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RAMAN EFFECT IN DEUTERO-NITRIC ACID

By Dr. G. B. BANERJI, M.Sc., Ph.D. (Lond.)

AND

B. MISHRA, M.Sc.

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Plate XVIII.

ABSTRACT. Deutero-nitric acid has been prepared by the action of nitrogen pentoxide on heavy water. The Raman spectra of the acid have been photographed and consist of frequencies 166, 589, 667, 790, 905, 1017, 1293, 1536, 1640, 1849, 1972 and 2455 (band). By comparison with HNO_3 it has been found possible to calculate the isotope shifts and also to explain the origin of the vibrations in DNO_3.

INTRODUCTION

Since the isolation of heavy water, a large number of experimenters have studied the Raman frequencies of various compounds in which hydrogen is replaced by deuteronium. The results have led to measurable isotope shifts and have served as a check to theoretical developments in this connection. Leckie[1] prepared Deutero-sulphuric acid and photographed the Raman spectra of the 100% acid and also of the acid in various dilutions of heavy water. Small but definite isotope shifts have been recorded. Nitric acid has a number of Raman frequencies and it was thought desirable to prepare Deutero-nitric acid and study the Raman effect in 100% acid.

EXPERIMENTAL ARRANGEMENTS

After various trials, DNO_3 was prepared by the action of N_2O_5 on heavy water. In order to prepare N_2O_5, a mixture of strong nitric and sulphuric acid was first distilled. The nitric acid thus obtained was mixed with phosphorus pentoxide and distilled. The distillate was cooled by freezing mixture and consisted of solid N_2O_5. This was purified and a small weighed quantity of the solid was taken and to it a definite quantity of heavy water(100%) was added as required by the reaction $D_2O + N_2O_5 = 2DNO_3$. For this work only 5 c.c. of the acid was prepared. The acid thus obtained looked slightly brown due to the presence of nitrous fumes. To make it transparent a small current of perfectly dry air was passed through it for about an hour, care being taken to avoid contamination with moisture. After the completion of the work, the strength of DNO_2 was tested and found to be 98%.

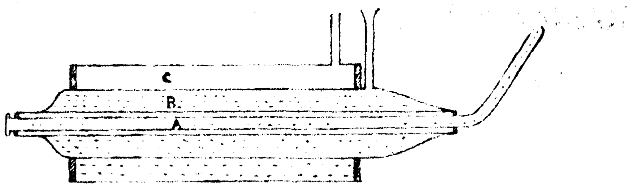

FIG. 1

The acid was transferred to a glass tube A (Fig. I) with one end blown flat and the other end was quickly sealed off. The tube was about 25 cm. long and had a bore of 4 mm. only. Some 3 c.c. of liquid was sufficient for investigation.

To avoid complications, Raman spectra was produced by filtering out all lines of the mercury arc other than the 4358 group. With this view, a simple piece of pyrex glass apparatus (Fig. I) was blown. The experimental tube was surrounded by two jackets B and C containing a very dilute solution of iodine in carbon tetrachloride and a concentrated solution of sodium nitrite in water respectively. The former solution absorbed the wave-lengths longer than 4358 Å, while the latter absorbed shorter wave-lengths. The whole arrangement was quite handy.

A bent mercury arc of pyrex glass, like the one devised by Ananthakrishnan [2] was employed. This surrounded the central part of the apparatus.

Two card-boards were slipped over the jacket C at its two ends and these allowed the light from the mercury arc to fall only over the middle part of the experimental tube.

The mercury arc was run at 4 amperes and the exposure lasted for 80 hours in the case of DNO_3. For photographing a Hilger spectrograph with a very dense flint glass prism was employed.

RESULTS

The wave-lengths of all the Raman lines were measured with the help of Hartmann's formula, taking known lines of copper arc as standard. Nearly all the lines are rather broad and there may be a maximum error of 5 in the reported frequencies.

Plate XVIII is a reproduction of the spectrum obtained, in which the stronger Raman lines of DNO_3 can be seen. All the Raman lines for DNO_3 are listed in the following table :—

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PLATE VIII.

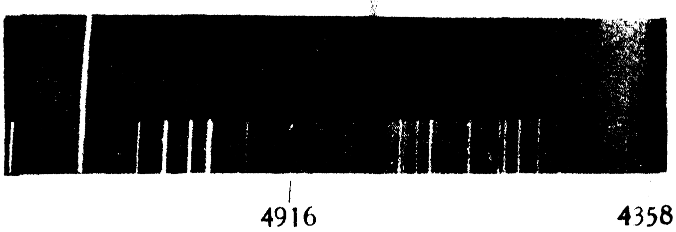


TABLE I

Raman shifts for DNO_3 (98%)

Wave-lengths of Raman lines	Frequencies	Shift in $cm.^{-1}$
4391.41 (2d)	22772	166
4474.48 (0)	22349	589
4480.20 (2)	22281	667
4515.01 (0)	22148	790
4538.73 (4)	22033	905
4561·76 (1)	21921	1017
4619.92 (10)	21645	1293
4672.47 (2)	21402	1536
4695.17 (2b)	21298	1640
4741.80 (0)	21089	1849
4769.53 (0)	20966	1972
4882.1 (Band)	20483	2455

For correlating the Raman spectra of DNO_3 with HNO_3, we have taken a few photrgraphs with a sample of 80% HNO_3. In table II, the Raman frequencies obtained by us are listed as also those by other workers working with 100% acid. It will be seen that a new broad line with a shift of 1779 $cm.^{-1}$ has been obtained by us.

TABLE II

Raman Frequencies for 100% Nitric acid

Angus and Leckie [3]	Dadieu and Kohlrausch [4]	Medard and Volkringer [5]	Aderhold and Weiss [6]	Present Authors (80% acid)	Mean
608 (3)	607	613	607	627 (2)	613 (2)
679 (4)	667	675	667	682 (2b)	674 (2b)
924 (6)	916	923	—	935 (5)	924 (5)
1064 (2)	—	1048	—	1041 (2)	1051 (2)
1126 (0)	—	1103	—	—	1115 (0)
1297 (8b)	1292	1295	1291	1302 (10b)	1296 (10)
1407 (1)	—	—	—	—	1407 (1)
1516 (1)	—	1537	—	—	1527 (1)
1611 (0)	—	—	—	—	1611 (0)
—	1665	1679	1665	1674 (2)	1679 (2)
1699 (4)	1687	—	1687	—	—
—	—	—	—	1779 (2b)	1779 (2b)
—	3420 (Band)	—	—	—	3420 (Band)

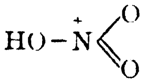
From the intensities and natures of the lines for HNO_3 and DNO_3 acids it is easy to find out the wave-numbers for similar modes of vibrations. This is done in table III.

TABLE III

Raman frequencies for HNO_3	Raman frequencies for DNO_3	Isotope shift in cm.$^{-1}$	Origin of vibration
—	166 (2d)	—	—
613 (2)	589 (0)	26	p_1
674 (2b)	667 (2)	7	p_2
—	790 (0)	—	—
924 (5)	905 (4)	19	ω_1
1051 (2)	1017 (1)	34	ionic
1115 (0)	—	—	p_3
1296 (10)	1293 (10)	3	ω_2
1407 (1)	—	—	ionic
1527 (1)	—	—	—
1647 (0)	—	—	—
1685 (2)	1536 (2)	149	p_4
1779 (2b)	1640 (2b)	139	—
—	1849 (0)	—	—
—	1972 (0)	—	—
3420 (Band)	2455 (Band)	935	OH. OD bands

DISCUSSIONS

Let us first consider the modes of vibrations in HNO_3. In dilute solutions, the only line which gains in intensity is 1051 cm.$^{-1}$ and hence this line is regarded as due to the dissociated molecule of nitric acid. The NO_3 ion has probably a plano-symmetric structure and the frequency 1051 represents the symmetric and parallel vibrations of the nitrogen atom.

Venkateswaran[7] has attributed the formula  $HO-\overset{+}{N}{<}^{O}_{O}$ to nitric acid and taking the configuration AB_3, where all the B atoms are different and the atom A at the apex of the pyramid, the Raman frequencies of Nitric acid can be adequately explained. The two strong frequencies 924 and 1296 are to be attributed to the two parallel vibrations of the AB_3 group in nitric acid. These two vibrations are represented by ω_1 and ω_2 in table III. The four perpendicular vibration frequencies are 613, 674, 1115 and 1685. These are represented by p_1, p_2, p_3 and p_4 in table III. In Deutero-nitric acid the two corresponding parallel vibrations are 905 and 1293. In DNO_3 three of the four perpendicular vibrations have appeared, namely 589, 667 and 1536.

Venkateswaran has pointed out that the excitation of the line with an apparent shift of 1685 $cm.^{-1}$ is due to 4046 line of mercury arc. The authors took a number of photographs by avoiding the 4046 group of lines with a concentrated sodium nitrite solution and confirmed that the line is actually excited by 4358 line of mercury arc. There is also a similar type of line in DNO_3 at 1536 with an isotopic shift of 149 cm^{-1}.

The band at 2455 with DNO_3 extends over 150 wave-numbers and is due to the OD bond. The double lines, recorded as 167 in DNO_3 are probably to be attributed to lattice structure.

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