. For those compounds which are ionic the bands seen in this region arise from lattice vibrations of the individual ions. Since the vibrations occur throughout the lattice and are not concerned with a single unit cell these vibrations are often observed as broad peaks which represent a composite band of several vibrations. For such compounds the mass of the ions concerned plays an important role in determining the frequency of absorption. Since compounds such as LiOH show lattice frequencies in the 600-cm⁻¹ region,¹⁷ whereas with KBr the bands arise at ~ 120 cm⁻¹, it is evident that the vibrations can be found over a very wide range of frequency. However, within a class of similar compounds (e.g., alkali-metal halides) a regular decrease in frequency is observed with increasing size and mass and decreasing polarizing power of the cation.

For those lattices containing covalent molecules the vibrations likely to be observed in the far infrared arise from two sources, namely: (a) molecular lattice vibrations which would occur at very low frequencies due to the mass of the molecules; and (b) internal vibrations of the molecule. Within this second class fall the stretching and bending vibrations involving heavy atoms such as metal-oxygen bonds and the "hindered rotation" of ligands attached to a central metal atom. Recent work¹⁸ on metal-aquo complexes has illustrated the presence of such hindered rotations of the water molecules, which are coordinated to the metal atom, and have been termed the rocking, twisting, and wagging modes. Thus for covalent metal nitrates one should observe metal-to-oxygen stretching and bending frequencies together with the hindered rotations of the nitrate groups in the region below 600 cm^{-1} , all the other internal vibrations of the nitrate groups being observed above 600 cm⁻¹. A further complication is that in low symmetry, coupling between these low-frequency vibrations is likely to be large so that a particular absorption peak may contain the character of different vibrations.

The anhydrous metal nitrates demonstrate very rich far-infrared spectra from 350 to 70 cm⁻¹. The absorptions in this region for the anhydrous metal nitrates which show splitting of the ν_3 degenerate frequency of the ion¹⁻⁷ are tabulated in Table I. Neodymium nitrate has been shown in this investigation to show similar

TABLE I. Far-infrared absorptions of covalent nitrates $(350-70 \text{ cm}^{-1}).$ *

$Cu(NO_3)_2$	336(s), 299(sh), 253(w, sh), 209(m), 170(vw) 138(vw), 94(vw)
$Zn(NO_3)_2$	317(s, sp), 284(s, sp), 188(w), 141(m, sh), 127(m, sp), 119(m, sp), 96(w, sh)
Co(NO ₃) ₂	316(w, sh), 271(s), 217(sh), 185(s, sp), 170(m, sp), 162(m, sh), 138(w, sp), 108(w, sp), 88(s, sp)
$Mn(NO_3)_2$	231(s), 199(sh), 138(m, sp), 96(w, sh)
$Nd(NO_3)_3$	226(s), 178(s), 112(sh)
$Cd(NO_3)_2$	199(s, sp), 162(sh), 116(m)

^a All strong bands are also broad. No absorption in 650--350 cm⁻¹ except for $Nd(NO_2)_3$ [505(w), 610(vw), 640(w)]. Abbreviations: s, strong; sh, shoulder; m, medium; w, weak; vw, very weak; sp, sharp.

¹⁸ I. Nakagawa and T. Shimanouchi, Spectrochim. Acta 20, 429 (1964).

 ¹⁴ K. Narahari Rao, R. V. DeVore, and E. K. Plyler, J. Res. Natl. Bur. Std. (U.S.) A67, 351 (1963).
 ¹⁵ J. R. Ferraro, J. S. Ziomek, and G. Mack, Spectrochim. Acta

 ¹⁶ J. R. Ferraro, Spectrochim. Acta 20, 901 (1964).
 ¹⁷ S. S. Mitra, Solid State Phys. 13, 1 (1962).

loss of degeneracy $[\nu_4 = 1480 \text{ cm}^{-1}(s, br), \nu_1 = 1325 \text{ cm}^{-1}$ (s, br), $\nu_2 = 1023 \text{ cm}^{-1}(\text{m})$, $\nu_6 = 798 \text{ cm}^{-1}(\text{w})$] and is thus included in this table. In most cases two strong, broad absorptions are found along with several weak bands and weak shoulders. The strongest bands are always located at highest frequencies and are asymmetric in shape.

The results obtained for the ionic nitrates are listed in Table II. Two strong bands and several weaker ones are observed, similar to the covalent nitrates. The most intense band is usually at the highest frequency.

As illustrated in Table III the high-frequency band for both groups of nitrates decreases in frequency with increasing ionic radius and decreasing polarizing power of the cation. It can be observed that the frequencies for lithium and sodium nitrates overlap those for the transition-metal nitrates. This presents the problem of deciding whether the latter frequencies arise from

(350–70 cm ⁻¹). ^a		
LiNO3	321(s), 275(sh), 166(m, sp), 152(w, sh), 96(w)	
NaNO3	217(s), 173(s, sp), 89(m, sp)	
AgNO ₃	170(s), 125(sh), 103(w), 80(w)	
KNO3	152(s), 130(sh)	
Pb(NO ₃	$)_2$ 226(w, sh), 180(w, sh), 92(s)	
Ca (NO ₃	$)_2$ 236(sh), 205(s)	
Sr (NO ₃)	$_{2}$ 206(m), 162(s), 145(m), 128(w), 108(w)	
Ba(NO₃	153(m), 94(w), 77(w)	

^a All strong bands are also broad.

genuine metal-oxygen stretching vibrations or lattice vibrations of essentially free ions.

The frequencies in the region 650-70 cm⁻¹ for a series of ionic alkali-metal salts are listed in Table IV. The observed frequencies for these compounds can be assigned to lattice vibrations of essentially unperturbed ions. For all three classes of compounds increasing the mass of cation or anion shifts the strongest absorption toward lower frequency. This behavior appears to be characteristic of lattice vibrations in compounds where the polarizing power of the cation is small.

By comparison no regular decrease in frequency with mass is found for the transition-metal nitrates, the frequencies for copper and zinc nitrates being much higher than for cobalt and manganese nitrates. Furthermore, if mass were the only parameter the vibrations should be observed at much lower frequencies. The predominant factor here must therefore be the much higher polarizing power of the cations over that of the alkali metals. This must accordingly lead to a far greater perturbation of the nitrate group in the transi-

TABLE III. Relation of ionic radius with frequency for anhydrous metal nitrates.

Anhydrous nitrate	Strongest, high- frequency band (cm ⁻¹)	Ionic radius ^a of cation (Å)	Polarizing power ^b e/r ²
Cu (63.5)	336	0.74	3.65
Zn(65.4)	317, 284	0.83	2.90
Co (58.9)	271	0.82	2.97
Mn (54.9)	231	0.91	2.41
Nd (144.2)	226, 178	1.15	2.27
Cd (112.4)	199	1.03	1.88
Li (6.9)	321	0.78	1.64
Na (23.0)	217	0.98	1.04
Ag (107.9)	170	1.13	0.78
K (39.1)	152	1.33	0.51
Pb (207.2)	92	1.32	1.14

^a All ionic radii, except for copper are Goldschmidt values taken from T. Moeller, Inorganic Chemistry (John Wiley & Sons, Inc., New York, 1952). The copper value used was taken from the Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, Ohio, 1963).

^b As defined by V. M. Goldschmidt, Verteilungsgesetze 7, 60 (1926).

tion-metal nitrates, with a resultant formation of a metal-oxygen bond.

X-ray studies^{8,9} for anhydrous solid Cu(NO₃)₂ show that the copper-oxygen bond distance is about 1.9 Å. As a contrast, the potassium-oxygen distance¹⁹ in ionic KNO₃ is 2.9 Å. For anhydrous Cu(NO₃)₂, using the harmonic oscillator equation, and a force constant of 1. the Cu-O stretching frequency is calculated as 360 cm⁻¹. In Co(III) carbonato complexes, Nakamoto et al.20 and

TABLE IV. Comparison of alkali carbonates, nitrates, and halides $(650-70 \text{ cm}^{-1})$.

	Carbonates
Li	500(s), 409(s), 258(m), 137(m)
Na	240(m), 137(m)
K	195(m), 94(w)
Ca	325(s), 227(s), 106(s)
	Nitrates
Li	321(s), 275(sh), 166(m, sp), 152(w, sh), 96(w)
Na	217(s), 173(s, sp), 89(m, sp)
K	152(s), 130(sh)
	Halides
NaCl	175(s)
KCl ^a	144(s)
NaBr ^a	135(s)
KBr	115(s)

^a M. Davies, Infrared Spectroscopy and Molecular Structure (Elsevier Publishing Company, Inc., New York, 1963), p. 104.

 ¹⁹ D. A. Edwards, Z. Krist. 80, 154 (1931).
 ²⁰ K. Nakamoto, J. Fujita, S. Tonaka, and M. Kobayashi, J. Am. Chem. Soc. 79, 4904 (1957).

$Cu(NO_3)_2 \cdot 3H_2O$	580(m), 460(m), 325(s, sp), 257(sh), 180(w), 126(w), 104(m, sp) 233(m), 160(m)
$Cu(NO_3)_2$	336(s), 299(sh), 253(w, sh), 209(m) 170(vw), 138(vw), 94(vw)

TABLE V. Comparison of Cu (NO₃)₂·3H₂O and anhydrous $Cu(NO_3)_2$ spectra (cm⁻¹).

Fujita et al.²¹ have found the Co-O stretching frequency in the region of 340-450 cm⁻¹. Anhydrous Cu(NO₃)₂ shows a very strong band at 336 cm⁻¹ at room temperature, which splits into a doublet at liquid nitrogen temperatures. The complex structure⁸ of anhydrous solid Cu(NO₃)₂ indicates that several different Cu-O bonds are possible, and these might result in a multiple broad absorption band, as is observed for this vibration. Infrared evidence in molten salts^{22,23} and Raman evidence^{24,25} for aqueous nitrate solutions indicate possible metal-oxygen stretching vibrations occurring in the region of 250-450 cm⁻¹.

We consider, therefore, that for the nitrates listed in Table I, the strong high-frequency bands may be assigned to metal-oxygen stretching vibrations while the weak bands observed at lower frequencies arise from the rocking and wagging modes of the NO₂ groups attached to the M-O bonds. The bending vibrations would be expected at much lower frequencies. In addition if the nitrate is bonded to the metal as a bidentate ligand, a ring breathing vibration is possible. Very low energy motions of the chains as in solid $Cu(NO_3)_2$ can also occur.

In order to assign the various types of vibrations that are possible in this region, and to make definite frequency assignments a normal coordinate analysis for anhydrous solid $Cu(NO_3)_2$ is being attempted, and will be reported in a separate publication.

The far-infrared frequencies observed for Li₂CO₃, which are listed in Table IV, appear unusually high for lattice vibrations. We therefore determined the spectrum in the NaCl region and found that it could only reasonably be assigned on the basis of a coordinated carbonate. The bands observed are assigned as follows:

$$\begin{split} \nu_4 &= 1485 \ \mathrm{cm}^{-1}(\mathrm{s}), \qquad \nu_1 &= 1425 \ \mathrm{cm}^{-1}(\mathrm{s}), \\ \nu_2 &= 1071 \ \mathrm{cm}^{-1}(\mathrm{m}), \qquad \nu_6 &= 849 \ \mathrm{cm}^{-1}(\mathrm{s}). \end{split}$$

Thus, the frequencies found at 500 cm⁻¹ and 409 cm⁻¹ in Li₂CO₃ are probably Li-O stretching vibrations

- ²¹ J. Fujita, A. E. Martell, and K. Nakamoto, J. Chem. Phys. **36**, 339 (1962).
- ²³G. J. Janz, T. R. Kozlowski, and S. C. Wait, J. Chem. Phys. 39, 1809 (1963).
 ²³G. E. Walrafen and D. E. Irish, J. Chem. Phys. 40, 911
- (1964).²⁴ R. E. Hester, R. A. Plane, and G. E. Walrafen, J. Chem.
- Phys. 38, 249 (1963)

rather than lattice modes. A similar assignment for Li₂CO₃ has already been made.²⁶

Certain discrepancies occur between this work and previous investigations in the case of NaNO₃ and CaCO₃. The infrared absorptions in NaNO₃ are found at 217, 173, and 89 cm⁻¹. Only the lower frequency band was found in the Raman spectra in the present work. Raman et al.27 found bands at 185 and 98 cm⁻¹, only if the Raman measurements were made with the incident light vector along the optic axis of the crystal. Liebisch and Rubens²⁸ reported bands at 71, 133, and 218 cm⁻¹ for NaNO₃, using residual ray techniques. An infrared absorption band in molten NaNO₃ has been reported at 238 cm^{-1.29} Hexter³⁰ has attempted to arrive at the lattice frequencies for NaNO3 by an infrared study of the overtone region, and has postulated a band at 315 cm^{-1} , which was not observed in this study. Similarly, two additional frequencies postulated for calcite³¹ at 270 and 416 cm⁻¹, were not observed.

Metal-Water Vibrations

The region from 700 to 350 cm^{-1} for hydrated and anhydrous nitrates, was first studied by Miller and co-workers.¹¹ They reported that nitrates lack absorption in this region. Table V shows the comparison of the results for $Cu(NO_3)_2 \cdot 3H_2O$ and anhydrous



FIG. 1. Spectrum of anhydrous Cd (NO₃)₂.

- ²⁶ P. Tarte, Spectrochim. Acta **20**, 238 (1964). ²⁷ C. V. Raman and T. M. K. Nedungadi, Nature **143**, 679 (1939).
- ¹²⁸ T. Liebisch and H. Rubens, Sitzber. Deut. Akad. Wiss. Berlin, Kl. Math. Phys., Tech. **1919**, 198.
- ²⁹ J. K. Wilmshurst and S. Senderoff, J. Chem. Phys. 35, 1078 (1961).
 - ³⁰ R. M. Hexter, Spectrochim. Acta 10, 291 (1958).
 - ³¹ R. M. Hexter, Spectrochim. Acta 10, 281 (1958).

²⁶ R. E. Hester and R. A. Plane, J. Inorg. Chem. 3, 769 (1964).

Cu(NO₃)₂. It is observed that absorption occurs at 460 cm⁻¹ and 580 cm⁻¹ in the hydrate which is absent in the anhydrous salt. Recent infrared evidence¹⁸ with chlorides and sulfates and Raman evidence³² with aqueous solutions, show that bands due to the librational modes of coordinated water can be found in this region. In CuSO₄·5H₂O the Cu-OH₂ stretching absorption occurs at 440 cm⁻¹ and the bound water wagging vibration is at 535 cm⁻¹. The discrepancy in this region for Cu(NO₃)₂·3H₂O between the present and the previous work,¹¹ is probably due to the precautions used in this work in mulling in the dry box. If the hydrated salt is mulled in the open or if the drybox mull is exposed to the air for a few minutes all bands in the 700-350 cm⁻¹ region disappear.

Upon exposure of the covalent nitrates to moist air the infrared spectrum quickly reverts to that of an ionic nitrate in the NaCl region. The ν_4 , ν_1 separation decreases and ultimately coalesces to a strong band at about 1400 cm⁻¹, and the frequency in the 1000-cm⁻¹ region diminishes in intensity. This is caused by the replacement of the nitrate in the coordination sphere of the metal by water, and an ionic nitrate ensues.

The far-infrared region also shows marked changes on exposure to moist air. The bands at 336 cm^{-1} and below for anhydrous Cu(NO₃)₂ quickly disappear on exposure to air. Similar effects are observed with all the other anhydrous covalent nitrates. Figure 1 shows a comparison of a mull of anhydrous cadmium nitrate before and after exposure to moist air. Thus, as water enters the coordination sphere of the metal, the nitrate is displaced and the metal-to-nitrate bond is no longer observed. Finally, when excess water is present and liquid droplets are formed, as occurs when either $Cu(NO_3)_2$ or $Cu(NO_3)_2 \cdot 3H_2O$ is exposed to air, even the metal-water frequencies in the region 800 to 350 cm⁻¹ disappear. Further discussion of differences in the spectra of anhydrous and hydrated salts will be made in a separate publication.³³

TABLE VI. Raman displacements for several anhydrous salts $(500-0 \text{ cm}^{-1})$.

LiNO ₃	238(s), 95(w)	
NaNO ₃	98(m)	
KNO3	85(s)	
CaCO ₃	115(w)	
Li_2CO_3	No bands	
Na_2CO_3	No bands	
K_2CO_3	No bands	

Low-Temperature Studies

In an attempt to differentiate between lattice vibrations and internal stretching modes, spectra were obtained at liquid nitrogen temperatures. The lattice vibration of NaNO₃ at 217 cm⁻¹ was investigated and observed to sharpen and shift about 10 cm⁻¹ toward higher frequency. Observations of the 336 cm⁻¹ band in Cu(NO₃)₂ and the 321 cm⁻¹ band in LiNO₃ failed to show a shift, although sharpening occurred, and in the case of Cu(NO₃)₂ splitting into a doublet was observed. However, the broadness of the peaks precluded observation of any small shift. The sharp band at 325 cm⁻¹ in Cu(NO₃)₂·3H₂O was observed not to shift.

Raman Studies

Raman displacements for several carbonates and nitrates are listed in Table VI. Attempts to make Raman measurements of the covalent nitrates proved unsuccessful. The covalent nitrates were prepared by the method of Addison *et al.*^{6,12,13} and are formed as very fine powders. Raman spectra of these are impossible to obtain. Pelletizing techniques to improve powder spectra¹⁶ were not possible because pellets of KBr and the anhydrous covalent nitrates interact. Pellets of the pure material failed to hold together. In addition, several of these nitrates are colored and Raman spectra are not possible with mercury radiation, which was the only source available to us.

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²² R. E. Hester and R. A. Plane, J. Inorg. Chem. 3, 768 (1964). ²³ J. R. Ferraro and A. Walker, J. Chem. Phys. 42, 1278 (1965) (following paper).