

Derivatives of Hydrazine

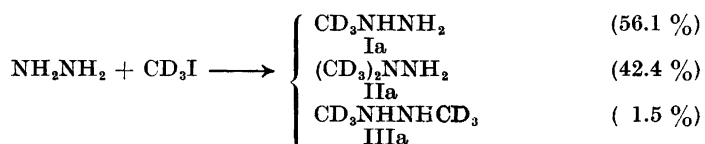
I. Preparation and Infrared Spectra of Partially Deuterated Mono- and Dimethylhydrazines

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The preparation of *C*-deuterated methylhydrazine, 1,1-dimethylhydrazine and 1,2-dimethylhydrazine from hydrazine and methyl- d_3 iodide is described. The corresponding *N*-deuterated compounds have been prepared from the parent hydrazines by exchange with deuterium oxide. The infrared spectra of these six deuterated hydrazines together with those of the parent compounds, in solution and as the pure liquids, have been recorded. The results enable assignment of a series of group frequencies.

In connection with work on *N*-isothiocyanatoamines,¹ methyl- d_3 -hydrazine (Ia) and 1,1-dimethyl- d_6 -hydrazine (IIa) were prepared together with small amounts of 1,2-dimethyl- d_6 -hydrazine (IIIa), by treatment of an excess of anhydrous hydrazine with methyl- d_3 -iodide. The method is based upon a principle introduced by Howitz in a patent.² In the crude reaction mixture, most of the methylhydrazines are present as hydriodides. The essential feature of the method is that the methylhydrazines may be removed by careful distillation, by virtue of their lower boiling point in comparison to hydrazine. Since equilibrium is continuously reestablished, only the excess hydrazine and hydrazinium iodide are left. The crude mixture of Ia—IIIa thus obtained was finally separated by vapour-phase chromatography.



Although the infrared and Raman spectra of I,³⁻⁵ II,^{3,6,7} and 1,2-dimethylhydrazine (III)^{3-5,7,8} have been studied by several workers, there are major differences in assignment of fundamentals in the low-frequency region. Only recently, Bürger and Höfler⁷ used 1,1-dimethylhydrazine-*d*₂ (IIb) for identification of the bands arising from the amino group in II. The infrared spectrum of 1,2-dimethylhydrazine-*d*₂ (IIIb)⁹ has not been recorded. We have therefore investigated the infrared spectra of all the above-mentioned compounds and of methylhydrazine-*d*₃ (Ib). They have been recorded for the pure liquids and for solutions in tetrahydrofuran and methylene chloride. Owing to the very small quantities of IIIa available, the spectrum was only determined in tetrahydrofuran. This solvent was chosen because with the other hydrazines it proved to give the spectra most like those of the pure liquids.

It should be pointed out that the following discussion is based only on results obtained by selective isotopic substitution and, strictly speaking, allows deductions only as to the location of group frequencies of the hydrazines. The present interpretation is, of course, also limited by our lack of knowledge of important vibrations below 500 cm⁻¹. Also, no regard has been taken to the variation in line intensity which is known to occur between "allowed" transitions. Furthermore, complications may arise from the presence of several conformers in equilibrium and from hydrogen bond effects. However, we feel that the evidence obtained is sufficient to allow firm conclusions to be reached.

1,1-Dimethylhydrazine and its deuterated species II—IIb. Even in the most symmetric arrangement, these compounds have only one plane of symmetry and would belong to the point group *C*_s. All 30 fundamentals are therefore expected to be infrared active. They may roughly be classified as 21 modes characteristic of the (CH₃)₂N radical, 3 modes from the NH₂ radical and 6 modes arising from the joining of these radicals. The fundamentals of the dimethylamino group are anticipated as follows (summarized in Table 1): 6 ν (C—H) stretching vibrations (2700—3000 cm⁻¹), 6 δ (CH₃) deformation vibrations (1400—1500 cm⁻¹), 4 ρ (CH₃) rocking modes (1000—1300 cm⁻¹), 2 ν (C—N) stretching modes (see below), and three vibrations below the range (500—4000 cm⁻¹) investigated. The amino group gives rise to 2 ν (N—H) stretching vibrations (3100—3400 cm⁻¹) and a δ (NH₂) deformation mode around 1600 cm⁻¹. By the joining of the groups we get an ω (NH₂) wagging mode and a ρ (NH₂) rocking mode (700—1300 cm⁻¹) and a ν (N—N) vibration which probably couples heavily with the two ν (C—N) modes mentioned above to give three skeletal stretching vibrations. The three remaining skeletal vibrations are expected to give bands situated below the region investigated.

The proposed assignment of the infrared absorption maxima for II—IIb is given in Table 1. The number and position of the bands largely agree with those earlier reported.^{6,7} However, we were unable to detect in any of our spectra the band at 1180 cm⁻¹ which was reported by Bürger and Höfler⁷ and assigned by them to an amino group vibration. The band cannot be found in the Raman spectrum either,^{3,6,7} and since the amino vibrations can be satisfactorily assigned, we believe this band to be due to an impurity. Similarly, the unassigned band reported⁷ at 870 cm⁻¹ apparently arose from an impurity.

Table 1. Observed infrared spectra of 1,1-dimethylhydrazine (II), 1,1-dimethyl- d_6 -hydrazine (IIa), and 1,1-dimethylhydrazine- d_2 (IIb) and proposed assignments for 24 fundamentals in the 500–4000 cm^{-1} spectral region.

Assignment and expected number of fundamentals	II		IIa		IIb		
	liquid	solution ^a	liquid	solution ^a	liquid	solution ^a	
$\nu(\text{N-H})/\nu(\text{N-D})$	2	3308s — 3220msh 3140m	3342w 3300w 3200w 3141w	3308s — 3220msh 3138m	3337m 3290w 3199w 3140w	2458s — 2336m 2292m	2483w 2460w 2345w 2318w
$\nu(\text{C-H})/\nu(\text{C-D})$	6	2990ssh 2973vs 2942vs — 2890s 2850vs 2820vs 2775vs	2990ssh 2981s 2948vs 2920wsh 2886m 2848vs 2810vs 2768vs	2302w 2240s 2229msh 2190vs 2110s — 2088m 2040vs	— 2237m 2183vs 2110w 2099w 2080vw 2031vs	2990ssh 2976s 2954vs 2940vs 2898s 2843vs 2806vs 2762vs	2990ssh 2980s 2952vs — 2894s 2848vs 2814vs 2768vs
Unassigned		—	—	—	2688m	2693w	
$\delta(\text{NH}_2)/\delta(\text{ND}_2)$	1	1605s	1596s	1606s	1593s	1184s	1182s
$\delta(\text{CH}_3)\delta(\text{CD}_3)$	6	— 1486s 1456vs 1426msh 1390w	1474wsh 1464s 1451s 1425msh 1398w	1209m 1161s 1106m 1059s —	1206w 1160m 1104m 1058m —	— 1466s 1446s — 1400w	1472msh 1466s 1454s 1432msh 1400w
$\omega(\text{NH}_2)/\omega(\text{ND}_2)$	1	1319m	1311m	1320m	1303m	958m	950m
$\rho(\text{CH}_3)/\rho(\text{CD}_3)$	4	1246w 1210m 1147m 1093m	1244w ^b 1209m 1144m 1092m	868m 842w 807w —	868m 842w 807w —	1255m 1233m 1165msh 1095m	1253m ^b 1232m 1156w 1094m
Skeletal stretch	2	1060vs 1015s	1056vs 1014s	1050s 985vsbr	1051s 982vs	1026s 1005s	1024s 1005s
$\rho(\text{NH}_2)/\rho(\text{ND}_2)$	1	945vsbr	947vs	939vs	937vs	793vs	786vs
Skeletal stretch	1	810vs	807vs	752vs	754vs ^b	810vs	800vs

^a In methylene chloride except ^b in tetrahydrofuran. vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad.

The hydrogen stretching region offers no clear path to detailed assignments since there are generally more strong bands than are needed for fundamentals. In the pure liquid phase and in dioxane solution, three bands in the 3100–3400 cm^{-1} range are observed for II, the highest of which shows a

further splitting in methylene chloride solution. In the Raman spectrum⁷ the four bands are similarly located at 3143, 3202, 3309, and 3334 cm^{-1} . Now it is well known that this region is often complicated by the appearance of hydrogen-bonded N—H stretching modes¹⁰ and by the overtone of the $\delta(\text{NH}_2)$ mode at 1605 cm^{-1} ,¹¹ so several assignments are possible. However, by analogy with hydrazine¹⁰ and methylamine¹¹ it is inferred that the bands at 3308 and 3140 cm^{-1} in the liquid phase are the two $\nu(\text{N—H})$ fundamentals and the band at 3220 cm^{-1} the Fermi resonance enhanced overtone of the NH_2 scissoring mode at 1605 cm^{-1} . Similar considerations may be applied to the $\nu(\text{N—D})$ region, in which the overtone of the $\delta(\text{ND}_2)$ fundamental might appear.

Without gas-phase contour measurements, it is not possible to distinguish the $\nu(\text{C—H})$ fundamentals from the overtones and combinations of the $\delta(\text{CH}_3)$ modes intensified by Fermi resonance. In considering this region, comparison was profitably made with the assignments by Gayles¹² for $(\text{CH}_3)_2\text{N—CD}_3$. The $\nu(\text{C—H})$ regions of the spectra of this compound and II are in fact so similar that the assigned modes at 2970, 2945, 2862, 2820, and 2770 cm^{-1} (solid film) might be transferred directly. Other possibilities, however, especially in the assignment of the 2820 cm^{-1} band, are not to be overlooked. It has been shown that the band at 2820 cm^{-1} in $(\text{CH}_3)_2\text{NH}$ ¹³ originates from an overtone, and in $(\text{CH}_3)_2\text{N—PF}_2$ ¹⁴ the fundamentals are located between 2814 and 2998 cm^{-1} (liquid phase), which means that the 2814 cm^{-1} band for the latter compound is the lowest $\nu(\text{C—H})$ fundamental. Though it is thus confirmed that the presence of at least one band in the 2760—2820 cm^{-1} region¹⁵ is a useful criterion for an N—CH₃ group, it seems to be a doubtful extension⁷ of this rule to identify the $\text{N}(\text{CH}_3)_2$ group by means of a strong band between 2810 and 2830 cm^{-1} if this band has a multiple origin. The infrared spectrum of the complex between II and borane displays only two bands due to C—H stretching at 2980 and 3020 cm^{-1} . This confirms the idea that observation of low frequency bands in this region¹⁵ is intimately correlated with the presence of an unshared electron pair on the nitrogen.

The assignment of the band at 1605 cm^{-1} to the $\delta(\text{NH}_2)$ scissoring vibration in liquid II is unambiguous. Since the $\delta(\text{ND}_2)$ mode in ND_2ND_2 gives rise to a band at 1194 cm^{-1} (liquid),¹⁰ it is safe to choose the band at 1184 cm^{-1} for the corresponding mode in IIb. In discussing the two external deformation modes of the amino group in this region, we have to consider the various models possible for II. The *cis* conformation is rather unlikely, but good arguments can be advanced for both the *gauche* (staggered or semi-eclipsed), hydrazine-like model and the *trans* (C_s) model, analogous to methylamine. The most recent assignment for liquid hydrazine is as follows:¹⁰ $\omega(\text{NH}_2)$ at 1324 + 1283 cm^{-1} ($\omega(\text{ND}_2)$ at 987 + 1032 cm^{-1}) and $\rho(\text{NH}_2)$ at 1042 + 871 cm^{-1} ($\rho(\text{ND}_2)$ at 787 + 727 cm^{-1}). In methylamine the $\omega(\text{NH}_2)$ band¹¹ has been observed at 780 cm^{-1} in the gaseous state and as a doublet at 909 + 948 cm^{-1} in the solid state (624 and 718 + 759 cm^{-1} , respectively, in CH_3ND_2). Considerable confusion seems to exist as to the location of the NH_2 "twisting" frequency in methylamine, but current evidence^{11,16} points to the region around 1000 cm^{-1} . From Table I it is seen that by adopting the hydrazine model the differences between II and IIb are satisfactorily explained through attri-

buting the band at 1319 cm^{-1} to the $\omega(\text{NH}_2)$ mode and the band at 945 cm^{-1} to the $\rho(\text{NH}_2)$ mode. This choice is further justified on the ground that the corresponding bands are found in methylhydrazine at 1305 and 990 cm^{-1} , whilst 1,2-dimethylhydrazine has no strong bands at all between 1200 and 1400 cm^{-1} . It should be mentioned that Stewart¹⁷ suggested that the band at 810 cm^{-1} in II was a counterpart of the strong band around 800 cm^{-1} found in primary aliphatic amines and attributed to the amino group. Our results leave no doubt that this cannot be correct.

In the $\delta(\text{CH}_3)$ region, an overlapping of bands occurs, but it is interesting to note the coincidence of the two strongest bands at 1468 and 1456 cm^{-1} with two of the fundamentals of $(\text{CH}_3)_2\text{N}-\text{CD}_3$, assigned by Gayles¹² to 1468 and 1454 cm^{-1} (solid film). In terms of the local symmetry of the methyl groups (C_{3v}), they would be due to asymmetric $\delta(\text{CH}_3)$ modes. Gayles also assigned the lowest (symmetric) $\delta(\text{CH}_3)$ fundamental in $(\text{CH}_3)_2\text{N}-\text{CD}_3$ to the band at 1405 cm^{-1} . This might reasonably be correlated with the peak in II at 1390 cm^{-1} , also observed in the Raman spectrum⁷ as a strong band at 1397 cm^{-1} . The assignment of the $\delta(\text{CD}_3)$ modes in IIa to the bands situated in the region from 1209 cm^{-1} downwards is consistent with the results obtained with $(\text{CD}_3)_2\text{N}-\text{CH}_3$ and $(\text{CD}_3)_3\text{N}$.¹²

The vibrations of the dimethylamino group have recently been treated from a theoretical point of view by Finch *et al.*¹⁸ From their results we may deduce that the $\rho(\text{CH}_3)$ modes of II should give rise to one band at *ca.* 1215 cm^{-1} , one band around 1160 cm^{-1} , one band near 1050 cm^{-1} , and one band extensively coupled with the skeletal stretching vibrations. The bands of II assigned to $\rho(\text{CH}_3)$ in Table 1 at 1246 , 1210 , 1147 , and 1093 cm^{-1} agree well with the calculated values if the complications introduced by the amino group are taken into account. The $\rho(\text{CD}_3)$ modes of IIa appear as three bands in the region between 800 and 900 cm^{-1} . This region is otherwise free of absorption and the assignment can be considered fairly safe. It is noteworthy that the two bands at 1210 and 1147 cm^{-1} in II show a shift to 1233 and 1165 cm^{-1} in IIb. This is very probably due to a coupling in the latter compound with the $\delta(\text{ND}_2)$ fundamental at 1184 cm^{-1} .

In each of the compounds II–IIb, only three strong bands are now left unassigned, and these are accordingly attributed to the skeletal stretching vibrations. The band at 1060 cm^{-1} in II is only slightly shifted on *C*-deuteration but shows a major shift to 1026 cm^{-1} on *N*-deuteration. On the contrary, the bands at 1015 and 810 cm^{-1} in II are little affected by *N*-deuteration but are shifted to 985 and 752 cm^{-1} on *C*-deuteration. Tentatively, therefore, we assign the band at 1060 cm^{-1} in II to a skeletal vibration involving mainly the N–N bond and the bands at 1015 and 810 cm^{-1} to skeletal vibrations of the C–N stretching type. We note that the bands due to C–N stretching vibrations in trimethylamine probably occur¹² at 1043 and 825 cm^{-1} and the corresponding bands in $(\text{CH}_3)_2\text{N}-\text{CD}_3$ at 1013 and 792 cm^{-1} , in close agreement with the results obtained here. The bands assigned to the $\nu(\text{N}-\text{N})$ mode in hydrazine and tetradeuteriohydrazine in the liquid phase are found,¹⁰ respectively, at 1098 and 936 cm^{-1} , in fair agreement with the value for II. Very probably, though, heavy couplings occur in this region. Thus, the only main points of difference between the spectra of the condensed phase and the vapour

phase of II⁶ are that the three bands at 1060, 1015, and 945 cm⁻¹ appear to be shifted to 1046 cm⁻¹ (vs), 961 cm⁻¹ (m), and 904 cm⁻¹ (s). The shifts of the first and the third band may be accounted for by the breaking of hydrogen bonds present in the liquid state, but the shift of the band at 1015 cm⁻¹ by ca. 50 cm⁻¹ is hard to explain if the assignment to a pure skeletal C—N stretching mode is literally upheld.

Methylhydrazine and its deuterated species, I—Ib. Chemical reasoning argues that these compounds have a *gauche* (hydrazine-like) conformation. Accordingly, the twenty-one normal vibrations are all infrared active. Apart from the three skeletal modes occurring beyond the range investigated, the following fundamentals are expected for I: 3 ν (N—H) stretching modes (3100—3400 cm⁻¹), 3 ν (C—H) stretching modes (2700—3000 cm⁻¹), 1 δ (NH₂) deformation vibration (ca. 1600 cm⁻¹), 3 δ (CH₃) deformation modes (1400—1500 cm⁻¹), 2 δ (NH) skeletal bending modes (one at 1200—1500 cm⁻¹ and one at 700—900 cm⁻¹),¹³ 2 ρ (CH₃) rocking modes (1000—1300 cm⁻¹), 1 ρ (NH₂) and 1 ω (NH₂) external deformation mode (700—1300 cm⁻¹), and finally two skeletal stretching vibrations with partly C—N, partly N—N stretching character as summarised in Table 2. The infrared frequencies observed under various conditions are also tabulated in Table 2 together with assignments. It was impossible to detect a band at 1042 cm⁻¹ in liquid I, reported by Axford *et al.*⁴ to occur with medium strength. Furthermore, we were unable to resolve the broad band with apparent maximum at 990 cm⁻¹ into two bands around 950 and 985 cm⁻¹ as claimed by the same authors. We note that neither the band at 1042 nor that at 950 cm⁻¹ have been observed⁴ in the Raman spectrum of liquid I. Apart from these minor discrepancies, the results agree satisfactorily. Since the absorptions were very broad in many cases, indicative of extensive hydrogen bonding, their exact positions were difficult to decide.

No detailed assignments can be given for the ν (N—H) region. The discussion of this region for II also applies to I, but the pattern is further complicated by the occurrence of an extra fundamental. Equally unsatisfactory is the situation for the ν (C—H) region, exhibiting a total of eight bands of which only three can be due to fundamentals. The position of the four strongest bands at 2980, 2930, 2850, and 2780 cm⁻¹ is close to the observations for CH₃—N(CD₃)₂ by Gayles.¹² By using the frequency product rule he was able to pick the three bands at ca. 2970, 2840, and 2770 cm⁻¹ as fundamentals, allowing a similar tentative assignment of the fundamentals for I.

Arguing by analogy to II—Ib, the three bands arising from the δ (NH₂), the ω (NH₂), and the ρ (NH₂) modes should be those observed at 1615, 1305, and 990 cm⁻¹, respectively. The two first assignments are obvious from comparison of II and Ib, but the third band shows an interesting behaviour on change in medium. Thus, in tetrahydrofuran we observe 988 + 948 cm⁻¹, in methylene chloride 990 + 928 cm⁻¹, and in the vapour Axford *et al.*⁴ reported 969 + 886 cm⁻¹. This band, therefore, consists of 1) an absorption between 969 and 990 cm⁻¹, nearly independent of the medium and assigned below to a skeletal vibration, and 2) an absorption assigned to the ρ (NH₂) mode on account of the marked lowering in frequency on passing from the liquid to the vapour state. This assignment is substantiated by comparison with the spectrum of Ib.

Table 2. Observed infrared spectra of methylhydrazine (I), methyl- d_3 -hydrazine (Ia) and methylhydrazine- d_3 (Ib) and proposed assignments for 18 fundamentals in the 500–4000 cm^{-1} spectral region.

Assignment and expected number of fundamentals	I		Ia		Ib		
	liquid	solution ^a	liquid	solution ^a	liquid	solution ^a	
$\nu(\text{N}-\text{H})/\nu(\text{N}-\text{D})$	3	3300vsbr	3348s	3300vsbr	3348s	2460vs	2460m
		—	3305ssh	—	3300ssh	—	—
		—	3255ssh	—	3250ssh	2388s	2390w
		3190vssh	3183m	3180vs	3190m	2335s	2330w
$\nu(\text{C}-\text{H})/\nu(\text{C}-\text{D})$	3	2980vssh	2985vs	2290wsh	2286w	2968vs	2972vs
		—	2947vssh	2235s	2233m	2940vs	2942vs
		2930vs	2937vs	2198vs	2194s	—	—
		—	2922msh	2131m	2125m	—	—
		2885ssh	2885m	2098m	2096m	2879vs	2882s
		2850vs	2858s	2061vs	2056s	2855vs	2856s
		—	2842s	—	—	2835vs	2843s
		2780s	2783s	—	—	2784vs	2783s
$\delta(\text{NH}_2)/\delta(\text{ND}_2)$	1	1615s	1611s	1618vs	1607s	1202s	1199s
$\delta(\text{CH}_3)/\delta(\text{CD}_3)$	3	{1480s	1480s	1140s	1141s	1470s	1469s
		{1465s	1446s	1061m	1060m	1444s	1445s
		{1447s	—	1047m	1049m	1412w	—
		{1414w	—	—	—	—	—
$\delta(\text{NH})/\delta(\text{ND})$	1	{1480s	1480s	1471m	1456w	1048m	1049m
		{1465s	—	—	—	—	—
$\omega(\text{NH}_2)/\omega(\text{ND}_2)$	1	1305m	1299m ^b	1296m	1295m ^b	945m	940m
$\rho(\text{CH}_3)/\rho(\text{CD}_3)$	2	1203s	1195m	908s	902m	1202s	1199s
		1100s	1099s	816s	808m	1099m	1100m
Unassigned		1123s	1126m	—	—	1141m	1138m
Skeletal stretch	1	990vsbr	990s	983sbr	968s	978m	970m
$\rho(\text{NH}_2)/\rho(\text{ND}_2)$	1		928s	946s	943m	840vsbr	830vs
$\delta(\text{NH})/\delta(\text{ND})$	1	820vsbr	815ssh	772sbr	769s ^b	680sbr	660s
Skeletal stretch			1			792vs	790vsbr

^a see Table 1.

The $\delta(\text{NH})$ bending modes in dimethylamine¹³ are found at 735 cm^{-1} (a' mode) and 1486 cm^{-1} (a'' mode) in the gas and at 881 and 1525 cm^{-1} in the crystalline state. This makes the bands at 820 cm^{-1} and at 1465 or 1480 cm^{-1} the $\delta(\text{NH})$ candidates for I. The band at 820 cm^{-1} shows a tendency to

split when I is in solution, and on *N*-deuteration a new absorption appears at 680 cm^{-1} , leaving the main band at 790 cm^{-1} . The shift is of the same order of magnitude as that observed on *N*-deuteration of methylamine and indicates the band at 820 cm^{-1} in I to be an unresolved doublet originating from the $\delta(\text{NH})$ and one of the skeletal stretching modes. The same conclusion was reached from different reasoning by Axford *et al.*⁴ They observed that the strongest Raman line in this region was at 816 cm^{-1} , nearly coinciding with the absorption in the infrared, and selected this as the lowest skeletal stretching mode by comparison with spectra of related compounds. They argue that such modes are usually weak in the infrared and hence an accidental degeneracy (with the band due to the $\delta(\text{NH})$ mode) has to be assumed. However, it is difficult to see why the same argument should not apply to II, for which a very strong Raman line at 809 cm^{-1} parallels the infrared absorption at 810 cm^{-1} . Since there is no other indication of a double origin of this band, the argument is probably not valid. The high-frequency $\delta(\text{NH})$ mode is expected in the $\delta(\text{CH}_3)$ region and is unambiguously identified in Ia by comparison with Ib. Apart from this, the assignments of the $\delta(\text{CH}_3)$ modes present no difficulties. Comparison of I and Ib also leaves no doubt as to the location of the $\rho(\text{CH}_3)$ bands, and the band at 1123 cm^{-1} , observed⁴ as a weak band at 1122 cm^{-1} in the gas phase and in the Raman spectrum at $1117 + 1137\text{ cm}^{-1}$, is left unassigned. The two composite bands at 990 cm^{-1} and 820 cm^{-1} contain the skeletal stretching modes as discussed above and might be allocated to the $\nu(\text{N}-\text{N})$ and the $\nu(\text{C}-\text{N})$ stretching modes, respectively, by analogy to II. A trial run of the spectrum of I in chloroform showed that only one weak band at 445 cm^{-1} was present in the region down to 400 cm^{-1} . A corresponding line was found in the Raman spectrum at 443 cm^{-1} and attributed⁴ to one of the skeletal deformation modes. In view of this, it appears likely that the band at 1122 cm^{-1} is not an overtone, but is rather a combination band.

1,2-Dimethylhydrazine and its deuterated species, III—IIIb. The thirty normal vibrations of III may be divided into the following groups: 2 $\nu(\text{N}-\text{H})$ stretching vibrations ($3100\text{--}3400\text{ cm}^{-1}$), 6 $\nu(\text{C}-\text{H})$ stretching vibrations ($2700\text{--}3000\text{ cm}^{-1}$), 6 $\delta(\text{CH}_3)$ deformation modes ($1400\text{--}1500\text{ cm}^{-1}$), 4 $\rho(\text{CH}_3)$ rocking modes ($1000\text{--}1300\text{ cm}^{-1}$), 3 skeletal modes ($700\text{--}1100\text{ cm}^{-1}$), 4 $\delta(\text{NH})$ bending modes (2 around 1500 cm^{-1} and 2 around 800 cm^{-1} by analogy to I—Ib), and finally 5 skeletal modes occurring below the region investigated. All vibrations are expected to be active in the infrared. The assignments given in Table 3 are discussed briefly below. One of the $\delta(\text{NH})$ modes was identified by Bürger and Höfler⁷ with a weak band at 1665 cm^{-1} . This band has no counterpart in the Raman spectrum and disappears on scrupulous drying of III over barium oxide. The strong shoulder at 940 cm^{-1} on the band at 915 cm^{-1} has not hitherto been noted, but it is also revealed in the Raman spectrum as a shoulder at 950 cm^{-1} . The rest of the spectrum is in substantial agreement with reported evidence.

The hydrogen stretching region requires no special comments. Two of the $\delta(\text{NH})$ modes are expected in the $\delta(\text{CH}_3)$ region and cannot be assigned with certainty. In IIIa, however, there is a band of medium strength at 1475 cm^{-1} which is assigned to one of the $\delta(\text{NH})$ fundamentals. In IIIb there can be little doubt that the corresponding modes give rise to the bands at 1158 and 1118

Table 3. Observed infrared spectra of 1,2-dimethylhydrazine (III), 1,2-dimethyl- d_4 -hydrazine (IIIa) and 1,2-dimethylhydrazine- d_2 (IIIb) and proposed assignments for 25 fundamentals in the 500–4000 cm^{-1} region.

Assignment and expected number of fundamentals	III		IIIa	IIIb		
	liquid	solution ^a	solution ^b	liquid	solution ^a	
$\nu(\text{N}-\text{H})/\nu(\text{N}-\text{D})$	2	3290s 3223s —	3335m 3285s 3225s	3340s 3240ssh —	2444s 2410m 2370s	2472m 2440mbr 2374mbr
$\nu(\text{C}-\text{H})/\nu(\text{C}-\text{D})$	6	2975vs 2940vs — 2850vs — 2780s	2966s 2946vs 2885ssh 2866s 2840s 2784s	2305w 2230s 2195s 2125m 2090m 2055s	2975s 2945vs 2885s 2860s 2835s 2785s	2977vs 2948vs 2883s 2861s 2841s 2782s
$\delta(\text{NH})/\delta(\text{ND})$	2	— —	— —	— 1475m	1158m 1118m	1158m 1118m
$\delta(\text{CH}_3)/\delta(\text{CD}_3)$	6	1507m 1495ssh 1478s 1461ssh 1455s 1410m	1510m — 1485s — 1453s 1412w	1160m 1130m — — — —	1510wsh — 1469s — 1442s 1411m	1500wsh — 1467s 1448msh 1442s 1410m
$\rho(\text{CH}_3)/\rho(\text{CD}_3)$	4	1202s — 1111m 1095m	1198s — 1110m 1094m	889s — 800msh 782s	1212m 1196m 1094m 1078m	1210m 1193m 1092m 1078m
Skeletal stretch	1	1039s	1037s	1046vs	979s	977s
$\delta(\text{NH})/\delta(\text{ND})$	1	940ssh	970msh	936msh	758ssh	740ssh ^b
Skeletal stretch	1	915vsbr	920vs	955s	940m	936m
$\delta(\text{NH})/\delta(\text{ND})$	1	880ssh	886s	889s	662s	657vs
Skeletal stretch	1	755sbr	748vs	709s	728sbr	713sbr ^b

^a In methylene chloride. ^b In tetrahydrofuran.

cm^{-1} , which vary in strength with the percentage of deuteration. The assignment of the two remaining $\delta(\text{NH})$ modes in III to the shoulders at 940 cm^{-1} and 880 cm^{-1} seems justified by comparison with IIIa and IIIb. In further support we note that the band at 880 cm^{-1} is displaced to 865 cm^{-1} in the gas phase ⁴ as expected for a vibration sensitive to hydrogen bonding. Axford *et al.*⁴ proposed that the strong band at 755 cm^{-1} (720 cm^{-1} in the gas phase)

was one of the $\delta(\text{NH})$ fundamentals. However, this seems excluded by the observation that IIIb does not absorb between 500 and 650 cm^{-1} . Instead, this band must be due to a skeletal stretching vibration that, by analogy to I and II, is expected around 800 cm^{-1} . The assignment of the remaining skeletal stretching vibrations and the $\delta(\text{CH}_3)$ and $\rho(\text{CH}_3)$ modes is straightforward.

EXPERIMENTAL

The infrared spectra were obtained at room temperature on a Perkin-Elmer Model 337 Grating Infrared Spectrophotometer, with the occasional use of a Hitachi Perkin-Elmer Model 159 scale expander. The instrument was calibrated according to the instructions of the manufacturer. Frequencies should be accurate to about $\pm 2 \text{ cm}^{-1}$ below 1333 cm^{-1} and about $\pm 5 \text{ cm}^{-1}$ above. The tetrahydrofuran used as solvent was distilled over lithium aluminium hydride immediately before use.

Methyl-d₃ iodide was prepared following essentially the method of Cotton *et al.*¹⁹ In the first step of this synthesis (deuterium exchange of trimethylsulfoxonium iodide with 99.7 % deuterium oxide catalyzed by potassium carbonate) the temperature required for optimum yield was found by us to be 90°C. If the temperature is raised much higher, the formation of a yellow colour and small amounts of oily drops is observed. Yield 60 % with 98.7 % deuteration. The yield is slightly lower than reported by Cotton¹⁹ which is perhaps partly due to recirculation of the low-percentage deuterium oxide. Thermolysis of the salt was most readily effected by working at 30 mm Hg and at 180°C at the beginning, slowly lowering the temperature to 140°C at the end. The thermolysis flask was connected through an air-cooled reflux condenser to two liquid nitrogen cooled traps in series. In this way, only the methyl-d₃ iodide distilled during decomposition of the salt. Yields ranging from 88 to 93 % were repeatedly obtained. The dimethyl-d₆ sulfoxide served as solvent for the thermolysis and could be distilled separately after decomposition of the salt was completed.

Reaction between hydrazine and methyl-d₃ iodide. Anhydrous hydrazine (43 ml), cooled in an ice-bath, was treated with methyl-d₃ iodide (21 ml) added with stirring at a rate of one drop per sec. When the addition was completed, the ice-bath was removed and the reaction mixture stirred for another $\frac{1}{2}$ h. By careful heating, the precipitate was brought into solution and the crude mixture of methylhydrazines (8.5 g, b.p. 60–95°C) was collected through a short Vigreux column. The gas chromatographic separation was carried out with the aid of a column prepared according to the instructions given by Bigli and Saglietto.²⁰ Finally, the deuterated methylhydrazines Ia–IIIa were dried over barium oxide.

N-deuterated methylhydrazines, Ib–IIIb. Each of the parent hydrazines was subjected to the procedure described by Bürger and Höfler⁷ for 1,1-dimethylhydrazine. The treatment was repeated until the infrared bands originating from the undeuterated amino groups had disappeared.

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