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# Raman and infrared spectra of crystalline dinitrogen tetroxide

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Raman and infrared spectra of polycrystalline samples of  $\text{N}_2\text{O}_4$  at low temperatures have been recorded. The number and activities of the fundamentals are compared with the predictions of group theory, based on the known molecular and crystal geometries. Several additional peaks are attributed to Fermi resonances of combinations with fundamentals. A new low frequency internal mode and five lattice modes have been observed.

## INTRODUCTION

In the gas and liquid phases, nitrogen dioxide coexists in monomeric and dimeric forms. The percentage of dimer  $\text{N}_2\text{O}_4$  increases from zero at the critical point ( $158^\circ\text{C}$ ) to 100 at the freezing point ( $-11.2^\circ\text{C}$ ) and the solid consists entirely of  $\text{N}_2\text{O}_4$  molecules.<sup>1</sup> The molecular and crystal structures of  $\text{N}_2\text{O}_4$  have been determined.<sup>2,3</sup> The molecule is planar, with point symmetry  $D_{2h}$ , as shown in Fig. 1. The bond lengths and angle indicated there are the values at 25 K. The fact that the length of the N-N bond is so much larger than that for the N-O bond is an indication of the relatively weak binding between the two halves of the dimer.

The crystal lattice of  $\text{N}_2\text{O}_4$  is body-centred cubic, with space group  $T_h^5(Im\bar{3})$ . The three molecules in the primitive unit cell are on sites of  $D_{2h}$  symmetry, with the arrangement shown in Fig. 2. The cubic lattice constant has the value  $a = 7.655 \text{ \AA}$  at 25 K. Metastable forms of both the molecule<sup>4,5</sup> and the crystal<sup>6</sup> are also known to exist.

A group theoretical analysis of the  $\text{N}_2\text{O}_4$  molecule, in its stable  $D_{2h}$  symmetry, shows that the irreducible representations are distributed as follows:

$$\Gamma(\text{internal}) = 3A_g + A_u + 2B_{1g} + B_{1u} + B_{2g} + 2B_{2u} + 2B_{3u},$$

$$\Gamma(\text{rotational}) = B_{1g} + B_{2g} + B_{3g},$$

$$\Gamma(\text{translational}) = B_{1u} + B_{2u} + B_{3u}.$$

All *gerade* modes are Raman active and all *ungerade* modes except  $A_u$  are infrared active. The form of the molecular normal modes has been given by Bibart and Ewing.<sup>7</sup> The correlation diagram showing the number and activities of the internal and lattice modes of the  $\text{N}_2\text{O}_4$  crystal is shown in Fig. 3. It is seen that the separation between *gerade* and *ungerade* modes is maintained in the crystal. The three totally symmetric modes are each expected to give rise to two Raman components, while the other three Raman modes remain singlets. All five infrared modes also give singlets in the crystal. The inactive  $A_u$  mode (torsion about the N-N bond) leads to two components in the solid, but neither are Raman or infrared active. Three Raman librational modes, two infrared translational modes, and one zero-frequency acoustic mode are also predicted, all triply degenerate.

There have been many previous spectroscopic studies of  $\text{N}_2\text{O}_4$ ,<sup>7-13</sup> most of which have concentrated on the

higher frequency internal modes. A comprehensive assignment of these modes, based on vibrational-rotation band shape theory, has been given by Bibart and Ewing.<sup>7</sup> On the basis of entropy data, they predicted that the  $\nu_{10}$  mode (in-phase rocking motion of the  $\text{NO}_2$  groups) should have a frequency of about  $270 \text{ cm}^{-1}$ , whereas previous workers gave values between  $370$  and  $450 \text{ cm}^{-1}$  for this mode. Several additional peaks have been interpreted as combinations between internal and lattice modes<sup>4,10,11</sup> or an overtone in Fermi resonance with a fundamental.<sup>12</sup>

The purpose of the present work is to obtain Raman and infrared spectra on similarly grown samples of crystalline  $\text{N}_2\text{O}_4$  in its stable form over wide temperature and frequency ranges. Particular emphasis is given to the region below  $350 \text{ cm}^{-1}$ , to obtain information on the lattice modes and low-lying internal modes, and thus attempt to resolve some of the remaining uncertainties and ambiguities associated with the vibrations of this molecular crystal.

## EXPERIMENTAL TECHNIQUES

The gas used in these experiments was obtained from Matheson Company, and was stated to be 99.5% pure. However, preliminary spectra indicated that further purification was necessary and this was achieved by repeated fractional distillations using flasks immersed in dry ice-acetone slush ( $-78^\circ\text{C}$ ). The main impurity was  $\text{N}_2\text{O}_3$ , which colored the solid bright blue. The pure-white solid  $\text{N}_2\text{O}_4$  eventually obtained gave mid-infrared spectra in complete agreement with previous

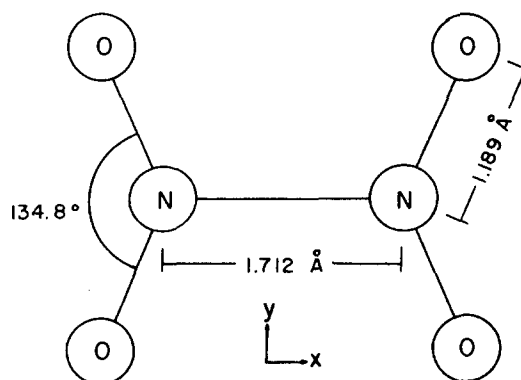
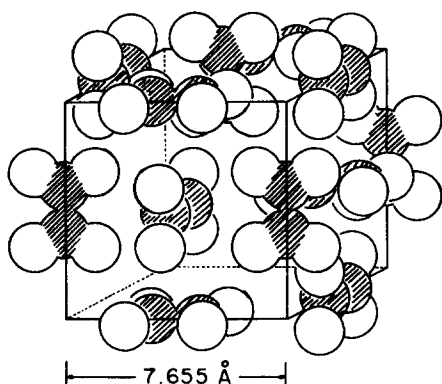


FIG. 1. Geometry of the  $\text{N}_2\text{O}_4$  molecule (from Ref. 3).

FIG. 2. Crystal structure of N<sub>2</sub>O<sub>4</sub> (from Ref. 2).

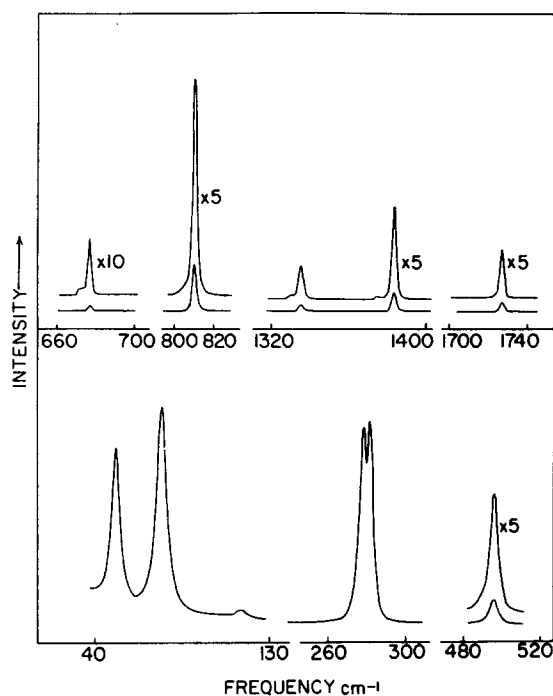
studies, with no peaks attributable to N<sub>2</sub>O<sub>3</sub>.<sup>14</sup> The gas was first deposited onto substrates at liquid nitrogen temperature in conventional cryostats. Samples grown in this way gave complex spectra with broad peaks which were not reproducible from run to run, presumably because of varying amounts of metastable forms of the N<sub>2</sub>O<sub>4</sub> molecule and crystal in the sample. On annealing to about 170 K and then recooling, reproducible simple spectra with sharp features were consistently obtained, which are interpreted as characteristic of the stable cubic crystal.

Spectroscopic equipment and techniques used in these experiments have been described in a recent review paper<sup>15</sup> and only an outline will be repeated here. Raman spectra were excited by the 514.5 nm line of an argon-ion laser (Spectra-Physics, 165) operating at about 0.4 W, analyzed with a Spex 1401 double monochromator, and detected by a cooled photomultiplier (RCA C31034) and photon counting electronics. Mid-infrared spectra (300–2000 cm<sup>-1</sup>) were obtained with a Beckman IR 12 filter-grating spectrometer with thermocouple detector. Far-infrared spectra (20–360 cm<sup>-1</sup>) were recorded with a Beckman-RIIC FS 620 Fourier spectrometer fitted with a germanium bolometric detector operating at 4 K. Substrates used were silver chloride or silver bromide in the mid-infrared, and copper blocks with inclined surfaces for the Raman<sup>16</sup> and far-infrared<sup>17</sup> experiments, as described previously.

## RESULTS

The observed Raman spectra of annealed samples cooled to 20 K are shown in Fig. 4, and corresponding

	Molecule	Site	Unit Cell	Activity
	D <sub>2h</sub>	D <sub>2h</sub>	T <sub>h</sub>	
$\nu_1 \quad \nu_2 \quad \nu_3$	A <sub>g</sub>	A <sub>g</sub>	A <sub>g</sub>	R
$\nu_5 \quad \nu_6 \quad R_z$	B <sub>1g</sub>	B <sub>1g</sub>	E <sub>g</sub>	R
$\nu_8 \quad R_y$	B <sub>2g</sub>	B <sub>2g</sub>	F <sub>g</sub>	R
$R_x$	B <sub>3g</sub>	B <sub>3g</sub>	F <sub>g</sub>	R
$\nu_4$	A <sub>u</sub>	A <sub>u</sub>	A <sub>u</sub>	—
$\nu_7 \quad T_z$	B <sub>1u</sub>	B <sub>1u</sub>	E <sub>u</sub>	—
$\nu_9 \quad \nu_{10} \quad T_y$	B <sub>2u</sub>	B <sub>2u</sub>	F <sub>u</sub>	IR
$\nu_{11} \quad \nu_{12} \quad T_x$	B <sub>3u</sub>	B <sub>3u</sub>	F <sub>u</sub>	IR

FIG. 3. Correlation diagram for crystalline N<sub>2</sub>O<sub>4</sub>.FIG. 4. Raman spectra of crystalline N<sub>2</sub>O<sub>4</sub> at 20 K (resolution  $\approx 1$  cm<sup>-1</sup>). For certain weak features, signal gain has been increased by the indicated factor.

infrared spectra are displayed in Fig. 5. The instrumental resolutions used for the various spectral regions are indicated in the captions for these figures. Frequencies of maximum intensity (Raman) and absorption (infrared) are listed in Table I with proposed assignments. Most of these are based on the work of Bibart

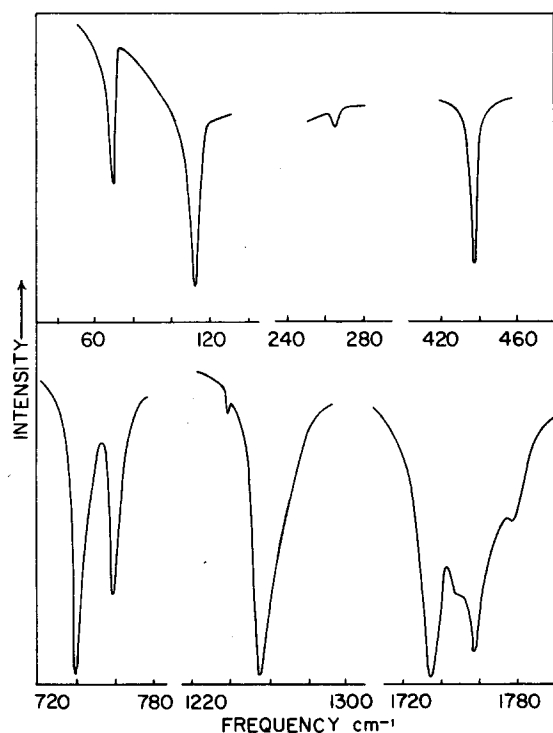
FIG. 5. Infrared spectra of crystalline N<sub>2</sub>O<sub>4</sub> at 20 K (resolution  $\approx 1$  cm<sup>-1</sup>).

TABLE I. Raman and infrared frequencies of solid  $N_2O_4$  at 20 K.

Raman		Infrared	
Frequency	Assignment	Frequency	Assignment
52	$\nu_{R1}$	71	$\nu_{T1}$
76	$\nu_{R2}$	113	$\nu_{T2}$
119	$\nu_{R3}$	265	$\nu_{10}$
180	$(\nu_{T1} + \nu_{T2})$	439	$\nu_7$
279	$\nu_3$	742	$\nu_{12}^a$
283		761	$(\nu_6 + \nu_{10})^a$
496	$\nu_6$	1240	$\nu_{11}$
677	$\nu_8$	1257	
$\sim 804^b$	$\nu_2$	1737	$\nu_9^a$
811			
$\sim 1330^b$	$2\nu_8^a$	1750	$(\nu_6 + \nu_{11})^a$
1336		1759	
1377	$\nu_1^a$	1780	
1384			
1727	$\nu_5$		

<sup>a</sup>Suggested Fermi resonances.<sup>b</sup>Observed as shoulders.

and Ewing,<sup>7</sup> while others will be discussed in the next section.

## DISCUSSION

### Raman spectra

The totally symmetric modes  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  are predicted to be doublets in the crystal, as a result of coupling between molecules in the unit cell. The  $\nu_3$  vibration near 280  $cm^{-1}$  most clearly shows this splitting, with two peaks of approximately equal intensity, separated by about 4  $cm^{-1}$ , clearly resolved. A weak low frequency component of  $\nu_1$  is also detected (7  $cm^{-1}$  from the strong peak at 1384  $cm^{-1}$ ), and a weak low frequency shoulder is also seen in the  $\nu_2$  region ( $\sim 810$   $cm^{-1}$ ). These are probably the result of correlation field splittings, since the peaks from isotopic species ( $^{15}N^{14}N^{16}O_4$  and  $^{14}N_2^{18}O^{16}O_3$ ) are expected to be even weaker than those observed, on the basis of their natural abundances. The remaining three Raman molecular fundamentals  $\nu_5$ ,  $\nu_6$ , and  $\nu_8$  are all observed as singlets in accord with group theoretical predictions. An additional peak is observed at 1336  $cm^{-1}$ , which is most probably the overtone  $2\nu_8$  in Fermi resonance with  $\nu_1$ , as first suggested by Begun and Fletcher.<sup>12</sup>

In the lattice region, two strong peaks and a much weaker band at higher frequency are observed. These are assigned as the three predicted fundamental librational modes, corresponding to rotations about the molecular axes; that about the N-N axis should have the highest frequency (smallest moment of inertia), that about an axis perpendicular to the plane of the molecule should have the lowest, if it is assumed that the intermolecular restoring forces for these librations are comparable. However, since the three modes are all of the same symmetry ( $F_g$ ), substantial mixing may occur, with the result that the above labels would at best be only approximate. The two strong peaks were observed in the early study by Sutherland,<sup>8</sup> who also recorded a weak feature at 29  $cm^{-1}$  in the anti-Stokes

spectrum. Careful checks were made in the present work, with the use of a third monochromator (Spex 1442), and a weak shoulder on the tail of the exciting line was sometimes detected in this region, but only from samples which had been poorly annealed. A very weak peak is also observed at 180  $cm^{-1}$ , which is probably a combination of the two fundamental infrared lattice modes (71 + 113  $cm^{-1}$ ). An alternative assignment is that this peak is the overtone of the inactive torsional mode  $\nu_4$ , which has been predicted<sup>7</sup> to have a frequency of about 79  $cm^{-1}$ .

### Infrared spectra

We will first deal with the lattice region, since the location of all predicted lattice modes is an important step in the assignment of some higher frequency absorptions. In the far-infrared region ( $< 200$   $cm^{-1}$ ), two strong peaks are observed which are readily assigned as the two fundamental translational modes predicted for the  $N_2O_4$  cubic crystal. It is noted that all zone-center lattice fundamentals (Raman and infrared) fall in the 50–120  $cm^{-1}$  range. A weak peak is also seen at 265  $cm^{-1}$ . This is assigned as the "missing" internal mode  $\nu_{10}$  predicted<sup>7</sup> to have a frequency of around 270  $cm^{-1}$ . To our knowledge, this is the first direct observation of this fundamental.

According to group theory, all five infrared active molecular fundamentals should remain as singlets in the crystal. This is confirmed for  $\nu_{10}$ , mentioned above, and also  $\nu_7$ , which has a frequency of 439  $cm^{-1}$ . However, multiplets are observed for the other three modes  $\nu_9$ ,  $\nu_{11}$ , and  $\nu_{12}$ , in agreement with other experimental studies, but in apparent violation of theoretical predictions.  $\nu_{11}$  is seen as a strong peak at 1257  $cm^{-1}$ , with a weak low frequency component at 1240  $cm^{-1}$ , which probably corresponds to an isotopic molecular species.

The strong doublet, with separation between components of 19  $cm^{-1}$ , observed in the  $\nu_{12}$  ( $\sim 750$   $cm^{-1}$ ) region has been interpreted as the fundamental and a combination with lattice mode.<sup>4,10,11</sup> However, the higher frequency component appears to be too strong and sharp for this to be the correct interpretation. Moreover, there is no evidence from the present work that lattice modes with this low a frequency (except, of course, acoustic modes) are present in  $N_2O_4$ . A preferred explanation is that the extra peak results from a Fermi resonance, similar to that postulated for the  $\nu_1$  region of the Raman spectrum.<sup>12</sup> The symmetry species of the  $\nu_{12}$  mode is  $B_{3u}$ . Of the various combinations having this symmetry (from the direct product rules<sup>18</sup>), that corresponding to  $\nu_6$  ( $B_{1g}$ ) +  $\nu_{10}$  ( $B_{3u}$ ) has a sum frequency of 496 + 265 = 761  $cm^{-1}$ , which corresponds (exactly!) to the weaker higher frequency component observed in the  $\nu_{12}$  region.

In the vicinity of the  $\nu_9$  fundamental (1720–1800  $cm^{-1}$ ), a complex absorption is observed with two strong peaks and two shoulders instead of the predicted singlet. For reasons similar to those discussed above, the explanation in terms of combinations with lattice modes is unlikely, and once again a Fermi resonance interpreta-

tion is preferred. The combination  $\nu_6(B_{1g}) + \nu_{11}(B_{3u})$  has the same  $B_{2u}$  symmetry as  $\nu_9$  and approximately the same frequency ( $496 + 1257 = 1753 \text{ cm}^{-1}$ ), in this case within  $6 \text{ cm}^{-1}$  of the weaker higher frequency component of the doublet. The additional shoulders observed could result from combinations of these fundamentals throughout the Brillouin zone, the final absorption profile depending on the small dispersion effects and densities of states for these branches. Alternatively, these shoulders could result from ternary combinations.

## CONCLUDING REMARKS

In this spectroscopic investigation of crystalline N<sub>2</sub>O<sub>4</sub> in its stable form (planar  $D_{2h}$  molecules in a cubic  $T_h^5$  lattice), all molecular fundamentals (except the optically inactive torsional mode  $\nu_4$ ) have been observed with the expected activities and number of components. A new low frequency internal mode is observed in infrared absorption with a wave number close to that predicted from entropy considerations. Additional peaks are attributed to combination bands in Fermi resonance with fundamentals. Five lattice modes have been detected and assigned, and form the experimental basis for a lattice dynamical calculation of the N<sub>2</sub>O<sub>4</sub> crystal, based on the rigid molecule approximation and using Lennard-Jones potentials to represent the atom-atom interactions. Such a computation is in progress in this laboratory and details will be presented in a future publication.

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- <sup>1</sup>*Encyclopedie des Gaz* (Elsevier, Amsterdam, 1976).
- <sup>2</sup>J. S. Broadley and J. M. Robertson, *Nature* (London) **164**, 915 (1949).
- <sup>3</sup>B. S. Cartwright and J. H. Robertson, *Chem. Commun.* **3**, 82 (1966).
- <sup>4</sup>W. G. Fateley, H. A. Bent, and B. Crawford, *J. Chem. Phys.* **31**, 204 (1958).
- <sup>5</sup>I. C. Hisatsune, J. P. Devlin, and Y. Wada, *J. Chem. Phys.* **33**, 714 (1960).
- <sup>6</sup>P. Groth, *Acta Chem. Scand.* **17**, 2419 (1963).
- <sup>7</sup>C. H. Bibart and G. E. Ewing, *J. Chem. Phys.* **61**, 1284 (1974).
- <sup>8</sup>G. B. B. M. Sutherland, *Proc. R. Soc. London Ser. A* **141**, 535 (1933).
- <sup>9</sup>P. Gray and A. D. Yoffe, *Chem. Rev.* **55**, 1069 (1955).
- <sup>10</sup>R. G. Snyder and I. C. Hisatsune, *J. Mol. Spectrosc.* **1**, 139 (1957).
- <sup>11</sup>R. N. Wiener and E. R. Nixon, *J. Chem. Phys.* **26**, 906 (1956).
- <sup>12</sup>G. M. Begun and W. H. Fletcher, *J. Mol. Spectrosc.* **4**, 388 (1960).
- <sup>13</sup>I. C. Hisatsune, *Adv. Mol. Spectrosc.* **3**, 982 (1959).
- <sup>14</sup>C. H. Bibart and G. E. Ewing, *J. Chem. Phys.* **61**, 1293 (1974).
- <sup>15</sup>A. Anderson, J. W. Leech, and B. H. Torrie, *Ind. J. Pure Appl. Phys.* **16**, 243 (1978).
- <sup>16</sup>A. Anderson, T. S. Sun, and M. C. A. Donkersloot, *Can. J. Phys.* **48**, 2265 (1970).
- <sup>17</sup>A. Anderson and H. A. Gebbie, *Spectrochim. Acta* **21**, 883 (1965).
- <sup>18</sup>E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955), p. 331.