# THE RAMAN SPECTRA OF TRI-METHYL-AMINE AND SOME COMPOUNDS OF HYDROXYLAMINE AND HYDRAZINE.

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Received July 31, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

## 1. *Introduction.*

The importance of a detailed study of the Raman spectra of comparatively simple molecules has been pointed out by the author in earlier communications to these *Proceedings*.[1] In the present paper, the Raman spectra of $N(CH_3)_3$, $NH_2OH.HCl$, $(NH_2OH)_2.H_2SO_4$, $HCl.N_2H_4.HCl$ and $N_2H_4.H_2O$ are reported on, and discussed in some detail.

## 2. *Experimental.*

10 grams of tri-methyl-amine (Kahlbaum, 'wasserfrei') distilled in vacuum was employed in the investigation. The hydrochloride and hydrosulphate of hydroxylamine were studied in the crystalline state as well as in concentrated aqueous solution. In the case of hydrazine, the hydrochloride and a 50% solution of the hydrate were examined. A Hilger two-prism spectrograph was used for photographing the spectrum in the case of tri-methyl-amine; a Fuess spectrograph of somewhat higher dispersion was employed for the rest of the work.

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[1] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1936, 3, 527; 4, 74, 82.

## 3. *Results.*

TABLE I.

*Raman spectrum of tri-methyl-amine* : $N(CH_3)_3$.

| No. | $\nu$ | Assignment | Int. | $\rho$ |
|---|---|---|---|---|
| 1 | 19960 | *e*—2978 | 2*b* | D |
| 2 | 19987 | *e*—2951 | 4 | P |
| 3 | 20110 | *e*—2828 | 2 | P |
| 4 | 20166 | *e*—2772 | 6 | P |
| 5 | 20200 | *e*—2738 | 0 | P |
| 6 | 21464 | *e*—1474 | 3 | D |
| 7 | 21494 | *e*—1444 | 3 | D |
| 8 | 21536 | *e*—1402<br>*i*—2980 | ½ | D |
| 9 | 21572 | *i*—2924 | 1 | P |
| 10 | 21658 | *e*—1280 | 0*bd* | D ? |
| 11 | 21729 | *k*—2976 | 6*b* | D |
| 12 | 21756 | *e*—1182<br>*k*—2949 | 10*b* | P |
| 13 | 21785 | *k*—2920 ? | 0*d* | ? |
| 14 | 21884 | *k*—2821 | 8 | P |
| 15 | 21934 | *k*—2771 | 12 | P |
| 16 | 21969 | *k*—2738 | 3 | P |
| 17 | 22109 | *e*—829 | 6*s* | P |
| 18 | 22206 | *k*—2499 ? | 0*bd* | D |
| 19 | 22510 | *e*—428 | 2*b* | D |
| 20 | 22564 | *e*—374 | 2 | P |
| 21 | 22663 | *e*—275 | 2*bd* | D |
| 22 | 23236 | *k*—1469 | 3 | D |
| 23 | 23267 | *k*—1438 | 3 | D |
| 24 | 23299 | *k*—1406 | 1 | D |
| 25 | 23425 | *k*—1280 | 0*d* | D |
| 26 | 23518 | *k*—1187 | 3*s* | P |
| 27 | 23663 | *k*—1402 | 2*b* | D |
| 28 | 23878 | *k*—827 | 4*s* | P |
| 29 | 24282 | *k*—423 | 1*d* | D |
| 30 | 24407 | *p*—2946<br>*q*—2981 | 4*b* | P |
| 31 | 24443 | *q*—2945 | 5*b* | P |
| 32 | 24473 | *o*—2820 | 1*d* | P |
|  | 24516<br>(Hg) | *o*—2777<br>*p*—2837 | — | — |
| 34 | 24535 | *p*—2818 | 1*d* | P |
| 35 | 24570 | *q*—2818 | 2 | P |
| 36 | 24591 | *p*—2762 | 2 | P |
| 37 | 24628 | *p*—2725<br>*q*—2760 | 6 | P |

| $\Delta\nu$ (cm.$^{-1}$). | 275 | 374 | 428 | 828 | 1042 | 1187 | 1280 | 1404 | 1442 | 1472 |
|---|---|---|---|---|---|---|---|---|---|---|
| Int. .. | 2*bd* | 2 | 2*b* | 6*s* | 2*b* | 3*s* | 0*d* | 1 | 3 | 3 |
| $\rho$ .. | D | P | D | P | D | P | D | D | D | D |

| $\Delta\nu$ (cm.$^{-1}$). | 2499? | 2738 | 2770 | 2820 | 2920? | 2948 | 2978 |
|---|---|---|---|---|---|---|---|
| Int. .. | *Obd* | 2 | 12 | 8 | 0*d* | 10*b* | 6*bd* |
| $\rho$ .. | D | P | P | P | ? | P | D |

TABLE II.

*Raman spectra of* $NH_2OH.HCl$ *and* $(NH_2OH)_2.H_2SO_4$.

| $NH_2OH.HCl$ | $(NH_2OH)_2.H_2SO_4$ |
|---|---|
| *Crystal*<br>$\Delta\nu$ = 1000·5 cm.$^{-1}$ (3*s*)<br>*Aq. solution*<br>$\Delta\nu$ = 1008 cm.$^{-1}$ (6)<br>2962 (2*b*)<br>*Water* 3227 (1*b*)<br>3435 (6*vb*)<br>3620 (1*b*) | *Aq. solution*<br>$\Delta\nu$ = 450 (5*b*)<br>624 (4*b*)<br>982 (10)<br>1008 (8)<br>1112 (2*b*)<br>2987 (1*b*)<br>*Water* 3227 (1*b*)<br>3435 (6*vb*)<br>3620 (1*b*) |

TABLE III.

*Raman spectra of $HCl.N_2H_4.HCl$ and $N_2H_4.H_2O$.*

| $HCl.N_2H_4.HCl$ | | $N_2H_4.H_2O$ | |
|---|---|---|---|
| *Crystal* | $\Delta\nu$ = 1024 cm.$^{-1}$ (1*s*) | 50% *solution* | $\Delta\nu$ = 916 (0*d*) |
| *Aq. solution* | $\Delta\nu$ = 967 (1) | | 1126 (1) |
| | 1029 (3) | | 3215 (½) |
| | 1108 (½*d*) | | 3286 (3) |
| | 3190 (1*d*) | | 3350 (2) |
| *Water* | 3284 (½*d*) | | |
| | 3432 (6*vb*) | | |
| | 3640 (1*b*) | | |

### 4. *Discussion of Results.*

1. *Tri-methyl-amine*: $N(CH_3)_3$.—So far as the author is aware,[2] the Raman spectrum of tri-methyl-amine has been studied only by Dadieu and Kohlrausch.[3] As the following table will show, their results are very incomplete.

TABLE IV.

| Dadieu-Kohlrauch | Author | | |
|---|---|---|---|
| $\Delta\nu$ (Int.) | $\Delta\nu$ | Int. | $\rho$ |
| | 275 | 2*bd* | D |
| | 374 | 2 | P |
| | 428 | 2*b* | D |
| 826 (1) | 828 | 6*s* | P |
| | 1042 | 2*b* | D |
| 1182 (½) | 1187 | 3*s* | P |
| | 1280 | 0*d* | D |
| 1439 (0) | 1404 | 1 | D |
| | 1442 | 3 | D |
| | 1472 | 3 | D |
| | 2499 ? | 0*bd* | D |
| 2770 (3) | 2738 | 2 | P |
| | 2820 | 8 | P |
| | 2920 ? | 0*d* | ? |
| 2942 (3*br*) | 2948 | 10*b* | P |
| 2977 (1*br*) | 2978 | 6*bd* | D |

A noteworthy feature of the Raman spectrum of this substance is the extreme feebleness of the rotational wings accompanying the Rayleigh lines.

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[2] *See* J. Weiler, "Raman Effekt," *Landolt-Börnstein Tabellen*, 1935, p. 1026.

[3] A. Dadieu and K. W. F. Kohlrausch, *Wien. Bericht.*, 1930, 139, 459.

This suggests that the optical anisotropy of the molecule is very small so that the depolarisation of the Rayleigh scattering for the liquid as well as for the vapour might be expected to be comparatively low.

If we confine our attention to the frequencies below 1100 cm.$^{-1}$ then, as a first approximation we can disregard the H atoms and treat the molecule of tri-methyl-amine as the general $AB_3$ type having the symmetry $C_{3v}$. In the region with which we are concerned, there are five Raman lines of which two are polarised, and three depolarised. This is rather surprising, since the model in question has only four distinct frequencies, two, totally symmetric ($\rho \ll \frac{6}{7}$) and two doubly degenerate ($\rho = \frac{6}{7}$). From a comparison with the Raman spctrum of iso-butane, H.C $(CH_3)_3$ which has been recently discussed by the author[4] we are led to the following classification of the observed frequencies :

| Substance | Totally symmetric | | Doubly degenerate | |
|---|---|---|---|---|
| | $\nu_1(CH_3)$ | $\delta_3(CH_3)$ | $\nu_{2,3}(CH_3)$ | $\delta_{1,2}(CH_3)$ |
| $H \cdot C(CH_3)_3$ .. | 795 (10)<br>P | 437 (1)<br>P | 965 (4*b*)<br>D | 370 (4*b*)<br>D |
| $N(CH_3)_3$ .. | 828 (6*s*)<br>P | 374 (2)<br>P | 1042 (2*b*)<br>D | 428 (2*b*)<br>D |

This leaves the broad and depolarised Raman band at 275 cm.$^{-1}$ unexplained. This band appears to be quite analogous to the low frequency Raman band observed by the author in the spectra of liquid $H_2O$ and $D_2O$[5]. A similar intense depolarised Raman band at about 200 cm.$^{-1}$ has been observed in the case of liquid formic acid. These bands owe their origin, perhaps, to the hindered rotation of the liquid molecules, but their presence in certain cases and absence in others is rather difficult to understand.

The fact that the assignment of the frequencies of iso-butane given by Kohlrausch is incorrect in view of the author's polarisation measurements has been pointed out in a previous communication.[6] It follows therefore that the calculations of Kohlrausch and Köppl[7] in the case of iso-butane are not significant.

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[4] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 527.

[5] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 291; 1936, **3**, 201.

[6] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 527.

[7] K. W. F. Kohlrausch and F. Köppl, *Z. f. Phys. Chem.*, B, 1934, **4**, 630.

Howard and Wilson[8] have discussed the normal frequencies of vibration of the symmetrical pyramidal molecule $AB_3$ using a general potential energy function involving six constants. The central force system adopted by Dennison,[9] and the valence force system employed by Lechner[10] involve two constants and give identical expressions for the ratio $\left(\frac{\omega_1\omega_2}{\omega_3\omega_4}\right)^2$ where $\omega_1$ and $\omega_2$ are the totally symmetric and $\omega_3$ and $\omega_4$ the doubly degenerate frequencies of the $AB_3$ molecule. From this ratio, it is possible to make an estimate of the angle $\beta$ between the edge and the height of the pyramid. A rough computation (neglecting the H atoms) gives $\beta = 62° 30'$ in the case of iso-butane, and $\beta = 70° 16'$ in the case of $N(CH_3)_3$. If the carbon valencies in iso-butane are assumed to be tetrahedral, we should find $\beta = 70° 32'$. The fact that the carbon valencies in saturated compounds tend to preserve at least approximately, the tetrahedral structure is supported by chemical evidence as well as by evidence derived from electron diffraction experiments. The large deviation of the calculated value from the expected one is therefore to be ascribed to the fact that neither the central nor the valence force system is applicable for the present case. Indeed, Howard and Wilson[11] as well as Redlich and Pordes[12] have found that even in the case of very simple molecules such as the tri-halides, $CHCl_3$, $CDCl_3$, etc., the central force system and the valence force system are equally unsatisfactory.

A characteristic difference between the Raman spectra of $H.C(CH_3)_3$ and $N(CH_3)_3$ revealed by the polarisation photographs is the striking reversal in the state of polarisation of the two lowest fundamental frequencies (370 and 437 in the case of iso-butane and 374 and 428 in the case of tri-methyl-amine). In the spectrum of iso-butane, the frequency $\Delta\nu = 370$ is depolarised and $\Delta\nu = 437$ polarised, whereas in the spectrum of tri-methyl-amine $\Delta\nu = 374$ is polarised and $\Delta\nu = 428$ is depolarised.

In the frequency interval between 1100 cm.$^{-1}$ and 1500 cm.$^{-1}$ we find marked differences between the spectra of tri-methyl-amine and iso-butane as will be seen from the table below.

The splitting of the 1450 Raman band which arises from the $\delta$ (C–H) vibration of the $CH_3$ groups into three components is very exceptional, and is therefore a significant feature of the Raman spectrum of tri-methyl-amine.

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[8] J. B. Howard and E. B. Wilson, *Jour. Chem. Phys.*, 1934, 4, 630.

[9] D. M. Dennison, *Phil. Mag.*, 1926, 1, 195.

[10] F. Lechner, *Wien. Bericht.*, 1932, 141, 633.

[11] J. B. Howard and E. B. Wilson, *Loc. cit.*

[12] O. Redlich and F. Pordes, *Monat. f. Chem.*, 1936, 67, 203.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H.C $(CH_3)_3$ | $\Delta\nu$ | 1170 | | 1325 | | 1452 | |
| | Int. | 4*b* | | 3*b* | | 7*b* | |
| | $\rho$ | D | | D | | D | |
| N $(CH_3)_3$ | $\Delta\nu$ | 1187 | 1210 | | 1404 | 1442 | 1472 |
| | Int. | 3*s* | 0*d* | | 1 | 3 | 3 |
| | $\rho$ | P | D | | D | D | D |

2. *Hydroxylamine hydrochloride and sulphate*: $NH_2\ OH.\ HCl$, $(NH_2\ OH)_2.\ H_2SO_4$.—The Raman spectrum of pure $NH_2OH$ (liquid) has been studied by Medard[13] who has found the following frequencies[14]:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\Delta\nu$ .. | 897 | 921 | 1045 | 1108 | 1311 | 1605 | 3259 | 3306 |
| Int. .. | 6 | 6 | 0 | 1 | 0 | 3 | 5 | 3 |

He has remarked that due to the rapid decomposition of the substance with evolution of bubbles, the spectrum obtained was quite mediocre. It is rather surprising that neither of the two strong lines 897 and 921 is observed in the Raman spectra of the salts investigated by the present author. The Raman spectrum of crystalline $NH_2OH.HCl$ consists of a single sharp line with a frequency shift of 1000·5 cm.$^{-1}$ In solution, this line is slightly shifted towards the longer wave-length side ($\Delta\nu = 1008$) but remais still the strongest line in the spectrum. This line occurs with equal prominence in the aqueous solution of the sulphate, and is well polarised in both cases. Besides, the aqueous solution of the hydrochloride shows a band extending over about 60 wavenumbers and with its centre at 2962 cm.$^{-1}$ The water bands are, of course, a prominent feature of the spectra of the aqueous solutions, but there is a considerable strengthening of the central component of the band—which extends roughly over 150 wave-numbers—due, no doubt, to the superposition of the O–H and N–H vibrations of $NH_2OH$. Besides the Raman bands referred to above, the aqueous solution of the sulphate shows also the Raman frequencies 450 (5*b*), 624 (4*b*), 982 (10), and 1112 (2*b*) which are the characteristic frequencies of the tetrahedral ($SO_4$) ion.

From the chemical standpoint, the constitution of hydroxylamine is a problem of some interest. If, as is generally accepted, hydroxylamine is thought of as being derived from ammonia by the substitution of one of the H atoms by the hydroxyl group (OH), then the constitutional formula of hydroxylamine will be represented by $H_2 = N - OH$, the nitrogen being

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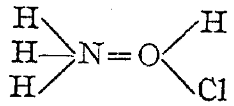
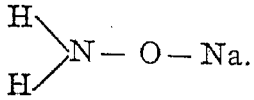
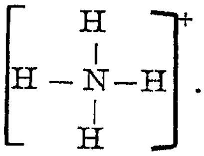
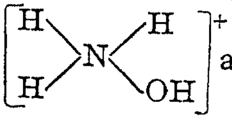
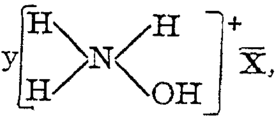
[13] L. Medard, *C.R.*, 1934, **199**, 421.

[14] *See* J. Weiler, "Raman Effekt," *Landolt-Börnstein-Tabellen*, 1935, p. 949.

trivalent. While this is in conformity with the larger body of chemical evidence, there are certain cases where the behaviour of hydroxylamine appears to accord better with the constitution $H_3 \equiv N = O$, the nitrogen being pentavalent. "In alkaline solutions, hydroxylamine plays the rôle of an amido-acid $H_2 = N - OH$, and acts as a reducing agent, while in acid solutions, it behaves like ammonia oxide $H_3 \equiv N = O$, and acts as an oxidising agent.[15]" According to this view, the structure of a salt of hydroxylamine, say, the hydrochloride will be represented by  while sodium hydroxylamate in which $NH_2OH$ functions as an acid will have the constitution 

It is interesting to point out the relation between tri- and quinqevalent nitrogen on the basis of the electronic theory of valency.[16] Nitrogen (atomic number 7) has five valency electrons and so can complete its octet by taking up three hydrogen atoms. Thus in ammonia, $NH_3$, there are six shared electrons, and two unshared. If a fourth neutral H atom were taken up, this would introduce another electron and the valency group would consist of nine, as it does in sodium (2, 8, 1). Hence neutral $NH_4$ behaves like a univalent metal. The valency group is, however, very unstable. It readily loses one electron, and forms the stable ammonium ion  $\left[\begin{array}{c} H \\ | \\ H-N-H \\ | \\ H \end{array}\right]^+$.

This explains why that one of the five valencies of pentavalent nitrogen must always be an electrovalency. A nitrogen atom which has lost one electron ($N^+$) behaves like tetravalent carbon. The fifth group, the anion, is not attached to the ammonium ion in any fixed position, but is merely attracted to it as a whole.

If we extend the ammonium group theory to hydroxylamine, the hydroxylammonium ion will be represented by  and the salt of hydroxylamine, say, the hydrochloride will be represented by 

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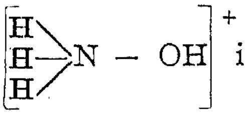
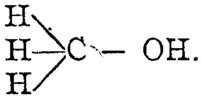
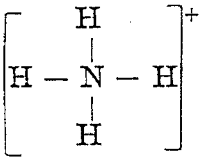
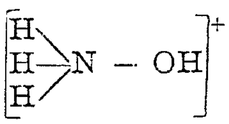
[15] *See* J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 1928, **8**, 297.

[16] N. V. Sidgwick, *The Electronic Theory of Valency*, 1927, 65.

where X stands for the anion. Since ionic bindings do not give Raman effect, we should expect, the anion and the cation to give their own characteristic frequencies. This is in fact what is actually observed. The characteristic Raman lines at 1000·5 and 1008 cm.$^{-1}$ observed respectively in the spectra of the crystal and aqueous solution of the salts of hydroxylamine arise no doubt from the mutual vibration of the N and O atoms of the  ion. Indeed, on the analogy between C and $N^+$ we can compare this Raman line to the intense line at 1035 cm.$^{-1}$ observed in the Raman spectrum of methyl alcohol,  If as a rough approximation we ignore the H atoms and consider the hydroxylammonium ion as a diatomic N–O, we get for the force constant (putting $\Delta\nu = 1008$) $f = 4{\cdot}45 \times 10^5$ dynes/cm.

The complete elucidation of the frequencies in the 3 $\mu$ region is of great interest in the case of the  $\left[H-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}-H\right]^+$ and  ions in view of the analogy with the corresponding carbon compounds. The great intensity of the water bands which fall practically in the same region renders the matter one of extreme difficulty in the case of aqueous solutions. The use of heavy water as solvent would obviate this difficulty, and the author hopes beforelong to take up this problem.

(3) *Hydrazine hydrochloride and Hydrazine hydrate*: $HCl.N_2H_4.HCl$, $N_2H_4.H_2O$.—The Raman spectrum of pure hydrazine as well as that of the pure hydrate has been studied by Imanishi.[17] Aqueous solutions of the hydrate have been studied by Pal and Sen Gupta.[18] The spectra of the pure susbtance and of the hydrate do not seem to differ appreciably. The author's results for the hydrate are in fair agreement with those of the previous workers.

The spectrum of hydrazine hydrochloride in the crystalline state shows a single sharp line at 1024 cm.$^{-1}$ In the aqueous solution this line is the most prominent and is shifted by about 5 wavenumbers to the longer wavelength side. Besides, two fainter lines are also observed in the aqueous solution, one at 967 and the other at 1108 cm.$^{-1}$ The 3 $\mu$ region shows certain details as will be seen from Table III, but the use of heavy water as

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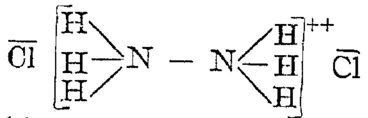
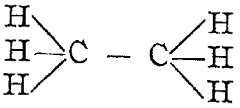
[17] S. Imanishi, *Sci. Pap. Inst. Phys. Chem. Res.*, 1931, **16**, 1.

[18] N. N. Pal and P. N. Sen Gupta, *Ind. Jour. Phys.*, 1930, **5**, 13.

solvent might be expected to show many new features. The configuration of $HCl.N_2H_4.HCl$ can be written as  $\overline{\mathrm{Cl}}\left[\mathrm{H_3N}-\mathrm{NH_3}\right]^{++}\overline{\mathrm{Cl}}$ so that the vibrations of the hydrazinium ion should be somewhat analogous to those of ethane,  $\mathrm{H_3C}-\mathrm{CH_3}$. It may not be wrong to compare the Raman line $\Delta\nu = 1029$ of the hydrazinium ion to the strong Raman line 992 of ethane. A rough computation gives for the magnitude of the N–N force constant, $f = 4 \cdot 35 \times 10^5$ dynes/cm.

In conclusion, the author wishes to express his respectful thanks to Professor Sir C. V. Raman for his kind interest in the present work.

## 5. *Summary.*

The Raman spectrum of tri-methyl-amine has been investigated and the observed frequencies are discussed with the aid of polarisation data. Certain conclusions regarding the proper assignment of the frequencies have been drawn from a comparison with the spectrum of iso-butane which has been investigated on a former occasion. The hydrochlorides of hydroxylamine and hydrazine show but a single Raman line in the crystalline state. This line remains quite strong even in aqueous solutions, but the latter also show certain additional features. The constitution of these salts is discussed on the basis of the electronic theory of valency; the conclusions drawn therefrom seem to be supported by the Raman effect.