Infrared Spectrum of α-Aminoisobutyric Acid and the Assignment of the Vibrational Frequencies

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As has been shown in our previous papers[1,2], the infrared absorption measurement is an effective means for detecting differences in the molecular configurations of amino acids in different environments. In order to investigate further in detail such differences in the molecular configurations, it is necessary to know the vibrational mode for each of the bands given by these amino acids. For glycine[3] and DL-alanine[4], complete assignments of the vibrational modes have been made to the bands observed in the NaCl (and also KBr for glycine) region. This paper refers to another simple amino acid, α-aminoisobutyric acid. The vibrational frequencies observed in the solid state infrared spectra of this compound and its deuterated (ND_3^+) one, and also of its hydrochloride will be shown, and then, to all of these observed frequencies, approximate vibrational modes will be assigned on the basis of the results of analyses of normal vibrations made by previous authors for simpler molecules.

It may be worthwhile to point out here that, in these molecules (probably because of their branched-chain structures), the couplings between the skeletal stretching vibrations and the CH_3 or NH_3^+ rocking vibrations are not so strong as in alanine. Therefore, detailed discussions may be made on the couplings between the CH_3 rocking vibrations and the NH_3^+ rocking vibrations.

Experimental

The sample of α-aminoisobutyric acid was purified with active charcoal and repeated recrystallization from water. The deuterated product (ND_3^+) was obtained by dissolving the acid in D_2O and then by evaporating the solvent in vacuum. During the procedure, the D_2O and the acid were kept away from the atmospheric moisture by use of a dry box. By repeating the procedure twice an almost completely deuterated product, practically free from the NDH_2^+ and ND_2H^+ groups, was obtained. α-Aminoisobutyric acid hydrochloride was obtained by dissolving the free acid in concentrated aqueous solution of hydrochloric acid (1.1 equivalents) and was purified by recrystallization from aqueous alcohol.

The infrared absorption measurements were made with Nujol mulls, hexachlorobutadiene mulls, and KBr disks. The instruments used were a Perkin-Elmer 21 spectrometer equipped with an NaCl prism and a Hilger H800 spectrometer equipped with an NaCl prism or with a KBr prism.

Results

Infrared absorption curves obtained for α-aminoisobutyric acid and its deuterated product are shown in Fig. 1, and that for the hydrochloride in Fig. 2. The observed frequencies of the bands are listed in Table I, and are graphically shown in Fig. 3, with their intensities. As to assignments given in the table and Fig. 3, discussions will be given below.

Assignments of the Vibrational Frequencies of Trimethylacetic Acid

Before discussing the vibration frequencies of α-aminoisobutyric acid, considerations will be made on the frequencies of trimethylacetic acid, $(CH_3)_3CCOOH$, which is iso-electronic with α-aminoisobutyric acid cation, $\begin{matrix} NH_3^+ \\ CH_3 \\ CH_3 \end{matrix}\!\!>\!C\text{-}COOH$, the NH_3^+ group of the latter being substituted by the CH_3 group in the former. The frequencies (in the region of 650~1800 cm^{-1}) of $(CH_3)_3CCOOH$, as read from Sadtler Standard Spectrum No. 6355*, are listed in Table II.

For comparison, the frequencies of *tert*-butyl chloride, as observed by Sheppard[5]

1) M. Tsuboi, T. Takenishi and Y. Iitaka, This Bulletin, **32**, 305 (1959).
2) M. Tsuboi and T. Takenishi, ibid., **32**, 726 (1959).
3) M. Tsuboi, T. Onishi, I. Nakagawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **12**, 253 (1958).
4) K. Fukushima, T. Onishi, T, Shimanouchi and S. Mizushima, ibid., **13**, 236 (1959).
5) N. Sheppard, *Trans. Faraday Soc.*, **46**, 527 (1950).
* See also reference 7.

are also given in the parallel column. The assignment of the frequencies of *tert*-butyl chloride was made by Nakagawa[6] with the result as given in Table II and Fig. 3.

The vibrational frequencies of trimethylacetic acid can be assigned readily by comparing the frequencies with those of *tert*-butyl chloride and by taking the characteristic frequencies of the carboxyl group[7] into consideration (see Table II and Fig. 3).

The frequencies, 1695, 1408, 1192 and 935 cm^{-1}, (shown in Fig. 3 by thick vertical lines) are assigned to four vibrations of the carboxyl group; i. e., 1695 cm^{-1} to the C=O stretching vibration, 1408 and 1192 cm^{-1} to two vibrations including the C–O stretching and the OH in-plane deformation, and 940 cm^{-1} to the OH out-of-plane deformation vibration. The frequency 865 cm^{-1} is assigned to the C–C (carboxyl) stretching mode, as 895 cm^{-1} in acetic acid dimer[8] or 846 cm^{-1} in acetic acid monomer[8]. All the other frequencies of trimethylacetic acid are correlated (see Fig. 3) with the frequencies of *tert*-butyl chloride, although provisos should be added as follows: The CH_3 degenerate deformation frequency 1460 cm^{-1} in the latter splits into two, 1479 and 1456 cm^{-1}, in trimethylacetic acid. The CH_3 symmetric deformation frequency 1370 cm^{-1} in *tert*-butyl chloride is lowered to 1359 cm^{-1} in trimethylacetic acid; $C\begin{smallmatrix}\diagup C\\ -C\\ \diagdown C\end{smallmatrix}$ asymmetric stretching frequency 1240 cm^{-1} is raised to 1295 cm^{-1}, and the symmetric stretching frequency 812 cm^{-1} lowered to 766 cm^{-1}. This lowering and raising is explained as the result of interactions of the vibrations of the $(CH_3)_3$–C group with the vibrations of the carboxyl group, interactions between the 1359 and 1408 cm^{-1} vibrations, between 1295 and 1192 cm^{-1} vibrations, and between 766 and 865 cm^{-1} vibrations. The band due to the CH_3 rocking vibration observed at 910 cm^{-1} in *tert*-butyl chloride is probably obscured in trimethylacetic acid by the strong band at 935 cm^{-1}.

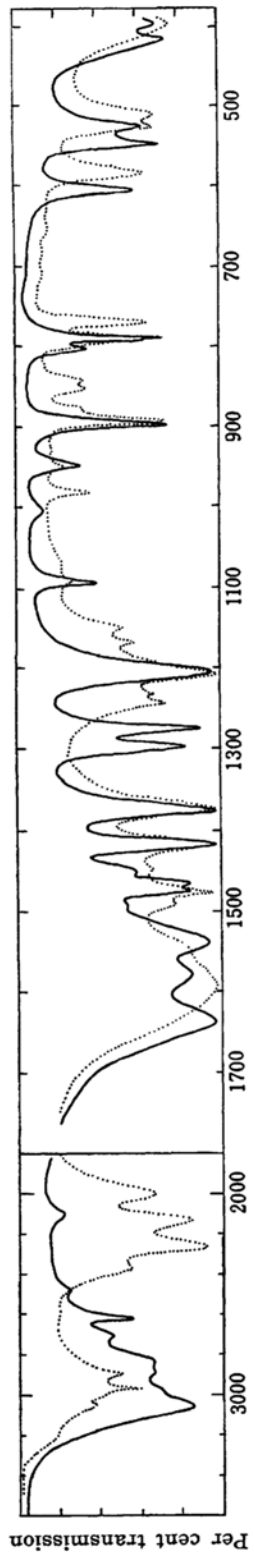


Fig. 1. Infrared absorption spectra of α-aminoisobutyric acid (——) and α-aminoisobutyric acid—ND_3 (……).

6) I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 602 (1956). Nakagawa based his assignment (somewhat different from Sheppard's assignment) on his series of theoretical investigations of the normal vibrations of the molecules with the CH_3 groups and on the comparisons of the frequencies with those of other related molecules such as $CH(CH_3)_3$, etc.

7) D. Hadzi and N. Sheppard, *Proc. Roy. Soc.* (*London*), **A216**, 247 (1953).

8) J. K. Wilmshurst, *J. Chem. Phys.*, **25**, 1171 (1956).

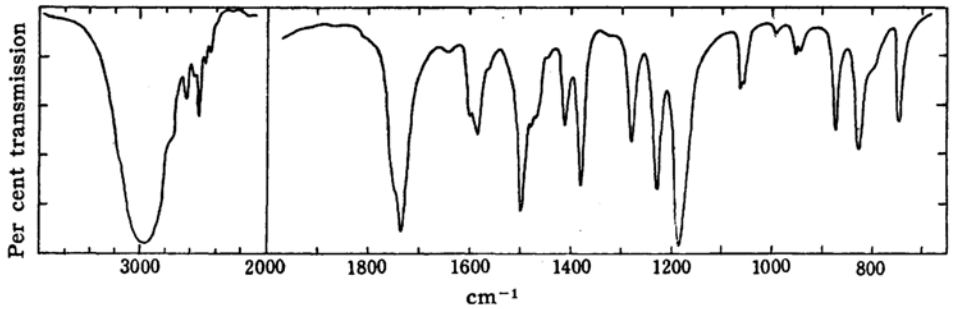


Fig. 2. Infrared absorption spectrum of α-aminoisobutyric acid hydrochloride.

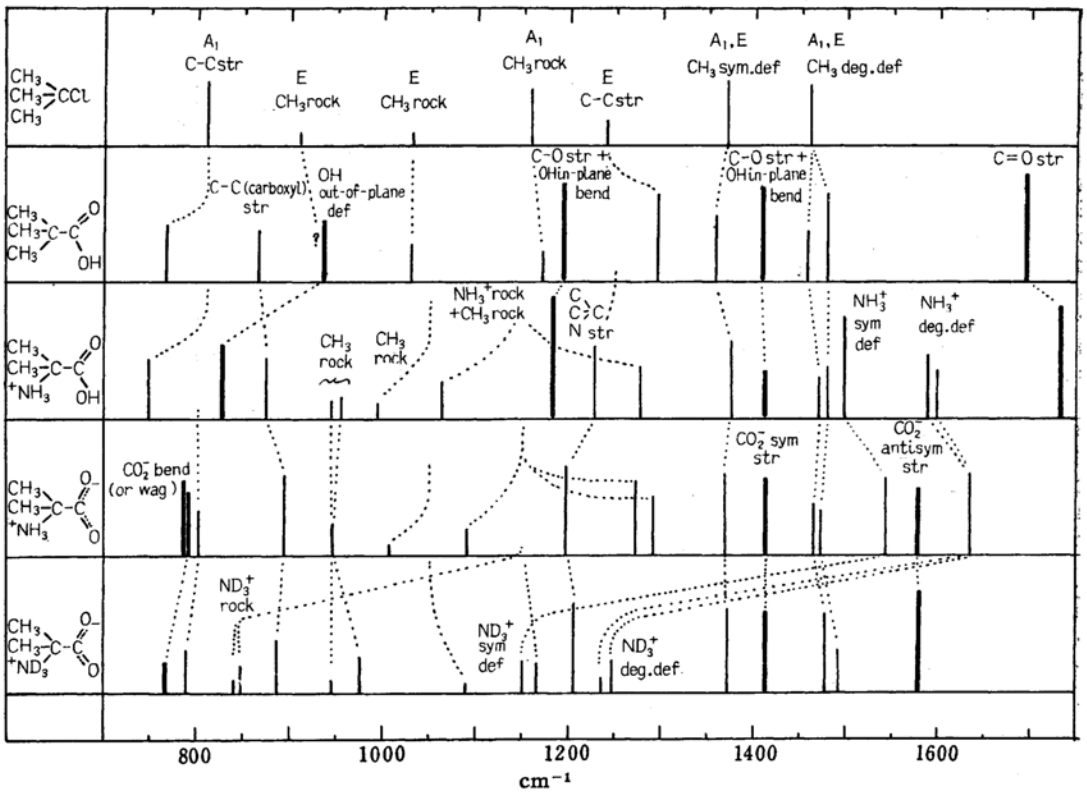


Fig. 3. Positions and intensities of the absorption bands of α-aminoisobutyric acid and related compounds.

Assignments of the Vibrational Frequencies of α-Aminoisobutyric Acid, its Deuterated (ND_3^+) Product, and its Hydrochloride

In the three crystals in question, α-aminoisobutyric acid, its deuterated product, and its hydrochloride, the molecules take the structures expressed by the formulae: $NH_3^+C(CH_3)_2COO^-$, $ND_3^+C(CH_3)_2COO^-$ and $NH_3^+C(CH_3)_2COOH$, respectively. These may be referred to in the following discussions as the zwitterion, the deuterated zwitterion, and the cation, respectively. In all of these three ions there seems to be no strong coupling between the four types of vibrations: the vibrations of the carboxyl group, the skeletal stretching vibrations, the hydrogen deformation vibrations (NH_3^+ and CH_3^+ deformation vibrations), and the hydrogen rocking vibrations. Discussions will, therefore, be presented below of these four types of vibrations in separate paragraphs.

A) Vibrations of the Carboxyl Group (shown in Fig. 3 by thick vertical lines).—In the cation, the carboxyl group takes the form,

TABLE I. OBSERVED FREQUENCIES (cm^{-1}) OF α-AMINOISOBUTYRIC ACID, ITS DEUTERATED PRODUCT (ND_3^+), AND ITS HYDROCHLORIDE, WITH THEIR ASSIGNMENTS
(s: strong, m: medium, w: weak)

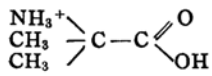
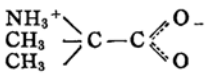
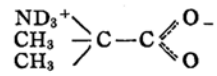
						Assignment
~3000						OH str.
2630 2570 2535 2490 2440		3035 2875 2820 2690 2610 2480 2100				NH_3^+ and CH_3 str.
				2962		CH_3 deg. str.
				2889		CH_3 sym. str.
				2367 2262 2112 2043 1990		ND_3^+ str.
1732	s					C=O str.
1599 1587	s s	1635	s	1237 1247	w w	NH_3^+ or ND_3^+ deg. def.
		1578	s	1580	s	CO_2^- antisym. str.
1495	s	1544	m	1151	m	NH_3^+ or ND_3^+ sym. def.
1480 1470	m m	1473 1465	m m	1492 1478	m s	CH_3 deg. def.
		1413	s	1415	s	CO_2^- sym. str.
1411	m					C-O str.+OH in-plane def.
1376	s	1370	s	1373	s	CH_3 deg. def.
1277	m	1293 1273	s s	849 842	m w	NH_3^+ or ND_3^+ rock.
1229	s	1199	s	1206	s	 asym. str.
1183	s					C-O str.+OH in-plane def.
1064 994	m w	1091 1008	w w	1167 1090	m w	CH_3 rock.
955 945	w w	946	w	976 947	m w	CH_3 rock.
875	m	895	s	888	s	C-C (carbonyl) str.
828	s					OH out-of-plane def.
748	m	803	m	790	m	 sym. str.
↑		792 787	m s	768	m	CO_2^- bend. (or wag.)
		602	m	587	m	CO_2^- wag. (or bend.)
not observed		547 531	m m	529 519	m m	CO_2^- rock.
↓		430 407	m m	404	m	skeletal def.

TABLE II. ASSIGNMENTS OF THE FREQUENCIES (cm^{-1}) OF *tert*-BUTYL CHLORIDE AND TRIMETHYLACETIC ACID
(s: strong, m: medium, w: weak, b: broad)

$(CH_3)_3C-Cl$		$(CH_3)_3C-C(=O)OH$		Assignment
		1695	sb	C=O stretching
1460	s	1479	s	CH_3 deg. def.
		1456	m	
		1408	m	C-O str.+OH in-plane def.
1370	s	1359	m	CH_3 sym. def.
1240	m	1295	sb	C-C str. (E)
		1192	sb	C-O str.+OH in-plane def.
1159	s	1170	w	CH_3 rock. (A_1)
1031	w	1029	m	CH_3 rock. (E)
		935	sb	OH out-of-plane def.
910	w	masked ?		CH_3 rock.
		865	s	C-C (carboxyl) str.
812	m	766	s	C-C str. (A_1)

$C(=O)OH$ The bands due to the vibrations of this group are picked out on account of their frequencies, intensities, or breadth. These are at 1732 (C=O stretching), 1411 (C-O stretching+OH in-plane deformation), 1183 (C-O stretching + OH in-plane deformation), and 828 cm^{-1} (OH out-of-plane deformation).

The frequency of the last vibration is much lower than that (930 cm^{-1}) of carboxylic acids without the NH_3^+ group. This is also the case for glycine hydrochloride and DL-alanine hydrochloride. This fact may be understood, if we assume that the carboxyl groups in amino acid hydrochlorides are in different hydrogen bondings from those of the carboxylic acids containing no NH_3^+ groups; in the latter the ring dimer is mostly formed through the two OH·····O=C bondings, while in the former the NH_3^+ group, a strong proton donor, interrupts the hydrogen bondings in the ring dimer.

In the zwitterion and the deuterated zwitterion, the carboxyl group takes the form, $C(=O)O$ The antisymmetric and symmetric stretching vibrations of this group are observed around the usual positions, 1600 and 1400 cm^{-1},— 1578 and 1413 cm^{-1} in the undeuterated zwitterion, and 1580 and 1415 cm^{-1} in the deuterated zwitterion.

The COO^- rocking vibration has the frequency 504 cm^{-1} in glycine[3], and 540 cm^{-1} in DL-alanine[9]. Therefore, the band at 540 cm^{-1} (doublet with the peaks at 547 and 531 cm^{-1}) in the zwitterion of α-aminoisobutyric acid is assigned to the COO^- rocking vibration. In the deuterated zwitterion, the band at 520 cm^{-1} is picked up as the corresponding one.

The COO^- bending and wagging vibrations have the frequencies 607 and 694 cm^{-1} respectively in glycine[3]. According to the result of the calculation of the normal vibrations in alanine by Fukushima[10], the COO^- bending frequency must be much higher than 607 cm^{-1}, and the band at 746 cm^{-1} was assigned to this vibration. The COO^- wagging vibration in this molecule was assigned to the band at 642 cm^{-1}. α-Aminoisobutyric acid gives two strong bands at 602 cm^{-1} and 790 cm^{-1} (doublet with the peaks at 792 and 787 cm^{-1}) in the region 600~800 cm^{-1}. By analogy with the case of DL-alanine, the band at 602 cm^{-1} is tentatively assigned to the COO^- wagging vibration and that at 790 cm^{-1} to the COO^- bending vibration.

A difficulty of this assignment is due to the fact that, very close to by the band at 790 cm^{-1}, there is another band observed at 805 cm^{-1}, which is later shown to be assigned to the $C-C(-N^+)C$ symmetrical stretching vibration. The two vibrations, COO^- bending and $C-C(-N^+)C$ symmetrical stretching, with dipole oscillations in almost the same direction, would couple strongly, so that the two bands due to these two

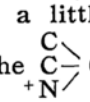
9) M. Tsuboi, to be published.

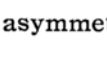
10) K. Fukushima, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 370 (1958).

vibrations appear much more apart from each other. From this point of view, the band at 790 cm^{-1} is notlikely due to the COO^- bending vibration. Therefore another choice to assign the 790 cm^{-1} to the COO^- wagging and the 602 cm^{-1} to the COO^- bending is not entirely eliminated.

B) Skeletal Stretching Vibrations. — The skeletal stretching frequencies of the  structure are expected to be close to those of the  structure (see above), the symmetrical one being expected to be around 800 cm^{-1} and the asymmetrical one around 1200 cm^{-1}.

Actually, however, a band in the cation that may be assigned to the  symmetrical stretching vibration is observed at 748 cm^{-1}, a little lower than 800 cm^{-1}. This is attributed to a lowering of the frequency of the vibration in question due to its coupling with the C–C (carboxyl) stretching vibration. The band that may be assigned to the C–C (carboxyl) stretching vibration is observed at 875 cm^{-1}, a little higher than usual (835 cm^{-1} in trichloroacetic acid dimer[7]) just as is expected from the above-mentioned coupling of the two vibrations.

In the zwitterion, the C–C (carboxyl) stretching frequency is 895 cm^{-1}, a little higher than in the cation; and the  symmetrical stretching frequency is 803 cm^{-1}, a usual value.

The band of the cation at 1229 cm^{-1} and that of the zwitterion at 1199 cm^{-1} are assigned to one of the  asymmetrical stretching vibrations**.

In the deuterated zwitterion, the three skeletal stretching frequencies, namely, the symmetrical and asymmetrical stretching frequencies of the  structure and the C–C (carboxyl) stretching frequency, are found to be 790, 1206 and 888 cm^{-1}, respectively.

C) NH_3^+, ND_3^+ and CH_3^+ Deformation Vibrations.—As to the assignments of these vibrations, the results of studies on the vibrations of the glycine molecule[3] as well as of some simple molecules with the CH_3 group[11] are to be referred to. In the cation, the NH_3^+ degenerate deformation vibration is assigned to the doublet with the peaks at 1599 and 1587 cm^{-1}, and the NH_3^+ symmetric deformation vibration to the strong band at 1495 cm^{-1}. In the undeuterated zwitterion, the bands corresponding to the above two are at 1635 and at 1544 cm^{-1} respectively, 30~50 cm^{-1} higher than in the cation. This difference in the positions of bands may be explained by considering that the intermolecular (interionic) hydrogen bonding is stronger for the zwitterion than for the cation.

In the deuterated zwitterion, the doublet with peaks at 1237 and 1247 cm^{-1} and the band at 1151 cm^{-1} are interpreted as corresponding to the above two bands. Then, the factors of the shiftings of these bands are respectively 1.32 and 1.34, in agreement with the expected values, 1.37 and 1.31, respectively.

CH_3 degenerate deformation is assigned to a doublet around 1470 cm^{-1} and CH_3 symmetric deformation to a band near 1370 cm^{-1} in any of the cations, the undeuterated zwitterion, and the deuterated zwitterion.

D) NH_3^+, ND_3^+ and CH_3 Rocking Vibrations.—In any of the above three ions now under discussion, six rocking vibrations are expected, two from the NH_3^+ (or ND_3^+) group and four from the two CH_3 groups. In glycine, both of the two NH_3^+ rocking vibrations are observed in the vicinity of 1150 cm^{-1} [13]; and in isopropyl chloride, the four CH_3 rocking vibrations are observed at 1160, 1062, 949 and 932 cm^{-1} [10]. The location of the bands corresponding to the six rocking vibrations may be made around these frequencies.

Actually, in the cation, there are two weak bands observed, at 955 and 945 cm^{-1}, and these may correspond to the above two frequencies at 949 and 932 cm^{-1} of isopropyl chloride. Instead of bands around 1160 and 1062 cm^{-1}, however, three bands are observed at 1277, 1064 and 994 cm^{-1}. This fact may be explained as a result of interactions of the CH_3 rocking and the NH_3^+ rocking vibrations; thus, the two CH_3 rocking frequencies, originally at 1160 and 1062 cm^{-1} are lowered respectively to 1064 and 994 cm^{-1} and the two

** Only one band could be observed though two are theoretically expected.

11) I. Nakagawa and S. Mizushima, This Bulletin, 28, 589 (1955).

NH_3^+ rocking frequencies, originally around 1150 cm^{-1} are both raised to 1277 cm^{-1}.

In the undeuterated zwitterion, a band with a medium intensity is observed at 946 cm^{-1}. This band is considered to be an unresolved doublet and to correspond to the two CH_3 rocking vibrations observed at 949 and 932 cm^{-1} in isopropyl chloride and at 955 and 945 cm^{-1} in the α-amino-isobutyric acid hydrochloride. Besides this, four bands are observed at 1008, 1091, 1273 and 1293 cm^{-1}. These four bands are again explained as resulting from interactions of two of the four CH_3 rocking vibrations with the two NH_3^+ rocking vibrations, all of which are considered to be originally in the vicinities of 1160 and 1062 cm^{-1} (see Fig. 3).

This explanation is supported by what was observed of the rocking vibrations in the deuterated zwitterion. In the deuterated zwitterion, in which the NH_3^+ group is substituted by the ND_3^+ group, the above-mentioned interactions between the CH_3 and NH_3^+ rocking vibrations should be absent, and hence, the almost pure CH_3 rocking vibrations are expected to occur in the vicinities of 1160 and 1062 cm^{-1}. Actually, two bands are observed at 1167 and 1090 cm^{-1} in the deuterated zwitterion. It is also expected from the above explanation, that the two ND_3^+ rocking vibrations occur around $1160/1.32 = 880$ cm^{-1}. Actually, two bands are observed at 849 and 842 cm^{-1}. The observed frequencies of the bands are sufficiently close to the expected ones to support the above explanation.

Going into detail, however, the observed frequencies of the two CH_3 rocking vibrations are somewhat higher, and those of the two ND_3^+ rocking vibrations are somewhat lower, than the corresponding expected frequencies. This fact suggests that there are interactions of another type between the CH_3 and ND_3^+ rocking vibrations.

Corresponding to the other two CH_3 rocking vibrations in the deuterated zwitterion, expected around the 940 cm^{-1}, two bands are actually observed at 976 and 947 cm^{-1}. That the band at 976 cm^{-1} is situated at a little higher position than the expected position, 940 cm^{-1}, may again be attributed to the interactions of the CH_3 and ND_3^+ rocking vibrations***.

We wish to express our sincere thanks to Professor San-ichiro Mizushima, Dr. Takehiko Shimanouchi and Dr. Haruomi Oeda for their kind encouragement and valuable suggestions and to Miss Chie Yamazaki for helpful assistance.

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12) N. Sheppard, *Trans. Faraday Soc.*, **46**, 533 (1950); G. Radinger and H. Wittek, *Z. physik. Chem.*, **B45**, 329 (1940); I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 602 (1956).

*** Under the assumption that all the rocking vibrations are independent of vibrations of other kinds in the zwitterion and in the deuterated zwitterion, the assignment, above made, of the six rocking frequencies is almost consistent with the product rule. Thus, the observed ratio, $1293\times1274\times1091\times1008\times946\times946/849\times842\times1167\times1090\times976\times947 = 1.93$, is close to the calculated ratio, 1.81. However, it is to be noted that the observed and calculated ratios are not in complete agreement. This is probably to be explained by considering that the assumption is not entirely valid, in other words, that some other vibrations, e. g., CH_3, NH_3^+, or ND_3^+ degenerate deformation vibrations and C-N stretching vibrations are coupling a little with the rocking vibrations.