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Force Constants in MethylamineA Determination by the Use of 15N Isotope Shifts

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ponents. This molecule is a very interesting example of an almost prolate top along the a axis but with its dipole moment almost entirely in the b direction.

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Force Constants in Methylamine—A Determination by the Use of ^{15}N Isotope Shifts

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Infrared absorption spectrum of methylamine—^{15}N has been examined in the gaseous state, and the amounts of ^{15}N isotope shifts have been determined for 12 absorption bands of undeuterated methylamine. Force constants in the methylamine molecule were adjusted on the bases of the vibrational frequencies of CH_3NH_2, CH_3ND_2, CD_3NH_2, and CD_3ND_2 and of the ^{15}N isotope shifts of CH_3NH_2 by the method of the least squares. The ^{15}N isotope shifts have been found to be useful data for selecting the best set of force constants among several sets which are equally good as far as only the agreement of the observed and calculated frequencies are taken into account.

I. INTRODUCTION

There have been a number of reports published on the normal coordinate treatment of methylamine. All of the recent three works[1–3] were made on the assumption of the Urey–Bradley force field (or a simplified valence force field) and on the basis of the vibrational frequencies given by Gray and Lord[4] of the four isotopic species, namely, CH_3NH_2, CH_3ND_2, CD_3NH_2, and CD_3ND_2. What we are going to present here involves the following advancement. First, we have added ^{15}N isotope shifts in the vibrational frequencies of CH_3NH_2 as new data for the force constant determination. Secondly, we have removed the Urey–Bradley assumption. We adopted the local symmetry force field which is one of the general force fields. Although we could not determine all of the force constant values without any assumptions, we could classify force constants into groups: what can be estimated mainly by the vibrational frequencies, what can be estimated by the ^{15}N isotope shifts, and what should be estimated by the ^{13}C isotope shifts. The results will be summarized in this paper.

II. ^{15}N ISOTOPE SHIFTS

Methylamine–^{15}N was prepared from corresponding hydrochloride. The latter was prepared by Dr. A. Nakamura, Central Research Laboratories, Ajinomoto Co., Inc., from ammonium sulfate in which 98% of nitrogen was ^{15}N, and kindly placed by him at our disposal. The procedure of the preparation was similar

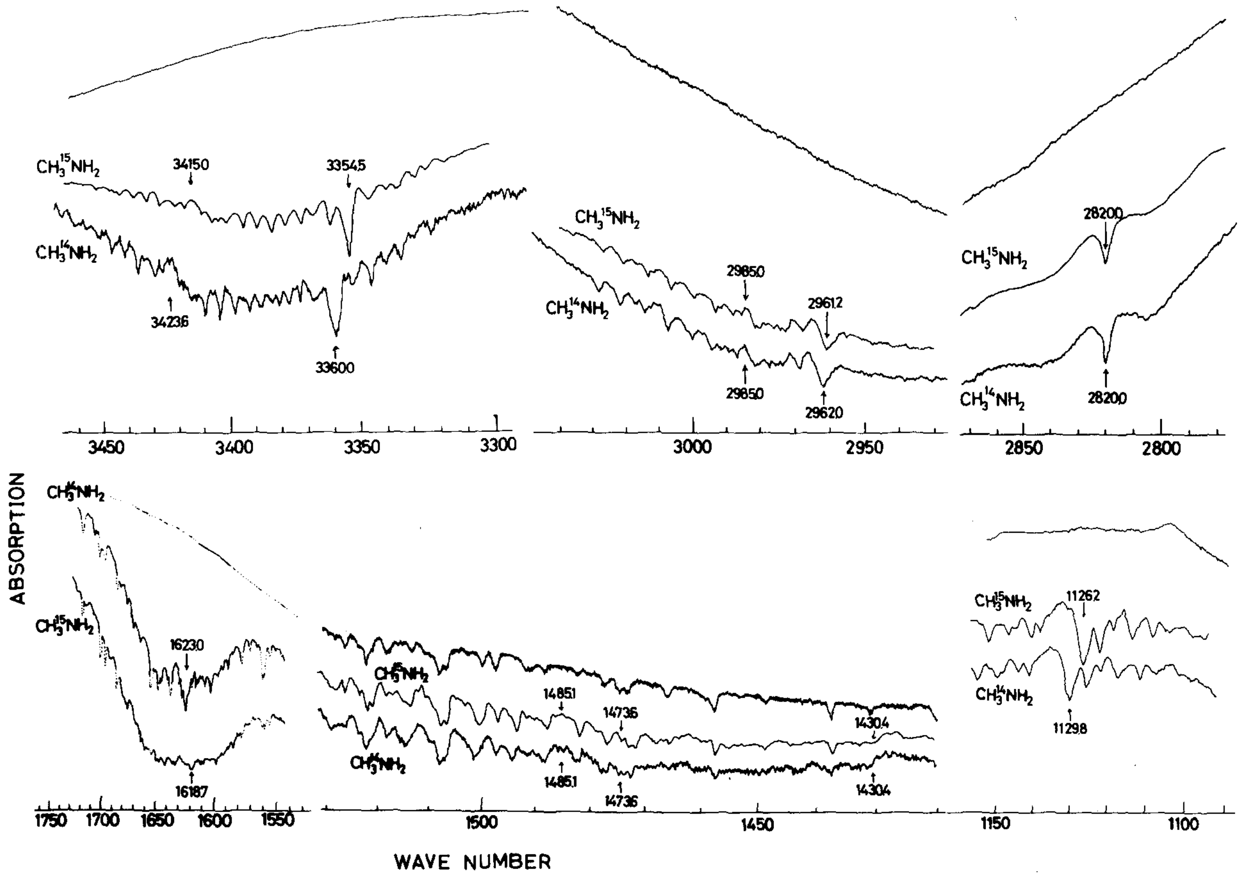
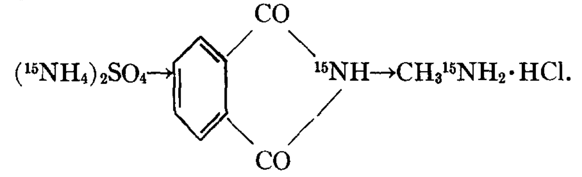


FIG. 1. ^{15}N isotope shifts observed for six absorption bands of methylamine. The three curves shown in each spectral region are what are recorded by the use of a single-beam spectrophotometer (Perkin–Elmer Model 112G): for infrared radiation passed through an empty gas cell, through the cell with CH$_3{}^{14}$NH$_2$ gas, and through the cell with CH$_3{}^{15}$NH$_2$ gas.

to that of DL-alanine–^{15}N[5] and involves the following steps:



The infrared absorption measurements were made by the use of a Perkin–Elmer Model 112G spectrometer with a 75 line/mm grating blazed at 12 μ and a KBr foreprism. A gas cell with optical path length of 10 cm was used. The pressure of the gas in the cell was 5–300 mmHg. The calibration of the frequency scale of the instrument was made by observing several absorption lines with known frequencies of H$_2$O and CO$_2$.

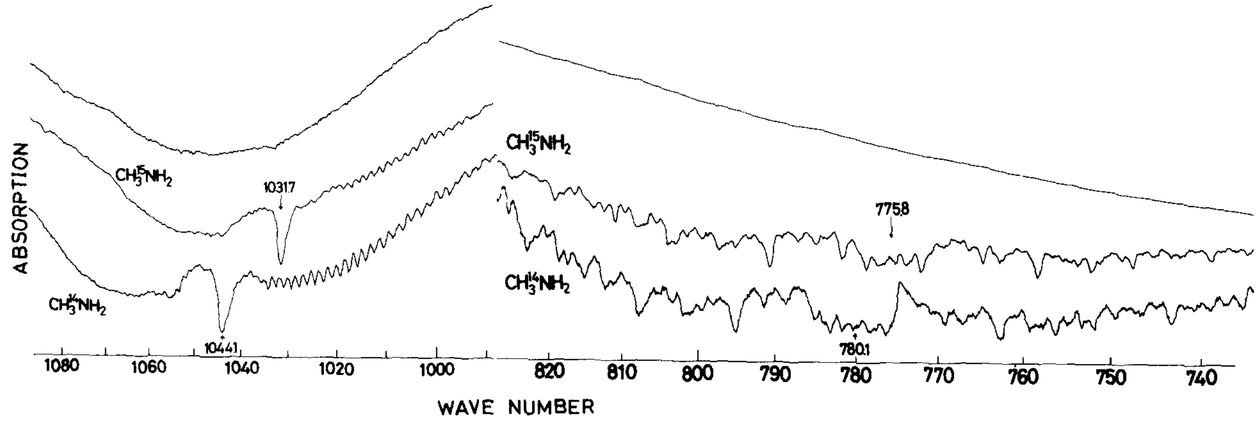


FIG. 2. ^{15}N isotope shifts observed for the 1044 and 780 cm^{-1} bands of methylamine; see the legend of Fig. 1.

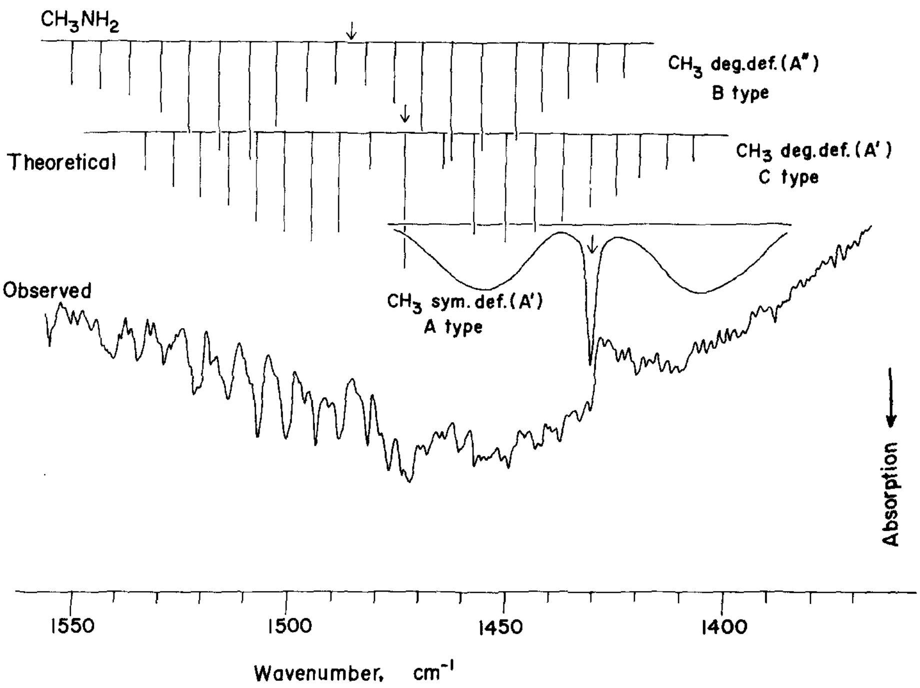


FIG. 3. Infrared absorption curve of CH_3NH_2 in the gaseous state in the 1550–1370 cm^{-1} region, and its interpretation.

In Figs. 1 and 2, some of the reproductions of the recorded curves are illustrated. The frequency of the band center of each of the absorption bands is given in Table I with the isotope shift determined.

III. AMINO TWISTING FREQUENCIES

As was pointed out by Dellepiane and Zerbi,[3] one of the difficulties in the vibrational assignment of CH_3NH_2 and deutero-derivatives is the location of the NH_2 and ND_2 twisting motion.

Gray and Lord[4] tentatively located the NH_2 twisting vibration of CH_3NH_2 at 1455 cm^{-1}. This assignment, however, is not supported by our recent reexamination of the infrared absorption spectrum of CH_3NH_2. Figure 3 is a reproduction of a transmission curve of CH_3NH_2 gas in the 1550–1370 cm^{-1} region recorded by the use of a Perkin–Elmer Model 621 spectrophotometer which has probably a slightly better resolution (about 0.3 cm^{-1}) than that which was used by Gray and Lord.[4]

TABLE I. ^{15}N isotope shifts in the vibrational frequencies of methylamine in gaseous state.

Frequency, cm^{-1}		Shift, cm^{-1}	Assignment	
^{14}N Species	^{15}N Species			
3423.6	3415.0	-8.6	NH_2 antisym.str.	(A")
3360.0	3354.5	-5.5	NH_2 sym.str.	(A')
2985.0	2985.0	0	CH_3"deg."str.	(A")
2962.0	2961.2	-0.8	CH_3"deg."str.	(A')
2820.0	2820.0	0	CH_3 sym.str.	(A')
1623.0	1618.7	-4.3	NH_2 scissor.	(A')
1485.$_1$	1485.$_1$	0	CH_3"deg."def.	(A")
1473.6	1473.6	0	CH_3"deg."def.	(A')
1430.4	1430.4	0	CH_3 sym.def.	(A')
1129.8	1126.2	-3.6	CH_3 rocking	(A')
1044.1	1031.7	-12.4	C-N str.	(A')
780.1	775.8	-4.3	NH_2 wag.	(A')

TABLE II. Local symmetry coordinates.

A'	S_1 ;	$(\Delta r_1+\Delta r_2)/\sqrt{2}$	NH_2 sym. str.
	S_2 ;	$(\Delta r_3+\Delta r_4+\Delta r_5)/\sqrt{3}$	CH_3 sym. str.
	S_3 ;	$(2\Delta r_3-\Delta r_4-\Delta r_5)/\sqrt{6}$	CH_3 deg. str.
	S_4 ;	ΔR	CN str.
	S_5 ;	$(2\Delta\alpha_1-\Delta\beta_1-\Delta\beta_2)/\sqrt{6}$	NH_2 scissor.
	S_6 ;	$(\Delta\alpha_1+\Delta\beta_1+\Delta\beta_2)/\sqrt{3}$	NH_2 wag.
	S_7 ;	$(2\Delta\alpha_3-\Delta\alpha_4-\Delta\alpha_5)/\sqrt{6}$	CH_3 deg. def.
	S_8 ;	$(\Delta\alpha_3+\Delta\alpha_4+\Delta\alpha_5-\Delta\beta_3-\Delta\beta_4-\Delta\beta_5)/\sqrt{6}$	CH_3 sym. def.
	S_9 ;	$(2\Delta\beta_3-\Delta\beta_4-\Delta\beta_5)/\sqrt{6}$	CH_3 deg. rock.
A"	S_{10};	$(\Delta r_1-\Delta r_2)/\sqrt{2}$	NH_2 antisym. str.
	S_{11};	$(\Delta r_4-\Delta r_5)/\sqrt{2}$	CH_3 deg. str.
	S_{12};	$(\Delta\beta_1-\Delta\beta_2)/\sqrt{2}$	NH_2 twist.
	S_{13};	$(\Delta\alpha_4-\Delta\alpha_5)/\sqrt{2}$	CH_3 deg. def.
	S_{14};	$(\Delta\beta_4-\Delta\beta_5)/\sqrt{2}$	CH_3 deg. rock.
	S_{15};	$\Delta\theta$[a]	torsion

[a] As for the definition of $\Delta\theta$ see "Computer Programs for Normal Coordinate treatment of Polyatomic Molecules," Ref. 12.

TABLE III. Numbering of F-matrix elements and the definition of force constants.

	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9
S_1 NH_2 sym.str.	1(37)[a]								
S_2 CH_3 sym.str.	10	2(38)							
S_3 CH_3 deg.str.	11	–[b]	3(39)						
S_4 CN str.	12	18	–	4					
S_5 NH_2 scissor.	13	19	22	26	5				
S_6 NH_2 wag.	14	20	23	27	29	6(40)			
S_7 CH_3 deg.def.	15	–	24	–	30	33	7		
S_8 CH_3 sym.def.	16	21	–	28	31	34	–	8	
S_9 CH_3 deg.rock.	17	–	25	–	32	35	36	–	9

	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}
S_{10} NH_2 antisym. str.	41(62)					
S_{11} CH_3 deg.str.	47	42(63)				
S_{12} NH_2 twist.	48	52	43			
S_{13} CH_3 deg.def.	49	53	56	44		
S_{14} CH_3 deg.rock.	50	54	57	59	45	
S_{15} torsion	51	55	58	60	61	46

[a] The force constants Nos. 1, 2, 3, 6, 41, and 42 are for the *hydrogenated* (NH_2 and/or CH_3) molecules. Because of the anharmonicities of the C–H and N–H stretching and the NH_2 wagging vibrations, appreciably different effective values of force constants are expected for the deuterated (ND_2 and/or CD_3) molecules. These force constants are denoted respectively by Nos. 37, 38, 39, 40, 62, and 63.

[b] The off-diagonal elements of mutually perpendicular local symmetry coordinates are zero. These elements are written by bar, namely, any force constants are *not* assigned, on the assumption of local symmetry force field.

As may be seen in the figure, most of the stronger absorption lines observed, including those in the 1450–1460 cm^{-1} region, can be assigned to those belonging to the B-type band at 1485.1 cm^{-1} (A'' type CH_3 "degenerate" deformation), the C-type band at 1473.6 cm^{-1} (A' type CH_3 "degenerate" deformation), or A-type band at 1430.4 cm^{-1} (CH_3 symmetric deformation). There are very weak absorptions in the vicinity of 1415 cm^{-1} in CH_3NH_2 (see Fig. 3) and of 1416 cm^{-1} in CD_3NH_2.[4] It is probable, however, that they are the overtone bands of the amino wagging vibrations, rather than the NH_2 twisting bands now in question.

Dellepiane and Zerbi[3] located the amino twisting frequencies of CH_3NH_2, CD_3NH_2, CH_3ND_2, and CD_3ND_2 respectively at 995, 1100, 766, and 713 cm^{-1}, on the basis of their normal coordinate calculation. This set of frequencies, however, is not fully acceptable because of the following two reasons: First, no absorption band nor Raman line has even been observed at any of these frequencies. Second, it has been shown that, on the basis of the general force field, the twisting frequency cannot be estimated from the observed frequencies of NH_2 scissoring, ND_2 scissoring, NH_2 wagging, and/or ND_2 wagging vibrations. In the course of determining the force constant values, they made an assumption: the off-diagonal elements in the potential energy matrix F corresponding to the cross terms of the CNH bending and the HNH bending coordinates, for example, are either zero or under the constraint of the Urey–Bradley force field. The amino twisting frequencies are determined only upon such an assumption, whereas such an assumption is not justified by the observed frequencies. We found that there are several sets of force constants, which reproduce the observed frequencies of the four isotopic methylamine molecules as well as the set presented by Dellepiane and Zerbi,[3] and which give greatly different frequency values for the amino twisting vibrations. For example, our set a, set b, and set c give the NH_2 twisting frequency of CH_3NH_2 at 1455, 1339, and 1256 cm^{-1}, respectively.

Hydrazine (gas) gives one of its amino twisting frequencies at 1260 cm^{-1},[6,7] and partly deuterated ammonia, NH_2D, at 1394 cm^{-1}.[8] Ethylamine (gas) gives two weak absorption bands at 1294.0 and 1238.4 cm^{-1}, both of which show ^{15}N isotope shifts of 1.7 cm^{-1}.[9] This is explained by considering that there is a coupling between the NH_2 and CH_2 twisting vibrations in the ethylamine molecule. The two frequencies 1294.0 and 1238.4 cm^{-1} are assigned these two coupled twisting vibrations. The amounts of the ^{15}N isotope shifts are compatible with this assignment. In the spectrum of CH_3NH_2, now in question, there are weak bands at 1335 and 1246 cm^{-1} which remain unassigned. The weak band at 1335 cm^{-1} of CD_3NH_2 also remains unassigned. On taking these data into account, it is probable that the NH_2 twisting frequency of CH_3NH_2

TABLE IV. Force constants on the local symmetry force field (for the *A′* type vibrations).

		Set I	Set II	Set III
1	$f(NH_2ss)$[a]	6.444(0.009)[b]	6.443(0.005)	6.436
2	$f(CH_3ts)$	4.616(0.007)	4.615(0.004)	4.615
3	$f(CH_3ds)$	4.739(0.007)	4.743(0.004)	4.743
4	f(CN)	5.123(0.039)	5.126(0.023)	5.178
5	$f(NH_2sc)$	0.661(0.004)	0.655(0.006)	0.546
6	$f(NH_2wa)$	0.566(0.097)	0.674(0.048)	0.699
7	$f(CH_3dd)$	0.567(0.010)	0.535(0.016)	0.561
8	$f(CH_3sd)$	0.642(0.003)	0.645(0.002)	0.647
9	$f(CH_3dr)$	0.789(0.009)	0.817(0.023)	0.789
10	f(ss-ts)	0.0	0.0	0.0
11	f(ss-ds)	0.0	0.0	0.0
12	f(ss-CN)	0.474	0.499	0.324
13	f(ss-sc)	0.069	0.062	0.106
14	f(ss-wa)	0.299	0.308	0.247
15	f(ss-dd)	0.0	0.0	0.0
16	f(ss-sd)	0.0	0.0	0.0
17	f(ss-dr)	0.0	0.0	0.0
18	f(ts-CN)	0.825	0.836	0.853
19	f(ts-sc)	0.0	0.0	0.0
20	f(ts-wa)	0.0	0.0	0.0
21	f(ts-sd)	-0.093	-0.096	-0.100
22	f(ds-sc)	0.0	0.0	0.0
23	f(ds-wa)	0.0	0.0	0.0
24	f(ds-dd)	-0.093	-0.093	-0.093
25	f(ds-dr)	0.316	0.321	0.327
26	f(CN-sc)	-0.230(0.045)	-0.242(0.012)	-0.158
27	f(CN-wa)	0.325	0.487(0.017)	0.491
28	f(CN-sd)	-0.499(0.022)	-0.506(0.023)	-0.517
29	f(sc-wa)	-0.197(0.154)	-0.307(0.041)	0.182
30	f(sc-dd)	0.0	0.0	0.0
31	f(sc-sd)	0.023(0.016)	0.026(0.008)	-0.008
32	f(sc-dr)	0.030(0.029)	0.006(0.014)	0.021
33	f(wa-dd)	0.0	0.0	0.0
34	f(wa-sd)	0.037(0.017)	-0.001(0.033)	-0.008
35	f(wa-dr)	-0.024(0.007)	-0.025(0.006)	-0.015
36	f(dd-dr)	-0.057(0.025)	0.001(0.021)	-0.042
37	$f(ND_2ss)$	6.729(0.012)	6.733(0.007)	6.711
38	$f(CD_3ts)$	4.890(0.011)	4.882(0.006)	4.883
39	$f(CD_3ds)$	4.788(0.010)	4.794(0.006)	4.797
40	$f(ND_2wa)$	0.602(0.097)	0.706(0.049)	0.742

[a] Unit: mdyn/Å for stretch–stretch elements, mdyn for stretch–deform elements, and mdyn·Å for deform–deform elements.

[b] Statistical uncertainties calculated in the course of the least squares procedure are given in parentheses.

TABLE V. Observed and calculated frequencies ν and ^{15}N isotope shifts $\delta\nu$ in cm^{-1}.

ν_{obs} (cm^{-1})	$\nu_{obs}-\nu_{calc}$ (cm^{-1})		
	Set I	Set II	Set III
CH_3NH_2			
ν_1 3360	-1	-1	-1
ν_2 2962	1	1	1
ν_3 2820	2	2	2
ν_4 1623	-2	-3	-2
ν_5 1474	3	3	3
ν_6 1430	-2	0	0
ν_7 1130	0	0	-2
ν_8 1044	-1	-1	-2
ν_9 780	0	1	-1
CH_3ND_2			
ν_1 2479	2	2	2
ν_2 2961	0	-1	-1
ν_3 2817	-2	-2	-2
ν_4 1234	-1	1	2
ν_5 1468	-3	-3	-3
ν_6 1430	0	0	-3
ν_7 1117	0	1	2
ν_8 997	-1	1	-1
ν_9 625	2	2	1
CD_3NH_2			
ν_1 3361	0	1	1
ν_2 2203	0	0	1
ν_3 2077	0	2	2
ν_4 1624	2	2	1
ν_5(1065)	--	--	--
ν_6 1142	1	-1	1
ν_7 913	4	1	1
ν_8 973	3	0	3
ν_9 740	4	1	1
CD_3ND_2			
ν_1 2477	-1	-2	-2
ν_2 2202	0	0	-1
ν_3 2073	-3	-2	-2
ν_4 1227	1	0	-1
ν_5(1065)	--	--	--
ν_6 1123	1	0	1
ν_7 880	-3	-1	-1
ν_8 942	4	0	1
ν_9 601	1	-1	-1
^{15}N shift			
$\delta\nu_{obs}$ (cm^{-1})	$\delta\nu_{obs}-\delta\nu_{calc}$ (cm^{-1})		
$\delta\nu_1$ -5.5	-1.2	-1.3	-1.1
$\delta\nu_2$ -0.8	-0.8	-0.8	-0.8
$\delta\nu_3$ 0.0	0.2	0.2	0.2
$\delta\nu_4$ -4.3	0.2	0.4	1.4
$\delta\nu_5$ 0.0	0.0	0.3	0.0
$\delta\nu_6$ 0.0	0.2	0.1	0.2
$\delta\nu_7$ -3.6	-0.4	0.6	-1.0
$\delta\nu_8$ -12.4	2.1	0.2	0.3
$\delta\nu_9$ -4.3	-0.9	-0.3	0.3

is in the 1200–1450 cm^{-1} region. We do not attempt to locate the amino twisting frequency in any further detail. We shall present below only the results which are independent of the location of the amino twisting frequency in this region.

IV. NORMAL COORDINATE TREATMENT

The purpose of our present normal coordinate treatment is to reach the best set of force constants on

TABLE VI. The P_{AB} matrix elements for force constant Set II for the A' type vibrations.

k_B (fix) / k_A (variable)	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	30	33
1	.	.	.	.1	.	.	.	-.1	.	.	.	.	.	.	.	.	.	.
2	.	.	.	.	.	.	.	.	.1	-.1	.	.3	.	.	.	.	.	.
3	.	.	.	.	.	.	.	.	.	.	.	.	.1	-.1	-.3	.1	.	.
4	.	.	.1	.	.	-.1	.	.2	.3	.	.	.1	.1	.	.	.	.	.2
5	.	.	.	.	.	-.1	.	.	.	.2	.	.	-.3	.	.	.	-2.7	.5
6	.	.	.	.	.1	.6	.	.	-.2	-1.3	.1	-.3	2.0	-.1	.3	-.3	21.1	-3.9
7	.	.	.	.	.	.	.	.	.1	.1	.	.1	-.1	.	-.1	.1	-1.7	.3
8	.	.	.	.	.	.	.	.	.	.	.	-.1	.	.	.	.	.2	.
9	.	.	.	.	.	.	.	.	-.1	-.1	.	-.1	.1	.	.1	-.1	1.6	-.3
26	.	.	.	.	.	.	.	.	.	.1	.	.	.2	.	.	.	1.5	-.2
27	.	.	.	.	.1	.1	.	-.1	-.1	-.1	.1	-.1	.1	.	.	.	1.8	-.4
28	.	.	.	.	.	-.1	.	-.1	.	.4	-.1	.1	-.7	.	-.1	.1	-6.4	1.1
29	.	.	.	.	.	-.5	.	.	.2	1.1	-.1	.2	-1.6	.1	-.2	.3	-17.6	3.3
31	.	.	.	.	.	.	.	.	.	.	.	.	-.2	.	.	.	-1.3	.2
32	.	.	.	.	.	-.2	.	.	.1	.3	.	.1	-.5	.	-.1	.1	-5.5	1.1
34	.	.	.	.	.	.2	.1	.1	-.1	-.6	.1	.	1.1	.	.1	-.1	9.6	-1.6
35	.	.	.	.	.	.	.	.1	.	-.1	.	.	.2	.	.	.	2.1	.
36	.	.	.	.	.	.1	.	.	-.1	-.1	.	-.1	.2	.	.1	-.2	2.4	-.4

the basis of the data so far obtained of the methylamine molecule. As the data we use fundamental frequencies of four isotopic methylamines, CH_3NH_2, CH_3ND_2, CD_3NH_2, and CD_3ND_2, and the ^{15}N isotope shifts observed for CH_3NH_2. Because of the anharmonicity of the internal potential, the fundamental frequencies are in general appreciably different from the normal frequencies for the equilibrium conformation (i.e., at the potential minimum). These differences, however, are not taken into account. In other words, we do not attempt, in our present treatment, to reach a set of force constants at the very potential minimum. Instead, we try to obtain an effective set good for reproducing the actually observed fundamental frequencies. For the NH, ND, CH, and CD stretching vibrations, however, the anharmonicities are so great that it is impossible to fit both of the NH and ND (or CH and CD) fundamental frequencies with the same value of force constant. We assume a different value for the effective force constant of ND (or CD) from that of NH (or CH).[10] The NH_2 and ND_2 wagging vibrations are also strongly anharmonic, and the force constant for the former is assumed to be different from that for the latter.

The relation between the force constants and the vibrational frequencies is given by the secular equation

$$|GF-E\lambda|=0, \tag{1}$$

where G is the inverse kinetic energy matrix, F the potential energy matrix, E the unit matrix, and λ is equal to $4\pi^2c^2\nu^2/N$, c being the light velocity, N the Avogadro number, and ν the vibrational wavenumber.

The relation between the force constants and ^{15}N isotope shifts is now given as

$$|\delta G\cdot F-E\cdot\delta\lambda|=0, \tag{2}$$

where δG is the difference in the G matrices of ^{15}N and ^{14}N species,

$$\delta G=G(^{15}N)-G(^{14}N), \tag{3}$$

and $\delta\lambda$ is the corresponding difference in λ. As the basis of the G and F matrices, we choose a set of symmetry coordinates[10] S defined in Table II. The notations of the bond lengths and bond angles are defined in Fig. 4. The set of normal coordinates Q is given as

$$S=LQ. \tag{4}$$

In our treatment we chose the local symmetry force field.[10] The force constants are called by numbers which are given in Table III.

As for the bond lengths, the following values given by Itoh[11] were used: C–N 1.474 Å, C–H 1.093 Å, and N–H 1.014 A. All the bond angles were assumed to be tetrahedral. In addition, the C–N bond was assumed to be exactly along the symmetry axis of the CH_3 group.

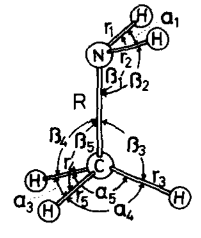


FIG. 4. Structure of the methylamine molecule. The bond lengths and bond angles are denoted as shown here.

TABLE VII. Force constants on the local symmetry force field (for the A'' type vibrations).

Force constants	Set a	Set b	Set c
41	6.382(0.006)[a]	6.383(0.007)	6.383(0.013)
42	4.814(0.005)	4.815(0.006)	4.815(0.011)
43	1.102(0.004)	0.977(0.003)	0.835(0.010)
44	0.581(0.004)	0.585(0.004)	0.581(0.005)
45	0.939(0.004)	0.939(0.004)	0.952(0.010)
46	0.048(0.001)	0.048(0.001)	0.048(0.001)
47	0.0	0.0	0.0
48	0.216	0.216	0.216
49	0.0	0.0	0.0
50	0.0	0.0	0.0
51	0.0	0.0	0.0
52	0.0	0.0	0.0
53	-0.093	-0.093	-0.093
54	0.321	0.321	0.321
55	0.0	0.0	0.0
56	0.074(0.007)	0.083(0.015)	0.050(0.020)
57	-0.185(0.013)	-0.176(0.009)	-0.186(0.007)
58	0.0	0.0	0.0
59	-0.074(0.010)	-0.083(0.012)	-0.080(0.013)
60	0.0	0.0	0.0
61	0.0	0.0	0.0
62	6.539(0.008)	6.542(0.010)	6.546(0.017)
63	4.931(0.007)	4.934(0.008)	4.935(0.015)

[a] Statistical uncertainties calculated in the course of the least squares procedure are given in parentheses.

Numerical calculations were made by a Hitac 5020E at the Computing Center of the University of Tokyo, by the use of programs LSMB and LSMC.[12]

The adjustments of force constants have been made according to the least squares method by the use of the equation[13]

$$\tilde{J}WJ\Delta k=\tilde{J}W\Delta\nu^0. \tag{5}$$

Here,

$$\Delta k=k-k^0, \tag{6}$$

where k^0 is the set of force constants to be refined and k is the refined set of force constants. $\Delta\nu^0$ means

$$\Delta\nu^0=\nu^{\text{obs}}-\nu^0, \tag{7}$$

where ν^{obs} is the set of data, which consists of the observed frequencies and the observed amounts of the ^{15}N isotope shifts. ν^0 is the corresponding set of calculated values, i.e., the vibrational frequencies ν_n and the amounts of the ^{15}N isotope shifts $\delta\nu_n$ calculated from the set of force constants k^0. J is the Jacobian matrix whose elements are $\partial\nu_n/\partial k_m$ and $\partial(\delta\nu_n)/\partial k_m$. The $\partial\nu_n/\partial k_m$ values can be calculated by the method designed by Miyazawa[14] and King *et al.*[15] For an ^{15}N isotope shift, the element of J is given[16] by

$$\frac{\partial(\delta\nu_n)}{\partial k_m}=\frac{N\nu_n}{4\pi^2c^2}\sum_{i(\neq n)}\frac{(L_0^{-1}\delta G\tilde{L}_0^{-1})_{ni}(\tilde{L}_0A_mL_0)_{ni}}{\nu_n^2-\nu_i^2}, \tag{8}$$

where A_m is a matrix by which the F matrix and k_m are related as

$$F=\sum_m A_mk_m, \tag{9}$$

and L_0 is the L matrix [Eq. (4)] calculated on the set of force constants k^0. W in Eq. (5) is a weight matrix whose diagonal elements represent the statistical weights of the observed frequencies and of the amounts of the isotope shifts.

TABLE VIII. Observed and calculated (indicated by asterisk) frequencies ν and ^{15}N isotope shifts $\delta\nu$ in cm^{-1} (for A'' vibration).

	ν_{obs} (cm^{-1})	$\nu_{\text{obs}}-\nu_{\text{calc}}$ (cm^{-1})		
		Set a	Set b	Set c
CH_3NH_2				
ν_{10}	3424	-2	-2	-2
ν_{11}	2985	0	0	0
ν_{12}	1485	-2	-3	-1
ν_{13}	~	(1424)*	(1339)*	(1256)*
ν_{14}	1195	2	2	16
ν_{15}	264	-3	-3	-3
CH_3ND_2				
ν_{10}	2556	0	0	0
ν_{11}	2985	0	0	0
ν_{12}	1485	-1	-1	-1
ν_{13}	-	(1058)*	(994)*	(916)*
ν_{14}	1187	-4	-6	-12
ν_{15}	225	3	3	3
CD_3NH_2				
ν_{10}	3427	2	2	2
ν_{11}	2236	-1	-1	-1
ν_{12}	1077	3	2	3
ν_{13}	~	(1416)*	(1335)*	(1230)*
ν_{14}	–	–	–	–
ν_{15}	–	–	–	–
CD_3ND_2				
ν_{10}	2556	0	0	0
ν_{11}	2238	1	1	1
ν_{12}	1077	-2	2	0
ν_{13}	–	(1051)*	(996)*	(926)*
ν_{14}	910	4	6	11
ν_{15}	–	–	–	–
^{15}N shift				
	$\delta\nu_{\text{obs}}$ (cm^{-1})	$\delta\nu_{\text{obs}}-\delta\nu_{\text{calc}}$ (cm^{-1})		
$\delta\nu_{10}$	-8.6	1.0	1.0	1.3
$\delta\nu_{11}$	0.0	0.0	0.0	0.0
$\delta\nu_{12}$	0.0	0.1	0.2	0.0
$\delta\nu_{13}$	–	–	–	–
$\delta\nu_{14}$	–	–	–	–
$\delta\nu_{15}$	–	–	–	–

TABLE IX. Force constants[a] for the general valence force field.

	Δr_1	Δr_2	Δr_3	Δr_4	Δr_5	ΔR	$\Delta\alpha_1$	$\Delta\beta_1$	$\Delta\beta_2$	$\Delta\alpha_3$	$\Delta\alpha_4$	$\Delta\alpha_5$	$\Delta\beta_3$	$\Delta\beta_4$	$\Delta\beta_5$	$\Delta\theta$
Δr_1 [b]	6.413 (6.638)															
Δr_2	0.030 (0.046)	6.413 (6.638)														
Δr_3	0.0	0.0	4.652 (4.732)													
Δr_4	0.0	0.0	-0.055 (0.006)	4.760 (4.939)												
Δr_5	0.0	0.0	-0.055 (0.006)	-0.055 (0.006)	4.760 (4.939)											
ΔR	0.353	0.353	0.483	0.483	0.483	5.126										
$\Delta\alpha_1$	0.162	0.162	0.0	0.0	0.0	0.084^{*}	0.372									
$\Delta\beta_1$	0.216	0.0	0.0	0.0	0.0	0.380^{*}	-0.066	0.967 (1.015)								
$\Delta\beta_2$	0.0	0.216	0.0	0.0	0.0	0.380^{*}	-0.066	-0.010	0.967 (1.015)							
$\Delta\alpha_3$	0.0	0.0	0.0	0.093	0.093	0.0	0.0^{**}	0.0^{**}	0.0^{**}	0.436						
$\Delta\alpha_4$	0.0	0.0	0.093	0.0	0.093	0.0	0.0^{**}	0.0^{**}	0.0^{**}	-0.074^{++}	0.511					
$\Delta\alpha_5$	0.0	0.0	0.093	0.093	0.0	0.0	0.0^{**}	0.0^{**}	0.0^{**}	-0.074^{++}	-0.074^{++}	0.511				
$\Delta\beta_3$	0.0	0.0	0.321	0.0	0.0	0.413	-0.013^{+}	-0.005^{+}	-0.005^{+}	0.0	-0.074^{++}	-0.074^{++}	0.682			
$\Delta\beta_4$	0.0	0.0	0.0	0.321	0.0	0.413	-0.013^{+}	-0.005^{+}	0.037^{+}	-0.074^{+}	0.0	-0.074^{++}	-0.074^{++}	0.865		
$\Delta\beta_5$	0.0	0.0	0.0	0.0	0.321	0.413	-0.024^{+}	0.037^{+}	-0.005^{+}	-0.074^{++}	-0.074^{++}	0.0	-0.074^{++}	-0.074^{++}	0.865	
$\Delta\theta$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.048

[a] Unit: mdyn/Å for stretch–stretch elements, mdyn for stretch–deform elements, and mdyn·Å for deform–deform elements. *, Calculated from Nos. 26 and 27; **, Assumed (not consistent with the value of No. 56); $^{+}$, Calculated from Nos. 31, 32, 34, and 35 (not consistent with the value of No. 57); $^{++}$, Calculated from Nos. 7, 8, 9, 44, and 45, with an assumption that all of these elements have the same value with one another (consistent with No. 59, but not with No. 36).

[b] See Fig. 4.

V. SIGNIFICANCE OF THE USE OF ^{15}N SHIFTS

In this section we show that the secular equation (2) may provide a quite different type of information on the F matrix from what the secular equation (1) can provide.

The relation between the force constants and the vibrational frequencies is more readily seen by expressing an approximate solution of Eq. (1) as

$$\lambda_i=(GF)_{ii}+\sum_{j(\neq i)}(GF)_{ij}(GF)_{ji}/[(GF)_{ii}-(GF)_{jj}], \quad (10)$$

with

$$(GF)_{ii}=g_{ii}f_{ii}+\sum_{k(\neq i)}g_{ik}f_{ik} \quad (11)$$

and

$$(GF)_{ij}=\sum_{k}g_{ik}f_{jk}, \quad (12)$$

where the g_{ik}'s and f_{ik}'s are the elements of G and F matrices, respectively. Let us first consider a case where the second term in Eq. (10) is small as compared with the first term. This corresponds to the case where the ith mode (symmetry coordinate) does not strongly couple with other modes, and it is nearly a normal mode of vibration. In this case, λ_i depends upon f_{ii} and the f_{ik}'s [see Eq. (11)]; but it is much more sensitive to f_{ii} than to f_{ik}'s, because $g_{ii}>g_{ik}$ for most k's. In fact, if i is the coordinate for C–H (or N–H) stretching or deformation vibration, the diagonal element g_{ii} is about ten times as great as most of the off-diagonal elements g_{ik}. Only when i and k are two bond-angle-deformation coordinates involving some N–H or C–H bonds in common (such as S_5 and S_6), the g_{ik} value has a comparable order of magnitude to the g_{ii} value. Secondly, we consider a case where $(GF)_{ii}-(GF)_{jj}$ has a small value. This corresponds to a case where there is a coupling between i and j coordinates. In this case λ_i is sensitive to $(GF)_{ij}$, and among the terms in the right side of Eq. (12), $g_{ii}f_{ji}$ should be most important because the coefficient g_{ii} is greater than the other coefficients g_{ik}. In other words, λ_i is sensitive not only to f_{ii} but also to f_{ji}. Thus, if a deuteration (H→D) brings about a new vibrational coupling (between i and j) the set of frequencies (ν_i^{H}, ν_j^{H}, ν_i^{D}, and ν_j^{D}) should be a useful datum for determining the force constants f_{ii}, f_{jj}, and f_{ij}.

TABLE X. *L*-

	ν_{10}	ν_{11}	ν_{12}	ν_{13}	ν_{14}	ν_{15}
CH_3NH_2(A")						
S_{10}	-1.042	0.020	0.001	-0.027	0.000	0.000
S_{11}	0.019	1.049	-0.013	0.018	-0.050	0.000
S_{12}	0.070	-0.081	0.090	1.021	0.264	0.003
S_{13}	0.008	0.147	1.471	-0.161	-0.228	-0.001
S_{14}	0.069	-0.061	0.318	-0.126	0.936	0.003
S_{15}	-0.050	0.010	-0.004	-0.047	-0.057	0.936
CH_3ND_2(A")						
S_{10}	-0.017	0.769	0.008	0.012	-0.009	-0.001
S_{11}	1.049	0.024	-0.014	-0.052	0.004	0.000
S_{12}	-0.072	-0.126	-0.017	0.105	0.785	0.004
S_{13}	0.147	-0.009	1.481	-0.211	-0.060	-0.001
S_{14}	-0.057	-0.108	0.321	0.938	0.058	0.002
S_{15}	0.008	0.070	0.001	-0.043	-0.069	0.776
CD_3NH_2(A")						
S_{10}	1.042	-0.008	-0.026	0.003	0.004	0.000
S_{11}	-0.005	-0.779	0.021	-0.019	-0.026	0.000
S_{12}	-0.071	0.131	1.047	-0.085	0.080	0.003
S_{13}	-0.004	-0.211	0.014	1.086	0.018	-0.001
S_{14}	-0.066	0.125	0.078	0.064	0.745	0.004
S_{15}	0.050	-0.015	-0.053	0.013	-0.060	0.849
CD_3ND_2(A")						
S_{10}	0.769	-0.018	0.003	-0.005	0.011	0.000
S_{11}	-0.018	-0.779	-0.019	0.004	-0.027	0.000
S_{12}	-0.122	0.116	-0.069	0.771	-0.146	0.003
S_{13}	-0.009	-0.211	1.086	-0.004	0.018	-0.001
S_{14}	-0.094	0.127	0.067	0.304	0.681	0.003
S_{15}	0.069	-0.016	0.012	-0.078	-0.030	0.668

	ν_1	ν_2	ν_3	ν_4
CD_3NH_2(A')				
S_1	1.018	-0.005	0.010	-0.009
S_2	-0.008	-0.008	0.721	-0.036
S_3	0.004	0.778	0.011	0.033
S_4	-0.025	-0.001	-0.049	0.081
S_5	-0.050	-0.099	0.067	1.492
S_6	-0.009	0.056	-0.019	-0.118
S_7	0.003	0.206	0.001	-0.038
S_8	0.015	0.004	-0.188	0.006
S_9	0.035	-0.120	0.002	0.038
CD_3ND_2(A')				
S_1	0.736	-0.017	0.027	-0.004
S_2	-0.027	-0.004	0.721	-0.029
S_3	0.018	0.778	0.006	0.013
S_4	-0.038	0.000	-0.051	0.213
S_5	-0.103	-0.054	0.029	1.033
S_6	-0.036	0.051	-0.015	-0.125
S_7	0.009	0.206	0.000	-0.096
S_8	0.023	0.003	-0.187	0.182
S_9	0.051	-0.121	0.004	0.066

The relation between the force constants and the ^{15}N isotope shifts will now be shown by an expression analogous to Eq. (10). Thus, from Eq. (2),

$$\delta\lambda_i=(\delta G\cdot F)_{ii}+\sum_{j(\neq i)}\frac{(\delta G\cdot F)_{ij}(\delta G\cdot F)_{ji}}{(\delta G\cdot F)_{ii}-(\delta G\cdot F)_{jj}}, \tag{13}$$

$$(\delta G\cdot F)_{ii}=\delta g_{ii}\cdot f_{ii}+\sum_{k(\neq i)}\delta g_{ik}\cdot f_{ik}, \tag{14}$$

and

$$(\delta G\cdot F)_{ij}=\sum_k \delta g_{ik}\cdot f_{jk}, \tag{15}$$

where δg_{ii} and δg_{ik} are the elements of δG matrix. The essential point is the fact that the relative amounts of the values of δg_{ii} and δg_{ik} are greatly different from the relative amounts of the g_{ii} and g_{ik} values. First, δg_{ii} and δg_{ik} are zero if corresponding g_{ii} and g_{ik} does not involve the mass of the nitrogen atom. Second, if they are not zero δg_{ii} has a comparable order of magnitude to δg_{ik}. In this way, it is clear that Eq. (13) is a relation quite independent of Eq. (10) for fixing the f_{ii} and f_{ik} values.

VI. WEIGHTS OF THE ^{15}N SHIFTS AS DATA FOR FORCE CONSTANT DETERMINATION

The amounts of the probable error in an observed ^{15}N isotope shift ($\delta\nu$) depends upon how precisely the position of the band center of each isotopic species can be determined. The *Q*-branch peak of the 1044 cm^{-1} band is especially sharp (see Fig. 2), and the analysis of the 780 cm^{-1} band has been made in detail.[17] Therefore, the ^{15}N isotope shifts of these two bands are considered to have smaller errors than those of other bands. The errors have been estimated to be ±0.1 cm^{-1} for the two bands and ±0.2 cm^{-1} for the others.

The error of an observed vibrational frequency itself should, of course, be almost equal to that of the ^{15}N isotope shift. When the anharmonicity factor is taken into account, however, the difference of 1 cm^{-1}, for example, between the observed and calculated frequencies is much less significant than the same amount of difference between the observed and calculated ^{15}N isotope shifts. As has been stated in Sec. IV, we do not make the anharmonicity corrections for the observed matrix elements.

ν_5	ν_6	ν_7	ν_8	ν_9
-0.028	-0.001	-0.019	-0.016	-0.031
0.009	-0.002	-0.048	0.021	0.010
-0.001	-0.021	0.004	0.019	-0.018
0.289	0.008	0.194	-0.139	-0.070
0.104	0.002	0.115	0.290	0.321
0.176	-0.026	0.194	0.514	0.674
0.029	1.053	0.057	0.236	-0.114
0.925	-0.005	-0.551	-0.002	-0.085
-0.078	0.260	-0.187	-0.573	0.363
-0.016	-0.002	0.007	0.003	-0.026
0.022	-0.005	0.043	-0.016	0.007
-0.004	-0.021	-0.006	-0.024	-0.011
0.222	0.013	-0.207	0.104	-0.046
-0.216	0.039	0.101	-0.305	0.309
0.097	-0.022	-0.106	-0.276	0.605
0.088	1.048	-0.052	-0.250	-0.055
0.975	-0.058	0.418	-0.039	-0.068
-0.074	0.262	0.266	0.622	0.182

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
CH_3NH_2 (A')									
S_1	1.018	-0.013	0.021	-0.008	-0.002	-0.013	0.017	-0.024	-0.037
S_2	-0.022	-0.002	1.007	-0.022	-0.002	0.038	0.016	-0.054	0.015
S_3	0.014	1.049	0.002	0.008	-0.021	0.000	-0.049	-0.018	-0.012
S_4	-0.024	0.000	-0.029	0.077	0.002	0.100	-0.095	0.344	-0.099
S_5	-0.051	-0.041	0.028	1.492	0.036	0.044	-0.227	0.020	0.409
S_6	-0.008	0.033	-0.010	-0.125	-0.028	0.058	-0.299	0.055	0.832
S_7	0.006	0.144	0.000	-0.100	1.428	0.046	-0.414	-0.129	-0.058
S_8	0.019	0.001	-0.149	-0.007	-0.035	1.412	0.029	0.072	-0.096
S_9	0.037	-0.057	0.002	0.058	0.465	-0.008	0.825	0.263	0.164
CH_3ND_2 (A')									
S_1	0.010	-0.032	0.736	-0.005	-0.014	-0.003	0.003	-0.012	-0.027
S_2	-0.004	1.006	0.044	-0.001	0.039	-0.033	0.020	-0.045	0.009
S_3	1.049	0.005	-0.015	-0.021	0.000	-0.010	-0.049	-0.015	-0.008
S_4	-0.001	-0.027	-0.041	-0.002	0.095	0.187	-0.123	0.300	-0.054
S_5	-0.034	0.026	-0.099	-0.044	-0.023	1.001	-0.295	-0.327	0.344
S_6	0.031	-0.007	-0.038	-0.011	0.038	-0.162	-0.161	0.007	0.654
S_7	0.144	0.000	0.008	1.433	0.034	-0.106	-0.403	-0.104	-0.034
S_8	0.001	-0.150	0.019	-0.024	1.412	0.081	0.001	0.068	-0.063
S_9	-0.056	-0.002	0.062	0.456	-0.014	0.281	0.812	0.192	0.101

vibrational frequencies. If it were to be done, the amount of correction for a fundamental frequency of a deuterated species would be different from the corresponding frequency of the undeuterated species. We estimate the difference to be 1–10 cm^{-1} in the order of magnitude (except for CH or NH stretching frequencies). While, the corresponding difference in the ^{15}N isotope shift would be only 0.01–0.1 cm^{-1} in the order of magnitude. Taking both of (a) the probable errors in the observations and (b) the probable amounts of ambiguities caused by neglecting the difference in the anharmonicity corrections between deuterated and undeuterated species into consideration, we set all the weight of ν_n's (vibrational frequencies for which the assignments are established) as 1, the weights of $\delta\nu_n$'s (^{15}N shifts) for the 1044 and 780 cm^{-1} bands as 20, and the weights of the other $\delta\nu_n$'s as 5.

VII. RESULT OF THE CALCULATION

In the course of our calculation, we first found that the least squares procedure by the use of Eq. (5) becomes divergent when all of the 63 force constants are set as variables. In all of our later calculations, therefore, we made the following assumptions:

(1) The off-diagonal elements, Nos. 10, 11, 15, 16, 17, 19, 20, 22, 23, 30, 33, 47, 49, 50, 51, 52, 55, 58, 60, and 61 are assumed to be zero. These values should be zero on the basis of the Urey–Bradley force field, but we do not intend to claim that they are actually zero. We assume that they are only for estimating the other force constant values. We shall later examine the effects of deviations of these values from zero upon the values of the other force constants determined.

(2) The off-diagonal elements, for which the gem-type nonbonded atom–atom interactions are included, are subjected to the Urey–Bradley constraints. In other words, the elements 12, 13, 14, 18, 21, 24, 25, 48, 53, and 54 are expressed by the repulsive force constants, F (HNH), F (HNC), F (HCH), and F (HCN). The values of F (HNC) and F (HCN) are calculated from the values of Nos. 26 and 28, and F (HNH) and F (HCH) values are fixed at 0.376 and 0.200 mdyn/Å,

respectively. This assumption is also made only for estimating other variable force constant values, and we shall examine again the effect of deviation of each value from its constrained value upon the values of the other variable force constants.

Every off-diagonal element subjected to assumption (1) or (2) (except Nos. 30 and 33) corresponds to a cross term of the NH stretching, CH stretching, or torsion coordinate (S_1, S_2, S_3, S_{10}, S_{11}, or S_{15}) and one of the other coordinates. Such an off-diagonal element is of less interest and usually small. At least, the values of more interesting force constants were expected to be almost independent of the assumed values of the off-diagonal elements mentioned above. It will be shown later that this is actually the case.

First, the least squares adjustment of the force constants for the A' type vibrations was made. Among a number of sets of force constant values obtained, the following three will be subjected to the present discussion.

Set I

Data: 34 observed frequencies (among the $36A'$ type frequencies, those of CD_3 "degenerate" deformation vibrations of CD_3NH_2 and CD_3ND_2 are not yet known).

Force constants assumed as variables: 21 constants. These are diagonal elements and off-diagonal elements, Nos. 26, 28, 29, 31, 32, 34, 35, and 36. (Force constant No. 27 is subjected to the Urey–Bradley constraints.)

Starting set of force constants: Force constants adjusted for the observed frequencies in the constraint of Urey–Bradley force field.[1]

Set II

Data: 34 observed frequencies and nine observed ^{15}N isotope shifts.

Force constants assumed as variables: 22 constants. Those given in Set I plus force constant No. 27.

Starting set: The same as Set I.

Set III

Data: 34 observed frequencies and 9 observed ^{15}N isotope shifts.

Force constants assumed as variables: 22. The same as Set II.

Starting set: Force constants Nos. 5, 6, and 29 are set arbitrarily at 0.546, 0.699, and 0.182 mdyn/Å, respectively, which are different from the values in Set II, 0.655, 0.677, and −0.307 mdyn/Å, respectively.

The force constant values in these sets are given in Table IV. The differences of the calculated and observed values of the frequencies and ^{15}N isotope shifts are given in Table V.

As may be seen in Table V, the Sets I, II, and III are almost equally good as far as only the degree of agreement of the observed and calculated *frequencies* is taken into account. When the ^{15}N isotope shifts are taken into consideration, however, the superiority of Set II becomes clear. Set I gives too small ^{15}N shift for the 1044 cm^{-1} (ν_8) band, while Set III gives too small ^{15}N shift for the 1623 cm^{-1} (ν_4) band. The ^{15}N shifts calculated on the set of Dellepiane and Zerbi have the same tendency as those on Set I.

As has just been shown, Set II is now the best set of force constants so far obtained. These values of force constants, however, were obtained on the assumptions (1) and (2) given above; many off-diagonal elements were assumed to be zero or to have fixed values. In order to estimate the possible deviation from the obtained values of force constants in Set II, we calculated the P_{AB} matrix elements, which are defined[10] as

$$k_A = k^0{}_A + P_{AB} \cdot \Delta k_B, \qquad (16)$$

where k_A is the force constant column vector, whose elements are set as the variables, and $k_A{}^0$ denotes the force constant vector obtained by the least squares procedure. k_B is the force constant column vector, whose elements are those assumed to be zero or to have fixed values. Elements of $P_{AB} \cdot \Delta k_B$ denote the magnitudes of the changes in the k_A elements caused by the small changes of k_B elements from the initially assumed values. The method of approximate estimation of the P_{AB} elements was given by one of the authors,[10] and the results of our calculation for the present case are given in Table VI.

Similar adjustments of the force constants were next made for the A'' type vibrations. Here we would like to mention the following three sets of force constants obtained. In all of these sets, the five vibrational frequencies (other than the NH_2 twisting frequency) of CH_3NH_2, three ^{15}N isotope shifts (see Table I) of CH_3NH_2, five vibrational frequencies (other than the ND_2 twisting frequency) of CH_3ND_2, three vibrational frequencies (other than the NH_2 twisting, CH_3 rocking, and C–N torsional frequencies) of CD_3NH_2, and four vibrational frequencies (other than the ND_2 twisting and C–N torsional frequencies) are used as data.

Set a

Data: 1416.0 cm^{-1} of CD_3NH_2, in addition to the 17 vibrational frequencies and 3 ^{15}N isotope shifts mentioned above.

Force constants assumed as variables: 11 constants, namely, Nos. 41, 42, 43, 44, 45, 46, 56, 57, 59, 62, and 63.

Starting set: Urey–Bradley force constants adjusted for the observed frequencies.[1]

Set b

Data: 1335.0 cm^{-1} of CH_3NH_2 and 1335 cm^{-1} of CD_3NH_2, in addition to the 17 frequencies and 3 ^{15}N shifts mentioned above.

Variable force constants and the starting set: The same as Set a.

Set c

Data: 1246.5 cm^{-1} of CH_3NH_2, in addition to the 17 frequencies and three ^{15}N shifts mentioned above.

Variable force constants and the starting set: The same as Set a.

The force constant values in those sets are given in Table VII. The differences of the calculated and observed values of the frequencies and ^{15}N isotope shifts are given in Table VIII. The three sets are different only because different frequencies are assumed for the NH_2 twisting vibration. The differences in the force constant values are very small except for No. 43, and they are equally good in providing an agreement between the observed and calculated frequencies and ^{15}N shifts. We may therefore consider that the 10 force constant values other than that of No. 43 are practically obtained here.

Let us now consider that the Set II for the A' type vibrations plus Set b for the A'' type vibrations forms the final set. The force constant values in this set have been converted into the values of the elements of the F matrix on the internal coordinates (instead of symmetry coordinate). The results are given in Table IX. The normal modes of vibrations (L matrix) are given in Table X, which are calculated again on the basis of the Set II+Set b.

VIII. DISCUSSION

As may be seen in Table VI, the P_{AB} matrix elements are all small except those in the columns of force constants Nos. 30 and 33. This fact means that the values of force constants determined in Set II are not greatly affected when the values of the force constants Nos. 10–25 are altered from what were assumed. They are greatly affected, however, when the values of the force constants Nos. 30 and 33 are changed. Unfortunately, the least squares procedure becomes divergent if the force constants Nos. 30 and 33 are set as the variables. This is caused by the fact that the CD_3 "degenerate" deformation frequencies of the CD_3NH_2 and CD_3ND_2 molecules are not yet determined.

In our present examination, it has been shown that the ^{15}N isotope shifts are very useful data for estimating force constants which take part in the vibration of N atom, or, in other words, for partly removing the ambiguity in the force constant determination. First, the data ^{15}N isotope shifts may cause an increase of the number of force constants which can be set as variables. Without the data of ^{15}N isotope shifts (Set I), the force constant No. 27 could not be determined; the least squares procedure became divergent if the force constant No. 27 was set as a variable. When the ^{15}N isotope shifts were added in the data, the procedure became convergent even if the force constant No. 27 was set as a variable.

Without the data of ^{15}N isotope shifts, there seem to be a number of minima of equal depth in the function whose value we are trying to make as small as possible in our least squares procedure. Set I or II corresponds to one of such minima and Set III to another. Addition of the ^{15}N isotope shifts as new data does not cause any great change in the position of a minima. The force constant values in Set II is not greatly different from those in Set I, for example (see Table IV). The addition of these new data is not powerful enough to lead us out of Set III, for example, and to lead us into Set II, in the least squares procedure. It is powerful enough, however, to cause a discrimination of superiority and inferiority of these minima. It has been shown, for example, that the minimum corresponding to Set II becomes lower than the minimum corresponding to Set III, if the ^{15}N isotope shifts are added in the data.

As is naturally supposed, the data of ^{15}N isotope shifts are of no use for determining some force constants. As may be seen in Table IV, the introduction of the ^{15}N data (Set I→Set II) causes an appreciable decrease in each of the uncertainties of the force constants Nos. 1, 4, 6, 26, 37, and 40, but no significant decrease for Nos. 28 and 36. For estimating the latter force constants, the ^{13}C isotope shifts would be useful data.

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