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Elastic constants of the orientationally disordered phase of C_2F_6 by Brillouin spectroscopy

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The elastic constants and elasto-optic coefficient ratios of the orientationally disordered β phase of C_2F_6 have been determined using the technique of high resolution Brillouin spectroscopy. Just below the triple point, at 169 K, the values of the elastic constants (in units of kbar) are $C_{11}=26.99\pm0.10$, $C_{12}=19.32\pm0.10$, and $C_{44}=4.44\pm0.04$. The temperature dependence of all three elastic constants was also determined and appears to be linear for the temperature range investigated, with $\Delta C_{11}/\Delta T=-0.335\pm0.010$, $\Delta C_{12}/\Delta T=-0.236\pm0.010$, and $\Delta C_{44}/\Delta T=0.005\pm0.011$ kbar/K. Values of the ratios of acoustic velocities in high symmetry directions in the crystal indicate near perfect elastic isotropy and that moderately strong rotation-translation coupling is present in β - C_2F_6 .

I. INTRODUCTION

Orientationally disordered (OD) solids¹⁻³ are characterized by long range translational order (although individual molecular center of mass displacements about fixed lattice sites may be large) and molecular orientational disorder. Of special interest in these solids is the coupling of the orientational degrees of freedom to translational phonon modes. Such coupling is known as rotation-translation (RT) coupling and the theory has been developed by Michel *et al.*^{4,5} In many cases the rotational motion of the molecules dampens or softens the translational motion and hence this coupling is often strong enough to alter the collective excitations of the solid. It is expected that transverse modes, in particular, will be sensitive to RT coupling and softening of the shear elastic constants and/or overdamping in certain wave vector regimes could be exhibited. Detailed knowledge of the elastic properties of OD solids is therefore of importance in understanding the nature and extent of this coupling. Because it permits accurate determination of the elastic constants, the technique of Brillouin spectroscopy is particularly well suited for studying such solids.

The hexasubstituted ethanes (C_2X_6 , where X is a halogen) comprise a class of solids all of which exhibit an OD plastic phase between their melting points and low temperature ordered phases. One of the members of this class is the high temperature phase of hexafluoroethane (C_2F_6). The OD β phase of C_2F_6 exists below the triple point of 173.1 K.⁶ The crystal structure is body-centered cubic⁷ with molecules of symmetry $\bar{3}m$ occupying sites of symmetry $m\bar{3}m$ in the cubic I lattice.⁸ (According to Ref. 9, however, the structure of the β phase is unknown). The existence of a transition to a low temperature phase at 104 K was indicated by heat capacity data⁶ as well as measurements of NMR linewidth¹⁰ and the ir vibrational spectra.¹¹ X-ray diffraction data at 83 K¹¹ indicate that the low tem-

perature phase has monoclinic structure with space group $P2_1/m$. The x-ray diffraction results also show that there is disorder in the α phase of the statistical type since only a few discrete diffraction spots were observed; this was substantiated by Koide *et al.*¹² Neutron diffraction experiments conducted by Powell *et al.*,⁸ suggest that the structure is body-centered cubic at both 110 and 95 K. The low temperature profiles cannot be indexed on the basis of the monoclinic space group suggested by the x-ray studies. In addition, they found that a sluggish structural transition begins at 70 K and persists to 40 K such that both α and β phases coexist in this temperature range. More recent neutron scattering experiments appear to indicate that a structural phase transition does occur between 91 and 117 K.⁷

According to molecular dynamics simulations calculations, the origin of the disorder in β - C_2F_6 is twofold.^{13,14} The molecular symmetry is lower than the site symmetry which leads to statistical disorder in the orientations of the C-C bonds. In addition, since the F_6 framework is nearly octahedral, the molecular symmetry is almost that of the site, and preliminary simulations of different models of C_2F_6 ^{13,14} indicate that orientational frustration exists as in SF_6 .¹⁵⁻¹⁷ The simulations suggest that orientational frustration is a significant feature in C_2F_6 and that many properties of the OD phase are related to the dynamics of the approximate F_6 octahedra (rather than the disorder of the C-C bonds) and are thus very similar to SF_6 .

Information concerning the single molecule motions in β - C_2F_6 has been obtained from the C-F bond orientation distribution functions determined at temperatures of 110 and 95 K by Powell *et al.*⁸ This function indicates that although the fluorines are predominantly localized on the crystal axes, the distribution about these directions is very broad with a significant probability for the fluorines to be off axis. This distribution is qualitatively similar to that for SF_6 ¹⁸ which also exhibits broad maxima in the $\langle 100 \rangle$ directions. In the case of SF_6 at 96.5 K,¹⁸ the overall form of the S-F bond orientation distribution function was attributed to large amplitude molecular librations about the cu-

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bic axes and substantial thermal reorientation. This may also be the case for C_2F_6 although motions more akin to rotational diffusion and/or low frequency reorientation have been proposed.¹⁰

Molecular dynamics simulations also predict that the collective dynamics of β - C_2F_6 are very similar to those of plastic SF_6 .^{13,14} In particular, it is stated that RT coupling in β - C_2F_6 will be strongest at $q=0$ and drop to zero at the Brillouin zone boundary, paralleling the simulation results for SF_6 . Neutron diffraction experiments have shown that correlations between translational and rotational displacements in C_2F_6 are important.⁸ Brillouin scattering experiments on SF_6 ,¹⁹ however, show no anomalous mode softening which could be interpreted as evidence for strong RT coupling near $q=0$.

It has been suggested by Koide *et al.*¹² that disorder can be acquired at the $\alpha \rightarrow \beta$ phase transition by internal rotation of one CF_3 group with respect to the other. They also state that, in the high temperature phase, the molecular axis (the central C-C bond) runs parallel to the four body diagonals in a random fashion and that the internal rotation about the molecular axis and overall molecular rotation around the molecular axis begin to be fully excited. In the low temperature phase these motions are essentially frozen-in.¹²

In order to examine the RT coupling mechanism in β - C_2F_6 and, in particular, to make a quantitative comparison to SF_6 it is important that its elastic constants be determined. This has been done, in the present work, using the technique of high resolution Brillouin spectroscopy.

II. EXPERIMENTAL TECHNIQUE

The crystals of β - C_2F_6 used in these experiments were grown and maintained in a liquid nitrogen cryostat (Sulfron Cryogenics Inc.) which was modified for the purpose of the present work. The tail section of this cryostat and the cell assembly are shown in Fig. 1. The sample cell consists of a (3 mm i.d., 5 mm o.d.) glass tube. The lower end is sealed with a polished glass plug and sits in a spring-loaded BeCu jacket which is connected to a brass heat sink via two flexible copper braids and allows for sample rotation. Rotation was achieved via a rotary-sealed knurled knob which was connected to the cell by two stainless steel tubes and a brass plate. One of these tubes was used for gas entry.

Cooling was accomplished by allowing a finely controlled flow of nitrogen through a thin capillary tube which was thermally linked to the bottom of the sample cell via the brass heat sink and copper braid-BeCu jacket assembly mentioned above. Three resistive heaters were strategically placed in close proximity to the cell for temperature control: (1) directly beneath the capillary tube at the top of the heat sink; (2) at the bottom of the cell on the BeCu jacket; and (3) near the top of the cell for controlling the temperature gradient. GaAs temperature sensors were used in conjunction with the heaters and a proportional feedback temperature controller to control and monitor the temperature near the top and bottom of the cell. It turned out that it was only necessary to control the heat

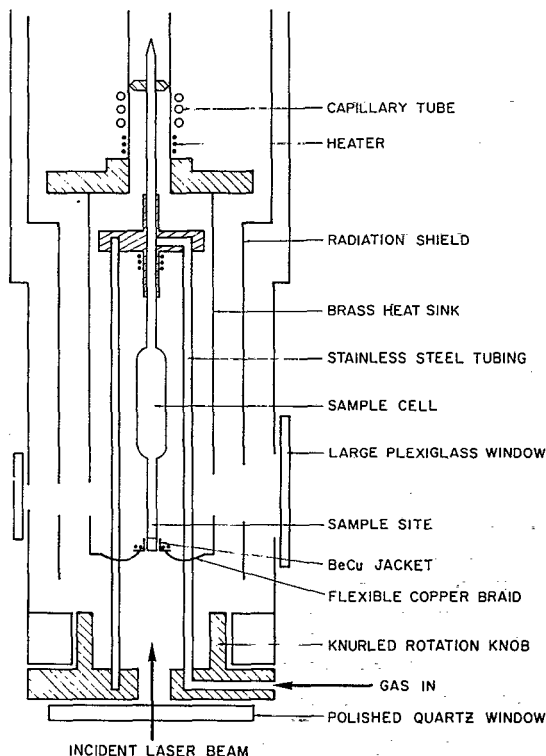


FIG. 1. The cryostat tail section and cell assembly.

sink temperature [i.e., with heater (1)]. To determine the temperature at the scattering center (located about 0.5 cm from the bottom of the sample), a constant and linear gradient was assumed to exist between the top and bottom of the cell.

The method used for growing crystals of C_2F_6 was similar to that used for other simple molecular solids grown in this laboratory.²⁰⁻²² Gaseous C_2F_6 of 99.6% purity was admitted into the sample cell where it was cooled and condensed. The sample temperature was then stabilized at 1 K above, and then abruptly lowered 1 K below, the triple point. This resulted in a solid 2–3 mm in height which was usually left for several hours to anneal. The quality of this “seed” was determined by using Laue x-ray diffraction. If the crystal was single, it was grown to a height of ~ 1 cm by cooling at a rate of about 0.1 K/h. Laue photographs were taken at various times during the cooling process. It was noted that as the crystal was grown it almost invariably became “twinned.” The diffraction spots, in all crystals kept for the light scattering experiments, remained fairly sharp and elliptical indicating little internal strain.

The crystal orientation with respect to the lab frame of reference was defined in terms of the usual Euler angles (θ , ϕ , χ). To determine these angles Laue x-ray diffraction photographs were taken as the crystal was rotated through intervals of 7.5° . The Laue spot coordinates served as input data for a least-squares computer program which utilized the method of stereographic projection to calculate possible sets of Euler angles for each photograph. Only orientations which gave an average error between measured and

TABLE I. Brillouin scattering data for β -C₂F₆ at 169 K.

XL #	Euler angles (°)			Observed (GHz)			Calculated (GHz)			Observed		Calculated	
	θ	ϕ	χ	ν_L	ν_{T_2}	ν_{T_1}	ν_L	ν_{T_2}	ν_{T_1}	I_{T_2}/I_L	I_{T_1}/I_L	I_{T_2}/I_L	I_{T_1}/I_L
1	141.9	231.3	316.4	4.19		1.61	4.16	1.64	1.59		0.05	0.02	0.03
	141.7	238.7	316.6	4.20		1.64	4.17	1.64	1.58		0.08	0.02	0.04
	141.4	246.1	316.8	4.20		1.60	4.17	1.64	1.57		0.03	0.02	0.03
	141.2	253.5	316.9	4.20		1.63	4.17	1.64	1.56		0.04	0.02	0.02
	141.2	261.0	316.9	4.19	1.68		4.17	1.65	1.56	0.02		0.02	0.02
	142.2	268.7	317.1	4.18	1.62		4.17	1.65	1.57	0.04		0.03	0.01
	142.2	276.2	317.1	4.16	1.71		4.16	1.66	1.58	0.02		0.03	0.01
	141.7	283.7	317.1	4.15	1.59		4.15	1.67	1.59	0.04		0.03	0.01
	141.6	290.9	317.1	4.12	1.63		4.14	1.67	1.61	0.06		0.03	0.01
	141.6	298.2	317.2	4.11	1.67		4.14	1.67	1.62	0.05		0.02	0.01
	141.4	305.6	317.2	4.11	1.67		4.14	1.67	1.63	0.05		0.02	0.01
	141.3	312.9	317.2	4.12	1.66		4.14	1.66	1.64	0.04		0.02	0.01
	141.6	320.6	318.1	4.12		1.62	4.14	1.66	1.64		0.06	0.01	0.03
	93.3	263.7	183.2	4.16	1.67		4.17	1.67	1.56	0.03		0.04	0.00
	94.6	271.2	183.4	4.14	1.68		4.16	1.67	1.55	0.04		0.04	0.00
2	94.6	278.2	183.6	4.14	1.68		4.16	1.67	1.55	0.04		0.04	0.00
	94.0	285.7	183.5	4.15	1.70		4.17	1.66	1.56	0.03		0.05	0.00
	93.4	293.2	183.4	4.15	1.68		4.17	1.65	1.56	0.05		0.06	0.00
	93.0	301.5	183.4	4.17	1.67		4.17	1.64	1.57	0.06		0.07	0.02
	92.3	308.6	183.0	4.17	1.59		4.18	1.62	1.58	0.10		0.06	0.03
	92.5	316.0	183.2	4.17	1.60		4.18	1.61	1.58	0.06		0.05	0.05
	92.6	323.4	183.4	4.17	1.58		4.18	1.62	1.58	0.06		0.05	0.04
	92.8	337.8	184.1	4.16	1.65		4.17	1.64	1.57	0.08		0.07	0.01
	141.9	185.7	309.4	4.15	1.73	1.63	4.12	1.67	1.66	0.03	0.03	0.03	0.02
	141.8	193.7	310.3	4.15	1.68	1.53	4.13	1.67	1.66	0.04	0.03	0.02	0.02
3	142.1	216.3	310.0	4.14		1.67	4.15	1.65	1.62		0.07	0.02	0.02
	142.2	238.2	310.1	4.15		1.54	4.17	1.65	1.57		0.05	0.02	0.04
	141.3	245.4	310.8	4.16			4.17	1.65	1.56			0.02	0.03
	141.4	253.4	310.7	4.18			4.17	1.65	1.56			0.02	0.02
	142.4	260.4	310.3	4.17	1.63	1.50	4.17	1.66	1.56	0.06	0.03	0.03	0.01
	142.4	267.9	310.3	4.18	1.71	1.56	4.16	1.66	1.57	0.02	0.03	0.03	0.01
	142.4	275.4	310.3	4.25	1.70	1.60	4.16	1.67	1.58	0.03	0.02	0.03	0.02
	142.4	282.9	310.3	4.18	1.69	1.60	4.15	1.67	1.59	0.03	0.03	0.02	0.02
	56.9	213.8	317.4	4.14		1.63	4.14	1.67	1.62		0.03	0.01	0.03
	57.2	221.0	317.5	4.10	1.67	1.61	4.13	1.67	1.64	0.03	0.03	0.01	0.03
4	56.3	265.7	318.4	4.11	1.68	1.60	4.14	1.67	1.62	0.03	0.03	0.01	0.03
	57.2	281.2	317.5	4.16		1.55	4.16	1.66	1.58		0.02	0.01	0.04
	57.2	296.3	317.5	4.16			4.17	1.66	1.56			0.01	0.02

calculated coordinate distances of < 1 mm for all pictures, and, which were consistent with crystal rotation (i.e., changes in angle ϕ only), were considered acceptable.

The optical system in the present work is the standard one used for Brillouin scattering experiments in this laboratory and has been described in detail elsewhere.²³ Incident radiation at 514.5 nm was provided by a single-mode argon ion laser (Spectra Physics 2020) which was filtered to a power level of about 50 mW. The light scattered at $90^\circ \pm 0.5^\circ$ was collected by $f/30$ optics and analyzed using a triple-pass piezoelectrically scanned Fabry–Perot interferometer set at a free spectral range of 10.99 GHz and a finesse of about 60. The light was detected by a water-cooled photomultiplier tube (ITT FW130) and the output was fed to a data acquisition and stabilization system (Burligh DAS-1) via an amplifier/discriminator. The DAS-1 employed photon counting electronics and provided continuous optimization of the interferometer finesse and compensation for frequency drift.

III. DATA ANALYSIS AND RESULTS

In total, 60 Brillouin spectra were recorded for four independent crystals of β -C₂F₆ at 169, 160, and 144 K. From Table I, it is evident that crystals 1, 3, and 4 have very similar and, therefore, preferred growth orientations. Most spectra were obtained at 7.5° intervals of rotation in the angle ϕ . In all spectra the longitudinal Brillouin component (L) was clearly visible but the transverse Brillouin components (T_1 and T_2) were very weak and both transverse components were observed in only nine of the spectra. A typical spectrum is shown in Fig. 2.

The observed Brillouin frequency shifts were obtained by direct measurement from the spectra and are shown in Tables I, II, and III. The Brillouin shifts for the crystal orientations studied here were nearly identical and corresponded to maximum variations of only 1% and 3% for the longitudinal and transverse shifts, respectively. These variations were not greatly different from the measurement

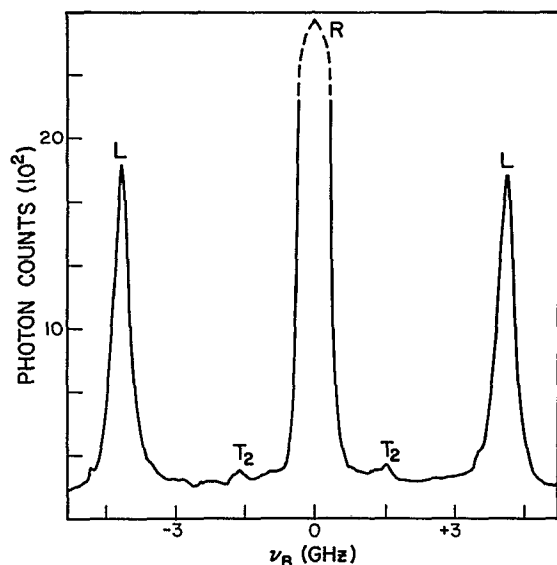


FIG. 2. A typical Brillouin spectrum of β -C₂F₆. The count rates are 2 and 35 counts/s for the T_2 and L components, respectively. The accumulation time is 26 h.

uncertainty which is estimated to be about 1–2 channels (i.e., about 0.05 GHz). The ratios of transverse Brillouin component intensities to longitudinal Brillouin component intensities, I_{T_1}/I_L and I_{T_2}/I_L , are also shown and are unusually small, varying from 0.01 to a maximum of only 0.10. These intensity ratios are probably accurate only to $\pm 15\%$ due to large variations in background intensity with channel number, weak signals, and the degeneracy of T_1 and T_2 .

In addition to the Brillouin frequency shift data, a knowledge of the density and refractive index of solid C₂F₆ was required to determine the elastic constants. Only one value for the density of solid C₂F₆ could be found in the literature, namely, $\rho = 1.85 \text{ g/cm}^3$ at the melting point (172.6 K).²⁴ The lattice parameter for the OD phase, how-

ever, has been determined by neutron diffraction experiments at 95 and 110 K.⁸ Because of the uncertainty of a phase transition at 104 K, only the 110 K value of the lattice parameter, $a = 6.1412 \text{ \AA}$, was used to yield a density of 1.98 g/cm^3 at 110 K. Linear interpolation was used to obtain the densities at 169, 160, and 144 K as noted in Table IV. The dependence of density on temperature for C₂F₆ was compared with that of SF₆.¹⁹ The slopes were nearly identical (-2.07×10^{-3} and $-2.06 \times 10^{-3} \text{ g/cm}^3 \text{ K}$ for C₂F₆ and SF₆, respectively), strengthening the reliability of the above density data.

A refractive index for solid C₂F₆ could not be found in the literature. A value of $n_l = 1.206$ at 199.9 K for the liquid,²⁵ however, was available. The density at this temperature was calculated from the empirical expression²⁴

$$\rho = 2.399 - 0.00406T \quad (1)$$

for the liquid densities.^{25,26} The Lorentz–Lorenz relation was then used to determine the refractive indices of the solid at the desired temperatures (see Table IV). It should be noted that the refractive indices are in excellent agreement with those obtained from the molar polarizability.⁹

The elastic constants were determined using a computerized iterative least-squares fit procedure described in detail in Ref. 23. The necessary input included the density, refractive index, Euler angles, and measured Brillouin shifts as well as initial guesses of the elastic constants. Initially, it was not possible to determine whether the single transverse peak observed in most of the spectra was the T_1 or T_2 component. Thus a complete analysis was first carried out assuming that the component was T_1 and then repeated assuming it was T_2 . The elastic constants obtained in both cases agreed with each other to better than 0.5%. The final assignments of the single transverse components were determined using the intensity ratio (I_{T_1}/I_L and I_{T_2}/I_L) fits calculated with an analogous computerized iterative least-squares program. The trans-

TABLE II. Brillouin scattering data for β -C₂F₆ at 160 K.

XL #	Euler angles (°)			Observed (GHz)			Calculated (GHz)			Observed		Calculated	
	θ	ϕ	χ	ν_L	ν_{T_2}	ν_{T_1}	ν_L	ν_{T_2}	ν_{T_1}	I_{T_2}/I_L	I_{T_1}/I_L	I_{T_2}/I_L	I_{T_1}/I_L
1	141.9	231.3	316.4	4.34		1.67	4.34	1.67	1.64			0.01	0.02
	141.4	246.1	316.8	4.32		1.63	4.34	1.67	1.63		0.03	0.01	0.02
	141.2	261.0	316.9	4.36	1.66		4.34	1.67	1.63	0.01		0.01	0.01
	142.2	276.2	317.1	4.34	1.69		4.33	1.68	1.64	0.01		0.02	0.01
	141.7	283.7	317.1	4.33	1.68		4.33	1.68	1.64	0.03		0.02	0.01
	141.6	298.2	317.2	4.32	1.68		4.32	1.68	1.66	0.04		0.02	0.01
	141.3	312.9	317.2	4.34	1.68		4.32	1.68	1.67	0.06		0.01	0.01
	141.6	320.6	318.1	4.31		1.67	4.32	1.68	1.67		0.07	0.01	0.02
2	94.0	285.7	183.5	4.34	1.70		4.34	1.68	1.62	0.05		0.03	0.00
	93.4	293.2	183.4	4.34	1.68		4.34	1.67	1.63	0.06		0.04	0.00
	93.0	301.5	183.4	4.34	1.66		4.34	1.67	1.63	0.05		0.04	0.01
	92.3	308.6	183.0	4.33	1.64		4.34	1.66	1.63	0.06		0.04	0.02
	92.5	316.0	183.2	4.33	1.66		4.34	1.65	1.64	0.06		0.03	0.03
	92.6	323.4	183.4	4.34	1.64		4.34	1.65	1.64	0.06		0.04	0.02
	92.1	330.9	182.8	4.34	1.66		4.34	1.66	1.63	0.05		0.04	0.01
	92.8	337.8	184.1	4.35	1.65		4.34	1.67	1.63	0.05		0.05	0.01

TABLE III. Brillouin scattering data for β -C₂F₆ at 144 K.

XL #	Euler angles (°)			Observed (GHz)			Calculated (GHz)			Observed		Calculated	
	θ	ϕ	χ	ν_L	ν_{T_2}	ν_{T_1}	ν_L	ν_{T_2}	ν_{T_1}	I_{T_2}/I_L	I_{T_1}/I_L	I_{T_2}/I_L	I_{T_1}/I_L
1	141.9	231.3	316.4	4.63		1.68	4.63	1.73	1.68		0.07	0.01	0.03
	141.4	246.1	316.8	4.64		1.74	4.62	1.75	1.68		0.02	0.01	0.03
4	57.5	236.0	317.4	4.64		1.64	4.67	1.65	1.64		0.03	0.01	0.03
	57.5	251.6	317.4	4.67	1.67	1.58	4.67	1.66	1.64	0.02	0.02	0.02	0.02
	56.3	265.7	318.4	4.67	1.67		4.66	1.70	1.64	0.02		0.01	0.01
	57.2	296.3	317.5	4.64			4.63	1.76	1.65			0.01	0.01

verse component with the greater calculated intensity ratio was the assignment given to the observed peak.

The best-fit elastic constants, given in Table IV, were those which minimized χ^2 . The uncertainties quoted in Table IV are those for which $\chi^2=1$ and are therefore the relative errors which express the quality of the least-squares fit. In addition, a systematic error of about 2%–3% is present due to uncertainties in the density, refractive index and scattering angle. This systematic error does not affect the elastic constant ratios nor the acoustic velocity ratios.

The temperature dependences of the elastic constants appear to be linear with slopes $\Delta C_{11}/\Delta T = -0.335 \pm 0.010$, $\Delta C_{12}/\Delta T = -0.236 \pm 0.010$, and $\Delta C_{44}/\Delta T = 0.005 \pm 0.011$ kbar/K in the range investigated. A graph of the elastic constants as functions of temperature is shown in Fig. 3.

As mentioned above, the elasto-optic coefficient ratios were determined using an iterative least-squares procedure such that reasonable agreement between the calculated and observed intensity ratios, I_{T_1}/I_L and I_{T_2}/I_L , was achieved. The assignments, either T_1 or T_2 for the single transverse components, which resulted in the smallest χ^2 were taken to be the correct ones and are given in Tables I, II, and III.

The resulting elasto-optic coefficient ratios and an estimate of the absolute values calculated from²⁷

$$p_{11} + 2p_{12} = \frac{(n^2 - 1)(n^2 + 2)}{n^4} \quad (2)$$

are given in Table IV. The uncertainties in the elasto-optic coefficient ratios are probably of the order of 10%–20% since, in fact, the sum of I_{T_1} and I_{T_2} was likely measured in many cases. The adiabatic bulk modulus, $B = (C_{11} + 2C_{12})/3$, and the elastic anisotropy, $A = 2C_{44}/(C_{11} - C_{12})$, were determined from the elastic constants and are also given in Table IV.

TABLE IV. Temperature dependent data for β -C₂F₆.

T (K)	ρ (g/cm ³)	n	C_{11} (kbar)	C_{12} (kbar)	C_{44} (kbar)	B (kbar)	A	p_{12}/p_{11}	p_{44}/p_{11}	p_{11}	p_{12}	p_{44}
169	1.857	1.243	26.99±0.10	19.32±0.10	4.44±0.04	21.9±0.1	1.16±0.04	1.10	0.12	0.25	0.28	0.03
160	1.876	1.246	29.76±0.07	21.34±0.05	4.53±0.02	24.1±0.1	1.08±0.03	1.06	0.09	0.26	0.28	0.02
144	1.909	1.251	35.32±0.29	25.21±0.41	4.33±0.09	28.6±0.4	0.86±0.08	1.04	0.12	0.27	0.28	0.03

IV. DISCUSSION

The Brillouin spectra of β -C₂F₆ are somewhat unusual in that the frequency shifts of the Brillouin components did not depend significantly on crystal orientation. Hence, β -C₂F₆ is elastically quite isotropic with an elastic anisotropy $A \sim 1$ for all temperatures investigated. This also accounts for the near degeneracy of T_1 and T_2 .

The Cauchy relation, $C_{12}/C_{44}=1$ for central intermolecular forces in cubic crystals, is not obeyed by β -C₂F₆. A high value of 4.4 was found at 169 K and implies that angle dependent forces play an important role in the dynamics of this OD solid.

A somewhat more quantitative estimate of the extent of the RT coupling in β -C₂F₆ can be obtained from the density-independent ratios of acoustic velocities in high symmetry directions. Large values of these ratios indicate softened transverse mode(s) which may be interpreted as being due to RT coupling.²⁸ These ratios have been calculated for β -C₂F₆ from the elastic constants determined in the present work and are given in Table V, where a comparison is made with those of the rare gas solids. As is evident, three of these ratios are substantially larger than the corresponding ratios for the rare gas solids and hence means that RT coupling is present in C₂F₆. The near equality of all four ratios for C₂F₆ is a consequence of its elastic isotropy.

As previously mentioned, preliminary molecular dynamics simulations of C₂F₆^{13,14} indicate that strong RT coupling exists in the $q=0$ wave vector regime. This is consistent with the values for the acoustic velocity ratios given in Table V in that they are significantly larger than those for the rare gas solids and are therefore indicative of significantly softened transverse modes. This suggests that moderately strong RT coupling exists near $q=0$. However, the molecular dynamics calculations also indicate that C₂F₆ is very similar to SF₆. This, from the present work, is

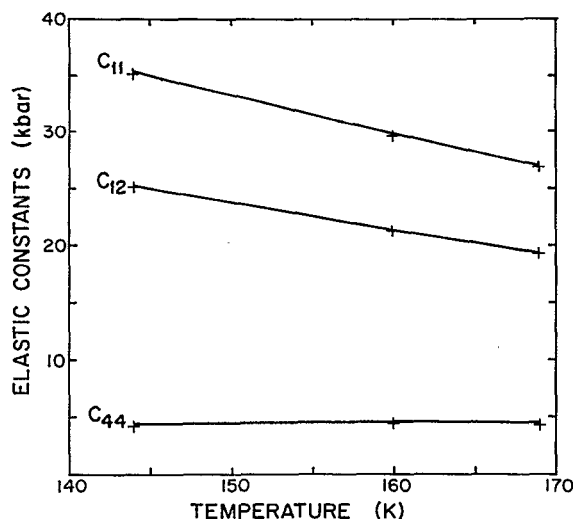


FIG. 3. Adiabatic elastic constants of β - C_2F_6 as functions of temperature.

clearly not the case because SF_6 behaves elastically much like a rare gas solid¹⁹ (see Table V). In addition, no anomalous mode softening evidence for RT coupling was observed for SF_6 near the Brillouin zone center.¹⁹

A possible explanation for the significant difference in behavior between C_2F_6 and SF_6 could be that the reorientational frequency of the molecules of C_2F_6 in the disordered phase is comparable to the frequency of the transverse acoustic phonons whereas in SF_6 these two frequencies may be quite different such that in SF_6 the molecular reorientational motion is effectively "smeared out."¹⁹

The ratios in Table V suggest that C_2F_6 is elastically quite isotropic and thus is qualitatively similar to the structurally identical cyclooctane-I and γ - O_2 although its acoustic velocity ratios are not quite as large. Brillouin scattering experiments on cyclooctane-I and γ - O_2 ²² have shown that strong RT coupling exists in these solids. In cyclooctane this strong coupling was, in part, attributed to the fact that

TABLE V. Temperature dependence of acoustic velocity ratios in high symmetry directions and Cauchy ratios for β - C_2F_6 and several other molecular solids.

SOLID	$\langle 100 \rangle$ $V_L/V_{T_2, T_1}$	$\langle 111 \rangle$ $V_L/V_{T_2, T_1}$	$\langle 110 \rangle$ V_L/V_{T_2}	$\langle 110 \rangle$ V_L/V_{T_1}	C_{12}/C_{44}
β - C_2F_6 (169 K)	2.47	2.62	2.49	2.68	4.35
β - C_2F_6 (160 K)	2.56	2.64	2.58	2.67	4.71
β - C_2F_6 (144 K)	2.87	2.67	2.83	2.62	5.82
Ne, Ar, Kr, Xe ^a	1.44	2.24	1.65	2.71	1.2–1.4
SF_6 ^b	1.60	2.29	1.76	2.64	1.68
C_8H_{16} (cyclooctane-I) ^c	3.49	3.35	3.48	3.29	9.98
γ - O_2 ^c	3.07	3.09	3.07	3.10	7.48
$(CH_2CN)_2$ ^d	2.79	2.60	2.76	2.54	4.98

^aReference 46.

^bReference 19.

^cReference 22.

^dReference 32. All data are near respective triple points unless otherwise indicated.

the molecular reorientation frequency (~ 1 GHz) is of the order of the transverse acoustic mode frequency (~ 2 GHz). A somewhat similar situation exists in γ - O_2 with respect to the frequencies of molecular vibrational dephasing.²⁹ It was suggested that the elastic isotropy exhibited by cyclooctane-I and γ - O_2 was due to an averaging out of the rotational motion of the disklike molecules (which are arranged in the form of long, mutually orthogonal chains) on the unit cell faces. The isotropy was found to be greatest near the triple point for O_2 and decreased with decreasing temperature; this feature is consistent with the proposed RT coupling mechanism.

As shown in Table V, the similarity between C_2F_6 and succinonitrile $(CH_2CN)_2$ is striking. Both are nearly elastically isotropic, the acoustic velocity ratios in the high symmetry directions for both solids are nearly equal and the Cauchy ratios are very similar (see Table V). $(CH_2CN)_2$ exists in an OD phase from its triple point, at 331 K, to 233 K.³⁰ Dielectric studies³¹ have shown very little change in the nature of the molecular reorientation between the liquid and OD phase. Light scattering experiments on $(CH_2CN)_2$ ³² have been carried out for temperatures in the range 243 to 323 K. A pair of peaks in the polarized spectra, thought to be due to transverse phonons, was observed above 283 K but did not appear below this temperature. The intensity of these peaks increased with increasing temperature and they could easily be seen at 323 K. It was argued that the temperature dependence of the shear phonon intensities is related to the temperature dependence of the reorientation mechanism, such that, at low temperatures, when the molecular reorientational frequency approaches the transverse phonon frequency, the slowly reorienting molecules dampen the shear phonons. Rayleigh-Brillouin measurements of the depolarized light scattering in $(CH_2CN)_2$ ³³ have found shear wave peaks with resonance line shapes. These spectra were understood to arise from coupling between acoustic phonons and molecular reorientational motions, and constitute evidence for RT coupling in $(CH_2CN)_2$. A hydrodynamic model developed by Courtens,³⁴ which included coupling between molecular reorientation and acoustic modes, correctly predicted the features of the depolarized light scattering spectra as well as the ultrasonic values of the elastic constants.³⁵ Further investigations by Descamps³⁶ indicated that steric hindrance is present in $(CH_2CN)_2$. It was later noted by Press *et al.*,³⁷ that in larger molecules, such as $(CH_2CN)_2$, steric hindrance introduces RT coupling. The above mentioned similarity between C_2F_6 and $(CH_2CN)_2$, therefore, clearly supports the importance of RT coupling in C_2F_6 .

More recent work on plastic $(CH_2CN)_2$ ³⁸ has deduced the RT coupling in the disordered phase of deuterated succinonitrile from x-ray diffraction measurements. It was shown that the coupling is directly related to the spatial siting of neighboring molecules and that it affects the positions of the *gauche* isomers. In a later study by the same group,³⁹ the structure of plastic $(CH_2CN)_2$ was re-examined through extended x-ray diffraction measurements. The structure was solved by using both the analytic

procedure of symmetry-adapted functions and a Frenkel model assuming discrete orientations and a possible RT coupling was included in the latter case. The nature of the rotational motions in $(\text{CH}_2\text{CN})_2$ has been examined by various other techniques including NMR,⁴⁰ dielectric relaxation,⁴¹ Rayleigh scattering,⁴² incoherent neutron scattering^{43,44} and molecular dynamics simulation.⁴⁵ All of these have revealed dynamic orientational disorder of the molecules with the rotational disorder being due to jumps from one cube diagonal to another and *trans-gauche* isomerization.

A major factor which accounts, at least in part, for the very different behavior of C_2F_6 and SF_6 , and which seems to have been overlooked in the molecular dynamics calculations,^{13,14} is the existence of internal rotational motion in C_2F_6 . In C_2F_6 , in addition to the molecular tumblinglike motions, there also exists rotation of one CF_3 group with respect to the other and overall rotation about the C–C bond. This type of motion also occurs in C_2Cl_6 ¹² and an analogous phenomenon takes place in $(\text{CH}_2\text{CN})_2$ ^{38,39} as the $\text{CH}_2\text{—C}\equiv\text{N}$ groups rotate about the central C–C bond and, in doing so, one isomer is changed into another. This certainly influences the RT coupling in C_2F_6 , especially if the frequency of these rotational motions is of the order of the frequency of the transverse acoustic phonons. The fact that C_2F_6 exhibits internal and molecular reorientational motions similar to those of $(\text{CH}_2\text{CN})_2$, as distinct from those of SF_6 , appears to account for both the similarities observed between C_2F_6 and $(\text{CH}_2\text{CN})_2$ and the differences between C_2F_6 and SF_6 .

The similarity between C_2F_6 and $(\text{CH}_2\text{CN})_2$, and difference from SF_6 , is also interesting from the point of view that all three have the same site symmetry and the OD phases form body-centered cubic lattices. All three, however, have different molecular symmetries. Molecular symmetry, therefore, probably does not play a significant role in the dynamics and, in particular, the RT coupling mechanism. Otherwise, C_2F_6 would be expected to behave like SF_6 due to their near identical molecular symmetries as suggested by the simulations of Dove *et al.* Instead, C_2F_6 was found to behave elastically like $(\text{CH}_2\text{CN})_2$ which has a significantly different molecular symmetry (the *gauche* isomers have symmetry 2 and the *trans* isomer has symmetry $2/m$ ³⁹).

V. CONCLUSIONS

In summary, the elastic and elasto-optic constants of the OD phase of C_2F_6 have been determined using the technique of high resolution Brillouin spectroscopy. The ratios of acoustic velocities calculated from the elastic constants show that C_2F_6 is quite isotropic and that it exhibits moderately strong RT coupling and in these respects is very similar to $(\text{CH}_2\text{CN})_2$. This is in contrast to the plastic phase of SF_6 which behaves elastically like a rare gas solid.

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