VIBRATIONAL ANALYSIS OF L-ALANINE AND DEUTERATED ANALOGS

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ABSTRACT

Raman spectra of the polycrystalline L-alanine analogs $CH_3CH(NH_3^+)COO^-$, $CH_3CH(ND_3^+)$-COO^-, $CD_3CD(NH_3^+)COO^-$, and $CD_3CD(ND_3^+)COO^-$ have been obtained. A normal coordinate analysis is carried out based on the experimental frequencies of the four isotopic analogs and a 34 parameter valence-type force field defined in terms of local symmetry coordinates. The final refinement, in which five stretching force constants are constrained to fixed values obtained from bond length data, results in an average error of 7 cm^{-1} (0.9%) for the observed frequencies of the four isotopically substituted molecules. Band assignments are given in terms of the potential energy distribution for local symmetry coordinates. For non-deuterated L-alanine, the vibrations above 1420 cm^{-1} and below 950 cm^{-1} may be described as localized group vibrations. By contrast, the eight modes in the middle frequency range, viz. the three skeletal stretching, the COO^- symmetric stretching, one NH_3^+ rocking, the symmetric CH_3 deformation, and the two methyne CH deformation vibrations, are very strongly coupled to one another. Some decoupling appears to take place in the perdeutero molecule, and all but five modes can be described as localized group vibrations.

INTRODUCTION

Several normal coordinate calculations have been reported for alanine and its *N*-deuterated analog [1—5]. These calculations have been based on a Urey—Bradley type force field with force constants transferred from related molecules. No refinement of force constants appears to have been carried out; no potential energy distribution has been presented, except for an oversimplified seven-body model [1, 2]; no calculations involving *C*-deuterated and perdeuterated species have been reported. Group-frequency assignments for alanine and some deuterated analogs have been proposed by numerous authors [1—13 and refs. therein], although it appears evident that, for a molecule of this size with no symmetry, extensive mixing of a number of normal vibrations must be expected.

Previous authors have published IR [11, 12] and Raman [4, 9] spectra of single crystals of L-alanine and the *N*-deuterated molecules. For the other

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two analogs, however, only partial IR spectra in polycrystalline form [8] are available. In addition, the Raman frequencies have been listed for polycrystalline L-alanine [10]. We have obtained complete Raman spectra of all four isotopic analogs in the polycrystalline form. To permit an overview, we present the four spectra in Fig. 1. The frequencies are in good agreement with previous work [4, 8—12], although not identical with the single crystal data because of resolved factor group splitting in the latter. A normal coordinate calculation was carried out on the bases of a valence-type force field and the Raman spectra of $CH_3CH(NH_3^+)COO^-(d_0)$, $CH_3CH(ND_3^+)COO^-(d_3)$, $CD_3CD(NH_3^+)COO^-(d_4)$, and $CD_3CD(ND_3^+)COO^-(d_7)$. A 34 parameter valence-type force field was employed to calculate a total of 132 frequencies. Assignments are discussed in terms of the potential energy distribution.

EXPERIMENTAL

A sample of L-alanine-d_4 (of isotopic purity >98%) was obtained from Merck, Sharp and Dohme, Canada, Ltd.,* and used without further purification. *N*-deuterated and perdeutero alanine were prepared by recrystallization of alanine-d_0 and -d_4, respectively, from D_2O. IR and Raman spectra revealed no isotopic impurities in any of the compounds. Raman spectra of the polycrystalline solids sealed in a melting point capillary were obtained from 40—3500 cm^{-1} on a Spex 1401 spectrometer with the 514.5 nm line of a

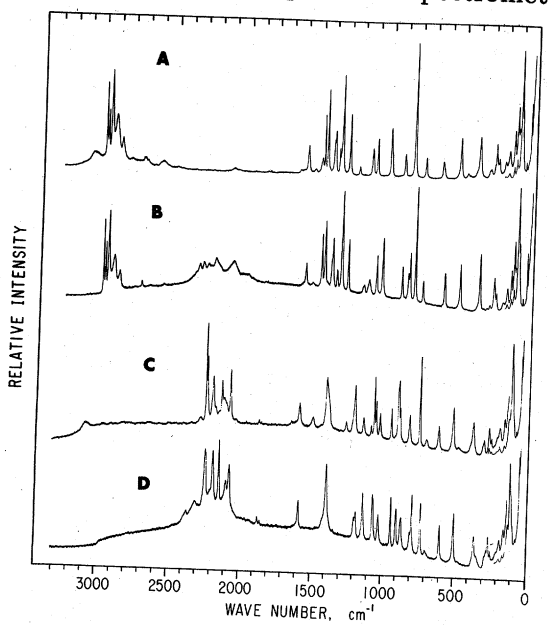

Fig. 1. Raman spectra of four isotopomers of polycrystalline L-alanine: A, d_0; B, d_3; C, d_4; D, d_7.

*Reference to any brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

Spectra-Physics Model 165—03 argon ion laser used for excitation. The laser power at the sample was ca. 250 mW and the spectral slit width, 3 cm^{-1}. Computations were carried out on an IBM 370/168-1 computer.

COMPUTATIONS

Numerical methods and structural considerations

Numerical calculations based on the *GF*-matrix formulation [14] were carried out by applying previously employed procedures and computer programs [15]. The *G*-matrix was based on structural data obtained by neutron diffraction studies on glycine [16], L-alanine [17], L-cysteine [18], and L-serine [19]. Except for the torsional angles of the skeletal atoms, average values for the bond distances and angles of these four molecules, which agree with the L-alanine data within experimental error, were used to facilitate future comparative computations with other amino acids. Figure 2 presents a schematic structural diagram of the L-alanine molecule. The atoms 2, 3, 4, 5 and the atoms 2, 3, 8, 11 were assumed to be in a *trans* conformation. The following mean bond length values were employed: C—O, 1.249 Å; C(2)—C(3), 1.529 Å; C(3)—C(8), 1.524 Å; C—N, 1.485 Å; C(3)—H, 1.098 Å; C(8)—H, 1.084 Å; N—H, 1.037 Å. The bond angles around C(3), C(8), and N(4) were assumed to be tetrahedral. The average values for the angles around C(2) were ∠CCO = 117.23° and ∠OCO = 125.55°. Hence, atoms O(1), O(6), C(2), and C(3) lie very nearly in

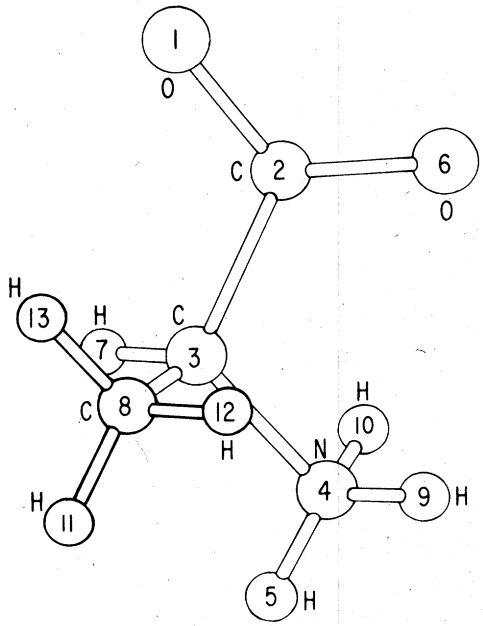

Fig. 2. Molecular structure of crystalline L-alanine.

a plane. The torsional angles O(1)—C(2)—C(3)—N and O(6)—C(2)—C(3)—N reported for L-alanine are +161.5° and −18.6°, respectively [17]. These values were not averaged because the four amino acids exhibited large variations in the size of these angles.

Symmetry coordinates and force field

The L-alanine molecule has no overall symmetry. Linear combinations of internal displacement coordinates corresponding to the local symmetries of the CH_3, NH_3^+, and COO^- groups were nevertheless defined. Such a procedure permits comparison of our work with previous studies by Destrade et al. [20] on glycine and makes it easier to choose significant interaction force constants. It also permits computation of the potential energy distribution (PED) in terms of generally accepted local modes of the CH_3, NH_3^+ and COO^- groups, and allows comparison with a variety of molecules containing methyl groups [21—23]. The local symmetry coordinates for the CH_3 and NH_3^+ groups were defined in the generally accepted manner [24]. The local symmetry coordinates for the COO^- grouping were constructed in the way reported by Destrade et al. [20] for glycine.

The torsional coordinates were defined in a manner analogous to that reported by Dempster and Zerbi [25] (see Fig. 2)

$$\tau(CH_3) = \tau_{\underline{11}832} + \tau_{\underline{12}837} + \tau_{\underline{13}834}$$

$$\tau(NH_3) = \tau_{5432} + \tau_{9437} + \tau_{\underline{10}438}$$

$$\tau(COO^-) = \tau_{7321} + \tau_{4326} + \tau_{8321}$$

The COO^- wagging mode was defined in terms of the angle between the C(2)—C(3) bond and the plane of the COO^- grouping. The sign is positive if the C(3) atom in Fig. 2 moves up.

The force constants are defined in terms of the previously described local symmetry coordinates for the COO^-, NH_3^+ and CH_3 groups, and in terms of bond stretching and bond angle bending coordinates for the central core containing the atoms C(2), C(3), C(8), N(4), and H(7) (Fig. 2) where there is no symmetry. Table 1 lists the diagonal force constants and the correspond ing displacement coordinates. Table 1 also lists the six interaction force constants which were included in the final refinements. All other interaction constants were fixed equal to zero.

Refinement of force constants

Initial values of force constants for a zero-order calculation were transferred from glycine [20] for the $C(NH_3^+)COO^-$ part of the molecule, and from hydrocarbons for the methyl and the methyne groups [26]. Despite the availability of the frequencies of four isotopic analogs for force constant refinement, it was not possible to refine all the force constants listed in Table 1 simultaneously. The following scheme was adopted: CO, CN, and

TABLE 1

Diagonal force constants and interaction force constants of L-alanine

Force constant	Local symmetry coordinate[a]	Value[b]	Dispersion[f]
Diagonal			
F (1)	ν_a NH_3^+	5.141	0.014
F (2)	ν_s NH_3^+	5.208	0.020
F (3)	δ_a NH_3^+	0.620	0.004
F (4)	δ_s NH_3^+	0.632	0.007
F (5)	$\rho_{\parallel}$ NH_3^+ [c]	0.731	0.019
F (6)	$\rho_{\perp}$ NH_3^+ [c]	0.803	0.017
F (7)	τ NH_3^+	0.045	0.001
F (8)	ν_a CH_3	4.771	0.013
F (9)	ν_s CH_3	4.878	0.020
F (10)	δ_a CH_3	0.532	0.003
F (11)	δ_s CH_3	0.573	0.012
F (12)	$\rho_{\parallel}$ CH_3 [d]	0.586	0.017
F (13)	$\rho_{\perp}$ CH_3 [d]	0.562	0.012
F (14)	τ CH_3	0.0097	0.0006
F (15)	ν CH	4.779	0.019
F (16)	δ CCH; δ NCH[e]	0.686	0.011
F (17)	ν_a COO^-	8.50	—
F (18)	ν_s COO^-	11.10	—
F (19)	δ COO^-	1.40	0.06
F (20)	ρ COO^-	1.42	0.08
F (21)	γ COO^-	0.541	0.015
F (22)	τ COO^-	0.063	0.004
F (23)	ν C—CH_3	4.46	—
F (24)	ν C—COO^-	4.39	—
F (25)	ν CN	3.89	—
F (26)	δ NC(3)C(8)	1.34	0.06
F (27)	δ NC(3)C(2)	1.18	0.09
F (28)	δ CCC	1.09	0.08
Interaction			
F (29)	ν CN, δ_s NH_3^+	−0.36	0.04
F (30)	ν C—CH_3, δ_s CH_3	−0.39	0.03
F (31)	ν_s COO^-, δ COO^-	1.71	0.09
F (32)	ν C—COO^-, δ COO^-	−0.34	0.06
F (33)	ν COO^-, ρ COO^-	1.23	0.04
F (34)	ν skel, δ CH	0.242	0.019

[a] ν_a, antisym. str; ν_s, sym. str; δ_a, antisym. bend; δ_s, sym. bend; ρ, rocking; γ, wagging; τ, torsion. [b] Units: stretching, mdyn Å^{-1}; bending and torsional, mdyn Å rad^{-2}; interaction, mdyn rad^{-1}. [c] Parallel and perpendicular to the plane containing atoms 2, 3, 4, 5 in Fig. 2. [d] Parallel and perpendicular to the plane containing atoms 2, 3, 8, 11 in Fig. 2. [e] The two orthogonal δ CH force constants were constrained to refine to the same value. [f] Estimated from the standard error in the frequency parameters.

CC stretching force constants (17, 18, 23, 24, 25) were constrained to values obtained from bond-length data, as described previously [15, 27, 28].

The derivation of the values shown in Table 1 for the two symmetry COO^-

stretching constants (17, 18) from that determined above for the valence CO constant (F_{CO} = 9.80 mdyne Å^{-1}) requires knowledge of the valence-type CO stretch—stretch interaction. Taking 1.1 mdyne Å^{-1} (as reported for this interaction in glycine [20]) as an initial estimate, small trial-and-error adjustments at the latter stages of refinement showed that a value of 1.3 mdyne Å^{-1} gives the best fit between the observed and calculated frequencies.

The force constants associated with the CH_3 and NH_3^+ bending modes (3, 4, 10, 11), which give rise to well-defined group frequencies, were initially adjusted by trial and error without refinement. Later, all force constants except the ones for the skeletal stretching modes (17, 18, 23, 24, 25) were refined together. At this stage small changes were made in the set of observed frequencies included in the calculation, to determine the best choice for the set of fundamental frequencies. The number of interaction force constants employed is relatively small, as shown in Table 1. Several other interaction force constants, such as $F(\nu_s\ COO^-, \nu\ C—COO^-)$ were introduced in various refinements on a trial-and-error basis, but the available data were insufficient to calculate them with a satisfactorily small computational uncertainty. They were omitted from later refinements of the data. The force field described in Table 1 thus appears as complete as can be expected on the basis of the available frequencies of L-alanine and three deuterated analogs.

RESULTS AND DISCUSSION

Table 1 gives the values of the refined force constants. The computational uncertainties of the final values are relatively small. It is obvious that the available data, although they are derived from four isotopic analogs, are sufficient for the calculation of only a severely constrained force field.

Tables 2—5 give the observed and calculated frequencies, the potential energy distribution (PED), and a group frequency assignment, where appropriate. To avoid confusion, generally not more than the three largest terms having values greater than 12% are included in the potential energy distribution. If the PED contribution to one local symmetry force constant is over 40%, an approximate group frequency description is given in the fourth column of the tables. Despite the general asymmetry of this molecule, a remarkable number of fundamental frequencies may be described approximately as group vibrations.

Table 2 shows that for normal, non-deuterated L-alanine, the vibrational modes in the middle frequency range (one NH_3 rocking mode, the three skeletal stretching vibrations, the COO^- symmetric stretching mode, the two bending modes of the methyne group and the symmetric CH_3 deformation) are extensively mixed. It is hardly possible to talk about localized group vibrations between ca. 950 and 1420 cm^{-1}. Above 1420 and to a lesser extent below 950 cm^{-1} such a classification is possible as a rough approximation, although in the range below 950 cm^{-1} the largest PED contribution to any single force constant is frequently only 40—50%. In all, 25 out of the 33 normal modes listed in Table 2 for the non-deuterated molecule can be

TABLE 2

Fundamental vibrations of $CH_3CH(NH_3^+)COO^-$

Frequency		Potential energy[a] distribution	Approximate[b] description
Raman	Calc.		
3082 (1.3)[c]	3088	1(99)	ν_a NH_3^+
3082 (1.3)	3088	1(99)	
(3001)	3001	2(100)	ν_s NH_3^+
3001 (7.4)	2998	8(99)	ν_a CH_3
2987 (5.6)	2997	8(99)	
2968 (10.0)	2965	15(98)	ν CH
2922[d]	2911	9(100)	ν_s CH_3
1648 (0.3)	1651	3(90)	δ_a NH_3^+
1648 (0.3)	1645	3(92)	
1596 (2.3)	1594	17(107), 20(12), 33(−26)	ν_a COO^-
1498 (1.2)	1500	4(99)	δ_s NH_3^+
1462 (6.7)	1460	10(90)	δ_a CH_3
1462 (6.7)	1458	10(94)	
1409 (3.2)	1424	24(30), 16(29), 18(20)	
1379 (1.5)	1381	11(51), 16(24), 18(10)	δ_s CH_3; δ CH
1359 (7.8)	1352	11(50), 16(35), 23(18), 30(−15)	
1305 (3.2)	1299	16(50), 18(45), 31(−15)	
1238 (0.5)	1217	6(45), 16(20)	$\rho_\perp$ NH_3^+
1143 (1.7)	1168	5(24), 25(18), 16(12)	
1112 (2.5)	1130	5(19), 18(19), 16(17)	
1020 (3.2)	1020	5(27), 23(25), 6(17)	
1010 sh	995	13(27), 12(19)	
921 (1.5)	925	12(50), 19(23), 24(15)	$\rho_\parallel$ CH_3
850 (10.0)	861	13(47), 25(23), 19(8)	$\rho_\perp$ CH_3
772 (1.3)	786	21(62), 23(12)	γ COO^-
653 (1.1)	663	19(44), 27(12), 20(12), 31(−16)	δ COO^-
531 (1.5)	526	20(41), 25(27)	ρ COO^-
477 (0.3)	474	7(83)	τ NH_3^+
399 (2.9)	401	26(63)	δ NC(3)C(8)
296 sh	294	28(49), 16(13), 24(12)	δ CCC
283 (2.1)	267	27(52), 20(20), 28(14)	δ NC(3)C(2)
219 (0.7)	217	14(93)	τ CH_3
192 (1.1)	189	22(89)	τ COO^-

[a]The first number designates the force constant, the second number (in parentheses), its % PED. [b]See Table 1 for designation of symbols (notes a, c, d). [c]The number in parentheses is relative Raman intensity. [d]Calculated from the Fermi resonance doublet at 2933 (5.4) and 2887 (1.6) cm^{-1}.

designated as approximately localized group vibrations. Somewhat surprisingly, some decoupling appears to occur for the totally deuterated molecule, and the number of such localized modes seems to increase. As seen in Tables 2—5, the number of group frequencies is 23 for both partially deuterated species but increases to 28 out of 33 for the perdeutero molecule.

The coupling of the three skeletal stretching vibrations is certainly not unexpected for a large, asymmetric molecule like alanine. By contrast, the extensive mixing of the symmetric COO^- stretching mode with the C—COO^-

TABLE 3

Fundamental vibrations of $CH_3CH(ND_3^+)COO^-$

Frequency		Potential energy[a] distribution	Approximate[b] description
Raman	Calc.		
3003 (6.9)[a]	2998	8(99)	ν_a CH_3
2990 (4.6)	2997	8(99)	
2972 (6.9)	2965	15(98)	ν CH
2917[c]	2911	9(100)	ν_s CH_3
2293[d]	2292	1(98)	ν_a ND_3^+
2293[d]	2290	1(98)	
2160[e]	2154	2(99)	ν_s ND_3^+
1591 (1.8)	1594	17(108), 20(12), 33(—25)	ν_a COO^-
1461 (5.5)	1460	10(91)	δ_a CH_3
1461 (5.5)	1458	10(94)	
1407 (3.8)	1414	24(33), 16(29), 18(25)	
1376 (1.7)	1381	11(52), 16(25), 18(10)	δ CH_3; δ CH
1355 (8.6)	1349	11(47), 16(42), 23(19), 30(—15)	
1299 (4.3)	1299	16(53), 18(42), 31(—14)	
1189 (0.4)	1192	3(63)	δ_a ND_3^+
1182 (0.6)	1181	3(94)	
1159 (0.6)	1162	3(29), 23(18), 4(17), 25(14)	
1148 (1.2)	1145	4(41), 25(13), 23(13)	δ_s ND_3^+
1098 (3.4)	1099	4(39), 16(12)	
1057 (4.9)	1074	18(14), 13(13), 12(12)	
916 (2.8)	927	12(57), 19(21), 24(14)	$\rho_\parallel$ CH_3
874 (2.0)	884	13(58), 6(21)	$\rho_\perp$ CH_3
863 (3.8)	842	5(52), 19(25)	$\rho_\parallel$ ND_3^+
825 (10.0)	808	6(48), 23(17), 25(11)	$\rho_\perp$ ND_3^+
771 (1.7)	778	21(63), 23(14)	γ COO^-
621 (2.6)	633	19(38), 5(15), 20(13), 31(—15)	
514 (3.5)	506	20(45), 25(28)	ρ COO^-
377 (4.3)	381	26(63)	δ NC(3)C(8)
335[f]	345	7(84)	τ ND_3^+
273 (2.6)	288	28(53), 21(12)	δ CCC
258 (1.2)	250	27(57), 20(19)	δ NC(2)C(3)
211 (0.6)	217	14(92)	τ CH_3
184 (3.0)	185	22(90)	τ COO^-

[a]See Table 2. [b]See Table 1 (notes a, c, d). [c]Calculated from the Fermi resonance doublet at 2930 (3.2) and 2893 (1.7) cm^{-1}. [d]Calculated from the Fermi resonance doublet at 2309 (1.6) and 2275 (1.5) cm^{-1}. [e]Calculated from the Fermi resonance doublet at 2224 (2.0) and 2095 (1.8) cm^{-1}. [f]IR frequency: corresponding Raman band was too weak to observe.

stretching vibration and one of the methyne CH bending coordinates may appear somewhat surprising, for both carboxyl stretching fundamentals have commonly been assumed to behave as clean group frequencies [1—12]. Nonetheless, the kinematic coupling found for these modes in alanine is also apparent in other substances having a COO^- moiety, such as glycine [20] and the acetate ion [29]. Species having the isoelectronic nitro group, like nitro-

TABLE 4

Fundamental vibrations of $CD_3CD(NH_3^+)COO^-$

Frequency		Potential energy[a] distribution	Approximate[b] description
Raman	Calc.		
3082 (0.8)[a]	3088	1(99)	ν_a NH_3^+
3082 (0.8)	3088	1(99)	
—	3001	2(100)	ν_s NH_3^+
2248 (10.0)	2239	8(94)	ν_a CD_3
2240 (8.0)	2238	8(97)	
2197 (5.1)	2200	15(91)	ν CD
2085[c]	2097	9(98)	ν_s CD_3
1643 (0.4)	1651	3(90)	δ_a NH_3^+
1643 (0.4)	1645	3(92)	
1592 (2.6)	1591	17(110), 20(12), 33(—26)	ν_a COO^-
1495 (1.1)	1498	4(102)	δ_s NH_3^+
1402 (5.4)	1399	18(44), 24(43), 31(—19)	
1263 (0.8)	1288	23(31), 6(18), 18(14), 16(14), 25(13)	
1202 (5.0)	1199	18(39), 25(25), 16(16)	
1142 (1.5)	1166	6(45), 5(20)	$\rho_\perp$ NH_3^+
1066 (7.1)	1071	11(74), 23(22), 30(—20)	δ_s CD_3
1053 (3.6)	1053	10(93)	δ_a CD_3
1053 (3.6)	1052	10(93)	
1025 (3.0)	1019	5(37), 16(18), 11(13)	
945 (2.9)	953	19(22), 16(20), 24(15)	
894 (5.8)	900	16(49)	δ CD
883 (3.2)	874	16(50)	δ' CD
816 (3.0)	799	19(28), 21(23), 12(16)	
747 (8.4)	730	21(37), 12(33)	
698 (0.7)	691	13(63), 25(15)	$\rho_\perp$ CD_3
614 (2.8)	614	19(25), 12(20), 20(18)	
514 (4.9)	514	20(37), 25(19), 7(13), 19(12)	
476 (0.6)	468	7(75)	τ NH_3
372 (3.3)	374	26(64)	δ NC(3)C(8)
293 (1.3)	276	27(28), 28(20), 16(16)	
261 (2.8)	257	28(42), 27(29)	δ NC(2)C(3)
187 (1.5)	185	22(88)	τ COO^-
155 (1.7)	154	14(95)	τ CD_3

[a]See Table 2. [b]See Table 1 (notes a, c, d). [c]Calculated from the Fermi resonance doublet at 2076 (6.1) and 2117 (1.6) cm^{-1}.

methane, exhibit similar behavior for the analogous symmetric NO_2 stretching coordinate [30].

The large isotope-induced frequency shifts observed in the IR spectrum of L-alanine-^{18}O for the four bands appearing between 1420 and 1300 cm^{-1} [31] lend further credence to the mixing evident in the calculated potential energy distribution for normal alanine (Table 1). The spectrum of the ^{18}O-substituted molecule also shows significant shifts for all five bands between 925 and 480 cm^{-1} [31]. Again, the calculation for the normal isotopic species clearly

TABLE 5

Fundamental vibrations of $CD_3CD(ND_3^+)COO^-$

Frequency		Potential energy[a] distribution	Approximate[b] description
Raman	Calc.		
2306 (2.4)[a]	2292	1(97)	ν_a ND_3^+
2306 (2.4)	2291	1(97)	
2242 (8.8)	2239	8(94)	ν_a CD_3
2236 (8.1)	2238	8(97)	
2188 (9.0)	2199	15(90)	ν CD
2147 (10.0)	2154	2(98)	ν_s ND_3^+
2084[c]	2097	9(98)	ν_s CD_3
1586 (3.8)	1590	17(110), 20(12), 33(—26)	ν_a COO^-
1394 (9.5)	1390	18(53), 24(46), 31(—22)	
—	1263	23(43), 25(20), 16(19)	ν C—CH_3
1199 (2.8)	1183	3(48), 18(19)	
1187 (3.3)	1183	3(88)	δ_a ND_3^+
1187 (3.3)	1178	3(53), 18(18)	
1137 (6.7)	1132	4(98)	δ_s ND_3^+
1066 (6.9)	1067	11(67)	δ_s CD_3
1045[d]	1053	10(96)	δ_a CD_3
1045[d]	1051	10(85)	
1026 (4.0)	1015	6(20), 11(16)	
928 (7.8)	926	16(43), 19(23)	δ CD
894 (5.9)	895	16(59)	δ' CD
860 (4.3)	845	5(36), 19(24), 16(13)	
797 (2.4)	790	6(48), 23(13)	ρ ND_3^+
785 (9.2)	769	5(30), 21(23)	
725 (7.8)	724	12(46), 21(30)	$\rho_{\parallel}$ CD_3
692 (0.9)	685	13(66), 25(14)	$\rho_{\perp}$ CD_3
590 (5.2)	598	19(27), 20(18), 12(15)	
497 (8.1)	497	20(43), 25(22), 19(14)	ρ COO^-
353 (4.5)	352	26(60)	δ NC(3)C(8)
337 (1.9)	341	7(84)	τ ND_3^+
279 (1.4)	267	28(44), 16(13)	δ CCC
255 (4.3)	245	27(52), 28(18), 20(18)	δ NC(2)C(3)
179 (2.8)	181	22(88)	τ COO^-
156 (5.8)	154	14(95)	τ CD_3

[a]See Table 2. [b]See Table 1. [c]Calculated from the Fermi resonance doublet at 2075 (6.7) and 2096 (4.5) cm^{-1}. [d]IR frequency: no corresponding band was observed in the Raman system.

indicates that the three COO^- bending modes contribute in varying degree to these five fundamental frequencies (Table 2).

In agreement with a recent publication by Machida et al. [4], we find that the $\gamma(COO^-)$ coordinate contributes strongly to the 772 cm^{-1} band in undeuterated alanine, while the largest contribution of the corresponding bending mode, $\delta(COO^-)$, is found at 653 cm^{-1}. This is in reverse order to that observed for these two modes in glycine [20] and the acetate ion [29].

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