with the viscosity of another ring molecule, naphthalene

$$\eta_{C_{10}H_8} = \frac{Nh}{112} e^{-6.7/R + 6{,}300/RT}$$

Both substances have rather high heats of activation, and positive entropies of activation.

The viscosity of polysulfur may be compared with the viscosity of a polyester

$$\eta_{\text{polyester}} = \frac{Nh}{500} e^{-6.8/R + 8{,}200/RT + 0.5\, Z_w^{1/2}/R}$$

Both substances have rather high heats of activation, and the two values of B are similar.

All of the above results provide a general confirmation, as well as a detailed description, of the postulated chain structure of polysulfur.

Acknowledgment.—The authors wish to express their appreciation to Drs. Bacon and Fanelli for permission to use their data in advance of publication, and for valuable discussion.

Summary

1. The available measurements of the equilibria between 8-membered sulfur rings and sulfur chains of all lengths are interpreted in terms of a quantitative thermodynamic theory.

2. Using the values of molecular composition so determined, the viscosity is formulated in terms of current theories and the calculated and experimental values compared. The decreases in viscosity due to impurities, observed by Bacon and Fanelli, are compared with theory.

PRINCETON, NEW JERSEY RECEIVED SEPTEMBER 18, 1942

[DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

Raman Spectrum and Molecular Vibrations of Nitric and Deuteronitric Acids

BY O. REDLICH AND L. E. NIELSEN[1]

The interpretation of vibration spectra has been considerably lagging behind the rapid accumulation of experimental data. While the Raman spectra of many hundreds of compounds have been recorded, a complete or nearly complete correlation of frequencies and vibration forms has been ascertained for only a small number of substances.

The Raman spectrum of few compounds has been investigated as frequently as that of nitric acid.[2] In addition, solutions of various concentrations have been examined by many authors.

Among the various attempts of interpretation,[3] that of Chédin is outstanding. This author made full use of all available methods, namely, Placzek's polarization rules, the comparison with the spectra of the nitrate ion, organic nitrates and nitro compounds, and Bjerrum's force systems. Nevertheless, even Chédin's results are far from complete and sufficiently certain. It was obvious that entirely new experimental data were necessary for any further progress.

New data may be obtained by an investigation of deuteronitric acid. The ratio of the corresponding frequencies of the hydrogen and deuterium compound, which will be called the "isotopic quotient" and denoted by q, is a measure of the extent to which the hydrogen participates in the vibration. The isotopic quotient assumes the value 1 if the hydrogen does not oscillate, and the value $\sqrt{2}$ if the vibration is carried out by the hydrogen alone. Thus the isotopic quotients furnish sometimes an immediate criterion of interpretation.

In addition, the regrouping of the lines in the spectrum of the deuterium compounds is sometimes instrumental in the discovery of anomalies of a purely experimental nature (superposition of lines) as well as in the frequencies themselves (Fermi resonance[4]).

Several authors made successful use of the so-called product formula, derived independently by Teller and by the senior author.[5] This formula furnishes relations between the vibration frequencies of isotopic molecules, the atomic masses

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[1] Present address: Department of Chemistry, Cornell University, Ithaca. N. Y.

[2] (a) A. Dadieu and K. W. F. Kohlrausch, *Naturwissenschaften*, **19**, 690 (1931). (b) L. Médard and H. Volkringer, *Compt. rend.*, **197**, 883 (1933). (c) W. R. Angus and A. H. Leckie. *Proc. Roy. Soc.* (London). **A149**, 327 (1935). (d) B. Susz and E. Briner, *Helv. Chim. Acta*, **18**, 387 (1935). (e) J. Chédin, *Ann. Chim.*, **8**, 243 (1937).

[3] (a) J. Chédin. *J. phys. radium*, **10**, 445 (1939). (b) C. S. Venkateswaran, *Proc. Indian Acad. Sci.*, **A4**, 174 (1936). (c) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **4**, 711 (1936); *cf.* also refs. 2a, **14**.

[4] *Cf.* the case of deuterobromoform, O. Redlich and W. Stricks, *Sitzber. Akad. Wiss. Wien, Math.-natur.-w. Klasse*, IIb, **145**, 192 (1936), or *Monatsh.* **67**, 213 (1936).

[5] O. Redlich, *Z. physik. Chem.*, **B28**, 371 (1935).

and the moments of inertia. It is strictly valid for harmonic frequencies, a fairly close approximation for the experimental values. The deviations can be roughly estimated, to some extent, by means of a few generalizations recently discussed.[6]

With the aid of the isotopic quotients and the product formula we hoped to secure a reliable interpretation of the six frequencies previously recognized as fundamentals. Beyond this expectation, the present report includes the complete spectra (nine frequencies) of both acids and a correlation to the proper vibrations which in the main is believed to follow necessarily from the experimental data.

Experimental Details

A spectrograph Type L256, Gaertner, with two glass prisms of 80-mm. height (Bausch and Lomb) was used. Since we wished a somewhat higher dispersion, the instrument had been equipped by the manufacturer with a Tessar camera lens of 500-mm. focal length instead of the 300-mm. of the standard type. The dispersion at 4000 and 5000 Å. is 76 and 138 cm.$^{-1}$ per mm., respectively. Owing to the large dimensions of the prisms and lenses, the intensity of this instrument is so high anyway that the gain in dispersion is well worth the loss in intensity. With 60 ml. of nitric acid and a slit width of 0.06 mm., an exposure of eight minutes was sufficient to produce a strong spectrum on Eastman Kodak Co. Ia-O plates.

Water-cooled mercury lamps of the U-shaped type first used by Yost were made of 10 mm. o. d. "Pyrex" tubing. The length of the arc was twice 200 mm. A current of 8 or 9 amp. was used at an arc voltage of about 60 v.

Two types of cells were used, made of 22 mm. and 12 mm. o. d. Pyrex tubing, with capacities of 60 and 15 ml., respectively. Only the smaller type was used for deuteronitric acid. The cell was mounted horizontally, the arc slightly (1:10) tilted, both were encased in an elliptic aluminum mirror. The center lines of the arc and the cell were 60 mm. apart.

Iron arc spectra were taken on the middle portion of the spectrum in the usual way. A large Gaertner comparator was used for measuring.

Three spectra each of nitric acid and deuteronitric acid were taken with slit widths of 0.01 and 0.06 mm. on Eastman Kodak Co. spectrographic plates Ia-O and I-J. Sodium nitrite solution was used as a filter in one nitric acid and all deuteronitric acid exposures. Exposure times were one-half to seven hours.

Samples of anhydrous nitric acid were prepared by one or two vacuum distillations from a sulfuric acid solution. Titration with sodium hydroxide solution gave values of 100.0 to 100.3% nitric acid.

Addition of the proper amount of heavy water to dry nitrogen pentoxide furnished anhydrous deuteronitric acid.

Two methods were considered for preparing nitrogen pentoxide, namely, dehydration of nitric acid by means of phosphorus pentoxide, and oxidation of dry nitrogen tetroxide by means of ozone. Following the kind advice of Professor F. Daniels, we chose the latter way, which is especially preferable where minute amounts of water are harmful.

All operations were carried out in a glass apparatus all parts of which were sealed to one another, except that the pentoxide receiver was connected to the main apparatus by means of a ground glass joint. The apparatus included an ozonizer similar to that constructed in this Laboratory by Levene.[7] Phosphorus pentoxide tubes were provided for in suitable places. Dry-ice was used for condensing.

Nitrogen tetroxide prepared from lead nitrate was twice redistilled through phosphorus pentoxide in an oxygen stream. The oxygen–ozone stream and nitrogen tetroxide, carried over by a suitably regulated oxygen stream, were mixed at such a rate that the mixture was colorless.[8] This operation required about thirty hours. The pentoxide, redistilled in an ozone stream, was pure white. Heavy water (99.5%) was added from a microburet to the container, which was kept in dry-ice. The reaction was started by cautiously warming the vessel, and proceeded smoothly. A slight yellow tinge was quickly removed by ozone. A sample of 35 g. of deuteronitric acid was prepared.

In order to allow for traces of water which might be absorbed in subsequent operations, we had added slightly less than the equivalent amount of heavy water. Two weight titrations with normal sodium hydroxide solution gave 100.34 and 100.28 g. of acid, calculated as $H_{0.005}D_{0.995}$-NO_3, in 100 g. of solution.

The acids were sealed in the cells and kept in the refrigerator. After a couple of exposures they showed slight decomposition and were easily reoxidized by means of ozone.

Density and Refractivity

The density of the deuteronitric acid was determined in a 12-ml. pycnometer at 25.00°. The result was 1.5239 g./ml. Correction for the excess of pentoxide and for the hydrogen content gives 1.5228 g./ml. for pure deuteronitric acid, the last place being uncertain.

The refractivity for sodium light of both acids was determined by means of a Pulfrich refractometer (Zeiss). As no cement would withstand

TABLE I

DENSITY AND REFRACTIVITY OF NITRIC AND DEUTERONITRIC ACIDS

	HNO_3	DNO_3
Density (25.00°)	1.50281[a]	1.5228
Molal volume	41.932[a]	42.04
Refractivity (25.0°)	1.3920[b]	1.3909
Molar refraction	9.99[b]	9.99

[a] Slightly extrapolated from the data of R. Lühdemann, *Z. physik. Chem.*, **B29**, 133 (1935). [b] Lühdemann gives 1.39316 and 10.01, respectively.

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(6) O. Redlich, *J. Chem. Phys.*, **9**, 298 (1941).

(7) A. A. Levene, *Northwest Science*, **3**, 19 (1929).

(8) *Cf.* O. R. Wulf, F. Daniels and S. Karrer, THIS JOURNAL, **44**, 2398 (1922).

TABLE II

FREQUENCIES OF HNO$_3$ AND DNO$_3$ IN CM.$^{-1}$

	HNO$_3$	HNO$_3$	HNO$_3$	HNO$_3$	HNO$_3$	HNO$_3$	DNO$_3$	Quotient	Vibration
	Dadieu	Médard	Angus	Susz	Chédin	This investigation		q	number
a	3420	3385	..	..	..	(b) 3386 ± 20	2476 ± 15	1.368 ± 0.010	7
b	1687	1679	1699	1683	1672	(8) 1680 ± 2	1336 ± 10	1.266 ± .008	8
c	1665	..	1611	1665	..	....	1645 ± 2	1.015 ± .002	4
d	..	1537	1516	1538	1516	(4) 1538 ± 1	1534 ± 2	1.003 ± .001	6
e	..	..	1407	..	1400	(4) 1394 ± 2	1393.5 ± 1	....	N$_2$O$_5$
f	1292	1293	1297	1297	1295	(20) 1301 ± 1	1305 ± 6	0.997 ± .005	1
g	..	1048	1064	1041	1050	(2) 1049 ± 6	1036 ± 3	....	N$_2$O$_5$
h	916	922	924	921	922	(15) 926 ± 1	924 ± 1	1.002 ± .002	2
i	667	675	679	668	674	(10) 675 ± 3	672.5 ± 1	1.004 ± .004	3
k	607	612	608	606	608	(8) 607 ± 3	570.5 ± 2	1.066 ± .007	5
l	..	..	..	..	..	(1) 480 ± 15	370 ± 10	1.30 ± .05	9

the action of the anhydrous nitric acid even for a few minutes, the glass ring cemented on the prism was removed. The metal cylinder which usually is dipped in the liquid to keep its temperature defined, was replaced by a glass tube with flat bottom. With proper adjustment one drop of the acid gave perfect readings. The results are given in Table I.

The instrument was first checked according to the directions given by the manufacturer and then, shortly before each of the measurements on nitric acid, by means of redistilled water and carbon tetrachloride[9] for which the values 1.3325 and 1.4574 (25.0°) were taken as standard.[10] Our readings were lower by 0.0003 and 0.0001 before the determinations on nitric acid and deuteronitric acid, respectively, and the corresponding corrections were applied. The correction for excess pentoxide is negligible.

Frequencies

The spectrographic results are listed in Table II, together with the data given for nitric acid by earlier observers.[2] The figures in parentheses as usual indicate the roughly estimated intensities. All frequencies were found as excited by the blue mercury line. In addition, the anti-Stokes lines of the frequencies denoted by h, i and k were found, and in the unfiltered spectrum most frequencies appeared as excited by the two strong violet mercury lines.

We were unable to detect the line 1103 (Médard) or 1126 (Angus) in HNO$_3$. We found three very weak lines in DNO$_3$, namely, (approximately) 2245; 1945; 1885. Obviously these are the combination frequencies: 1305 + 924; 1305 + 672; 924 + 924.

In order to establish a secure basis of the interpretation we have to discuss a few details.

The fairly broad line 1680, was resolved in a doublet (b and c) by two of the five earlier observers. Although our spectra were taken under widely varied conditions (for another purpose many more spectra were taken, though not measured) the resolution could not be confirmed; nor did a microphotometer tracing[11] show any irregularity to be interpreted as due to a doublet. We suppose that the resolution can be achieved by working at a low temperature though neither Dadieu and Kohlrausch nor Susz and Briner mention cooling during the exposure. Assuming that the centers of the two constituent lines are 22 cm.$^{-1}$ apart as found by Dadieu and Kohlrausch, we adopt 1691 and 1669 as final values.

We are unable to explain the value 1516 given for line d by two observers.

According to Susz and Briner and to Chédin, the lines e and g are undoubtedly due to nitrogen pentoxide. The remarkable sharpness of e has been pointed out by all observers. As a medium effect, the isotopic shift of g is surprisingly large.

In the spectrum of deuteronitric acid, the lines 1336 and 1305, denoted by b and f, are partially superimposed. The line b was discovered when our first measurements consistently gave the higher value 1312 for f in deuteronitric acid, as compared with 1301 in nitric acid. The superposition was then unmistakably found in all three spectra. We resolved the microphotometric curve (full line in Fig. 1) into the constituent curves (broken lines), assuming that the component curves are symmetric. In this graph we determined the frequencies of b and f by measuring the distances from e. No complexity of the line f was found in the spectra of nitric acid.

The weak, diffuse line l had been marked and measured in our routine procedure in one spec-

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(9) We are indebted to Dr. P. W. Schutz for a sample of highly purified carbon tetrachloride.

(10) "International Critical Tables," Vol. 7, pp. 13, 77.

(11) We wish to thank Mr. J. Bigeleisen, University of California, Berkeley, for taking the microphotometric curves.

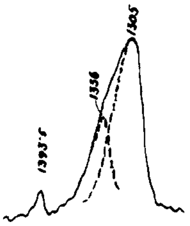

Fig. 1.—The full line represents a microphotometric curve of the lines e = 1393.5 and f = 1305 of deuteronitric acid. As line f of nitric acid is symmetric, the asymmetry of the curve in the region of f indicates the presence of another line. The broken lines represent the constituent curves, obtained by assuming that the constituent curves are symmetric.

trum each of nitric acid and deuteronitric acid. Later, when it was realized that this line represented the last fundamental, a careful inspection revealed its occurrence in one more spectrum of nitric acid and both remaining ones of deuteronitric acid. The reality of this line, not found by earlier observers, appears to be established.

Vibrations

The configuration of nitric acid has been determined by Maxwell and Mosley.[12] According to their electron diffraction measurements, the molecule most probably is plane, the parameters being

N═O	1.22 Å.	angle O═N═O	130°
N—O (hydroxyl)	1.41 Å.	angle O═N—O	115°

The position of the hydrogen cannot be determined by means of this method. Following Forsythe and Giauque,[13] we assume

O—H	0.96 Å.	angle N—O—H	90°

This configuration corresponds to the symmetry C_s, that is, the molecule possesses only one symmetry plane σ_x which is the plane of the molecule. However, it is useful to discuss, in addition, a simplified model in which the hydroxyl group is considered as a single unit, located in the place of the oxygen. The symmetry of this model is C_{2v}, consisting of a twofold symmetry axis, which will be taken as z-direction, and two symmetry planes σ_x and σ_y through the axis, the latter being normal to the plane of the molecule.

The simplified model implies the assumption that the hydroxyl group is rigid in six vibrations (1 to 6), the remaining three being carried out essentially by the hydrogen.

The classification of the vibrations for C_s and C_{2v} according to Placzek is given in Table III. As usual, the symbols s, a, T and R stand for symmetric, antisymmetric, translation and rotation.

TABLE III

SYMMETRY TYPES

Symmetry type	C_s	Proper vibr.	Improper vibr.	Proper vibr.	Symmetry C_{2v} C_2	σ_x	σ_y	Type
A'	s	1–5,7,8	T_z	1,2,3	s	s	s	A_1
			T_y,R_x	4,5	a	s	a	B_2
A''	a	6,9	R_z	..	s	a	a	A_2
			T_x,R_y	6	a	a	s	B_1

The diagrams in Fig. 2 indicate the approximate forms of the vibrations 1 to 6. The center circle in these diagrams represents the nitrogen, the upper the hydroxyl group, the two lower ones the oxygens. The vibrations 7, 8 and 9 are essentially the stretching, and the bending vibration of the hydrogen in the molecular plane, and the restricted internal rotation of the hydrogen around the z-axis.

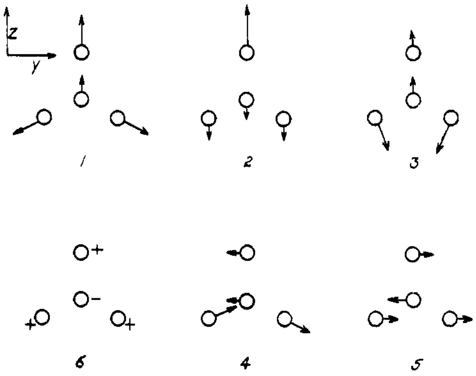

Fig. 2.—Approximate forms of the vibrations of (HO)-NO_2. The upper circles represent the hydroxyl group.

From the structural parameters the products of the isotopic quotients[5] were calculated according to Table III. The results are listed in Table IV.

TABLE IV

PRODUCTS OF THE ISOTOPIC QUOTIENTS AND QUOTIENTS FOR THE HYDROGEN VIBRATIONS

Type		Vibrations	Product calcd.	Product obs.
C_s	A'	1–5,7,8	1.938	1.875 ± 0.016
	A''	6,9	1.362	1.30 ± .05
C_{2v}	A_1	1,2,3	1.0211	1.006 ± .007
	B_2	4,5	1.0106	1.082 ± .008
	B_1	6	1.0013	1.003 ± .001
....	..	7	1.388	1.368 ± .010
....	..	8	1.403	1.266 ± .008
....	..	9	1.397	1.30 ± .05

In the simplified model, the symmetry axis or z-axis represents one of the principal axes of

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[12] L. R. Maxwell and V. M. Mosley, *J. Chem. Phys.*, **8**, 738 (1940).

[13] W. R. Forsythe and W. F. Giauque, THIS JOURNAL, **64**, 48 (1942).

inertia. However, in the model C_s this axis is turned opposite to the hydrogen atom by about 30° and the principal moments of inertia with respect to the two axes in the molecular plane are to be calculated by means of the formula

$$I = {}^1/_2(I_y + I_z) \pm 2D(I_y - I_z)[4D^2 + (I_y - I_z)^2]^{-1/2}$$

where D denotes the corresponding moment of deviation. While the more precise computation changes the values of the two moments of inertia quite appreciably, the product, which alone is involved in Table IV, is practically equal to I_yI_z.

The values of the isotopic quotients of the vibrations 7, 8 and 9, added to the product values in Table IV, were calculated from the assumption that the hydrogen oscillates against the rigid nitrate radical. This assumption involves an appreciable rotation of the nitrate radical around the x-axis in vibration 7. The similar effect is negligible in vibration 8.

The isotopic quotient of vibration 9 cannot be higher than the product 1.362 for type A''. The value 1.397 is found if vibration 9 is treated as a "restricted internal vibration." The discrepancy demonstrates the fact that the actual motion necessarily must be somewhat more complicated. This is not surprising as vibration 9 has to satisfy three conditions of conservation (linear momentum in the x-direction, angular momentum around the two principal axes in the molecular plane).

The two simplified models $(HO)NO_2$ and $H(NO_3)$ are by no means a strict consequence of the assumption that certain cross terms of the potential energy may be neglected. In addition, terms of the order of magnitude of the ratio of the masses $H:HNO_3$ are neglected. The errors involved do not cancel in the isotopic quotients. Therefore, not too much must be expected of the simplified models.

Correlation of Frequencies and Vibrations

Vibrations 1 and 2.—The interpretation of the lines f and h (Table II) as vibrations 1 and 2 (Table III, Fig. 2) has been unquestionably established by Chédin.[3] Both are strongly polarized and belong, therefore, to symmetry class A_1. The ratio of the two frequencies is $\sqrt{2}:1$ as to be expected for double and single bonds between the same atoms.

The results on deuteronitric acid agree with this assignment.

Vibration 7.—The reality of line a, which has been the subject of some discussion,[14] and its interpretation as the hydrogen stretching vibration cannot be doubted.[14a]

The isotopic quotient (Table IV) is 1.5 ± 0.7% below the value calculated for the $H(NO_3)$ model. This is about the amount of the anharmonicity correction to be expected. According to the accurate figures given by Darling and Dennison,[15] the corresponding quantity amounts to 1.79% for water; a somewhat higher value should be expected for a substance which contains only one hydroxyl bond.[6] The agreement indicates that vibration 7 does not mix to an appreciable amount with the vibrations of the nitrate radical.

Vibration 9.—The frequency of the restricted internal rotation has been estimated as 420 ± 30 by Forsythe and Giauque[8] from entropy data. The value 480 ± 15 for line l represents a satisfactory confirmation.

Actually the agreement is better than indicated by these figures. The model of the restricted internal rotation furnishes, except for cross terms in the potential energy, a correct limit for vanishing hydrogen mass. The motion can be approximated, therefore, as a rotation with an "apparent moment of inertia"

$$I_H = m_H d^2(1 - am_H)$$

where m_H denotes the mass of the hydrogen, and d its distance from the z-axis. The coefficient a is computed from the observed isotopic quotient according to $q^2 = I_D/I_H$. With the resulting value of I_H the estimate from entropy data is raised to 460 cm.$^{-1}$.

The interpretation is corroborated by the isotopic quotient (Table IV).

Vibrations 4 and 8.—Chédin and earlier authors assigned one line of the doublet b, c to the asymmetric stretching vibration 4 on account of a comparison with organic nitro compounds. The frequency 1645 in deuteronitric acid confirms this correlation.

The interpretation of the second line as the plane hydrogen bending vibration 8 is suggested by the occurrence of the frequency 1336 in the spectrum of deuteronitric acid. Indeed, there must be a corresponding frequency of nitric acid between

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[14] (a) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **4**, 711 (1936); (b) H. J. Bernstein, R. D. Romans, O. H. Howden and W. H. Martin, *Trans. Roy. Soc. Canada*, (III), **30**, 49 (1936); (c) C. S. Venkateswaran, *Proc. Ind. Acad. Sci.*, **A7**, 13 (1938); (d) O. Redlich, *Z. physik. Chem.*, **A182**, 42 (1938).

[15] B. T. Darling and D. M. Dennison, *Phys. Rev.*, **57**, 128 (1940).

1336 and 1336 $\sqrt{2} = 1889$. As the frequency 1538 appears practically unchanged in deuteronitric acid, only the doublet *b*, *c* remains. Moreover, this explanation of the second doublet line is corroborated by the fact that the hydrogen bending frequency generally is found in this region (1595.0 in water; 1178.7 in heavy water).

The low value of the observed isotopic quotient (*cf.* Table IV) of vibration 8 indicates that this vibration represents a mixture of the pure hydrogen bending vibration and some vibration of the nitrate radical. The isotopic quotients in Table II show immediately that the latter vibration corresponds to line *k*, as no pure NO_3 vibration can have an isotopic quotient as high as 1.066.

While we believe that the interpretation of the doublet *b*, *c* as vibrations 8 and 4 can hardly be questioned, the arguments for the more special assignment $b = 8$ and $c = 4$ are weak. According to Dadieu and Kohlrausch the line *c* is stronger than *b*, as to be expected for a stretching vibration in comparison with the usually weak hydrogen bending line.

Thus the correlation $b = 4$ and $c = 8$, while less probable, cannot be definitely excluded.

Vibrations 3 and 5.—These vibrations already have been correlated with the lines *i* and *k* by Chédin and this interpretation obviously accounts for the frequency region, the intensity and the fact that in dilute aqueous solutions both frequencies approach the corresponding degenerate nitrate ion frequency 718 cm.$^{-1}$. However, Chédin does not choose between $i = 3$; $k = 5$, and the reverse assignment. The first assignment is supported by the higher intensity and polarization of line *i*. Venkateswaran[3b] found the degrees of depolarization 0.62 and 0.71 for *i* and *k*, respectively. This result is in favor of $i = 3$ because vibration 3 is totally symmetrical not only in the symmetry C_s but also in the simplified model C_{2v}. As this correlation is based on a small difference in a quantity which cannot be measured with high accuracy, in this case too the reverse assignment cannot be safely excluded.

Vibration 6.—The only remaining line is $d = 1538$ cm.$^{-1}$. Chédin's interpretation as a combination $h + k = 926 + 607$ is definitely disproved by our results as the corresponding line in deuteronitric acid ought to be $924 + 570.5 = 1494.5$ while 1534 has been observed.

There does not appear to be any possible assignment but to the out-of-plane vibration 6. The low intensity is in favor of this correlation as the corresponding line of the nitrate ion is excluded from the Raman spectrum by Placzek's selection rules. Likewise the high degree of depolarization[3b] agrees perfectly with this assignment as vibration 6 is antisymmetric even in the symmetry C_s. However, we have no explanation for the large difference between the frequency of *d* and the out-of-plane frequency 830 of the nitrate ion as observed in the infrared.

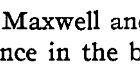
Products.—Considering the anharmonicity corrections previously discussed, the calculated and observed product values for A' and A'' (Table IV) agree very satisfactorily. This is a strong argument for the symmetry C_s or plane configuration of the molecule, although a lower symmetry can never be *strictly* excluded by means of the product formula.

The discrepancy of the product values for B_2 (model C_{2v}) reflects the interactions of vibrations 5 and 8, not taken into account in the simplified model.

When the manuscript of this paper was almost finished, we became acquainted with a recent paper of Banerji and Mishra.[16] These authors found for the Raman spectrum of deuteronitric acid: (band) 2455; (0) 1972; (0) 1849; (2b) 1640; (2) 1536; (10) 1293; (1) 1017; (4) 905; (0) 790; (2) 667; (0) 589; (2d) 166.

Except for the frequencies 790 and 166, these lines appeared also in our spectra, though the discrepancies are rather large in some cases. The hydrogen lines *b* and *l*, essential in our interpretation, are missing in this spectrum.

Banerji and Mishra assume a formula



$$\mathrm{HO{-}N^{+}}\begin{smallmatrix}/\mathrm{O^{-}}\\ \backslash \mathrm{O}\end{smallmatrix}$$

and a pyramidal configuration without any symmetry, first proposed by Venkateswaran.[3b] Consequently their interpretation is entirely different from ours. The assumption of an asymmetric pyramidal configuration does not appear to be in accord with common theory of valence and with the results of Maxwell and Mosley.[12] Considering the difference in the basic assumption,[17] we do not believe we should discuss all objections which are to be raised for theoretical reasons as

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[16] G. B. Banerji and B. Mishra, *Indian J. Phys.*, **15**, 359 (1941).

[17] The interpretation of Venkateswaran, Banerji and Mishra, especially with regard to the frequency 926 cm.$^{-1}$, is not consistent with assuming only a *slight* out-of-plane distortion of the nitrate group.

well as in view of our more complete spectra of both acids.

Grateful acknowledgment is made of a National Youth Administration grant which secured us the able assistance of Mr. J. De Young and Mr. R. O. Dhondt.

Summary

1. A new line 480 cm.$^{-1}$ was found in the Raman spectrum of anhydrous nitric acid and interpreted as the frequency of the restricted internal rotation of the hydrogen.

2. Anhydrous deuteronitric acid, free of lower oxides, has been prepared, and its Raman spectrum was determined.

3. All nine fundamentals were found in the spectra of nitric acid and deuteronitric acid. A complete interpretation is presented which, except for minor details, is believed to be a necessary consequence of the experimental results.

4. The results are in accord with the product formula applied to symmetry C_s (plane configuration).

5. The density of deuteronitric acid at 25.00° is 1.522$_8$.

6. The refractivities of nitric and deuteronitric acids at 25.0° are $n_D = 1.3920$ and $n_D = 1.3909$, respectively.

Pullman, Washington Received August 28, 1942

[Contribution from the Department of Chemistry, Ohio State University]

Deviations between Observed and Calculated Polarographic Diffusion Currents[1]

By W. M. MacNevin and Earl W. Balis[2,3]

This paper presents evidence to show that the deviations of observed from calculated polarographic diffusion currents have not been satisfactorily explained up to the present time. Further evidence is presented to show that the deviations are chiefly the result of a combination of the properties of ions and of stirring effects produced by the dropping electrode. The assumption of perfect drops at the electrode has been experimentally checked and validity of the Ilkovic equation has been reaffirmed.

Polarographic diffusion currents can be calculated from the Ilkovic equation,[4] $i_d = 605nD^{1/2}Cm^{2/3}t^{1/6}$ in which n is the number of faradays of electricity involved per mole of reactant, D is the diffusion coefficient of the reacting ion or molecule, C is the concentration in millimoles per liter of the reacting substance, m is the weight of mercury in milligrams flowing from the capillary per second, and t is the drop life in seconds; i_d is the average diffusion current in microamperes. Lingane and Kolthoff[5] have examined the Ilkovic equation at length and have concluded that it is essentially correct. Deviations, however, of the diffusion current from the theoretical have been observed by Ilkovic[4] and by Kolthoff and Lingane.[6] The latter authors report deviations as high as 8% between calculated and experimental diffusion currents. These authors have attributed the deviations to uncertainties in the values of the diffusion coefficients used in calculating the currents by the Ilkovic equation. An earlier suggestion was advanced by Lingane and Kolthoff[5] that the formation of the complex ions, $CdCl^+$ and $ZnCl^+$ may be responsible for the deviations found for these two metals.

In order to determine whether the deviations noted by Kolthoff and Lingane are peculiar to chloride solutions, we have determined the deviations using the nitrates in 0.1 molar potassium nitrate solution. It has been shown by Harned and Fitzgerald,[7] Bates,[8] and Robinson[9] that the activity coefficient for cadmium nitrate is quite different from that for cadmium chloride. Robinson, Wilson and Ayling[10] recently concluded from their values of the activity coefficient of cadmium nitrate that a complex nitrate ion does not exist.

Our data are shown in Table I together with

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[1] From a thesis submitted by E. W. Balis in partial fulfillment of the requirements for the Ph.D. Original manuscript received August 4, 1941.

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