Depolarization of Raman Scattering in LaCl₃†

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The first-order Raman spectrum of LaCl₃ is reexamined. Consideration of depolarization of the Raman scattering from the totally symmetric A_g vibration has led to a different assignment for the Raman-active lines: 108 cm⁻¹, E_{2g}; 180 cm⁻¹, A_g; 186 cm⁻¹, E_{1g}; 212 cm⁻¹, A_g; 219 cm⁻¹, E_{2g}. The depolarization scattering appears to result from optic axis wandering in the crystal as well as from converging or diverging light beams.

INTRODUCTION

THE Raman spectrum of LaCl₃ at 77°K is presented here. The experimental data indicate that one of the lines in certain polarizations results from depolarization scattering; the results suggest an interpretation of the Raman spectra which is different from that given previously.

A recent Raman study of depolarization in calcite by Porto et al.[1] appears to be pertinent to our study. The authors have shown that depolarization results when convergent incident or scattered light propagates along the crystalline optical axis of a uniaxial crystal. Residual depolarization is assigned to the wandering of the optic axis of the crystal.

The LaCl₃ crystal structure is briefly summarized. The x-ray studies by Zachariasen[2] have shown that LaCl₃ has a hexagonal dipyramidal type of symmetry and belongs to the space group $C_{6h}{}^2$. The $k=0$ factor group of $C_{6h}{}^2$ is isomorphic with the underlying C_{6h} point group,[3] so that the same character table can be used for both groups. The crystal symmetry contains the inversion operation, so that Raman and infrared vibrations are mutually exclusive.

The polarized Raman spectrum of the lattice vibrations of LaCl₃ has been studied by Hougen and Singh.[4] Five of the six Raman-active lines were observed. They were identified as three E_{2g} lines, one E_{1g} line, and one A_g line; an A_g line was found to be missing. The assignment does not conflict with that resulting from the vibronic studies of Cohen and Moos.[5]

However, in the present work we find that one of the lines previously identified as an E_{2g} line is actually an A_g line. A strong A_g line at 212 cm⁻¹ (crystal at 77°K) dominates the spectrum. When examining the E_{2g} spectrum with the scattered light propagating along the

crystal optic axis, a component of the 212-cm⁻¹ A_g line appears; however, the line does not appear in the E_{2g} spectrum when the scattered light is measured in a direction perpendicular to the c axis. The missing sixth Raman-active line was not found in the present work.

EXPERIMENTAL

The experimental technique consists of using a laser exciting source, passing the Raman scattered light through a double spectrometer, and counting the photomultiplier output pulses. A Hughes 1-W argon laser was used as the exciting source. Any of seven argon laser lines was selectable by rotating an internally mounted prism. The laser lines used for this study were the 5145, 4880, and 4765 Å lines; the power output of the first two lines was normally several hundred milliwatts. Narrow band-pass interference filters were placed at the exit position of the laser in order to reject gaseous discharge lines. A SPEX 0.75-m focal-length double spectrometer was used to minimize the Rayleigh scattered light emanating from the LaCl₃ crystal. An ITT FW-130 photomultiplier tube with an S-20 photocathode surface of 0.1 in. effective diameter was cooled with liquid nitrogen vapor in order to minimize dark current (1 to 5 counts/sec). The output pulses of the photomultiplier were amplified, height-discriminated, and shaped. The average rate of the resultant pulses was recorded; the rate was proportional to the intensity of the scattered light reaching the photomultiplier.

The crystals were grown by a technique described by Hutchison and Wong.[6] Lanthanum oxide was converted into a hydrated lanthanum chloride salt using HCl; dehydration of the material was accomplished by heating the sample under partial vacuum. The crystals were grown by the Bridgman process, in which a quartz growth capsule with a conical-to-capillary bottom is passed slowly through a furnace with a thermal gradient near the freezing point of the material. Several large clear crystals were grown in this manner.

A number of LaCl₃ crystals were shaped into rectangular parallelepipeds with dimensions of 2 to 3 mm on a side. The crystalline optic c axes were oriented to be perpendicular to a pair of parallel faces by means of

¹ S. P. S. Porto, J. A. Giordmaine, and T. C. Damen, Phys. Rev. 147, 608 (1966).
² W. H. Zachariasen, J. Chem. Phys. 16, 254 (1948).
³ J. Murphy, H. H. Caspers, and R. A. Buchanan, J. Chem. Phys. 40, 743 (1964).
⁴ J. T. Hougen and S. Singh, Proc. Roy. Soc. (London) A277, 193 (1964).
⁵ E. Cohen and H. W. Moos, Phys. Rev. 161, 268 (1967).
⁶ C. A. Hutchison and E. Wong, J. Chem. Phys. 29, 754 (1958).

crossed polaroids. Linde A powder on a rotating cloth lap was used to polish the samples. Many of the crystals showed distorted "rings and brushes" patterns, as a result of strain in the crystal. Several of the crystals showed definite polycrystalline features under crossed polaroids; small sections of the crystals appeared to be oriented in mutually different c-axis directions. The angular difference in directions appeared to be very small. The results described herein were taken on the best available samples; these showed only a slightly distorted pattern over most of the crystal.

The light from the laser was reflected upward into a Dewar by a diagonally placed front surface mirror. The crystal was located on a rotatable platform in the Dewar. The crystal was oriented so that the optic c axis (the z axis) was in the horizontal plane, perpendicular to the light-propagation direction (the x axis). By rotating the platform about the x axis, the scattered light could be observed along the y axis or the z axis.

The spectrometer slits were normally set so that resolution was 2 cm^{-1}. The instrument resolution was increased to 0.5 cm^{-1} in an attempt to observe any structure (the missing line). No structure was found.

DISCUSSION OF RESULTS

The polarization notation of Damen et al.[7] is used here, i.e., $x(yx)z$ means that the incident light is propagated in the x direction (first letter) while polarized in the y direction (second letter), and the scattered light is propagated in the z direction (fourth letter) while polarized in the x direction (third letter).

The Raman spectra of LaCl$_3$ at 77°K are shown in Figs. 1(a)–(e). Five lines appear in the spectra, the lines occurring at 108, 180, 186, 212, and 219 cm^{-1}. The species assignment of some of the lines is immediately evident. The point group for LaCl$_3$ is C_{6h}. The line at 180 cm^{-1} is caused by an A_g mode, according to Fig. 1(a), and the line at 186 cm^{-1} is E_{1g} according to Fig. 1(e). There is no inconsistency in assigning the lines at 108 and 219 cm^{-1} to E_{2g}, according to Figs. 1(b)–(d). Figure 1(d) shows that these are the only lines of the E_{2g} species. The assignment of these four lines agrees with previous studies.

However, the line at 212 cm^{-1} requires further discussion. This line has been previously assigned to E_{2g}, but the present work indicates that the line arises from depolarization of an A_g mode. The $x(yy)z$ polarization spectra should give rise to the A_g+E_{2g} modes. Since the lines at 108 and 219 cm^{-1} are E_{2g}, the line at 212 cm^{-1} can be assigned to A_g. The appearance of the 212-cm^{-1} line in the $x(yx)z$ [Fig. 1(c)] spectrum but not in the $x(yx)y$ spectrum [Fig. 1(d)] must be caused by depolarization scattering.[1]

In Fig. 1(c), the intensity of the 212-cm^{-1} line can be varied greatly relative to the 108- and 219-cm^{-1} lines

[7] T. C. Damen, S. P. S. Porto, and B. Tell, Phys. Rev. **142**, 570 (1966).
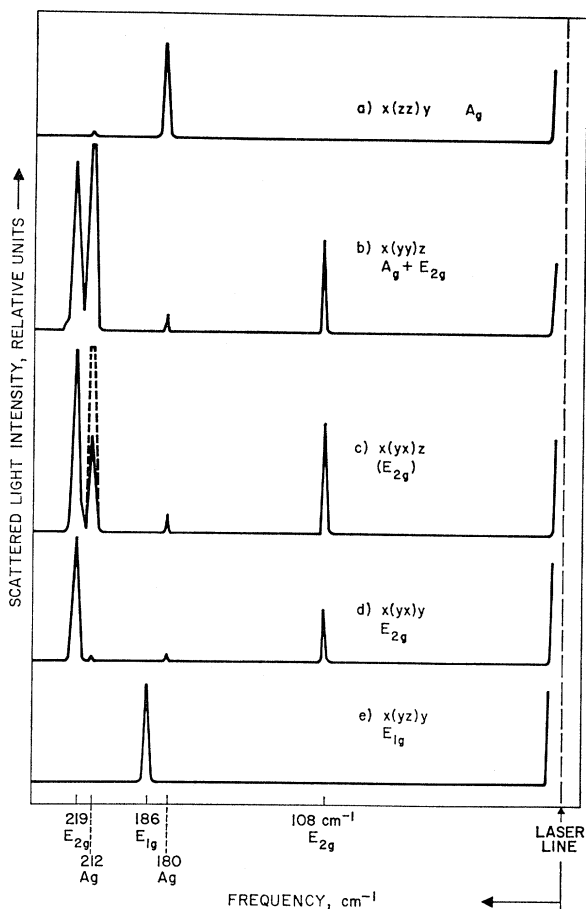

FIG. 1. The Raman spectrum of LaCl$_3$ at 77°K in various polarizations. The irreducible representations of the point group C_{6h} of LaCl$_3$ to which the various Raman-tensor components belong are indicated. (a) The $x(zz)y$ polarization (see text for notation). (b) $x(yy)z$. (c) $x(yx)z$; the A_g line at 212 cm^{-1} arises from depolarization about the optic-axis direction, the dotted line at 212 cm^{-1} shows the increased depolarization when the scattered light propagation direction is varied by a few degrees from the z axis, i.e., when the crystal is rotated about the x axis. (d) $x(yx)y$. (e) $x(yz)y$.

by merely rotating the crystals by a few degrees about the x axis, by examining different portions of the crystal, or by varying the aperture of the collecting lens between the sample and the spectrometer entrance slit. The minimum intensity ratio obtainable for the 212-cm^{-1} line relative to the 219-cm^{-1} line in the $x(yx)z$ polarization was 0.5. However, decreasing the aperture below about 4° did not affect the intensity ratio, but the examination of different portions of the crystal did affect the ratio. In addition, other crystals showing definite polycrystalline features, as mentioned above, showed minimum ratios larger than 0.5 ($\sim$1.0).

The relative intensity of the 212-cm^{-1} line is 3.5 times the intensity of the 219 cm^{-1} line in the $x(yy)z$ polarization [not shown in Fig. 1(b)]. The depolarization ratio is then about 0.15; i.e., 15% of the $x(yy)z$ spectrum appears in the $x(yx)z$ spectrum (correction

for depolarization of the 219-cm⁻¹ line can be made). The results suggest that the residual depolarization in the LaCl₃ crystals which we have examined is caused by wandering of the crystal optic axis.

The A_g lines in the $x(zz)y$ polarization [Fig. 1(a)] do not appear with the same intensities as the A_g lines in the $x(yy)z$ polarization [Fig. 1(b)]. This is discussed below. In addition, it is seen below that the (yy) polarization should give the same scattering intensity for the E_{2g} modes as the (yx) polarization; for this reason we rule out the possibility that the line at 212 cm⁻¹ in Fig. 1(b) is caused by E_{2g} appearing in (yy) polarization, since the intensity is so much larger than the same line in (xy) polarization [Fig. 1(d)].

The Raman scattering efficiency S (the ratio of the number of Raman scattered photon per unit solid angle to the number of incident exciting photons) is given by[8]

$$S = A[\Sigma e_i^\sigma R_{\sigma\rho} e_s^\rho]^2. \tag{1}$$

Here σ, $\rho = x$, y, z; A is a constant of proportionality and e_i^σ and e_s^ρ are the components of the unit vectors along the principal axes σ and ρ; and the subscripts i and s refer to incident and scattered photons, respectively. The $R_{\sigma\rho}$'s are the components of the Raman tensor. These have been conveniently listed by Loudon[8]; for the C_{6h} point group, the Raman-tensor components and the irreducible representations to which they belong are listed. These are

$$A_g: \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}, \quad E_{1g}: \begin{bmatrix} 0 & 0 & c \\ 0 & 0 & d \\ c & d & 0 \end{bmatrix}, \quad E_{1g}: \begin{bmatrix} 0 & 0 & -d \\ 0 & 0 & c \\ -d & c & 0 \end{bmatrix},$$

$$E_{2g}: \begin{bmatrix} e & f & 0 \\ f & -e & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad E_{2g}: \begin{bmatrix} f & -e & 0 \\ -e & -f & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

For the twofold degenerate photons, the contributions of each of the two matrices are added in Eq. (1) to give the total scattering efficiency, i.e., squared and then summed.[8] For the $x(yy)z$ polarization $(A_g + E_{2g})$,

$$S = A(a^2 + f^2 + e^2)(e_1^y e_s^y)^2, \tag{2}$$

and for the $x(yx)z$ or $x(yx)y$ polarizations (E_{2g}),

$$S = A(f^2 + e^2)(e_i^y e_s^x)^2. \tag{3}$$

In these polarizations the E_{2g} scattering intensity should therefore be the same. It is further noted that the A_g scattering intensity of $x(yy)z$ should be proportional to a^2, as seen in Eq. (2). On the other hand, the $x(zz)y$ polarization A_g yields a scattering efficiency proportional to b^2, which is not necessarily the same value as a^2. These statements are consistent with the conclusions given above.

In view of the fact that both A_g modes involve motions of the Cl atoms in the xy plane only,[3] one might

expect the change in polarizability $\alpha_{\sigma\rho}$, and hence Raman intensity, to be greater for incident polarization and induced moment in the xy plane than along z, i.e., $\alpha_{xx} = \alpha_{yy} > \alpha_{zz}$. For example, this is found to be the case in calcite, in which the symmetric stretching motion of the planar carbonate complex occurs in the xy plane. However, our results in LaCl₃ show that the 212-cm⁻¹ A_g mode agrees with such an argument, but the 180-cm⁻¹ A_g mode does not, viz., $\alpha_{zz} > \alpha_{yy}$. This undoubtedly results because LaCl₃ is not a layered structure.

It is of interest to compare the phonon frequencies and their symmetry assignments with those obtained from an analysis of the vibronic spectrum of Pr^{3+} in LaCl₃ by Cohen and Moos.[5] The results compare favorably in both frequency and assignment of irreducible representations if allowance is made for the fact that the vibronic spectra were observed at 4.2°K and our Raman spectra at 77°K. However, Cohen and Moos used the E_{2g} assignment of Hougen and Singh for the 210-cm⁻¹ phonon to eliminate a number of alternative assignments for these phonons. Among those eliminated from their Table II was the possibility that the 210-cm⁻¹ phonons belong to Γ_1^+ (A_{1g}). However, we wish to point out that the vibronic selection rules are also compatible with our result.

The missing sixth Raman-active E_{2g} line was not found in the present study. The scattered light in the spectral range from 15 to 300 cm⁻¹ from the 5145-Å laser line was examined with 0.5- and 2-cm⁻¹ resolution; no sixth line with intensity even one-twentieth of the weakest of the five Raman lines was found. With a further improved detection system, weaker lines should be detectable; however, the precise interpretation of weaker lines would require consideration of higher-order scattering processes. The Raman-scattering data were further checked using other excitation lines. Particularly useful was the 4765 Å argon laser line which, although weaker than the 5145- or 4880-Å lines, did not excite fluorescence from trace amounts of rare-earth impurities.

CONCLUSION

The spectrum of LaCl₃ has been reinterpreted since depolarization of scattered light near the crystal optic axis had previously led to the appearance of an extraneous line. Two E_{2g} lines, two A_g lines, and one E_{1g} line have been identified; one other E_{2g} line is missing in the spectrum.

[8] R. Louden, Advan. Phys. **13**, 423 (1964).