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Vibrational Dynamics of Crystalline L-Alanine

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Abstract

We report here a new, complete vibrational analysis of L-alanine and L-alanine-d_4 which utilizes IINS intensities in addition to frequency information. Our study clarifies a number of important issues on the vibrational dynamics of this molecule and presents a self-consistent force field for the molecular vibrations in crystalline L-alanine.

1. Introduction.

L-alanine ($CH_3CH(NH_3^+)CO_2^-$) is one of the simplest amino-acids and may be considered to be the basic building block constituting many polypeptides or alpha-helical proteins. The molecule is relatively flexible which results in significant coupling between some lattice modes and internal molecular vibrations[1]. It has been proposed[2] that localization of vibrational energy occurs in L-alanine as in related solids such as acetanilide or N-methylacetamide [3], where temperature dependent anomalies of the optical spectra have been attributed to localized, nonlinear excitations .

We initiated the present vibrational spectroscopic investigation of L-alanine and its partially deuterated isotopomer L-alanine-d_4 ($CD_3CD(NH_3^+)CO_2^-$) by incoherent inelastic neutron scattering (IINS) as a preliminary step in our study of the short polypeptide Tryp$[Ala]_{15}$. This has also been found to exhibit anomalies in the amide vibrations, which are thought to result from nonlinear or "polaronic " excitations by coupling the proton motion in the hydrogen-bond to lattice modes [4].

The crystal structure of zwitterionic L-alanine (space group $P2_12_12_1$) contains three networks of intermolecular hydrogen bonds linking a positively charged ammonium group to a carboxylate group on a neighboring molecule.The vibrational dynamics of L-alanine have previously been described [1,5,6]. Urey-Bradley or valence force fields have been also reported [7-9] as well as group frequency assignments[1,6,10].

We report here new IINS measurements and a vibrational analysis of L-alanine and L-alanine-d_4 which utilizes IINS intensities in addition to frequency information. The use of both isotopomers resulted in a self-consistent force field for and assignment of the molecular vibrations in L-alanine. Some details of the calculation as well as a comparison of calculated and observed IINS spectra are presented below.

2. Experimental details.

Polycrystalline samples of L-alanine were obtained from Aldrich, and L-alanine-d_4 from Cambride Isotope Laboratory (isotopic purity >98%). The IINS data reported in this work were collected on the FDS spectrometer at the Manuel Lujan Jr. Neutron Scattering Center of Los Alamos National Laboratory. The FDS spectra were obtained [11] by numerical deconvolution of the instrumental function from the raw data.

3.Results and Discussion.

The intermolecular force field was refined by fitting the vibrational frequencies and IINS intensities to force constants derived from a normal-coordinate analysis using the program CLIMAX [12] with structural parameters for the molecule given by Destro et al. [13]. The molecular vibrations can be described by 38 internal coordinates, which are associated with the force constants by means of a constraint matrix. The force constants are defined in terms of locally symmetric groups (CO_2^-, NH_3^+, and CH_3) and bond-stretching and bond angle-bending coordinates for the backbone of the molecule. Initial values of diagonal force constants for the zeroeth-order calculation were obtained from the work of Susi et Byler [8]. Table I lists the force constants for both isotopomers that were required to give a satisfactory fit of both intensities and frequencies. Since the number of interaction force constants employed is relatively small, the force field may not be expected to reproduce all vibrations equally well

Observed IINS spectra at 20K for L-alanine and L-alanine-d_4 are shown in Figure 1. for the frequency range 50 - 2000 cm^{-1}. Details of the frequency assignments will be reported in a future publication. We restrict our comments on assignments in the following to some of the more prominent bands in the IINS spectra. In the midfrequency region (800 - 1700 cm^{-1}) coupling between vibrational modes makes assignments of the modes difficult. However, the introduction of the interaction force constants 24 and 26 made it possibleto assign the rocking vibrations of the NH_3^+ and CH_3 groups in the same region in which the C-C-N stretching vibrations are also observed [5, 6].

Our results showed an extensive mixing of carboxyl stretching mode with the $\nu(C_2\text{-}C_1)$ vibration, the methyne CH bending coordinates and the NH_3^+ modes, and the fit is relatively poor in this region. A controversy exists in the literature concerning this mixing since the carboxyl stretching fundamentals are often thought to be localized modes, self-trapped by interaction with phonons. Nonetheless, a similar behavior is also observed in other substances having a CO_2 moiety such as glycine [14,15]. Furthermore, as the charges of the L-alanine are localized at the NH_3^+ and CO_2^- groups, one expects greater polarization effects, due to the charge centers interaction, on the NH_3^+ - CO_2^- intermolecular modes, and on the modes associated to these groups than on the other internal modes.

The NH_3 torsion at 480 cm^{-1} is the most intense band in the IINS spectrum. The frequency and width of this mode have been shown in the previous literature [1,16] to have a large and unusual temperature dependence which is currently under investigation by us. The CH_3 torsion is observed at 265 cm^{-1} in the IINS and at about 400 and 280 cm^{-1} in Raman scattering. Machida[5] calculated a rather large factor group splitting (around 100 cm-1) for the CH_3 modes resulting from the proximity of methyl from neighboring molecules. We do not, however, find any contribution from the methyl torsion in the IINS band 404 cm^{-1}.

The calculated spectra for both isotopomers of L-alanine are compared in Fig. 2. Reference to Fig. 1 shows that the agreement with experiment is satisfactory. This is particularly true in view of the fact that the present type of analysis treats the molecule as isolated. A computational treatment based on the crystalline unit cell with explicit use of intermolecular interactions would, however, be expected to improve this agreement substantially. Moreover, such a calculation is more realistic and would be of great importance in assessing issues [2-4] related to energy transport and localization in these biological model systems.

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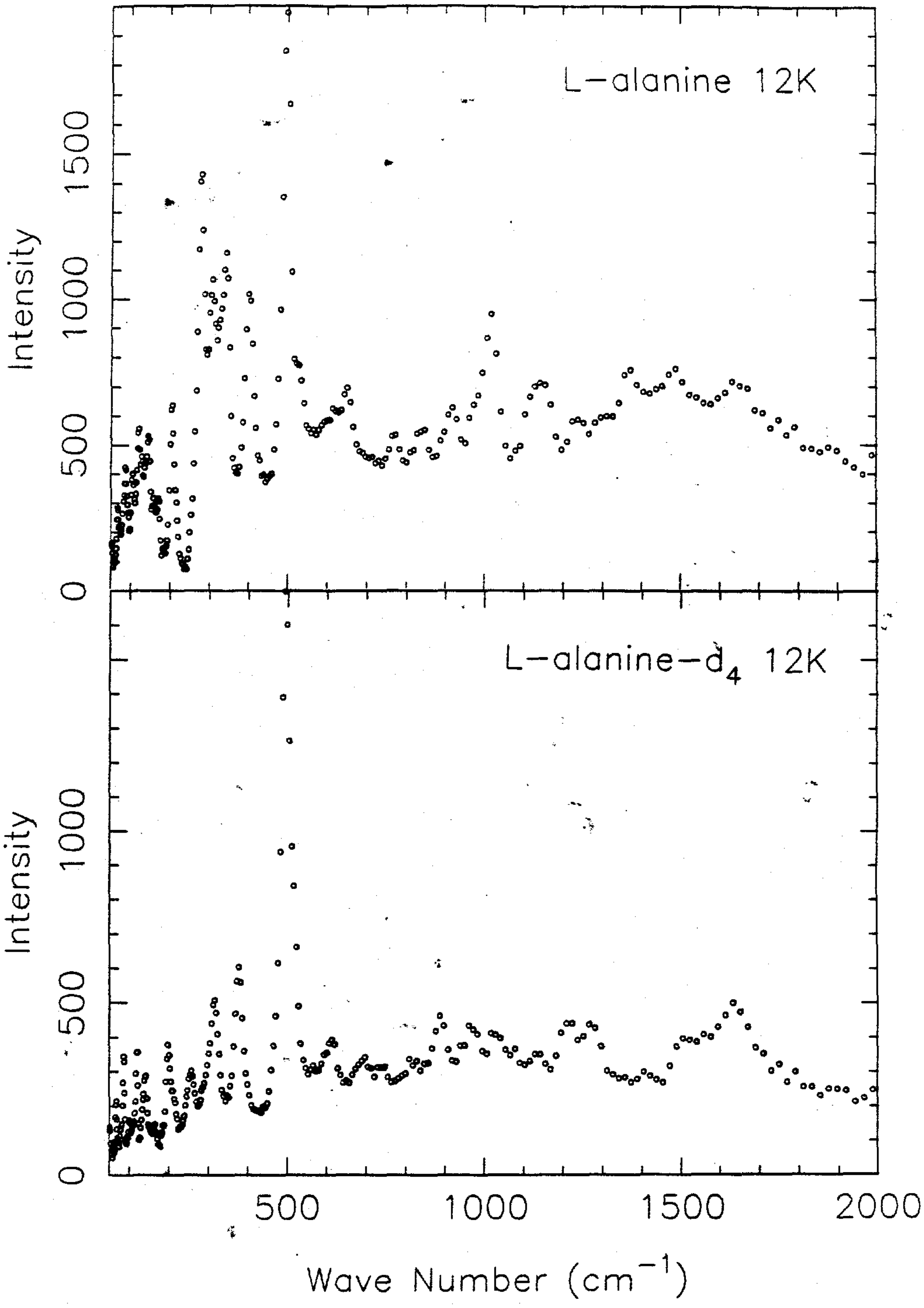
Table 1. Force constants (FC) obtained from fitting frequencies and IINS spectra of L-alanine (1) and L-alanine-d_4 (2) using CLIMAX [12]. C_1 is the carboxyl group carbon atom, C_2 the methyne- and C_3 the methyl group carbon atom.

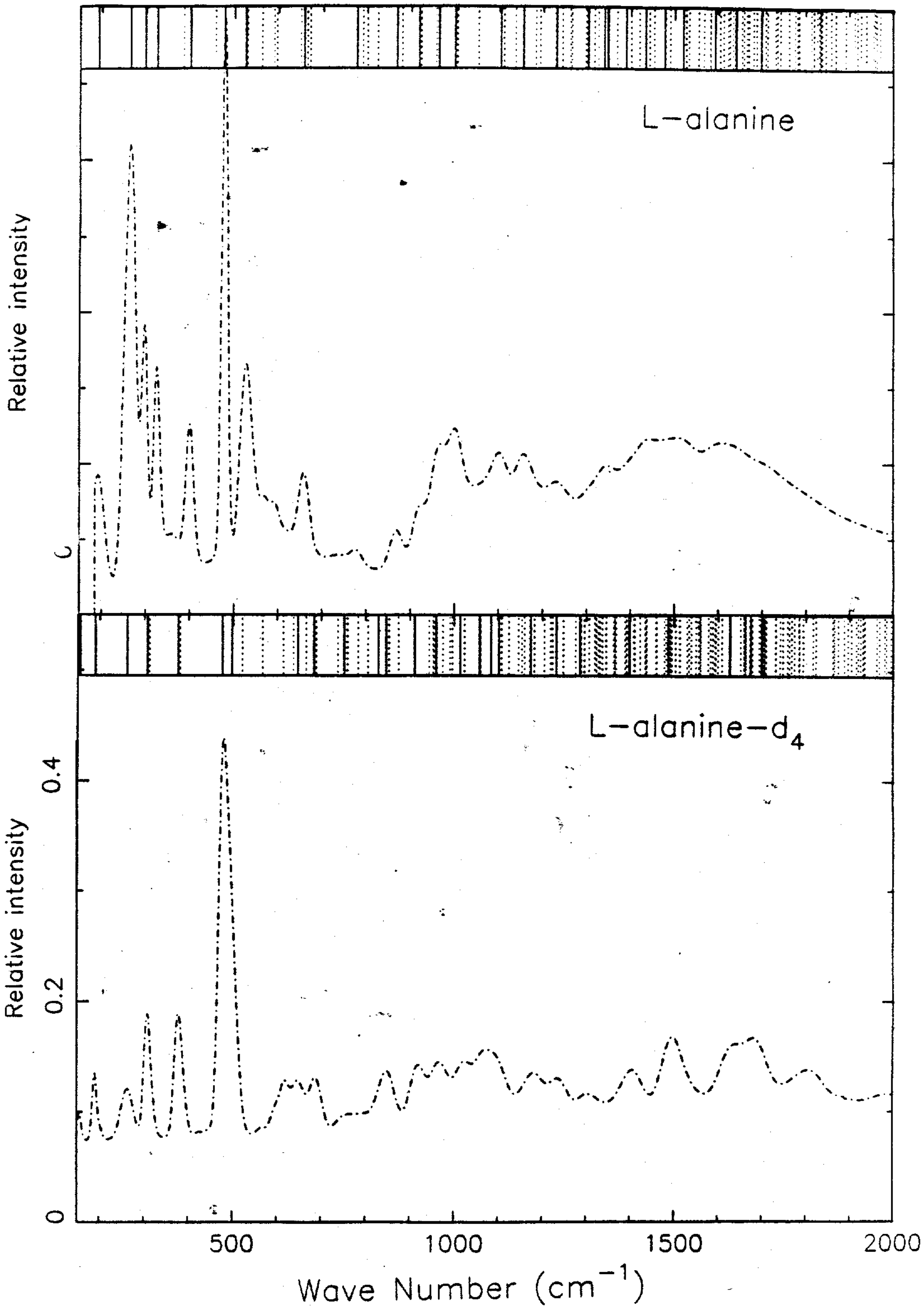
FC	1	2	coordinate	FC	1	2	coordinate
1	5.08	5.20	$\nu(NH_3^+)$	19	4.60	4.78	$\nu(C-N)$
2	0.51	0.53	$\delta(NH_3^+)$	20	1.47	1.23	$\delta(N-C_2-C_3)$
3	0.92	0.76	$\rho(NH_3^+)$	21	1.07	0.90	$\delta(N-C_2-C_1)$
4	0.005	0.005	$\tau(NH_3^+)$	22	1.38	0.99	$\delta(C_1-C_2-C_3)$
5	4.71	4.69	$\nu(CH_3)$	Interaction force constants			
6	0.45	0.48	$\delta(CH_3)$	23	-0.53	-0.92	$\nu(C-N)/\delta(NH_3^+)$
7	0.88	1.23	$\rho(CH_3)$	24	0.005	0.06	$\nu(C-N)/\rho(NH_3^+)$
8	0.001	0.001	$\tau(CH_3)$	25	0.081	0.14	$\nu(C_2-C_3)/\delta(CH_3)$
9	4.75	4.7	$\nu(C_2-H)$	26	0.48	0.58	$\nu(C_2-C_3)/\rho(CH_3)$
10	0.73	1.19	$\delta(C_2-H)$	27	1.19	1.21	$\nu(C_2-C_1)/\delta(CO_2^-)$
11	0.23	0.001	$\pi(C_1-C_2-H-C_3)$	28	1.00	1.32	$\nu(C_2-C_1)/\rho(CO_2^-)$
12	7.1	7.2	$\nu(C-O)$	29	0.57	0.63	$\nu(C-O)/\delta(CO_2^-)$
13	1.72	1.37	$\delta(CO_2^-)$	30	-0.13	-0.39	$\nu(C-O)/\rho(CO_2^-)$
14	1.24	1.40	$\rho(CO_2^-)$	31	1.41	0.49	$\nu(C_2-C_1)/\nu(C_2-C_3)$
15	0.53	0.50	$\gamma(CO_2^-)$	32	1.14	1.69	$\nu(C-O)/\nu(C_2-C_1)$
16	0.012	0.011	$\tau(CO_2^-)$	33	-0.10	-0.18	$\nu(C-O)/\delta(NH_3^+)$
17	5.07	5.31	$\nu(C_2-C_3)$	34	0.08	0.05	$\nu(C-O)/\rho(NH_3^+)$
18	3.69	4.53	$\nu(C_2-C_1)$	35	0.35	0.03	$\nu(C-O)/\delta(C_2-H)$

Figure Cations.

Fig. 1. Inelastic neutron scattering spectra for $CH_3CH(NH_3^+)CO_2^-$ (top) and $CD_3CD(NH_3^+)CO_2^-$(bottom) at 12K.

Fig. 2. Calculated IINS spectra for L-alanine (top) and L-alanine-d_4 (bottom). The bars at the top indicate the positions of the fundamental frequencies, overtones and combination bands.


L–alanine 12K
L–alanine–d4 12K
Intensity
Intensity
0
500
1000
1500
0
500
1000
500
1000
1500
2000
Wave Number (cm^{-1})


L-alanine
Relative intensity
0
L-alanine-d_4
Relative intensity
0.4
0.2
0
500
1000
1500
2000
Wave Number (cm^{-1})