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Deuterium Isotope Effect in L(+)-Glutamic Acid Hydrochloride

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A study of the effects of deuterium substitution in L(+)-glutamic acid hydrochloride is described. Solid state vibrational spectra depicting band shifts resulting from deuterium indicate that interatomic bond distances remain virtually unchanged. The cell volume expands only 0.05% upon deuteration, while the macroscopic linear and nonlinear polarizabilities are unaffected. The optical nonlinearity is therefore ascribed to the electronic nature of the hydrogen bonds.

Introduction

Recently L(+)-glutamic acid hydrochloride [$HOOC(CH_2)_2CH(NH_2)COOH \cdot HCl$] was shown to be phase matchable for optical second harmonic generation at 1.06 μm and has nonlinear optical coefficients comparable to CsH_2AsO_4 (*1*). Single crystals as large as 6 × 3 × 2 cm have been grown reproducibly from aqueous solutions and are optically transparent from 235.5 nm to 1.71 μm. This paper describes a study of the effects of deuterium substitution in L(+)-glutamic acid hydrochloride and ascribes the optical nonlinearity to the nonlinear polarizability of the hydrogen bonds.

Experimental

The preparation and impurity analysis of L(+)-glutamic acid hydrochloride crystals is the same as that previously described (*1*). Deuteration was accomplished by repeated recrystallization in 99.97% D_2O under dry argon to minimize $D \rightleftharpoons H$ exchange with the atmosphere.

Chemical ionization mass spectrometry (CIMS) was performed using a Finnigan model 3200 gas chromatograph mass spectrometer with a differentially pumped chemical ionization source. D_2O was used as the chemical ionization reagent and electron bombardment occurred at a pressure of 0.3 Torr.

Infrared spectra were recorded on Perkin–Elmer infrared spectrometers (Models 337 and 21), calibrated against the 1601 cm^{-1} band of polystyrene. Powdered samples (36–45 μm), ground from single crystals, were dried for 4 hr at 105°C prior to scanning. Solid-state spectra were run as Nujol mulls between KBr plates while solutions were examined using Irtran-2 windows.

Lattice parameters were measured with a Philips automatic single crystal diffractometer using Cu$K\alpha$ radiation.

Optical second harmonic powder analysis (SHA) was previously described (*2*). The SHA apparatus was recently improved by the addition of a digital signal integrator, which results in background noise that is less than 10^{-4} relative α-SiO_2 under optimum conditions with a reproducibility of better than 10%, and a standard deviation of ±30%.

Differential thermal analysis (DTA) was performed with a Columbia Scientific Instrument Model DTA-202 under static conditions. Recorded temperatures are considered accurate to ±1°C. Samples were on the order of 10 mg and Al_2O_3 was used as a reference. Platinum cups served as susceptors. Heating

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and cooling rates of 10°C $\min^{-1}$ were employed.

Results

Deuteration proceeds according to the following reaction

$$HOOC(CH_2)_2CH(NH_2)COOH \cdot HCl + D_2O \rightleftharpoons DOOC(CH_2)_2CH(ND_2)COOD \cdot DCl + H_2O,$$

where all but the five hydrogens of the three sp^3 carbons readily exchange. This was confirmed by CIMS with observed peaks at *m/e* 190, 152, 38, and 21. A deuteration level of $98 \pm 1\%$ was established by quantitative comparison of the intensity of the ν_2 and ν_3 fundamentals of H_2O, at 1595 and 3756 cm^{-1} to D_2O, at 1179 and 2789 cm^{-1}. The deuterate is therefore designated $d_5 - 0.98D$. This symbolism means that on the average each molecule has five deuteriums at a level of 98 mole%.

Crystals of L(+)- and D(−)-glutamic acid hydrochloride are orthorhombic with the space group $P2_12_12_1$ (3–5). Precession diagrams indicate that this symmetry is maintained upon deuteration. Table I lists the crystallographic data for the undeuterated and $d_5 - 0.98D$ salts. Within the resolution of our instrumentation the lattice parameters are not significantly affected by deuteration. The only detectable change is in the c_0 direction which increases by only 0.004 Å. More importantly, the cell volume increases by only 0.4 Å^3 or about 0.05%. This is somewhat surprising when one considers that deuterium substitution usually results in a marked lattice expansion for molecular crystals (*6–8*). The excellent agreement between experimental and calculated densities is indicative of the high deuteration level. In fact, accurate determination of the crystal density may be utilized in establishing the deuteration level in the crystal.

The SHA data shown in Table II exhibit a most unexpected result. Under identical

TABLE I

SINGLE CRYSTAL X-RAY DATA RECORDED AT 22°C

L(+)-glutamic acid hydrochloride	Undeuterated	$d_5 - 0.98D$
Lattice parameters (Å)		
a_0	11.737 ± 0.004	$a_0 = 11.736 \pm 0.004$
b_0	13.299 ± 0.004	$b_0 = 13.298 \pm 0.004$
c_0	5.1404 ± 0.0004	$c_0 = 5.1444 \pm 0.0004$
Cell volume (Å^3)	802.37	802.79
Z	4	4
ρ_{calcd} (g cm^{-3})	1.519	1.560
ρ_{exp} (g cm^{-3})	1.525 ± 0.005	1.559 ± 0.005

TABLE II

OPTICAL SECOND HARMONIC POWDER ANALYSIS DATA RECORDED AT 25°C

L(+)-glutamic acid hydrochloride	Particle size (μm)	$\bar{n}$ 5300 Å	Level relative α-SiO_2	Background noise
Undeuterated	212–300	1.558	1.0	10^{-4}
$d_5 - 0.98D$	212–300	1.558	0.9	10^{-4}

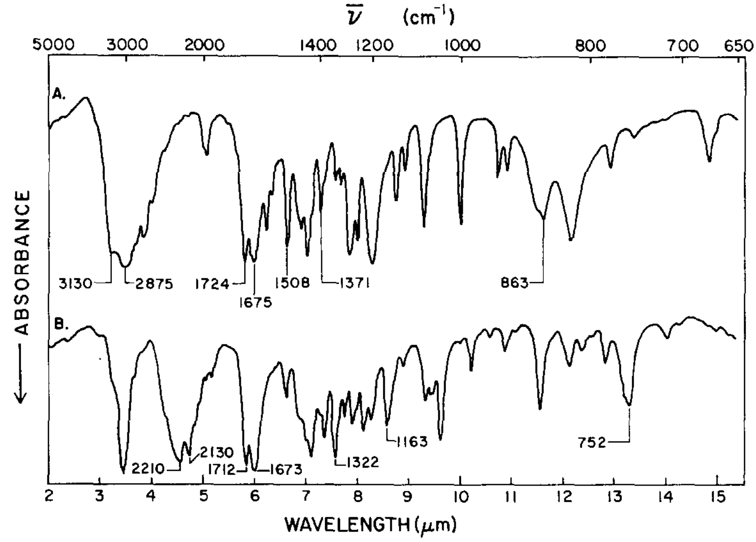

FIG. 1. Solid-state vibrational spectra for (A) L(+)-glutamic acid hydrochloride, and (B) d_5 – 0·98D L(+)-glutamic acid hydrochloride.

operating parameters, the second harmonic intensity, relative to an α-SiO_2 standard, is the same for the $d_5 - 0.98D$ salt. Selective deuterium substitution did not affect the optical nonlinearity. The estimated coherence length of 25 μm (*1*) was unaltered also.

Single crystal and powder samples were examined by DTA from –160°C and SHA from –60°C to the decomposition point. No transitions or anomalies of any kind were observed. The L(+)-glutamic acid hydrochloride decomposed at 202°C while the $d_5 - 0.98D$ salt decomposed at 206°C. The observed temperature difference of 4°C indicated that deuterium apparently has little effect upon bond strengths.

The solid-state spectra from 2 to 15 μm for the undeuterated and $d_5 - 0.98D$ salts are shown in Fig. 1, depicting band contours and frequency shifts. The assignments for some of the vibrational modes are listed in Table III for the undeuterated and for the $d_5 - 0.98D$ salt. These are based upon the crystal structure (*3–5*) and isotope shifts resulting from deuterium substitution. The isotope shifts confirm the conclusions drawn from the CIMS data that only those hydrogens which are directly bonded to a carbon are not replaced by deuterium. It should be noted that two C = 0

TABLE III

INFRARED SPECTRAL DATA AT 22°C

$\bar{\nu}$ (cm^{-1})	Intensity[a]	Assignment
(A) L(+)-glutamic acid hydrochloride		
3130	s, b	NH_3^+ sym. and asym. stretch
2875	s, b	OH stretch
1724	s	C = 0 stretch
1675	s	C = 0 stretch
1610	m	NH_3^+ asym. def.
1508	m	NH_3^+ sym. def.
1371	w	CH sym. def.
863	m, b	OH out-of-plane def.
(B) $d_5 - 0.98D$ L(+)-glutamic acid hydrochloride		
2928	s	CH_2 asym. H vib.
2890	s	CH stretch
2851	s	CH_2 sym. H vib.
2210	s, b	OD stretch
2130	s, b	ND_3^+ sym. and asym. stretch
1712	s	C = 0 stretch
1673	s	C = 0 stretch
1356	w	CH sym. def.
1322	m	NH_3^+ asym. def.
1163	m	NH_3^+ sym. def.
752	m, b	OD out-of-plane def.

[a] s = strong, m = medium, w = weak, b = broad, sym. = symmetric, asym. = asymmetric, def. = deformation, vib. = vibrational.

stretching frequencies occur since L(+)-glutamic acid hydrochloride is a dicarboxylic acid. The one at 1724 cm^{-1} is attributed to the alkyl carbonyl while the zwitterion carbonyl is at 1675 cm^{-1}. Upon deuteration, the alkyl $C=O$ stretch shifts to 1712 cm^{-1} while the zwitterion carbonyl remains nearly unchanged at 1673 cm^{-1}. Both carboxylic acid groups are in an unionized state as is expected from the structure work and from thermodynamic considerations (*3*, *5*).

Discussion

According to Dawson (*3*) and neutron-diffraction studies (*5*), four types of hydrogen bond predominate in the packing of the L(+)-glutamic acid hydrochloride lattice. These are listed in Table IV along with their respective bond distances. Previous workers (*9*, *10*) have shown a linear relationship between hydrogen bond distances and their corresponding stretching frequencies $\bar{\nu}_s$. Following their formalism, our calculated values for $\bar{\nu}_s$ are shown in Table IV. These are calculated from the reported bond distances (*3*, *5*) and are considered accurate to ±100 cm^{-1}. Based on these data, we can attempt to estimate the force constant for each bond and to predict the frequency shift resulting from deuterium. The force constant k for any AH---B bond is given by

$$k = 4\pi^2 c^2 \bar{\nu}_s \mu \qquad (1)$$

where c is the velocity of light, and μ is the reduced mass of the hydrogen bond. We assume that the shift in $\bar{\nu}_s$ is a consequence of the reduced mass of the bonding atoms and that the change in the force constant of the bond is negligible. Our calculated values of $\bar{\nu}_s$ for the isotope shift are shown in Table IV. These values are in excellent agreement with the observed frequency shifts obtained from the vibrational spectra (Fig. 1). It appears that the hydrogen bond distances remain fairly constant even after deuterium substitution and that the interatomic bond distances given by Dawson (*3*) and a neutron diffraction study (*5*) are correct.

X-ray measurements, DTA, and vibrational spectra indicated that interatomic bond distances remain virtually unchanged as a result of deuteration and the average nonlinear optical coefficient is unaltered also as shown by our SHA measurements. If we assume hydrogen bonding to play a key role in the optical nonlinearity, then deuterium substitution has certainly not affected the nonlinear polarizability of these bonds. If the linear polarizability were altered, only resulting from a change in bond distance, then the refractive index would have changed. We have already shown this not to be the case (Table II).

Following a similar analysis made by Bergman (*11*) the nonlinear optical coefficient d_{ijk} is related to the nonlinear bond polarizability β_{lmn} via,

$$d_{ijk} = V^{-1} \sum_{l,m,n} G_{il} G_{jm} G_{kn} \beta_{lmn} \qquad (2)$$

where V is the volume of the lattice, and G is a transformation matrix which relates the bond

TABLE IV

RELATION OF HYDROGEN BOND DISTANCES TO $\bar{\nu}_s$ (22°C)

Hydrogen bond	Bond distance (Å)	$\bar{\nu}'$ (cm^{-1}) Undeuterated Calculated	Undeuterated Observed	$d_5 - 0.98D$ Calculated	$d_5 - 0.98D$ Observed
NH---O	2.89	3100	3150	2257	2130
NH---Cl	3.18	2950	3000	2115	2250
OH---O	2.57	2625	2625	1910	2075
OH---Cl	3.06	3050	3100	2187	2175

coordinate system to the crystal coordinate system. For L(+)-glutamic acid hydrochloride the optical nonlinearity is assigned to the hydrogen bonds of the lattice, here Eq. (2) becomes

$$d_{ijk} = V^{-1} \sum_{l,m,n} \left(\sum_{\beta'} G_{il} G_{jm} G_{km} \beta'_{lmn}\right) + \left(\sum_{\beta''} G_{il} G_{jm} G_{km} \beta''_{lmn}\right) + \cdots \quad (3)$$

where β', β'' ... refer to the types of hydrogen bonds which are present, i.e., NH---O, NH---Cl, OH---O, and OH---Cl, of each bond symmetry. Summing is performed over the number of bonds in the lattice. Here we have neglected effects due to anisotropic polarization and inductive effects for reasons of simplicity.

Each β is treated as arising from the charge transfer resonance contribution of the hydrogen bond. Since hydrogen bonds are well known to be primarily electrostatic in character, the charge transfer structure contributes less than 6% of the total wave function for each hydrogen bond (*12*). Consequently the primary charge transfer mechanism is the anharmonic oscillatory motion of the hydrogen in the hydrogen bond. The electric field induced hydrogen displacement results in the nonlinear polarization. It therefore follows that since deuterium substitution affects the vibrational character and not the electronic character of the bond, that the nature of the optical nonlinearity is electronic and not vibrational.

Summary and Conclusions

We have shown that deuterium substitution has little effect upon the interatomic bond distances in L(+)-glutamic acid hydrochloride. At the same time no change in the optical nonlinearity is observed. Assuming the nonlinearity to arise from the hydrogen bonds leads us to conclude that the nonlinear polarizability is electronic and not vibrational in character. These observations may have important ramifications in the theory of nonlinear polarizabilities and linear polarizabilities.

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