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RAMAN SPECTRA OF L-ALANINE CRYSTAL**

EUGENE LOH

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INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11049 (Pinheiros)
CIDADE UNIVERSITÁRIA "ARMANDO DE SALLES OLIVEIRA"
SAO PAULO — BRASIL

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Eugene Loh

**Coordenadoria de Ciência e Tecnologia de Materiais
Instituto de Energia Atômica
São Paulo - Brasil**

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ABSTRACT

The low frequency $< 150 \text{ cm}^{-1}$ polarized Raman spectra of L-alanine single crystals by Wang and Storms can be interpreted more meaningfully in terms, instead of transverse and longitudinal phonons by Wang and Storms, of the intermolecular vibrations, i.e. librations and/or translations, of the four oriented alanine molecules in the unit cell of the orthorhombic crystal.

INTRODUCTION

The low frequency $< 150 \text{ cm}^{-1}$ polarized Raman spectra of L-alanine single crystals have been measured by Wang and Storms¹ and interpreted¹ in terms of transverse and longitudinal phonons with, however, large orientational anisotropy as well as polarization anomalies. To account for these unusual effects, a picture of dynamic disorder due to the protonic motion in the intermolecular hydrogen bonds between the NH_3^+ group of one molecule and the CO_2^- group of a neighboring molecule has been proposed¹.

In this note, we shall, by comparing the Raman intensities in the various polarized spectra, show that the polarized low frequency Raman spectra¹ of L-alanine single crystals can be interpreted physically more meaningfully in terms, instead of transverse and longitudinal phonons¹ of the intermolecular vibrations^{2,3}, i.e. librations and/or translations, of the four oriented alanine molecules within the unit cell of the orthorhombic alanine crystal, i.e. the oriented gas model.

ORIENTED GAS MODEL

To apply the oriented gas model, we need to approximate the three principle axes of the alanine molecule in the orthorhombic^{4,5} unit cell of alanine crystal by:

(i) u -- The projection of the u axis on the ac crystallographic^{4,5} plane is taken to be the same as that from the $\text{C}_\alpha\text{-C}$ bond, where C_α is the α carbon atom and C is the carbon from CO_2^- . u is perpendicular to the subsequently defined v . The direction of u defined in this manner is close to both the crystallographic c axis^{4,5} as indicated by the directional cosines in Table I, and the direction of the molecular chain^{4,5} in the crystal. u is, therefore, likely the "high" frequency axes, among u , v and w , of the intermolecular librations and translations.

(ii) v -- The direction of v is taken to be parallel to the line joining N of NH_3^+ and C_β of C_βH_3 in the alanine molecule and is close to that of the crystallographic^{4,5} a -axis, Table I.

(iii) w -- The direction of w is perpendicular to both u and v and is close to that of the crystallographic^{4,5} axis b , Table I.

	a	b	c
u	0.322	-0.202	0.923
v	0.935	0.225	0.275
w	-0.152	0.952	0.262

Table I

Direction cosines of the approximated molecular axes u, v and w of the alanine molecule with respect to the crystallographic axes a, b and c of the orthorhombic L-alanine crystal.

Following the steps by Suzuki et al⁶ in deriving the relative Raman intensities in various polarized spectra under the assumption of the oriented gas model:

The transformation matrices of molecules 1,2,3 and 4, in the $P2_12_12_1$ unit cell, between the molecule fixed co-ordinates u, v, w, and the crystal fixed coordinates a, b, c are expressed by

$$\begin{aligned}
 T_1 &= \begin{bmatrix} a_u & a_v & a_w \\ b_u & b_v & b_w \\ c_u & c_v & c_w \end{bmatrix}, & T_2 &= \begin{bmatrix} a_u & a_v & a_w \\ -b_u & -b_v & -b_w \\ -c_u & -c_v & -c_w \end{bmatrix} \\
 T_3 &= \begin{bmatrix} -a_u & -a_v & -a_w \\ b_u & b_v & b_w \\ -c_u & -c_v & -c_w \end{bmatrix} & \text{and } T_4 &= \begin{bmatrix} -a_u & -a_v & -a_w \\ -b_u & -b_v & -b_w \\ c_u & c_v & c_w \end{bmatrix} \quad (1)
 \end{aligned}$$

where a_u is the cosine of the angle between the a and u axes and so on. The values of a_u, a_v, \dots are listed in Table I. The molecular tensor with respect to the crystal fixed coordinates is therefore given by

$$\alpha_{m_i} = T_i \alpha'_m \tilde{T}_i \quad (2)$$

where $i = 1, 2, 3$ and 4 for molecules 1, 2, 3 and 4, respectively, and α'_m = derived polarizability tensor of the free molecule with respect to a normal vibration Q .

On the assumption of the oriented gas model we assume additive polarizabilities.

$$\alpha_u = \alpha'_{m_1} Q_1 + \alpha'_{m_2} Q_2 + \alpha'_{m_3} Q_3 + \alpha'_{m_4} Q_4 \quad (3)$$

where α_u is the polarizability tensor of the unit cell. Using symmetry coordinates⁶ S_{Ag}, S_{Bg1}, S_{Bg2} and S_{Bg3} appropriate to the four-molecule unit cell of D_2 , we find

$$\begin{aligned}
Q_1 &= (S_{A_0} + S_{B_{\theta_1}} + S_{B_{\theta_2}} + S_{B_{\theta_3}}) / \sqrt{4} \\
Q_2 &= (S_{A_0} + S_{B_{\theta_1}} - S_{B_{\theta_2}} - S_{B_{\theta_3}}) / \sqrt{4} \\
Q_3 &= (S_{A_0} - S_{B_{\theta_1}} + S_{B_{\theta_2}} - S_{B_{\theta_3}}) / \sqrt{4} \\
Q_4 &= (S_{A_0} - S_{B_{\theta_1}} - S_{B_{\theta_2}} + S_{B_{\theta_3}}) / \sqrt{4}
\end{aligned} \tag{4}$$

The derived polarizability tensors with respect to the unit cell vibrations, which can be obtained by taking the derivatives of equation(3) with substitutions of equations(1),(2) and(4), are⁷:

$$\begin{aligned}
\frac{\partial \alpha_u}{\partial S_{A_0}} &= \sqrt{4} \begin{bmatrix} A_{aa} & 0 & 0 \\ 0 & A_{bb} & 0 \\ 0 & 0 & A_{cc} \end{bmatrix}, & \frac{\partial \alpha_u}{\partial S_{B_{\theta_1}}} &= \sqrt{4} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & A_{bc} \\ 0 & A_{bc} & 0 \end{bmatrix} \\
\frac{\partial \alpha_u}{\partial S_{B_{\theta_2}}} &= \sqrt{4} \begin{bmatrix} 0 & 0 & A_{bc} \\ 0 & 0 & 0 \\ A_{bc} & 0 & 0 \end{bmatrix}, & \frac{\partial \alpha_u}{\partial S_{B_{\theta_3}}} &= \sqrt{4} \begin{bmatrix} 0 & A_{ab} & 0 \\ A_{ab} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}
\end{aligned} \tag{5}$$

where the A's are functions of the direction cosines and the elements of the derived polarizability tensor of the free molecule.

Following Adamowicz et al⁸, we approximate the L-alanine molecule, which is of C_1 symmetry, by a C_2 molecule with the two fold axis almost parallel to u. The character table and selection rules for C_2 molecule indicate that the non-vanishing elements of the derived polarizability tensor of the free molecule are α'_{uu} , α'_{vv} , α'_{ww} , and α'_{vw} for the libration R(u) or the translational vibration T(u) about the u-axis, α'_{uw} and α'_{uw} for that about v and w axes. Thus, we obtain simple analytical expressions of A's for the vibrations of different species of the molecule. They are given in Table II.

The squared values of A's, which are proportional to the expected intensities of a given lamen peak in the various polarized spectra, are listed in Table III. The values in the column of R(u), T(u) are more uncertain than that in the other two columns because of the presence of the α'_{uu} , α'_{vv} and α'_{ww} in the former as shown in Table II.

Table III shows that for intermolecular vibrations about the u-axis, the orders of intensities are

$$(A_{1b})^2 > (A_{aa})^2 > (A_{cc})^2 \tag{10a}$$

and

$$(A_{ab})^2 > (A_{ac})^2 > (A_{bc})^2 \quad (10b)$$

and are satisfied by the "high" frequency peaks¹, in Fig 1 and 2, at 105 cm⁻¹ and 113 cm⁻¹ for the inequality (10a) and at 105 cm⁻¹, 113 cm⁻¹ and 138 cm⁻¹ for inequality (10b)

For intermolecular vibrations about the v and w axes the intensity orders in the last column of Table III,

$$(A_{aa})^2 > (A_{cc})^2 > (A_{bb})^2 \quad (11a)$$

and

$$(A_{ac})^2 > (A_{bc})^2 > (A_{ab})^2 \quad (11b)$$

are satisfied by the "medium" frequency peaks¹ at 75 cm⁻¹ and 85 cm⁻¹ in Fig 1 and 2, for the inequality (11b). This indicates that these peaks are mostly of Bg mode in the D₂ factor group. However, for the lowered symmetry, e.g. C₂ factor group due to dynamic disorder¹, then these two "medium" frequency peaks¹ are also of Ag mode due to their strong intensities in (ac) spectra too.

The intensity orders in the next to last column are:

$$(A_{cc})^2 > (A_{bb})^2 > (A_{aa})^2 \quad (12a)$$

and

$$(A_{bc})^2 > (A_{ab})^2 > (A_{ac})^2 \quad (12b)$$

and are satisfied by the "low" frequency peaks at 48 cm⁻¹ and 40 cm⁻¹, in Fig 1 and 2, for both inequalities (12a) and (12b). These two peaks are again the mixture of the Ag and Bg modes.

CONCLUSION

The oriented gas model seems to be able to explain the relative Raman intensities in the polarized spectra of the low frequency vibrations in L alanine single crystals, which has hydrogen bonds as intermolecular bondings. The model assigns the intermolecular vibrations about the molecular axes u, v and w axes at (105 cm⁻¹, 113 cm⁻¹, 138 cm⁻¹), (75 cm⁻¹, 85 cm⁻¹) and (48 cm⁻¹, 40 cm⁻¹), respectively, of mixed A and B modes.

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Table II

Elements of the derived polarizability tensors of the approximated L-alanine molecular crystal

	R(u), T(u)	R(v), T(v) or R(w), T(w)
$\left\{ \begin{array}{l} A_{aa} \\ A_{bb} \\ A_{cc} \end{array} \right\}$ A_g	$a_{uu}^2 \alpha'_{uu} + a_{vv}^2 \alpha'_{vv} + a_{ww}^2 \alpha'_{ww} + 2a_u a_w \alpha'_{uw}$	$2a_u a_w \alpha'_{uw}$
	$b_{uu}^2 \alpha'_{uu} + b_{vv}^2 \alpha'_{vv} + b_{ww}^2 \alpha'_{ww} + 2b_u b_w \alpha'_{uw}$	$2b_u b_w \alpha'_{uw}$
	$c_{uu}^2 \alpha'_{uu} + c_{vv}^2 \alpha'_{vv} + c_{ww}^2 \alpha'_{ww} + 2c_u c_w \alpha'_{uw}$	$2c_u c_w \alpha'_{uw}$
$B_{g_1} A_{bc}$	$b_u c_u \alpha'_{uu} + b_v c_v \alpha'_{vv} + b_w c_w \alpha'_{ww} + (b_u c_w + b_w c_u) \alpha'_{uw}$	$(b_u c_w + b_w c_u) \alpha'_{uw}$
$B_{g_2} A_{bc}$	$a_u c_u \alpha'_{uu} + a_v c_v \alpha'_{vv} + a_w c_w \alpha'_{ww} + (a_u c_w + a_w c_u) \alpha'_{uw}$	$(a_u c_w + a_w c_u) \alpha'_{uw}$
$B_{g_3} A_{ab}$	$a_u b_u \alpha'_{uu} + a_v b_v \alpha'_{vv} + a_w b_w \alpha'_{ww} + (a_u b_w + a_w b_u) \alpha'_{uw}$	$(a_u b_w + a_w b_u) \alpha'_{uw}$

Table III

Squared values of the elements of the crystal tensors

	R(u), T(u)	R(v), T(v) or R(w), T(w)
$(A_{aa})^2$	$\sim 0.1 a_{vw}'^2$	0.1 $a_{uw}'^2$ 0.37 $a_{uv}'^2$
$(A_{bb})^2$	$> 0.18 a_{vw}'^2$	0.15 $a_{uw}'^2$ 0.08 $a_{uv}'^2$
$(A_{cc})^2$	$\sim 0.02 a_{vw}'^2$	0.23 $a_{uw}'^2$ 0.26 $a_{uv}'^2$
$(A_{ac})^2$	$\sim 0.1 a_{vw}'^2$	0.03 $a_{uw}'^2$ 0.6 $a_{uv}'^2$
$(A_{ab})^2$	$\sim 0.74 a_{vw}'^2$	0.11 $a_{uw}'^2$ 0.01 $a_{uv}'^2$
$(A_{bc})^2$	$\sim 0.04 a_{vw}'^2$	0.68 $a_{uw}'^2$ 0.07 $a_{uv}'^2$

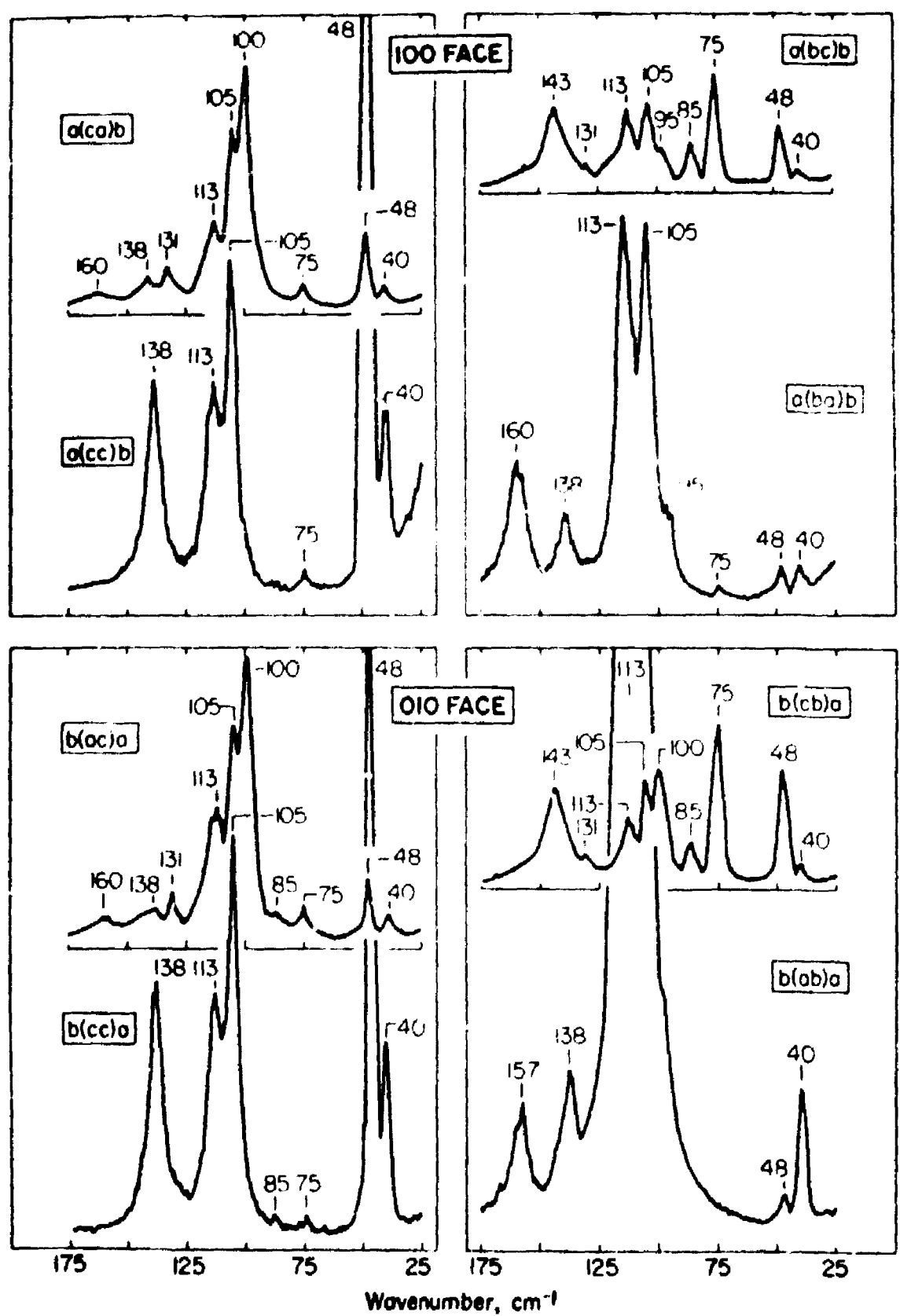


Figure 1
 The Raman spectra of L-alanine from 25 to 175 cm^{-1} for the (100) face and (010) face.
 (reproduced from reference 1)

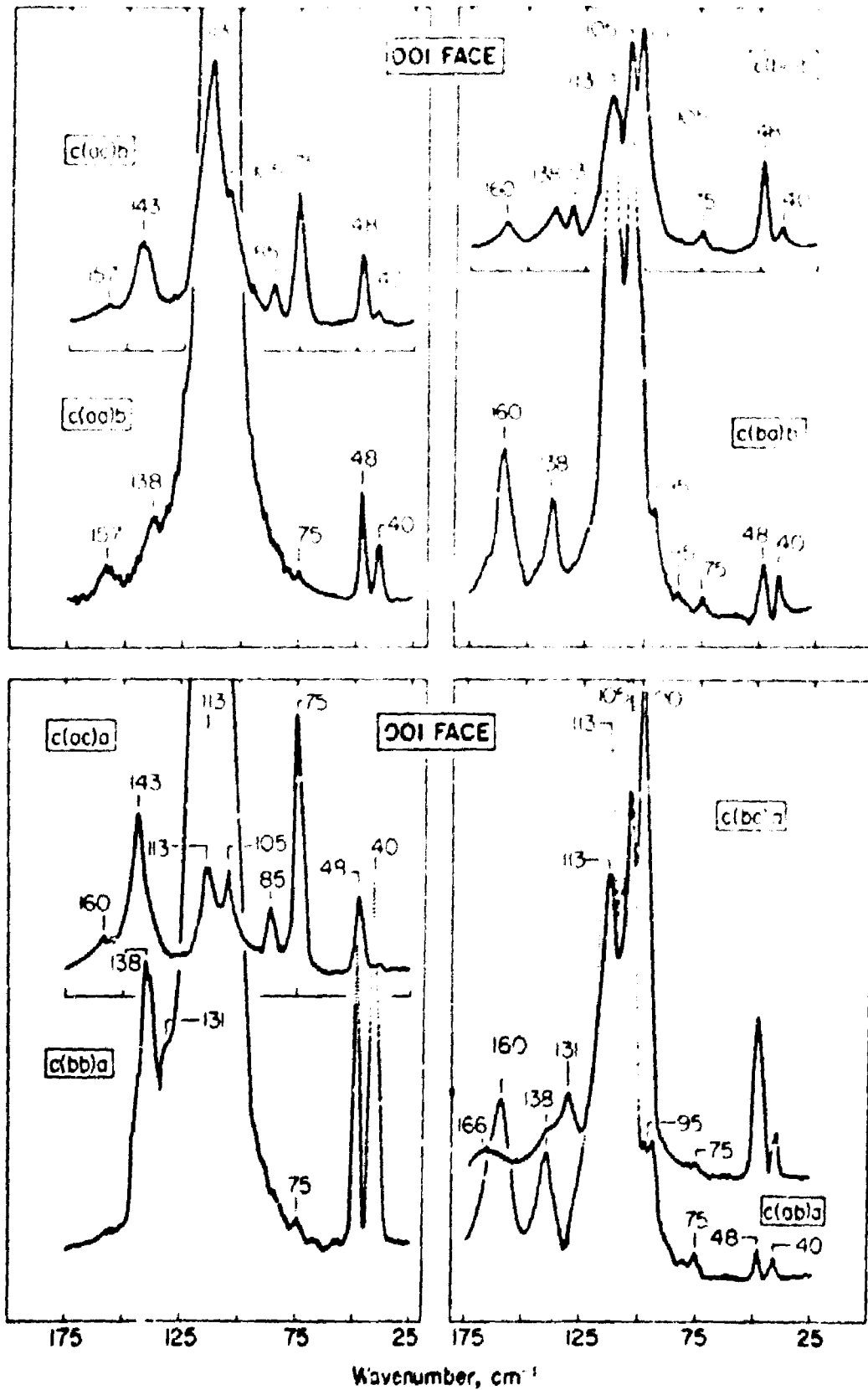


Figure 2

The Raman spectra of L-alanine from 25 to 175 cm⁻¹ for the (001) face.
(reproduced from reference 1)

RESUMO

Espectros Raman polarizados, de baixa frequência, $< 150 \text{ cm}^{-1}$ de monocristais de L-alanina, obtidos por Wang e Storms podem ser reinterpretados, mais significativamente, em termos, ao invés dos fonons transversais e longitudinais de Wang e Storms, das vibrações intermoleculares, i.e., "librations" e/ou translações, das quatro moléculas alanina orientadas na célula unitária do cristal ortorrômbico.

RÉSUMÉ

Les spectres Raman polarisés, de basse fréquence, $< 150 \text{ cm}^{-1}$, de monocristaux de L-alanine, obtenus par Wang et Storms peuvent être réinterprétés, plus significativement, en termes des vibrations intermoleculaires, c'est-à-dire, des librations et/ou translations, des quatre molécules alanine orientées dans la cellule unitaire du cristal orthorhombique.

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