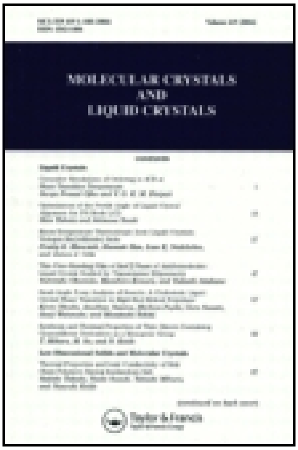

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Low Temperature Raman Spectra of Dibenzyl; Comparison with Biphenyl and Paraterphenyl

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The Raman spectra of crystal dibenzyl have been recorded from 293 down to 10 K. No typical temperature dependence which usually accompanies phase transitions has been observed in frequencies, intensities or background. A comparison is made with biphenyl and paraterphenyl whose evolution of Raman spectra with the temperature looks similar. The very broad bands observed at room temperature result from the superposition of the different modes which appear well separated at 10 K. This behavior is consistent with the large atomic thermal motion observed by X-ray analysis. Vibrational frequencies have been calculated using the intermolecular potential of the atom-atom type in the rigid phenyl approximation and compared with experimental data.

INTRODUCTION

The crystal structure of dibenzyl reported by Robertson[1] and Jeffrey[2] showed a molecule with a center of symmetry and a central —CH_2—CH_2— bond inclined at 70° to the plane of the benzene rings (Figure 1). However, a molecule with nonparallel rings was suggested by Mathur and Tabisz[3] from a far-infrared and laser Raman analysis. Teslenko[4] and Ryzhenkov[5] measuring the wave propagation velocities and thermal expansion obtained contradictory results. A new examination of X-ray data led to isotropic temperature factors of about 6 Å^2 for the carbon atoms. It is well known that large atomic thermal motion often characterizes disordered structures.

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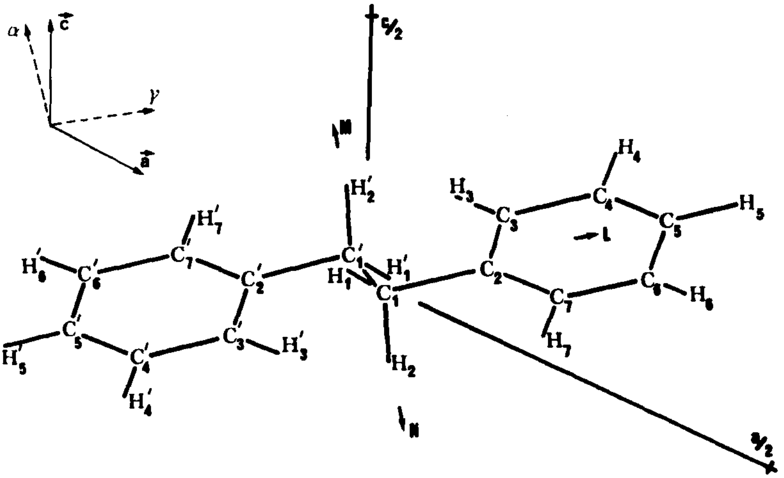


FIGURE 1 The crystal structure of dibenzyl: principal inertial axes; principal optical axes.

Therefore, the possibility of a phase transition should not be excluded and for these reasons, a large investigation by different techniques (X-ray, Brillouin, Raman) has been undertaken. We have previously reported[6] the refinement of the crystal structure at 293 and 110 K and the Brillouin scattering from 293 down to 10 K.

In the first part of this paper we deal with Raman spectra between 10 and 293 K, and we compare them with those of paraterphenyl and biphenyl; we also discuss the temperature dependence of the background. In the second part, the Raman active vibrational fundamentals are discussed by referring to the results of frequency calculations from atomic interaction potentials.

EXPERIMENTAL

The crystals used in the present work were grown from the melt by the Bridgman method. Several samples were cut with edges parallel to the principal optical axes α, b, γ with typical dimensions of $5 \times 4 \times 3$ mm^3. Laser Raman spectra were recorded with a LRDH 800 Coderg R. S. using the 4880 Å radiation from an Argon laser as an exciting line. The temperature of the sample, cooled in a Meric cryostat by a controlled stream of cold helium gas, was monitored by 2 AsGa diodes with an accuracy of ±0.1 K. The spectral slit width was 1.2 cm^{-1}.

TEMPERATURE DEPENDENCE STUDY AND COMPARISON WITH BIPHENYL AND PARATERPHENYL

Since no information concerning a possible solid state phase transition was available, Raman spectra were recorded from 293 down to 10 K along four different polarizations. Raman frequencies are summarized in Table I. Figure 2 shows the Raman spectra at 10 and 293 K. It is obvious that a change in crystal symmetry should affect the observed lattice vibrational spectra. High temperature spectra show four very broad bands while at 10 K we count eleven bands whose linewidth can be compared with the spectral slit width. Figure 3 shows the gradual change of spectrum for the $\gamma\,(bb)\alpha$ polarization. A similar evolution appears also in paraterphenyl[7,8] and biphenyl[9] where additional bands appear gradually when the temperature is lowered. To determine whether or not a phase transition occurs between 10 and 293 K it is necessary to detect a clear phenomenon connected with a structural modification. To this end, the behavior[10] of biphenyl and paraterphenyl provides a useful comparison.

In biphenyl, two phase transitions were detected at 17 K and 40 K by different methods. Observation by Raman spectroscopy of a soft mode revealed the displacive phase transition at 40 K.[11] The other transition at 17 K is a first-order transition between two incommensurate phases. We have measured the temperature dependence of frequency and intensity around this transition. The first-order transition is characterized by a sharp change at 17 K: $\Delta\nu = 2$ cm^{-1} for the 31 cm^{-1} mode and $\Delta I/I = 10\%$ for the 961 cm^{-1} internal mode.[12]

TABLE I

Observed Raman frequencies of dibenzyl (cm^{-1})

10 K	88 K	293 K
46.5	45.5	36
57	55.5	
65.5		
70	66	
86	84.5	75
95.5	95.5	93
105	104.5	
116.5	114.5	
128		
153	153	145
155		

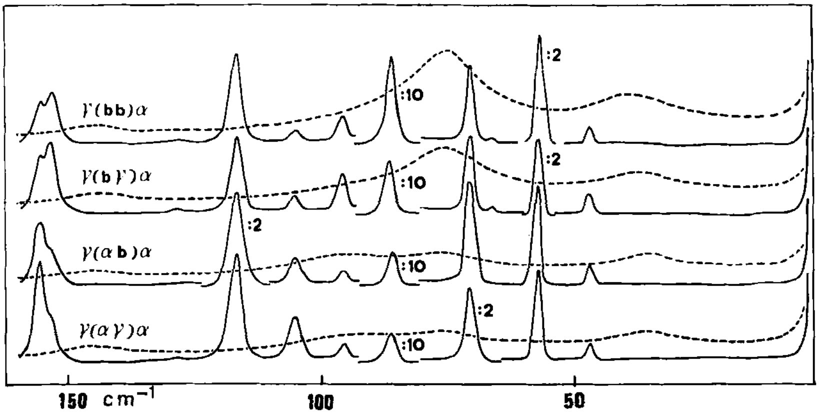


FIGURE 2 Raman spectra of dibenzyl: —— 10 K; ----- 293 K.

Paraterphenyl undergoes an order-disorder phase transition at 192 K. We have investigated variations with temperature of the linewidth for the 38.5 cm^{-1} band. The transition corresponds to an inflexion point on the curve.[7] None of theses typical features was observed in dibenzyl.

A last attempt to detect a phase transition was the study of the background,[13] which background can be considered as a measurement of anharmonicity in the crystal. We have applied this method to biphenyl, paraterphenyl and dibenzyl. Gratings have been set to explore a spectral region between the Rayleigh line and the first low frequency mode. Figure 4 which shows the temperature dependence of the background indicates unambiguously phase transitions in biphenyl and paraterphenyl but excludes such a possibility in dibenzyl. One point concerning biphenyl is worth noting: the soft mode vanishes in the background before reaching the experiment frequency (10 cm^{-1}).

From all these results it is clear that changes in Raman spectra of dibenzyl cannot be related to a phase transition. Thermal motion is probably the cause of the evolution of the Raman lines. The broad bands observed at 293 K (see Figure 2) are made of an addition of different modes which appear well separated at 10 K. This explains the slight frequency shift of maxima of these broad bands observed at 293 K for the different polarizations. It comes from the fact that intensities of the modes which form each broad band have different values along the four polarizations.

A study of the elastic properties of dibenzyl by Brillouin scattering[6] leads to a similar negative conclusion concerning an eventual phase transition. Therefore, we can use the crystal structure refined at 110 K to analyze the vibrational spectra recorded at 10 K, remembering however that there is a general shift toward low frequencies when the temperature rises.

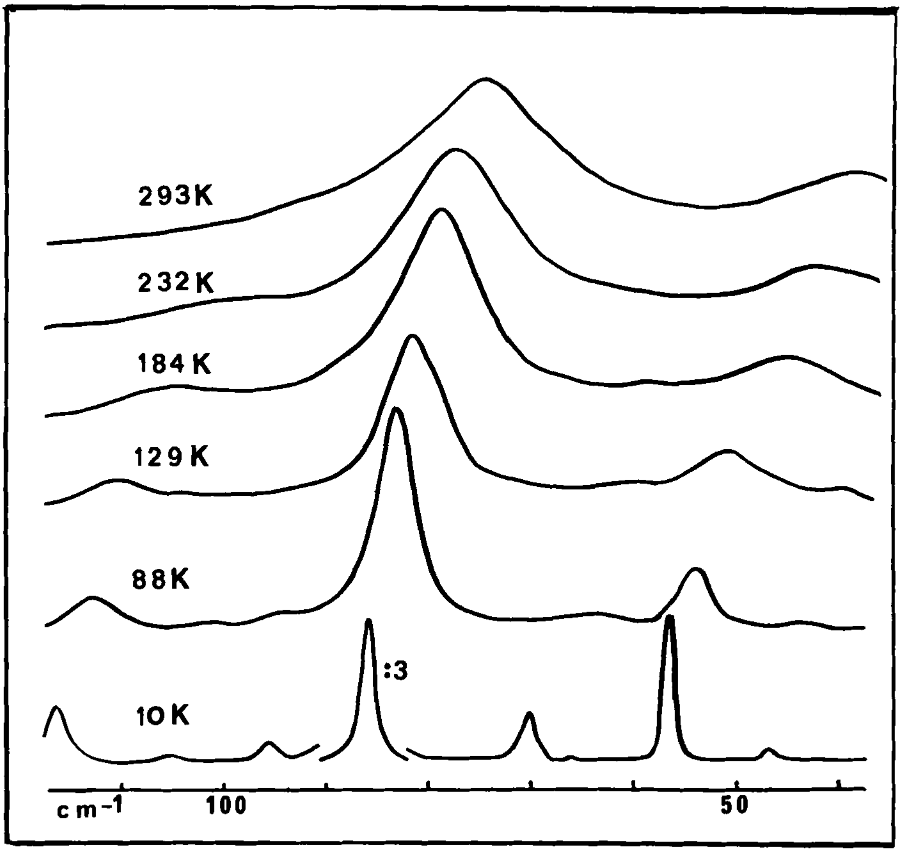


FIGURE 3 Temperature dependence of Raman spectrum of dibenzyl for the $\gamma(bb)\alpha$ polarization.

VIBRATIONAL ASSIGNMENTS

The crystal belongs to the monoclinic system: space group $P2_1/a$ (C^5_{2h}) with two molecules per unit cell, $a = 12.55$, $b = 6.12$, $c = 7.47$ Å, $\beta = 114.77°$. The molecules are located at C_i sites. The planes defining the two benzene rings are parallel and the angle between the central $C—CH_2—CH_2—C$ plane and the plane of the phenyl rings is 67.1°. Lattice vibrations predicted by the factor-group analysis can be classified into six rigid librational modes 3 Ag + 3 Bg and three translational modes 2 Au + 1 Bu. Each of the "u" internal modes in the site group C_i is split into a doublet Au + Bu in the point group C_{2h}. Similarly each "g" gives Ag + Bg. Torsion of the central bond $C_1—C_1'$ is only infrared active, while torsion of the bonds $C_1—C_2$, $C_1'—C_2'$ is both Raman and infrared active.

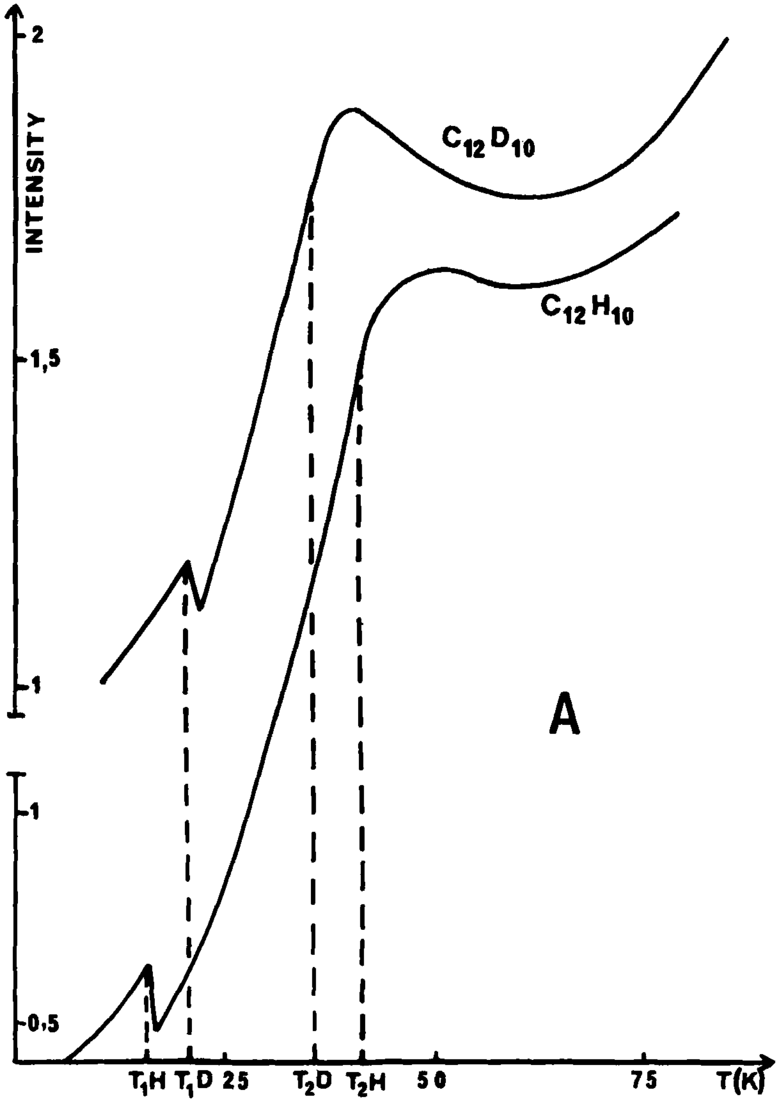
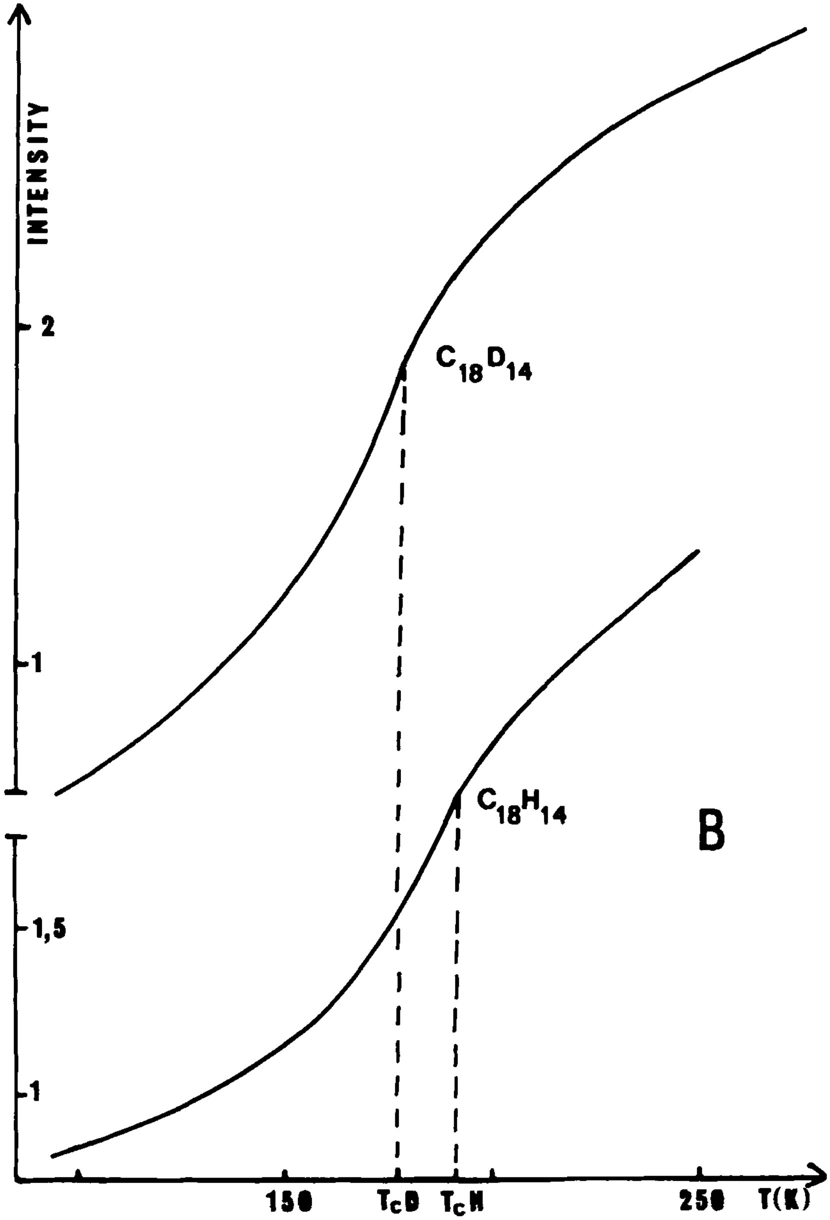
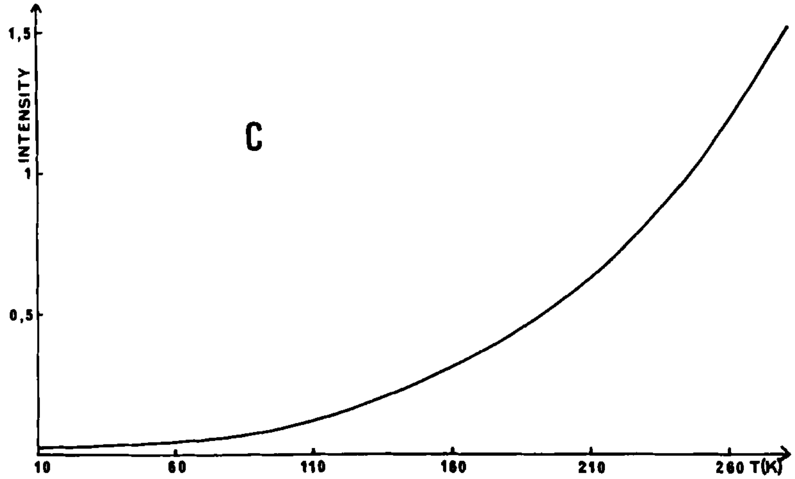


FIGURE 4 Temperature dependence of the background: A is biphenyl at 10 cm^{-1}, B is paraterphenyl at 15 cm^{-1}, C is dibenzyl at 18 cm^{-1}.

Although Ag-species fundamentals of dibenzyl should be observed only in polarized spectra of types *bb* and *aγ*, and those of Bg-species in *ba* and *bγ* polarized spectra, all the bands can be observed along each polarization (see Figure 2). Such a depolarization which is mainly due to defects in crystalline samples and misorientations will make measurements of the


INTENSITY
2
1
1,5
1
$C_{18}D_{14}$
$C_{18}H_{14}$
B
150
T_cD
T_cH
250
T(K)



relative line intensities necessary to allow assignments of the Raman fundamentals in A_g and B_g modes.

Calculation of the dynamical matrix[14] comes out to solve a secular equation of the following form:

$$|F^{\mu\nu} - (\lambda - \lambda_\mu)\delta^{\mu\nu}| = 0$$

with

$$F^{\mu\nu} = \partial^2 v/\partial S_\mu \partial S_\nu$$

where S is a dynamical variable which describes the molecular motion as a whole (rotation and translation) and the distortion of the molecule, λ_μ the free molecule eigenvalue corresponding to the internal mode S_μ. It is taken as zero for translations and librations. δ is the Kronecker symbol. The usual intermolecular potential V is written in the form of a sum of interatomic potentials:

$$v(r) = A\exp(-Br) - C/r^6$$

where r is the interatomic distance. The parameters[15] A, B, C used in this calculation are given in Table II.

The direction cosines of the three principal inertial axes are given in Table III. They define the basis set S for rigid librations and translations.

Calculations of the normal modes of the molecule of dibenzyl have been performed by using the valence force field of benzene for the phenyl rings and the valence force field of butane for the central chain. Force constants

TABLE II

Potential parameters

Atom pair	*A* (Kcal · mole^{-1})	*B* (Å^{-1})	*C* (Kcal · Å^6 · mole^{-1})
C—C	71782	3.60	512.50
C—H	8503	3.67	111.82
H—H	2171	3.74	24.39

TABLE III

Direction cosines of principal inertial axes

	a	*b*	*c**
L	0.17313	0.38864	0.90496
M	0.41500	0.80557	−0.42493
N	0.89413	−0.44732	0.02105

taken from benzene,[16,17] from butane[18] and from biphenyl[19] for the out of plane bendings of phenyl rings led to frequencies higher than the observed ones by about 20 cm^{-1}. They were adjusted to provide the best fit between observed and calculated frequencies. We have obtained the 78 frequencies and eigenvectors for the free molecule. Since we are interested in the interaction of lattice modes with internal modes, only the five frequencies below 200 cm^{-1} will be taken into account. Three are assigned to infrared active u modes and two to Raman active g modes. They correspond to torsions of the aliphatic chain mixed with out-of-plane displacements of the benzene rings. In these zero-order calculations the lowest mode attributed to benzene ring distortions has been found at 400 cm^{-1}. Therefore, a rigid-body approximation might have been used for the benzene rings. In fact the very low frequency internal modes depend only on two terms of the potential function which are the torsional diagonal term for the three aliphatic bonds and the out-of-plane deformation diagonal term for the benzene rings. It should be noted that calculations of internal lattice modes depend mainly on the form of the eigenvectors for the free molecule. In particular, taking into account the cross terms between torsional and out-of-plane deformations would change significantly the results.

Frequencies and eigenvectors for g modes are listed in Table IV. During calculations the value of the C_1—C_2 torsional force constant was adjusted from the standard value 0.03 mdyn Å down to 0.012 mdyn Å. This difference is probably due to the strains imposed on the molecule by the external field. Other results reinforce the assumption that intramolecular torsional

TABLE IV

Observed and calculated frequencies of dibenzyl

		Eigenvectors						
	$\nu_{calc.}$	L	M	N	I_1	I_2	$\nu_{exp.}$ 10 K	Assignment
Ag	59	0.11	0.32	0.84	0.36	0.18	57	Libration around N
	73	0.58	0.19	−0.44	0.64	0.08	86	Torsion of C_1C_2 bond
	100	0.71	−0.52	0.21	−0.36	0.20	105	Libration around L
	120	0.32	0.75	−0.02	−0.54	−0.12	128	Libration around M
	152	−0.18	0.13	−0.18	−0.12	0.94	155	Out of plane displacement of phenyl rings
Bg	46	−0.13	0.75	−0.59	−0.23	0.05	46.5	Libration around M
	73	0.49	−0.01	−0.42	0.74	0.11	70	Torsion of C_1C_2 bond
	93	0.34	0.59	0.65	0.11	0.29	95.5	Libration around N
	114	0.77	−0.15	−0.14	−0.59	−0.02	116.5	Libration around L
	151	−0.11	−0.22	−0.12	−0.14	0.94	153	Out of plane displacement of phenyl rings

Frequencies in cm^{-1}; I_1 internal torsion; I_2 out of plane deformation; no attribution is proposed for the very weak band at 65.5 cm^{-1}.

forces can be compared in value with intermolecular interactions. Thus, torsional modes around C_1—C_2 have been calculated at 59 cm^{-1} in A_u species and 60 cm^{-1} in B_u species (with the standard value of 0.03 mdyn Å for the central C_1—C_1' torsion constant). On the other hand the two g modes of the free molecule have been found at 39 and 98 cm^{-1}. All that explains why internal character of low frequency modes cannot be easily distinguished from lattice modes by conventional methods such as temperature dependence of frequencies.

The very intense 86 cm^{-1} band attributed to a torsion of the C_1—C_2 bond deserves some comment: Raman relative intensities have been calculated by using the oriented-gas model in the classical theory of polarizabilities. For lattice vibrations, in the case of rigid molecule librational motion around an inertial axis, Kastler and Rousset[20] showed that intensities mainly arise from the difference between principal polarizabilities in the plane perpendicular to the axis of rotation. This method was extended to the general case[21] where axes of librations do not coincide with inertial axes. Contribution of internal modes to Raman intensities have been evaluated by Long's theory.[22] Generally speaking, the above cited theories predict that librations around L and M should give values of the same order of magnitude as those of internal torsional modes. One explanation for the unexpected intensity of the 86 cm^{-1} band might be an important perturbation of the π-electronic system of the phenyl rings caused by a torsion of the molecule. No such feature is observed for the out-of-plane deformation 155 cm^{-1} band.

It seems quite reasonable to assume that the twisting of the molecule is caused by the external field. This situation has some analogy with the case of biphenyl which is nonplanar in the vapor phase but which is quasi-planar in the crystalline state.[23] In dibenzyl, the anomalous thermal factor observed by X-ray corresponds to the low frequency mode attributed to the L librations. It is worth noting that this frequency is lower than that attributed to M librations for A_g species although the inertial moment around M is ten times greater than that around L. One can say that anharmonicity of dibenzyl arises from low frequency lattice and internal modes, each benzene ring oscillating around C_1—C_2 in a very flat potential well. Far infrared and neutron spectroscopies might usefully complete this investigation of dibenzyl.

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