Raman Spectrum of Crystalline Benzil*

S. A. SOLIN AND A. K. RAMDAS

Department of Physics, Purdue University, Lafayette, Indiana 47907

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The Raman spectrum of the optically active organic crystal benzil, $C_6H_5COCOC_6H_5$, belonging to the point group D_3, is studied with the 6328 Å radiation from a He-Ne laser as the exciting radiation. From the correlation of the observed spectrum, consisting of 18 lines, with that of the melt and of benzene, it is concluded that most of the prominent lines with shifts > 100 cm^{-1} originate from the internal vibrations of the benzil molecule. The polarization of the Raman lines is studied to classify the normal modes which give rise to them into either the totally symmetric (A_1) or the doubly degenerate (E) Raman-active vibrations of the D_3 point group. The intensity variation of several Raman lines for right-angle scattering and plane-polarized radiation incident along the optic axis is studied as a function of the angle θ between the electric vector of the incident light and the normal to the scattering plane. The intensity of the A_1 vibrations exhibits oscillations as θ is varied externally, whereas the intensity of the E vibrations remains constant as a function of θ. The relative intensities of the various Raman-active lines originating from the coupling of specific benzene-ring vibrations in the molecule and the crystal are calculated in terms of the orientation of the benzil molecules in the crystal, and are compared with the experimentally observed polarization characteristics of such lines.

I. INTRODUCTION

THE organic compound benzil, $C_6H_5COCOC_6H_5$, crystallizes in the space group D_3^4 or the enantiomorphous D_3^6. The Raman spectra of crystals of this class are of interest in view of their high symmetry. It is interesting to note that α quartz,[1,2] which has this symmetry, was one of the first crystals for which the Raman spectrum was recorded. Since the advent of powerful laser sources, the Raman spectrum of α quartz has been reexamined.[3,4] Trigonal selenium[5,6] and cinnabar[7] are two other crystals of this space group whose Raman spectra have been reported recently. Unlike the other crystals mentioned above, benzil is a molecular crystal. Its Raman spectrum is of particular interest since Raman lines arising from both intermolecular (external) and intramolecular (internal) vibrations can be expected for it.[8] In the present paper we report and discuss the Raman spectrum of crystalline benzil,[9] including polarization studies as a function of crystallographic orientation.

II. EXPERIMENTAL PROCEDURE

Single crystals of benzil were grown by the Bridgman technique. The material was recrystallized several times in order to eliminate impurities. After crystallization, the crystal was brought to room temperature at a very slow rate since it is particularly susceptible to thermal shocks. The crystals are pale yellow in color, soft, and brittle. The dimensions of the specimens used in the present investigation were typically $1 \times 1 \times 0.5$ cm; single crystals 5 cm long and ~ 1 cm in diam have been frequently grown. The crystals were oriented with the use of x rays, the c axis being located to within $0.1°$, and further checked by observing the conoscopic figures with a polarizing microscope. Specimens of the desired dimensions and orientation were prepared by carefully grinding on #2 grit emery paper moistened with ethyl alcohol and polishing on AB Selvyt[10] polishing cloth with the use of $\frac{1}{4}$-μ and 1-μ diamond paste[10] and Matadi oil lubricant.[10] In this procedure, ethyl alcohol, besides serving as a lubricant, also effectively dissipates the heat generated in the grinding process. In the absence of the lubricant, the heat produced is sufficient to damage the crystals.

The 6328 Å radiation from a Spectra Physics[11] Model No. 125 He-Ne laser was used to excite the Raman spectrum. Except for the melt, the spectra were recorded with specimens at $\sim 300°$K. The lenses used in the optical system to focus the incident light at the scattering volume and to collect the scattered radiation were such that the angle of convergence and the angle of acceptance were ~ 13 and ~ 7 mrad, respectively. The radiation scattered at 90° was analyzed with a Perkin Elmer Model No. 210 monochromator equipped with a Bausch & Lomb[12] plane-reflection grating, blazed at 0.75 μ. A Jarrel-Ash[13] Model No. 82-410 grating

[1] G. Landsberg and L. Mandelstamm, Naturwiss. 16, 557 (1928).
[2] K. S. Krishnan, Indian J. Phys. 4, 131 (1929).
[3] J. F. Scott and S. P. S. Porto, Phys. Rev. 161, 903 (1967).
[4] J. F. Scott, L. E. Cheesman, and S. P. S. Porto, Phys. Rev. 162, 834 (1967).
[5] G. Lucovsky, A. Mooradian, W. Taylor, G. B. Wright, and R. C. Keezer, Solid State Commun. 5, 113 (1967).
[6] A. Mooradian and G. B. Wright (private communication).
[7] R. Zallen, G. Lucovsky, W. Taylor, A. Pinczuk, and E. Burstein, Bull. Am. Phys. Soc. 12, 422 (1967).
[8] S. Bhagavantam and T. Venkatarayudu, *Theory of Groups and Its Application to Physical Problems* (Andhra University Press, Waltair, India, 1962), p. 148.
[9] S. A. Solin and A. K. Ramdas, Bull. Am. Phys. Soc. 12, 421 (1967). In this preliminary report, it was incorrectly concluded that lines 1, 2, and 3 appear only in the crystalline state. The use

of a post monochromator has shown that lines 2 and 3 do occur in the spectrum of the melt. The strong line, 1, labelled S in this paper, is of instrumental origin and hence spurious.
[10] Manufactured by Buehler Ltd., 2120 Greenwood St., Evanston, Ill. 60204.
[11] Spectra Physics, 1255 Terra Bella Avenue, Mountainview, Calif. 94040.
[12] Bausch & Lomb, Rochester, N. Y. 14602.
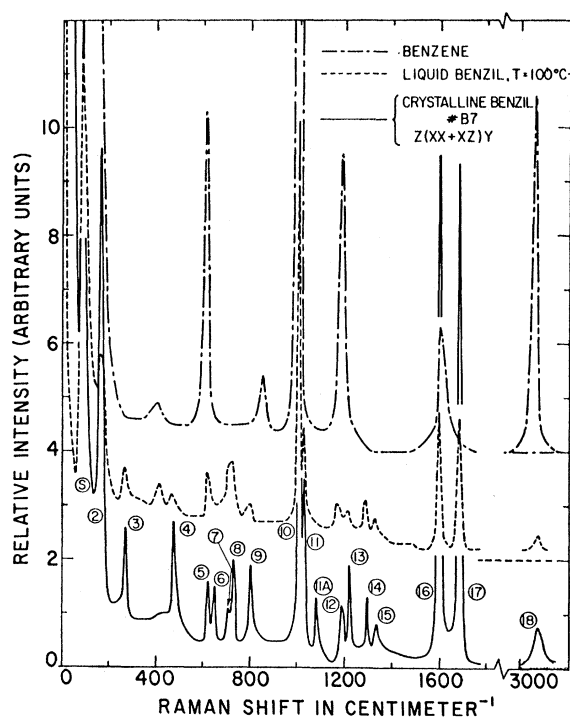[13] Jarrell-Ash, 590 Lincoln Street, Waltham, Mass. 02154.

FIG. 1. Comparison of the Raman spectra of crystalline benzil, liquid benzil (the melt), and benzene. The scales used for the relative intensities of the three spectra are not correlated in the figure. The spectra have been displaced vertically with respect to one another for the sake of clarity. The base lines (dashed) and (dot-dashed) at the right side of the figure correspond to the spectra of liquid benzil and benzene, respectively. The line labelled S is of instrumental origin and hence spurious.

monochromator equipped with a grating blazed at 0.6 μ was used as a "post monochromator." This monochromator was operated with a fixed entrance slit of 850 μ and without an exit slit; used in this manner, it served as a wide band-pass, tunable filter of ~ 800 cm^{-1} band width having sharp upper and lower cutoff characteristics. The use of the post monochromator resulted in a considerable reduction of the parasitic or stray radiation; with this arrangement Raman shifts ≥ 100 cm^{-1} could be detected. In the polarization studies, the plane of polarization of the linearly polarized laser radiation was rotated, when necessary, with the use of a Spectra Physics Model No. 310 polarization rotator.[11] A double Glan-Taylor prism was used as an analyzer. The polarization results in the present paper are labeled following the notation used by Damen, Porto, and Tell,[14] e.g., $X(YZ)Y$ denotes incident light along X, and polarized along Y while the scattered radiation is along Y and analyzed for polarization parallel to Z, thus giving the tensor component α_{YZ}. We shall take the Z direction to be along the c axis. A cooled RCA 7265 phototube was used as a detector. The incident radiation was chopped at 894 Hz and a

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

phase-sensitive detection technique was employed; a Princeton Applied Research Model No. HR-8 lock-in amplifier[15] was used in this connection. The details of the procedure and the technique used are essentially those given by Leite and Porto.[16]

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Raman Spectra

The Raman spectrum of crystalline benzil is shown in Fig. 1 for $Z(XX+XZ)Y$. Because benzil is an optically active crystal,[17,18] the plane of polarization is rotated as the plane-polarized radiation from the laser traverses the crystal along the c axis. The polarization rotator was used to compensate for this rotation such that the plane of polarization of the incident radiation was normal to the plane of scattering at the volume element scattering into the analyzing spectrometer. Figure 2 shows the Raman spectrum for $Y(ZZ+ZY)X$. No attempt has been made to take into account the effects of optical activity which also exist for propagation in directions other than the c axis; it is known that such optical activity introduces a small ellipticity in plane-polarized light.[19] The Raman spectrum of the melt was recorded by heating the crystal to a temperature above 95°C, the melting point of benzil; this is shown in Fig. 1. Also included in Fig. 1 is the Raman spectrum of liquid benzene. The positions of the Raman lines observed in Figs. 1 and 2 are listed in Table I.
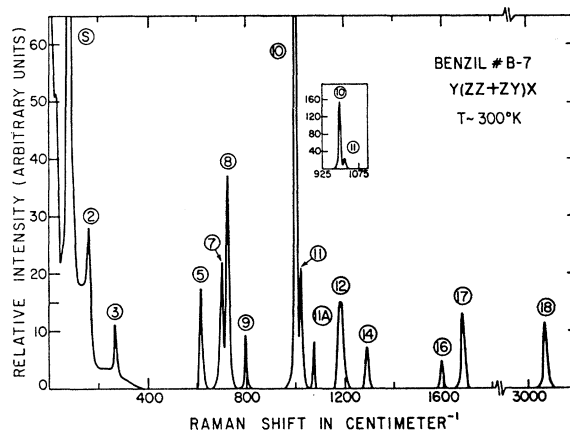

FIG. 2. Raman spectrum of crystalline benzil with the incident and the scattered radiation propagating at right angles to the optic axis.

[15] Princeton Applied Research Corporation, P. O. Box 565, Princeton, N. J. 08540.
[16] R. C. C. Leite and S. P. S. Porto, J. Opt. Soc. Am. 54, 981 (1964).
[17] S. Chandrasekhar, Proc. Indian Acad. Sci. 39A, 243 (1954).
[18] S. Chandrasekhar, Proc. Roy. Soc. (London) A259, 531 (1961).
[19] G. N. Ramachandran and S. Ramaseshan, in Encyclopedia of Physics, edited by S. Flügge (Springer-Verlag, Berlin, 1961), Vol. XXV/1, p. 1.

B. Structure of Benzil

In order to interpret the Raman spectrum of benzil, it is useful to summarize what is known about its molecular and crystalline structure. The benzil molecule consists of two

$$Ph-\overset{\mid}{C}=O$$
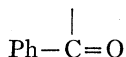
groups coupled by a carbon-carbon bond; here "Ph" denotes the C_6H_5 phenyl group. As mentioned in Sec. I, benzil belongs to the space group D_3^4 or D_3^6. The unit cell contains three molecules arranged spirally along the c axis. The x-ray studies of Sadanaga[20] show that the benzil molecule in the crystal possesses a skew structure, the angle 2ϕ between the two plane

$$Ph-\overset{\mid}{C}=O$$
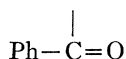
groups being 97.5°. (See Fig. 3.) The C—C bond which links the C=O group to the benzene ring makes an angle β of 105.4° with the c axis of the crystal. The diad axis of the crystal is perpendicular to the C—C bond coupling the two halves of the benzil molecule. Hence the site symmetry of the benzil molecule is C_2. The relatively low melting point of 95°C implies that the intermolecular forces in crystalline benzil are of the weak van der Waals type. The normal modes of crystalline benzil can thus be classified as those which can be correlated with the vibrations of the free benzil molecule and those in which the molecules in the unit cell vibrate as units against one another. The former are

TABLE I. Positions of the Raman lines in wave numbers.[a]

Serial No.	Crystalline benzil $Z(XX+XZ)Y$	$Y(ZZ+ZY)X$	Liquid benzil	Benzene[b]
2	159		159	
3	267		261	
4(a)			411	
4	469		463	
5	613	614	612	606 (ν_2)
6	642			
7	704	704	} 714[c]	
8	727	728		
9	794	795	800	
10	999	1000	1000	992 (ν_5)
11	1021	1022	1024	
11A	1076			
12	1168	1171	1163	1178 (ν_7)
13	1215		1212	
14	1293		1284	
15	1331		1323	
16	1594	1595	1596	1584–1606[d] (ν_9)
17	1671	1671	1681	
18	3067	3064	3063	3063 (ν_{11})

[a] The position of the Raman lines is accurate to ±5 cm⁻¹.
[b] The Raman lines of benzene have been labelled in this table following Mizushima (Ref. 28).
[c] This line is very broad in the spectrum of the liquid.
[d] These lines are due to an unresolved "resonance" doublet. See, e.g., G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1962).

[20] R. Sadanaga, unpublished results quoted by M. Leela and K. Lonsdale, Proc. Nat. Acad. Sci. India **A25**, 68 (1956).
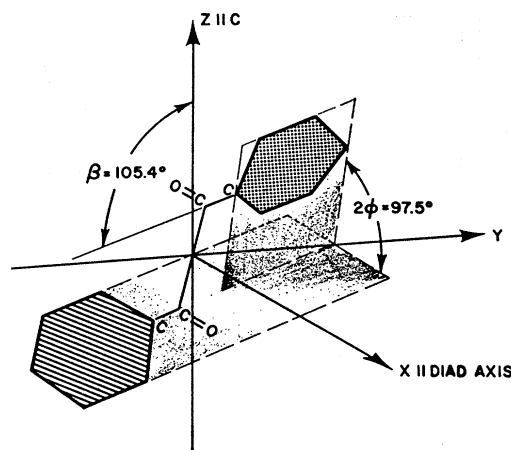

FIG. 3. Orientation of the benzil molecule with respect to the crystalline axes.

designated as "internal vibrations" and the latter as "external vibrations."[8]

C. Group-Theoretical Analysis and Symmetry Assignments

The number of normal modes of benzil with wave vector ~ 0, together with their symmetry characteristics, can be deduced group-theoretically following either the method of Bhagavantam and Venkatarayudu[8] or the method of coupling developed by Couture and Mathieu.[21] These are the vibrations which may be observed in the first order in the Raman effect and/or in infrared absorption. The results of such an analysis are presented in Table II.[22] As can be seen, the Raman-active modes belong to either the totally symmetric (A_1) or the doubly degenerate (E) irreducible representations. The Raman tensor corresponding to these two species of vibration can be shown to be[23]

$$A_1: \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix},$$

$$E: \begin{bmatrix} c & ic & d \\ ic & -c & -id \\ d & -id & 0 \end{bmatrix} \text{ and } \begin{bmatrix} c & -ic & d \\ -ic & -c & id \\ d & id & 0 \end{bmatrix}.$$

Thus the A_1 and E vibrations can clearly be distinguished on the basis of their polarization characteristics. The different tensor components are typically measured

[21] L. Couture and J. P. Mathieu, J. Phys. Radium **10**, 145 (1949).
[22] E. B. Wilson Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Co., New York, 1955).
[23] The tensors for the E vibrations were generated using the irreducible representations

$$\begin{bmatrix} e^{2\pi i/3} & 0 \\ 0 & e^{-2\pi i/3} \end{bmatrix} \text{ and } \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

for the threefold and the twofold symmetry axes, respectively. See Ref. 8, p. 272.
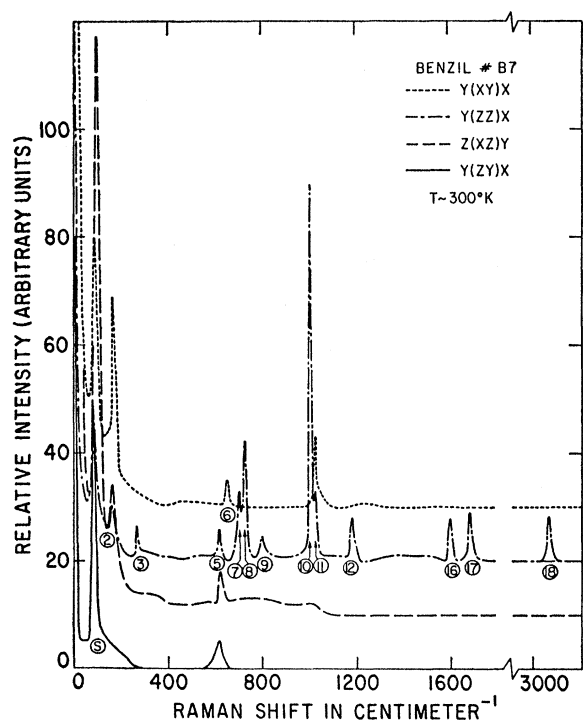
FIG. 4. Polarization features of the Raman lines of crystalline benzil, exhibiting the tensor components α_{xy}, α_{zz}, α_{xz}, and α_{yz}.

by sending polarized light along different crystallographic directions and analyzing the polarization of light scattered at 90° to the incident light. As mentioned earlier, in the case of benzil the optical activity has to be taken into account. The amount of ellipticity introduced by optical activity for propagation normal to the optic axis is small. This was shown by the distinct extinctions observed for polarization parallel and perpendicular to the optic axis when a section containing it was examined under a polarizing microscope. It thus appears that, at least in the case of benzil, the optical activity present normal to the optic axis can be ignored in the polarization measurements. The polarization of the Raman lines was studied for (i) $Y(ZZ)X$, (ii) $Y(ZY)X$, (iii) $Y(XY)X$, (iv) $Z(XZ)Y$, and (v) $Z(XX+XZ)Y$. In (iv) and (v) the polarization rotator was set such that the electric vector of the incident light was normal to the scattering plane at the scattering center. Some of the typical results are shown in Fig. 4.

Chandrasekharan[24] has exploited optical activity in order to identify the Raman-active vibrations of α quartz which is isomorphous with benzil. (See the Appendix.) In the present paper the following technique is used which makes it possible to determine polarization characteristics of the Raman lines. Plane-polarized exciting radiation from the laser is passed through the

polarization rotator and then through the crystal along the optic axis; the electric vector at the scattering center can be rotated to any desired angle θ with respect to the normal to the plane of scattering. A given Raman line is detected with the spectrometer set for the peak of the line. The variation of the peak intensity with the rotation of the polarization rotator is then recorded. The intensity for A_1 lines should vary from a maximum to zero as θ goes from 0° to 90°. On the other hand, the intensity of the E line is independent of θ. The experimental results following this technique are given in Fig. 5 for lines 2, 10, 16, and 17 of benzil.

D. Discussion of Data

As can be seen from Figs. 1 and 2 and Table I, all but two of the lines observed in the crystalline state of benzil can be correlated with those observed in the liquid state,[25] clearly indicating that the identity of the benzil molecule is preserved in the crystal. Lines 6 and 11A at 642 and 1076 wave numbers, respectively, are apparently too weak to be observed in the liquid state. It is also interesting that line 4(a) is observed only in the spectrum of the liquid. Also, some of the lines (i.e., 5, 10, 12, 16, and 18) are close to those of liquid benzene, a consequence of the benzene rings in the benzil molecule. The strong Raman line, line 17, is close to the characteristic carbonyl vibration[26] and is evidently due to the carbonyl constituent of the benzil molecule. The line at 469 cm^{-1}, line 4, could be interpreted as arising from a vibration in which the two halves of the benzil molecule, treated as point masses coupled by a C—C bond, vibrate against each other. A simple calculation based on this assumption, with a force constant of 5.6×10^5 dyn/cm,[27] yields a value of 425 cm^{-1} for such a vibration. This should be considered to be in fair agreement with the observed value in view

TABLE II. Symmetry classification of normal modes of crystalline benzil with wave vector ~ 0.

Point group D_3^a	External Translatory	Rotatory	Internal	Raman active	Infrared active
A_1	1	1	37	yes	no
A_2	1	2	35	no	yes
E	2	3	72	yes	yes

ª A_1, A_2, and E are the totally symmetric, the antisymmetric, and the doubly degenerate irreducible representations, respectively, of the D_3 point group (Ref. 22).

[25] Attention should be drawn to the measurements of Kohlrausch and Pongratz on liquid benzil as a part of their study on the effect of chemical constitution on the Raman spectrum of organic compounds. They reported Raman lines at 170, 260, 412, 503, 617, 810, 1170, 1322, 1490, 1600, 1683, and 3073 cm^{-1}; the use of a green filter prevented observations of lines in the range 810–1170 cm^{-1}. See K. W. F. Kohlrausch and A. Pongratz, Ber. Deut. Chem. Ges. **67B**, 976 (1934).

[26] See, e.g., S. Bhagavantam, *Scattering of Light and the Raman Effect* (Andhra University, Waltair, India, 1940), p. 293.

[27] See Ref. 22. These authors quote a value in the range 4.5–5.6 $\times 10^5$ dyn/cm for the force constant of the C—C bound.

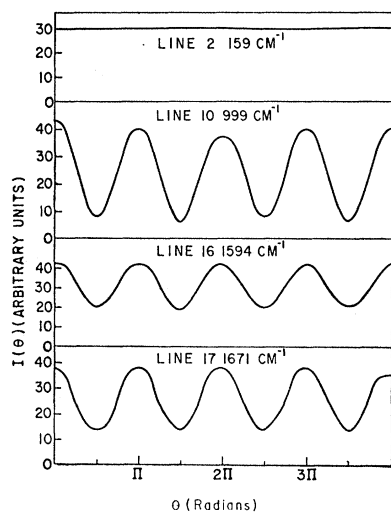[24] V. Chandrasekharan, Proc. Indian Acad. Sci. **28A**, 409 (1948); Z. Physik **154**, 43 (1959).

FIG. 5. Oscillations of intensity of the Raman lines, 2, 10, 16, and 17 of crystalline benzil as a function of θ, the angle between the electric vector of the incident radiation and the normal to the plane of scattering at the scattering center. Light is incident along the optic axis and scattered at right angles to it.

of the simplifying assumptions implicit in such a calculation. For example, the effect of the lattice on the force constant has been neglected.

As many as 109 internal Raman-active vibrations are expected on the basis of a group-theoretical analysis, as can be seen from Table II. Experimentally, however, only 18 are observed, indicating that the coupling between the three benzil molecules in the unit cell is very weak. In this context it is useful to consider the modifications in the normal modes of free benzene as it is incorporated in the benzil molecule which in turn becomes a part of the crystalline structure. The symmetry of the normal modes of benzil arising from the vibrations of the benzene ring are shown in Table III. The "free" vibrations have been labelled following Mizushima.[28] As can be seen, the coupling of the two benzene rings in the benzil molecule and the coupling of the three benzil molecules in the unit cell of crystalline

benzil lead to A_1+A_2+2E vibrations corresponding to the A_{1g} vibration of benzene. Similarly the E_{2g} vibration of free benzene generates $2A_1+2A_2+4E$ vibrations in the crystal. Of these, only the A_1 and E vibrations are Raman active. Experimentally, however, the 606-, 992-, 1178-, and 3063-cm^{-1} lines of benzene appear to give rise to only single lines in crystalline benzil rather than the expected multiplets. This situation could arise from (a) a lack of resolution of the multiplet and/or (b) one of the components being much stronger than the others. It is thus of interest to calculate the Raman tensors of the internal modes of the benzil crystal in terms of the Raman tensor for free benzene. Such a calculation can be performed following the techniques used by Couture[29] in the study of the Raman spectrum of barytes. These calculations lead to the following results: For the multiplet generated by the A_{1g} vibrations of free benzene,

$$\frac{I_E}{I_{A_1}} = \frac{Y(ZX)X \text{(for all } E \text{ vibrations in the multiplet)}}{Y(ZZ)X \text{(for all } A_1 \text{ vibrations in the multiplet)}}$$

$$= \frac{(b/a-1)^2(\cos^4\phi \sin^2 2\beta+\sin^2 2\phi \sin^2\beta)}{8[1+(b/a-1)\cos^2\phi \sin^2\beta]^2}. \quad (1)$$

Here b/a represents the ratio of the tensor components of the A_{1g} vibrations of free benzene given by

$$\begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix};$$

this ratio can be obtained from the depolarization ratio[30] for the lines measured for liquid benzene. This, of course, assumes that the ratio b/a remains unaltered in the passage to the crystalline state. The angles ϕ and β are defined in Sec. III B. Similarly the calculation of the relative intensities of the components of the multiplet generated by the E_{2g} vibrations of free benzene gives

$$\frac{I_E}{I_{A_1}} = \frac{[(\sin^2\phi+1)^2 \sin^2 2\beta+\sin^2 2\phi \sin^2\beta]+4(\sin^2\phi \cos^2 2\beta+\cos^2\phi \cos^2\beta)}{8\{[(\sin^2\phi+1) \sin^2\beta-1]^2-\sin^2\phi \sin^2 2\beta\}}. \quad (2)$$

The results of the calculations for the 992- and 3063-cm^{-1} A_{1g} vibrations and 606- and 1178-cm^{-1}, E_{2g} vibrations of benzene are compared with the experimental observations in Table III. As can be seen, the behavior of line 10, 999 cm^{-1}, and line 5, 606 cm^{-1} in crystalline benzil can be understood on the basis of the approach discussed above, i.e., the A_1 and E vibrations of the multiplet generated by the 606-cm^{-1} vibration of benzene are experimentally unresolved, while the E

vibrations in the multiplet generated by the 992-cm^{-1} benzene vibration appear to be too weak to be observed. The behavior of line 18 at 3067 cm^{-1} cannot be understood following the above analysis unless the ratio b/a is changed in the transition from the free to the crystalline state for the 3063-cm^{-1} benzene vibration. It is not clear why there is a discrepancy between the observed and the expected behavior of line 12 at 1178 cm^{-1} since

[28] S. Mizushima, in Encyclopedia of Physics, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. XXVI, p. 171.

[29] L. Couture, Ann. Phys. 2, 5 (1947).
[30] I. I. Kondilenko and P. A. Korotkov, Opt. i Spekroskopiya 22, 894 (1967) [English transl.: Opt. Spectry. 22, 488 (1967)].

TABLE III. Internal oscillations of crystalline benzil corresponding to free benzene vibrations.

Origin of the multiplets			I_E/I_{A_1}[a]		Free benzene lines
Free benzene (D_{6h})	Benzil molecule (C_2)	Benzil crystal (D_3)	Theory	Expt.[b]	
A_{1g}	$\begin{cases} A \\ \\ B \end{cases}$	$\begin{cases} A_1 \\ E \end{cases}$ $\begin{cases} A_2 \\ E \end{cases}$	0.03[c] 0.41[c]	≈ 0 ≈ 0	992 (ν_5) 3063 (ν_{11})
E_{2g}	$\begin{cases} A \\ \\ B \\ \\ A \\ \\ B \end{cases}$	$\begin{cases} A_1 \\ E \end{cases}$ $\begin{cases} A_2 \\ E \end{cases}$ $\begin{cases} A_1 \\ E \end{cases}$ $\begin{cases} A_2 \\ E \end{cases}$	1.2 1.2	1.2 ≈ 0	606 (ν_2) 1178 (ν_7)

[a] See Eqs. (1) and (2).
[b] The experimental values have been corrected to take into account the instrumental effects on polarization studies.
[c] The values for b/a were obtained from the depolarization ratio ρ_s for liquid benzene measured with linearly polarized incident radiation; the values of ρ_s (992 cm^{-1}) =0.020 and ρ_s (3063 cm^{-1}) =0.21 have been measured by Perkin Elmer Corp. (private communication).

its behavior should depend only on the orientation parameters ϕ and β.

In Table IV the assignments for the Raman lines deduced from their polarization characteristics are given; the origins of the lines are also indicated. The Raman lines 8, 9, and 15 have been interpreted as combinations, whereas line 14 appears to be an overtone; the symmetry characteristics of these lines are consistent with these assignments. The behavior of line 2 is anomalous since the results of the rotation

TABLE IV. Symmetry assignments and interpretation of the Raman lines.

Serial No.	Position in cm^{-1}	Symmetry	Interpretation[a]
2	159	A_1+E?	
3	267	A_1	
4	469	A_1	vibration of the two phenyl groups against each other
5	613	A_1+E	C−C−C∥bending (ν_2)
6	642	A_1+E	
7	704	A_1	
8	727	A_1	line 3+line 4= 731 cm^{-1}
9	794	A_1	line 6+line 2=801 cm^{-1}
10	999	A_1	C−C stretching[a] (ν_5)
11	1021	A_1+E	
11A	1076	?	
12	1168	A_1	C−H∥bending[a] (ν_7)
13	1215	A_1	
14	1293	A_1	2 (line 6) =1284 cm^{-1}
15	1331	A_1	line 2+line 12=1327 cm^{-1}
16	1594	A_1	C−C stretching[a] (ν_9)[b]
17	1671	A_1	C=0
18	3067	A_1	C−H stretching[a]

[a] See G. Herzberg, Infrared and Raman Spectra (D. Van Nostrand Company, Inc., New York, 1962), p. 363. The labels ν_2, ν_5, ν_7, and ν_9 follow Ref. 28.
[b] The "resonance" doublet splitting observed in benzene is absent in the crystal.

TABLE V. Comparison of infrared and Raman spectra of benzil.

Serial No.	Position of Raman line	Position of i.r. lines[a]
2	159	
3	267	
4	469	this region not studied
5	613	
6	642	
7	704	
8	727	719
9	794	797
		874
		930
10	999	995
11	1021	1016
		1046
11A	1076	1070
		1094
12	1168	≈ 1164[b]
13	1215	≈ 1208[b]
14	1293	$\left.\right\}$ 1290–1350[b]
15	1331	
		1395
		1450
		1490
16	1594	1586–1599
17	1671	1670
18	3067	3063

[a] See Ref. 31.
[b] The positions of these lines were estimated from the spectra published in Ref. 31.

technique described in Sec. III C indicate an E symmetry for it (see Fig. 5), whereas the results of Fig. 4 suggest a mixed symmetry of A_1+E. From the results for $Z(XX+XZ)Y$ in Fig. 1 and for $Z(XZ)Y$ and $Y(XY)X$ in Fig. 4, a value of $1:0.3:0.07$ was deduced for $a^2:c^2:d^2$. Thus the absence of oscillations for line 2 in Fig. 4 is inconsistent with the strength of the XX component of the A_1 vibration. The presence of a residual backrgound on which the oscillations for lines 10, 16, and 17 in Fig. 5 are superimposed could indicate an A_1+E symmetry for them. This is inconsistent with the absence of these lines in the spectrum for $Y(XY)X$ and $Z(XZ)Y$. It has been verified that the use of a finite slit with as well as the finite convergence of the incident and scattered radiation do not cause the residual background. The origin of this background is not clear.

The results of the present investigation show that none of the lines observed originates from external vibrations, whereas seven such vibrations are expected, as can be seen from Table II. These oscillations presumably have frequencies ≤ 100 cm^{-1}, a region for which reliable results could not be obtained with the present equipment.

The infrared absorption spectrum of crystalline benzil has been measured by Mann and Thompson[31]; their measurements cover the range 700–1300 cm^{-1}. The lines observed are listed in Table V along with the Raman lines. As can be seen, lines 10–18 have counterparts in the infrared spectrum. All these Raman lines

[31] J. Mann and H. W. Thompson, Proc. Roy. Soc. (London) 211A, 168 (1951).

are of A_1 symmetry, with the exception of lines 11 and 11A. Since only A_2 and E vibrations are infrared active, the lines observed in the infrared spectrum which coincide with the Raman lines must arise from the multiplets produced in the crystalline state by the coupling of the benzil molecules as discussed earlier. In this context a more detailed examination of the infrared spectrum with oriented samples and polarized radiation is of interest. Moreover, the infrared spectrum for wavelengths longer than ~ 15 μ has yet to be measured.

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APPENDIX

As discussed in Sec. III C, the presence of optical activity in benzil is a complicating factor in the polarization studies of Raman lines when these are carried out in the conventional fashion. Couture and Mathieu,[32] in their study of the optically active cubic crystals, sodium chlorate, and sodium bromate, circumvented this problem by sampling a small scattering volume; this was feasible for these crystals because of their small rotatory power. For uniaxial crystals like α quartz,[3] cinnabar,[7] and selenium,[5,6] measurements were made by confining the directions of incident and scattered radiation to a plane normal to the optic axis; the ellipticity introduced by the simultaneous presence of optical activity and birefringence is apparently very small.

Chandrasekharan[24] developed an elegant technique in which the optical activity rather than being a hindrance is exploited to yield information on polarization features. Consider linearly polarized light traveling
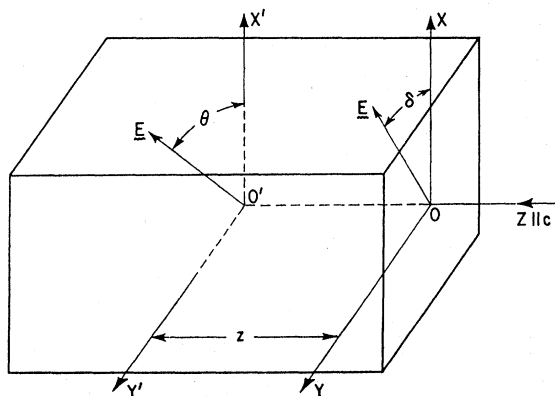
FIG. 6. Orientation of an optically active uniaxial crystal for observing the results shown in Figs. 5 and 7. Here δ and θ denote the angles between electric vector E of the incident radiation and the normal to the scattering plane at the entrance face and at the scattering center, O', respectively.

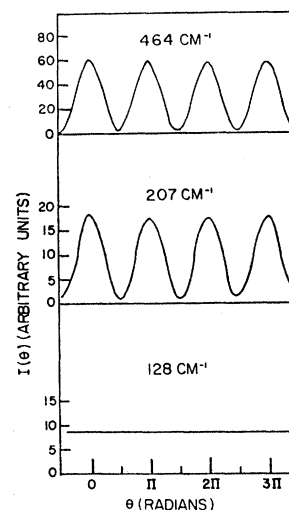[32] L. Couture and J. P. Mathieu, Ann. Phys. 3, 521 (1948).

FIG. 7. Oscillations of intensity of the 128, 207, and 464 cm^{-1} Raman lines of α-quartz observed under the conditions shown in Fig. 6.

along the optic axis of an optically active uniaxial crystal belonging to the D_3 point group; let the optic axis be parallel to the entrance slit of a spectrograph. As the incident light travels down the optic axis, the intensity of the A_1 lines scattered at 90° into the spectrograph varies from a maximum to zero, resulting in the appearance of banding in the Raman line recorded on the photographic plate; on the other hand, the E lines show no such banding. The variation of intensity with the azimuth of the polarization vector at a given scattering center is, following Chandrasekharan,

$$I_{A_1} \propto \cos^2\theta \quad \text{and} \quad I_E = \text{const}, \quad (A1)$$

where θ is defined in Fig. 6. In the present investigation, the plane of polarization at the scattering center is rotated by rotating the plane of polarization of the incident light as it enters the crystal. If the angle at the entrance face is δ with respect to the vertical, the angle at the scattering center is $\theta = (\delta + \rho z)$, where ρ is the rotatory power. The intensity of the Raman lines originating at z will thus vary as

$$I_{A_1} \propto \cos^2(\delta + \rho z) \quad \text{and} \quad I_E = \text{const}. \quad (A2)$$

In this experimental arrangement the entrance slit of the monochromator is parallel to OX, whereas in Chandrasekharan's experiments the slit is parallel to the Z axis. This technique was tested with the three well known lines of α quartz at 464 cm^{-1} (A_1), 207 cm^{-1} (A_1) and 128 cm^{-1} (E). The results are shown in Fig. 7. The lines having A_1 symmetry do show oscillations in intensity, the period of oscillation being π, whereas the line having E-type symmetry shows no such variation in intensity. The use of finite slit widths results in some departure from the predicted $\cos^2\theta$ type of oscillation but does not affect the qualitative difference between lines having A_1 and E symmetry. This technique, unlike Chandrasekharan's, is not limited to optically active crystals, i.e., the variation in θ is produced externally by varying δ. However, it is in an optically active medium that the technique has its maximum use.