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Depolarization of Raman Scattering in Calcite

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Measurements of depolarization of Raman scattering from the totally symmetric A_{1g} vibration in calcite ($\bar{\nu}=1086$ cm^{-1}) are reported. The results, obtained with highly collimated gas-laser exciting light, show no evidence of the anomalous values of α_{xy} previously reported, and are fully consistent with Raman selection rules based on point symmetry. The phenomenon of apparent depolarization due to interference effects in convergent polarized light is discussed in detail.

INTRODUCTION

The spectrum and polarization of Raman scattering in calcite have been extensively studied.[1–8] Group theory predicts for calcite, having point symmetry D_{3d}, five Raman active vibrations.[9–11] One, assigned to the totally symmetric breathing vibration of the CO_3^{2-} ion, is of symmetry character A_{1g} and is expected to have nonvanishing polarizability tensor components $\alpha_{xx}=\alpha_{yy}$ and α_{zz}. The other four vibrations have symmetry character E_g, with nonvanishing components $\alpha_{xz}=\alpha_{yz}$ and/or $\alpha_{xx}=\alpha_{xy}=-\alpha_{yy}$. Two of the E_g vibrations, as well as the A_{1g} vibration, have been assigned to internal vibrations[12] of the CO_3^{2-} ion, the remaining Raman-active E_g vibrations corresponding to external or lattice vibrations.

Previous experimental results indicate the following assignments[10]: $\bar{\nu}(A_{1g})=1088$ cm^{-1}; $\bar{\nu}(E_g)_{\text{external}}=156$ cm^{-1}, 283 cm^{-1}; $\bar{\nu}(E_g)_{\text{internal}}=714$ cm^{-1}, 1432 cm^{-1}. With the exception of the A_{1g} line, the measurements of depolarization of Raman scattering in both polarized and unpolarized incident light are compatible with the form of the polarizability tensor predicted on the basis of point symmetry.

However, the observations of many investigators[1–7] have shown strong anomalies in the polarization of the A_{1g} 1088 cm^{-1} scattering. These results take the form of a nonvanishing component α_{xy} forbidden by the selection rules, whose apparent value is found to be strongly dependent on the directions of both the incident and scattered light. The magnitude of α_{xy} is comparable to that of the fully allowed α_{xx}. The principal measurements of α_{xy}^2 are collected in Table I.

In the table the orthogonal xyz coordinate system is fixed to the crystal, the z and y axes representing respectively the trigonal (optic) axis and a binary axis. The notation *pol* indicates observations made with polarized incident light. The notation[13] $x(\alpha_{zz}^2)y$ indicates a measurement of α_{zz}^2 scattering along the y axis with incident light in the x direction. All the entries shown are on a scale in which $\alpha_{xx}^2=\alpha_{yy}^2=1$. The following paragraph contains a detailed discussion of certain entries and omissions from Table I.

The entries shown for observations with unpolarized incident light are inferred from the reported values of depolarization ρ, with the additional assumptions that $\alpha_{yz}=\alpha_{xz}=0$ and $\alpha_{xx}^2=\alpha_{yy}^2=5\alpha_{zz}^2$. These assumptions are consistent with the experiments to data.[3,5] Measurements in unpolarized incident light do not yield a value of $z(\alpha_{yx}^2)y$ or $z(\alpha_{xy}^2)x$. Quantities such as $y(\alpha_{xy}^2)z$ and $x(\alpha_{yx}^2)z$, differing only in an interchange of the x and y axes, are not distinguished in the table since both experimentally[3,6] and theoretically no difference is indicated. The value $\alpha_{xy}^2>1$ of Schaefer *et al.*[1] is asserted to be in error by Michalke.[3] Bhagavantum's observations[4] in polarized incident light include other measurements of α_{xy}, but allow a quantitative com-

Table I. Previously measure values of α_{xy}; $\bar{\nu}(A_{1g})=1086$ cm^{-1} $\alpha_{xx}^2=\alpha_{yy}^2=1$.

Observer	Polarization of incident light	$y(\alpha_{xy}^2)z$ or $x(\alpha_{yx}^2)z$	$z(\alpha_{yx}^2)y$ or $z(\alpha_{xy}^2)x$	$y(\alpha_{xy}^2)x$ or $x(\alpha_{xy}^2)y$
Couture-Mathieu and Mathieu[a]	*pol*	0.3	0.3	···
Aynard[b]	*pol*	0.7	0.7	0.1
Couture[c]	*unpol*	0.3	···	0.04
Bhagavantum[d]	*pol*	(0.6)	···	···
Michalke[e]	*unpol*	0.4	···	0.04
Cabannes and Osborne[f]	*unpol*	1	···	0
Schaefer[g]	*unpol*	<1	···	(>1)

[a] Reference 7.
[b] Reference 6.
[c] Reference 5.
[d] Reference 4.
[e] Reference 3.
[f] Reference 2.
[g] Reference 1.

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[1] C. Schaefer, F. Matossi, and N. Aderhold, Z. Physik, **65**, 289, 319, (1930).

[2] J. Cabannes and D. Osborne, Compt. Rend. **193**, 156 (1931).

[3] H. Michalke, Z. Physik **108**, 748 (1938).

[4] S. Bhagavantam, Proc. Indian Acad. Sci. **A11**, 62 (1940); S. Bhagavantam and B. P. Rao, Current Sci. (India), **9**, 409 (1940).

[5] L. Couture, Ann. Phys. (Paris) **2**, 5 (1947).

[6] R. Aynard, Compt. Rend. **234**, 2352 (1952).

[7] L. Couture-Mathieu and J. P. Mathieu, Compt. Rend. **236**, 1868 (1953).

[8] Further references to observations of the Raman spectrum of calcite are given by R. S. Krishnan, Proc. Indian Acad. Sci. **A22**, 182 (1945).

[9] G. Placzek, in *Handbuch der Radiologie*, edited by E. Marx (Akademische Verlagsgesellschaft, Leipzig, 1934), Vol. 6, Chap. 2, pp. 209–374.

[10] J. P. Mathieu, *Spectres de Vibration et Symétrie* (Hermann & Cie., Paris, 1945). p. 328.

[11] R. Loudon, Advan. Phys. **13**, 423 (1964).

[12] A. C. Menzies, Rept. Progr. Phys. **16**, 83 (1953).

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

TABLE II. Half-angular divergence, in degrees, of incident and collected scattered light (within crystal).

Laser unfocused	<0.01
Laser focused	0.5
Collected scattered light	3

parison with α_{xx} only for the case shown in the table. Repetition of these experiments by Bhagavantum and Rao[4] under more carefully controlled conditions showed a negligible value of α_{xy}. The observations of Couture-Mathieu and Mathieu[7] include the angular dependence of 90° α_{xy} scattering in the yz plane; the highest apparent values of α_{xy} are those entered in the table, observed with either the incident or scattered light along the optic axis.

To summarize, the apparent value of α_{xy} is small or negligible in comparison with α_{xx} when the directions of incident and scattered light are in the xy plane, or in the yz plane but removed from the optic axis; the apparent value of α_{xy} is high when either the incident or scattered light is directed along the optic axis.

The validity of the measurements of α_{xy} has been questioned by Bhagavantum,[4] who found that the anomalous depolarizations observed in his experiments were spurious and introduced by unspecified convergence and polarization errors. The importance of these errors can be understood from the fact that intense $x(\alpha_{yy}{}^2)z$ scattering, for example, diverging slightly from the optic axis, can be strongly depolarized due to interference of its ordinary and extraordinary components, giving rise to an apparent $x(\alpha_{yx}{}^2)z$ scattering. For a ray diverging as little as 1° from the optic axis, the depolarization can be *complete* after a 5-mm path in the crystal. The convergence errors are equally severe with polarized incident light convergent along the optic axis. In the experiments described in Table I, the incident and scattered beams include internal cone angles in the range 2^5 to 6^4 deg. In no case have the results been corrected for convergence errors.

Nevertheless the anomalous experimental results have stimulated a number of theoretical efforts to account for the apparent breakdown of the selection rules. It has been suggested, for example, that α_{xy} may become allowed as a result of a lowering of the symmetry from D_{3d} due to the Ca^{2+} ion vibration,[14] the influence of acoustic modes,[15] higher order dependence of polarizability on field strength,[16] and breakdown of the polarizability theory due to delocalized crystal orbitals.[17]

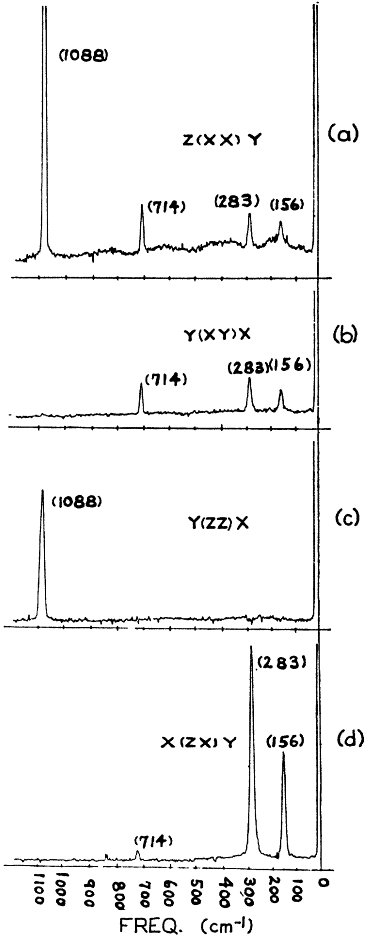

FIG. 1. Raman spectrum of calcite. The notation $x(zx)y$ indicates the spectrum with incident light directed along the *crystal* x axis and polarized along the z axis; the direction of observation of the x-polarized scattered light is the y axis.

In view of the importance of the experimental results and the question of their accuracy we have repeated some of the observations with a gas laser. The laser provides a unique tool for this purpose since its high brightness allows observation of Raman spectra with minimum convergence of the incident light. Section II contains our experimental results, which show no evidence for a significant nonzero value of α_{xy}. Section III contains discussion of convergence errors in uniaxial crystals.

II. EXPERIMENTAL RESULTS

The experimental apparatus has been described elsewhere[18]; it consists of a 50-mW He-Ne laser ($\lambda = 6328$ Å) chopped at 400 cps, the light of which passes through a focusing lens or directly through apertures into the crystal. Scattered light is collected at 90° from the incident beam, focused into an $f/6.8$ grating spectrometer and detected by an $S20$ photomultiplier. The photomultiplier signal is amplified in a lock-in amplifier and recorded. A polarizer in front of the entrance slit is used to observe the polarization of the scattered radiation. The slit widths used in our measurements

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[14] F. Matossi, *Der Raman-Effekt* (Frederick Vieweg und Sohn, Braunschweig, Germany, 1959).

[15] R. Soulmagnon, Compt. Rend. **236**, 796 (1953).

[16] F. Matossi and R. Mayer, Phys. Rev. **74**, 449 (1948).

[17] O. Theimer, Can. J. Phys. **34**, 312 (1956); O. Theimer and A. C. Saxman, J. Phys. Radium (to be published).

[18] R. C. C. Leite and S. P. S. Porto, J. Opt. Soc. Am. **54**, 891 (1964); S. P. S. Porto, Ann. N. Y. Acad. Sci. **122**, 643 (1965).

correspond to about 7 cm^{-1} and the integration time of the recordings was 3 sec.

The calcite sample was cut and polished in the form of a rectangular parallelepiped with approximately 2 cm sides, the x, y and z axes being normal to the faces. The angular divergence of the incident beam and collected scattered light are given in Table II. The entries indicate the maximum angular departure from the central ray of the beam, measured inside the crystal ($n \approx 1.6$).

Figure 1(a) shows the Raman spectrum of calcite when the crystal is illuminated along the z axis with the laser polarized in the x direction, and the x-polarized scattered light is collected in the y direction. The resulting $z(\alpha_{xx}^2)y$ spectrum should show all the A_{1g} and E_g lines. All lines were observed as expected. (The 1432 cm^{-1} line does not appear in any of the figures since to record it more sensitive gain settings had to be used.) Figure 1(b) shows the $y(\alpha_{xy}^2)x$ spectrum, including the E_g lines but no detectable A_{1g} scattering. Figure 1(c) shows the $y(\alpha_{zz}^2)x$ spectrum, in which only A_{1g} scattering was detected. Figure 1(d) shows the $x(\alpha_{zz}^2)y$ spectrum, including the E_g vibrations but no detectable A_{1g} scattering. All of the above results were obtained with focused laser light, and all are consistent with the selection rules.

When the $z(\alpha_{xy}^2)x$ spectrum was measured in focused laser light, it was found that the apparent value of $z(\alpha_{xy}^2)x \simeq 0.3z(\alpha_{yy}^2)x$, but also that the transmitted laser beam was largely depolarized. Under these conditions, the observed spectrum was a sum of $z(\alpha_{xy}^2)x$ and $z(\alpha_{yy}^2)x$ and as such should show strong A_{1g} scattering. With the laser beam unfocused and carefully aligned aloug the optic axis, the apparent $z(\alpha_{xy}^2)x$ scattering decreased to about 0.05 $z(\alpha_{yy}^2)x$. This value represents an upper limit since the minimum observed depolarization of the transmitted laser beam was also approximately 0.05. This residual depolarization is believed to be due to wandering of the optic axis in our crystal.

The observations of $x(\alpha_{yx}^2)z$ and $y(_{xy}^2)z$ spectra showed large apparent depolarization; since all the observations were made with a collection aperture $\approx 3°$, none of the results are significant (Sec. III).

The results relevant to α_{xy} are shown in Table III. In addition, $y(\alpha_{xz}^2)x$ was found to be less than 0.005.

In our observations of the E_g vibrations, it was found that the α_{xz} and α_{yz} components for the 156- and 283-cm^{-1} lines dominate the α_{xy} components, while the reverse is true for the 714- and 1432-cm^{-1} lines. This result is consistent with the identification of the 714- and 1432-cm^{-1} lines as internal modes, since in the limiting case of a completely isolated CO_3^{2-} ion (D_{3h}), α_{xz} and α_{yz} must approach zero for those lines.

TABLE III. Measured values of α_{xy} (upper limits); $\bar{\nu}(A_{1g}) = 1088$ cm^{-1}, $\alpha_{xx}^2 = \alpha_{yy}^2 = 1$.

$y(\alpha_{xy}^2)z$ and $x(\alpha_{yx}^2)z$	$z(\alpha_{yx}^2)y$ and $z(\alpha_{xy}^2)x$	$y(\alpha_{xy}^2)x$ and $x(\alpha_{yx}^2)y$
	≤ 0.05	≤ 0.005

III. DISCUSSION

Depolarization in calcite due to birefringence can be estimated as follows. Consider a measurement of $x(\alpha_{yx}^2)z$ for example. Assume that the detector receives scattered light propagating in a cone centered on the optic axis, of half-angle $\theta = \theta_0$ measured inside the crystal. Let φ be the aximuth angle of the scattered rays, measured around the z axis, where $\varphi = 0$ corresponds to the yz plane. The scattering source is assumed to be localized at a distance l cm below the crystal surface.

The detector analyzer is set to receive only light plane polarized along the x axis; however the ordinary and extraordinary components of the intense α_{yy} scattered light will in general interfere to produce nonzero x-polarized radiation.[19] The interference will occur for all rays having $\varphi \neq 0°$, $\varphi \neq 90°$.

Let n_0^0 and n_e^0 be the ordinary and extraordinary indices of refraction. For angles of propagation $\theta \leq \theta_0 \ll 1$ the refractive index difference between ordinary and extraordinary components is given to good approximation by Eq. (1):

$$\Delta n \equiv n_0 - n_e \approx [n_0^0 / 2(n_e^0)^2](n_0^{02} - n_e^{02})\theta^2 \equiv K\theta^2. \quad (1)$$

For scattering wavelengths near 4358 Å[1–8] $K_{4358} = 0.215$; near 6328 Å, $K_{6328} = 0.202$.

It is readily calculated that pure α_{yy} scattering, uniformly emitted into the cone $\theta \leq \theta_0$, leaves the crystal with a depolarization given by

$$\rho_a = (1 - \sin\psi/\psi)/(3 + \sin\psi/\psi), \quad (2)$$

where

$$\psi = (2\pi l/\lambda) K_\lambda \theta_0^2, \quad (3)$$

and where λ is the free-space wavelength of the scattered light. Figure 2 shows the dependence of ρ_a on ψ. The quantity ψ is the phase shift in traversing l, between ordinary and extraordinary components of a ray at $\theta = \theta_0$. The depolarization leads to an apparent ratio $x(\alpha_{yx}^2)z / x(\alpha_{yy}^2)z = \rho_a$.

The condition for negligible spurious depolarization is that $\psi \ll \pi$, or

$$\theta_0 \ll 1.2 \times 10^{-2} l^{-1/2}. \quad (4)$$

For $l = 0.5$ cm, for example, Eq. (4) requires observation with an f/number $\gg 29$. For $\psi \gtrless \pi$, $\rho_a \sim 0.33$; the maximum depolarization is $\rho_a = 0.44$ (Fig. 2).

All observations previously reported have apparently been carried out with $\psi \gg \pi$. We conclude therefore that the anomalous value of $x(\alpha_{yx}^2)z$ and $y(\alpha_{xy}^2)z \approx 0.3$

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[19] M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, Ltd., London, 1959), pp. 691–698.

reported by Michalke,[3] Couture,[5] and Couture-Mathieu and Mathieu[7] can be accounted for by interference of divergent scattered light. This conclusion is consistent with the observation of Couture-Mathieu and Mathieu[7] that the sum of the measured values of α_{xy}^2 and α_{xx}^2 remains unchanged as the observation direction is swept through the z direction in the yz plane: the apparent α_{xy}^2 is depolarized α_{xx}^2 scattering. The higher value $x(\alpha_{yx}^2)z\approx 0.6$ measured by Aynard[5] is inconsistent with those of other observers. It should be noted that the spurious depolarization can exceed 0.5 in observations with the cone axis deviating from the optical axis.

Observation of $z(\alpha_{xy}^2)x$ and $z(\alpha_{yx}^2)y$ with polarized light highly convergent along the optic axis are subject to depolarization error similar to that produced by divergent scattering along the optical axis. In this case apparent $z(\alpha_{xy}^2)x$ scattering arises from the introduction of a y-polarized component to the incident beam due to interference, giving rise to highly efficient α_{yy}^2 scattering. One measures an apparent ratio

$$\frac{z(\alpha_{xy}^2)x}{z(\alpha_{yy}^2)x}=\frac{1-(\sin\psi)/\psi}{3+(\sin\psi)/\psi}, \tag{5}$$

where ψ is defined by Eq. (3); in this case θ_0 indicates the half-angle of the incident cone centered on the optic axis, and l the distance from the entrance surface to the effective position of observation. Divergence of the scattering cone introduces only negligible errors for this case. The apparent ratio of Eq. (5) has the same form as the apparent ratio $x(\alpha_{yx}^2)z/x(\alpha_{yy}^2)z$ given by Eq. (2). It follows that measurements with the usual highly convergent incident and scattered beams would be expected to yield the same apparent value of α_{yx} (or α_{yx})≈ 0.33 with either incident or scattered light along the optical axis, irrespective of the particular aperture chosen. This symmetry is seen, for example, in the results of Couture-Mathieu and Mathieu.[7]

Straightforward considerations show that depolarization errors of the type described above do not enter into observations of α_{xz}, α_{yz}, α_{zx}, and α_{zy}. Measurements of α_{xy} with incident and scattered light in the xy plane are subject only to second order errors, arising from depolarization of *both* a convergent incident beam and a divergent scattered beam. These effects can be shown to be negligible. In all of these cases, neither the previous observations nor those reported here show any significant evidence of anomalous tensor coefficients.

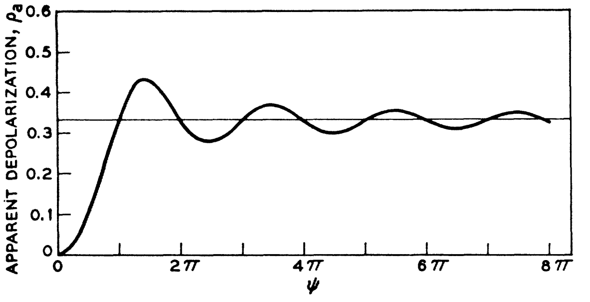

FIG. 2. Depolarization of Raman scattering in calcite due to birefringence, with incident or scattered light cone centered on the optic axis. The abscissa ψ is the phase shift between ordinary and extraordinary components of a ray on the cone envelope.

IV. CONCLUSION

Measurements of Raman scattering from the totally symmetric A_{1g} vibration of calcite with collimated He-Ne gas laser light show no evidence of the anomalous values of α_{xy} reported in earlier experiments. The earlier results, which are inconsistent with Raman selection rules based on point symmetry, can be explained by depolarization of the highly convergent incident and scattered light required in previous experiments. Such depolarization is especially important when either incident or scattered light propagates in a direction close to the crystal's optic axis.

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