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Low-Frequency Optical-Phonon Spectrum of Benzil*

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Raman spectra of single crystals of benzil in the region <100 cm^{-1} have been recorded. Six external vibrations that are expected on the basis of group theory could be detected, and their assignments are given. One phonon could be interpreted as a difference tone due to the decrease of intensity at lower temperatures.

INTRODUCTION

THE long-wave optical-phonon spectrum of a uniaxial crystal with two atoms in the unit cell has been described[1] in 1963 by an extension of the theory developed for cubic crystals by Huang.[2] Infra-red and Raman-active phonons with a lattice displacement parallel to the z axis (optical axis) will be of nondegenerate type A_1 and phonons with lattice displacements perpendicular to the z axis will be twofold degenerate of type E. When the phonon wave vector $\mathbf{k}_p$ is parallel to the z axis, the A_1 species corresponds to a longitudinal optical mode (LO). The E modes in this case correspond to a twofold degenerate transversal optical (TO) mode. Their linearly independent lattice displacements are lying in the xy plane, Fig. 1(a). However, when $\mathbf{k}_p$ is propagating perpendicular to the z axis the A_1 species correspond to nondegenerate TO modes and the E species correspond each to one TO and one LO mode, Fig. 1(b).

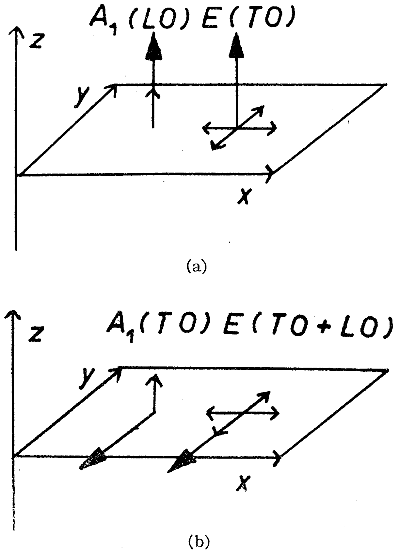

FIG. 1. (a) A_1 and E modes with the phonon wave vector parallel to the z axis. (b) A_1 and E modes with the phonon wave vector perpendicular to the z axis.

Like α quartz, the unit cell of the benzil crystal belongs to the point group D_3 and the site symmetry of the benzil molecule is C_2. There are three molecules in the unit cell arranged spirally along the optical axis (z axis) of the crystal. Unlike other similar organic molecules, for instance, tolane, dibenzyl, or azobenzene, benzil is a uniaxial crystal and has, therefore, sometimes been labeled as "the organic quartz." In the last few years, some interesting papers on Raman scattering in quartz have been published,[3,4] and, in particular, it has been found that for some phonons of E type, the splitting into LO and TO modes, as described by the Lyddane-Sachs-Teller relation, is quite noticeable. Benzil, therefore, seemed to be a very interesting material for investigations on the Raman effect. Two papers[5,6] reporting the internal vibrations of the crystal are known, but no experimental investigations in the external spectrum due to intermolecular vibrations have been published. In the present paper, these vibrations in the region <100 cm^{-1} will be presented and discussed.

EXPERIMENT

Two experimental arrangements were used: (1) The 5145-Å radiation from a Spectra Physics Ar$^+$ laser was used for excitation. The laser beam was focused with a lens of 40-cm focal distance, so that the focal region of the beam was formed inside the sample near and parallel to a surface. The emitted intensity of the laser had to be reduced to about 500 mW. Otherwise, the crystals could easily be damaged because of the great susceptibility to thermal gradients, caused by the high energy density along the beam. The samples were placed in front of the 2-cm-long vertical entrance slit of a Jarrell-Ash Model 25-102 Double Spectrometer with the laser

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[2] K. Huang, Proc. Roy. Soc. (London) **A208**, 352 (1951).

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[6] S. A. Solin and A. K. Ramdas, Bull. Am. Phys. Soc. **12**, 421 (1967).

beam parallel to the slit. The gratings had 1180 grooves per mm and the spectral slit width used was 3 cm^{-1}. The spectra were detected with a cooled EMI 9558QA multiplier with magnetic defocusing[7] and a two-channel dc amplifier made by H. Bock. (2) The spectra at lower temperatures were recorded by a Coderg Raman-spectrometer PH1 with excitation by a Spectra Physics He–Ne Laser Model 125. Since benzil is an optically active crystal, the plane of polarization of the laser beam will be rotated as the radiation traverses the crystal in the z direction. For other directions of propagation, the optical activity will introduce a small ellipticity. However, as could be shown before,[5] this ellipticity is very small in the case of benzil and in the present work no attempt has been made to take the effect into account, as no scattering geometry was used with the wave vector of light propagating along the z axis, and all lines observed could be assigned in an unambiguous way.

The two specimens used were nearly cubes with edges of about 10 mm and their orientations were (1) one edge parallel to the threefold axis (z) and one edge parallel to a twofold axis (x) and (2) one edge parallel to a twofold axis (x) and one edge at an angle of 45° with the threefold axis. The specimens were cut out of an optically clear single crystal with a miniature saw and were polished with fine corundum powder and water on a glass plate. The maximum transparence was obtained by glass slides which were attached on the surfaces of the specimens by paraffin oil. The single crystals were grown from a solution of benzil in m-xylene by slowly evaporating while mixing. The benzil material was recrystallized several times. The density of dislocations observed by the Lang method was less than 100 lines per cm^2.

DISCUSSION

The unit cell of the benzil crystal belongs to the point group D_3. The Raman-scattering tensors for the A_1 and E species are in this case[8]

$$A_1\begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}, \quad E(x)\begin{bmatrix} c & 0 & 0 \\ 0 & c & d \\ 0 & d & 0 \end{bmatrix},$$

$$E(y)\begin{bmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{bmatrix}.$$

The two tensors of $E(x)$ and $E(y)$ correspond to the two polarization components of the phonons along the principal axes x and y.

Adequate scattering geometries for identification of the symmetry properties of the phonons may be found by calculating the intensities which in uniaxial crystals are given by the tensor product

$$S=[e_i{}^{\sigma}R_{\sigma\rho}{}^{\tau}(\alpha\xi^{\tau}+\beta\zeta^{\tau})e_s{}^{\rho}]^2 \quad \rho,\sigma,\tau=x,y,z.$$

$R_{\sigma\rho}{}^{\tau}$ is the Raman-scattering tensor and τ is given in brackets after the symbols of the species $E(x)$ and $E(y)$. $e_i{}^{\sigma}=(e_i{}^x e_i{}^y e_i{}^z)$ and similarly $e_s{}^{\rho}$ are unit vectors in the directions of polarization of the incident and scattered photons, respectively. ξ^{τ} and ζ^{τ} are unit vectors in the directions of the mechanical polarization of the phonon and the **E** field associated with the LO phonons.[9] α and β are constants, and since β is proportional to the electric field strength $|\mathbf{E}|$ mentioned above, it is zero for transverse phonons. The number of Raman-allowed phonons due to translatorial and libratorial vibrations, respectively, are

$$n_t{}^{(\gamma)}=g^{-1}\sum_R k(R)\chi^{(\gamma)}(R)\chi_t(R)u_t(R)$$

and

$$n_r{}^{(\gamma)}=g^{-1}\sum_R k(R)\chi^{(\gamma)}(R)\chi_r(R)u_r(R),$$

where γ denotes the species of the phonon, g = the sum of all symmetry elements of the point group, $k(R)$ = number of symmetry elements in the class R, $\chi^{(\gamma)}(R)$ = character of the irreducible representation γ of the class R,[10] $\chi_t(R)$ and $\chi_r(R)$ = character of the reducible representation of a polar and an axial vector, respectively,[11] and $u_r(R)$ and $u_t(R)$ = number of molecules on a symmetry element and number of molecules less one, respectively.

Calculations show that there will be one Raman-active translation and one libration of type A_1 and, furthermore, two translatorial and three libratorial vibrations of twofold degenerate type E. Figures 2(a) and 2(b) show external vibrations of the benzil crystal with wave numbers 30, 39, and 69 cm^{-1}. These vibrations belong to the A_1 species. The scattering geometry used was $x(zz)y$, and since only the scattering tensor of the A_1 species has an element $R_{zz}(=b)$, the intensity of the E modes will vanish in an ideal scattering arrangement. In fact only one E mode can be detected as a slight shoulder of the line at 69 cm^{-1}. The isolation of the E modes was obtained by using the scattering geometry $x(zx)y$ or $x(yz)y$, Fig. 2(d). Referring to the formula for the scattering efficiency, it can be seen that the tensors for the $E(x)$ and $E(y)$ phonons will mix. However, using different scattering geometries one will be able to get different intensities due to different tensor elements. Figure 2(c), corresponding to $x(yx)y$, shows the scattering intensities due to the elements c and Fig. 2(d), corresponding to $x(zx)y$, those due to d. Both spectra show Raman lines with wave numbers 16, 39, 58, and

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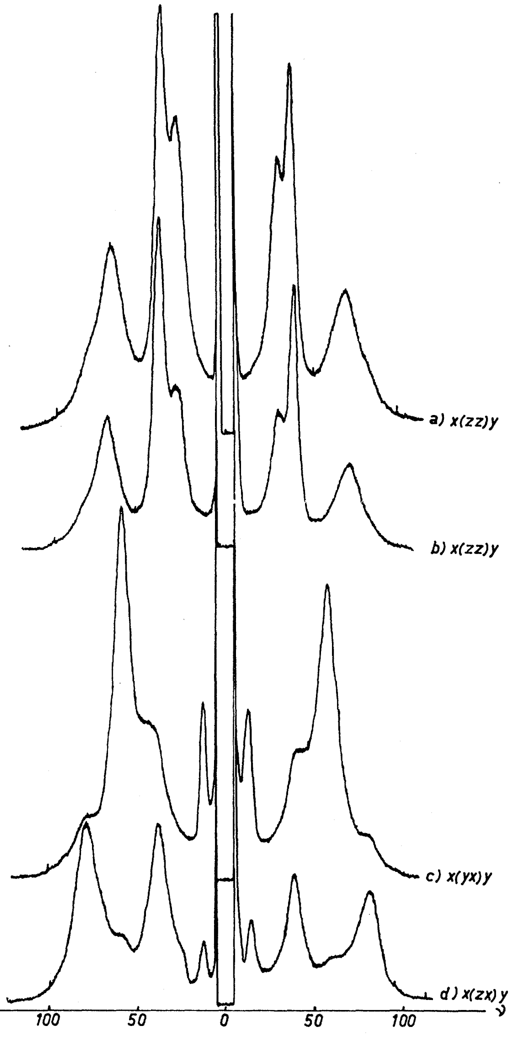

FIG. 2. Low-frequency Raman spectrum of benzil. (a) A_1 modes, $x(zz)y$ scattering at room temperature; (b) A_1 modes at −120°C; (c) E modes, $x(yx)y$ scattering at −120°C; and (d) E modes, $x(zx)y$ scattering at −120°C. The low-temperature spectra were recorded with an arrangement from Coderg. The spectral slit width used was 2 cm^{-1}.

78 cm^{-1}. Since the phonons at 16 and 58 cm^{-1} are stronger for $x(yx)y$ scattering follows $|c|>|d|$, while for the phonon at 78 cm^{-1} $|c|<|d|$. The only Raman line which appears with the same intensity in both spectra is that with wave number 39 cm^{-1}, so for this phonon $|c|\approx|d|$. The fifth E phonon cannot be identified on Figs. 2(c) and 2(d); however, at −150°C the long-wavelength side of the line at 39 cm^{-1} shows a very weak shoulder which may be the missing phonon. Table I shows that three phonons of A_1 symmetry could be observed. The spectra recorded at lower temperatures, however, showed that the line at 30 cm^{-1} can be interpreted as a difference vibration of the two A_1 species at 69 and 39 cm^{-1}.[10] Emission of a Stokes-Raman line corresponds to a transition from the activated energy level W_{39} to the W_{69} level. At lower temperatures, the W_{39} level will be less populated, so the intensity of the difference vibration will decrease. Figures 2(a) and 2(b) show the spectra of the A_1 species at room temperature and −120°C. The decrease of intensity of the phonon at 30 cm^{-1} is obvious. Ten spectra at equidistant temperatures between 20 and −120°C were recorded in order to eliminate the possibility of a phase transition. The scattering intensity, however, showed a continuous decrease with temperature. Since E phonons in uniaxial crystals have no LO components when $\mathbf{k}_p$ is propagating parallel to the z axis, Fig. 1(a), a corresponding scattering geometry can be used to identify the LO modes.[4] On the other hand, the LO modes will appear when $\mathbf{k}_p$ is perpendicular to the z axis. A great number of spectra were recorded in order to detect LO modes in this way, but none of the lines of E type showed a different behavior. The splitting described by the Lyddane-Sachs-Teller relation is, therefore, very small and might perhaps be observed only at He temperatures. The anisotropy in the case of benzil seems to predominate over the long-range electrostatic forces. All external E modes of benzil, as an organic analogon of α quartz, here show the inverse characteristics of some of the vibrations of α quartz.

Ignoring the interaction between lattice vibrations and molecular vibrations, in the case of translational vibrations, the polarizability tensor of the molecules will be simply displaced without any change with reference to the crystal axes. Librations, however, do change the polarizability, as the angles between molecular and crystal axes are changed when the two main polarizabilities, with reference to the axis of libration, are different. These latter vibrations should appear strongly in the Raman spectrum while translational vibrations appear mainly due to coupling with internal vibrations or librations of the same species.[11] Their intensities are, therefore, usually smaller than the intensity of the librations.[12]

Regarding the two A_1 vibrations at 39 and 69 cm^{-1}, it can be seen that the half-width of the latter one is greater and the maximum intensity smaller than the same data of the other phonon. Therefore, the phonon

TABLE I. Assignment of the observed external Raman-active phonons.

Wave numbers (±1.5 cm^{-1}) (cm^{-1})	Interpretation
16	E
30	A_1 (Difference tone)
39	A_1+E+E(?)
58	E
69	A_1
78	E

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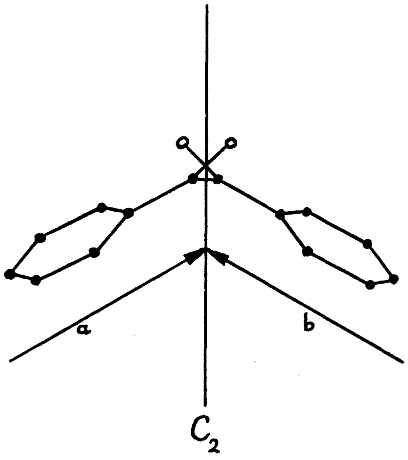

FIG. 3. Benzil molecule in projection on (0001), showing the C_2 symmetry axis.

at 39 cm^{-1} can tentatively be assigned as a libration. Since each molecule has a twofold symmetry axis coinciding with the twofold axis in the unit cell, the A_1 libration will correspond to the C_2 axis, Fig. 3. Furthermore the C_2 axis is the axis of the maximum moment of inertia, Θ, of the molecule, and calculations show that $\Theta \approx 1327$ (proton mass) Å^2. The structure data[13] used for this calculation differ from those quoted by Ramdas and Solin.[5] The new data[13] are more reliable because atomic coordinates of all atoms of the molecule in the crystal are given with very high accuracy. Comparing the mass of the molecule [210×(proton mass)] with the moment of inertia, the assignment of the libration may be confirmed. However, the force constant of the translation and the directional quantity of the libration must be assumed to be of approximately the same numerical magnitude for this reason. Since no corresponding data are known this is, of course, a very uncertain assumption, so the consideration may be appraised only as a hint. Crystals grown from deuterated benzil material will give more, and more reliable, information for the assignment of the librations, and especially for identifying the three librations and two translations of type E, for which calculations like those above would be without value at the present time.

APPENDIX

A detailed discussion of the internal vibrations of the Raman spectrum of benzil was recently published.[5] The internal spectra were also recorded by us. For this purpose, we used a spectral slit width of 5 cm^{-1} and photon counting in an arrangement described by Topp.[7] In addition to the 18 lines already found, we could record over 70 Raman lines and give their assignments. A great number of overtones and combinations were found, mainly in the region of 1900–2800 cm^{-1}. In most cases our assignments were in agreement with the previous interpretation, but two differences should be mentioned here: (1) The line denoted Nr. 2 by Ramdas and Solin could be resolved into three components [138 cm^{-1}: E, 158 cm^{-1}: $A_1(+E)$, and 168 cm^{-1}: E], and (2) the assignment of the line denoted Nr. 16 at 1593 cm^{-1} should obviously be $E+A_1$, since the E component was much stronger in our spectra. A more detailed discussion of the internal spectra will be published elsewhere.

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[13] C. J. Brown and R. Sadanaga, Acta Cryst. 18, 158 (1964).