

total energies of the more stable staggered form of  $C_2H_6$  and the eclipsed form is 2.90 kcal/mole. This may be compared with the experimental rotation barrier of 2.93 kcal/mole.<sup>7</sup> The most elaborate LCAO calculation for ethane is the one recently published by Veillard.<sup>6</sup> Using a large Gaussian basis set and the program IBMOL, Veillard calculated a barrier of 3.65 kcal/mole for the experimental geometry and a barrier of 3.07 kcal/mole for the optimized geometry. The close agreement with experiment obtained by the SCF- $X\alpha$ -SW method, in only a few minutes of computer time, is not fortuitous. The virial theorem is approximately satisfied by the  $X\alpha$  statistical total energy and kinetic energy for both the staggered and eclipsed conformations, indicating stable and metastable equilibrium, respectively. Close agreement between the  $X\alpha$  statistical binding energies of methane and experiment has also been obtained recently with the SCF- $X\alpha$ -SW method.<sup>8</sup>

In order to apply this technique correctly to the

problems of the inversion barrier in  $NH_3$  and the bond angle in  $H_2O$ , it is essential for one to include supplementary regions of spherically averaged  $X\alpha$  potential in the interatomic regions of the lone-pair electrons. These applications, along with more detailed results for the  $C_2H_6$  molecule, will be reported in a later publication.

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† Permanent address: Institute of Theoretical Physics, University of Stockholm, Stockholm, Sweden.

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## Localized In-Band Rotational Phonons in Mixed Molecular Crystals: Electronic Spectra of Naphthalene Doped Biphenyl and Durene\*

PETER H. CHERESON, PETER S. FRIEDMAN, AND RAOUL KOPELMAN

*Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104*

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The concept of localized phonons has been established in the last decade.<sup>1,2</sup> Originally it applied only to guest localized phonons with energy well above the fundamental host phonon band, but subsequently it was extended to bandgap phonons and in-band "resonance" phonons.<sup>1,2</sup> Some of the "resonance phonons" are by implication<sup>1,2</sup> *pseudolocalized*, that is, characterized by a large amplitude at the guest site and by small but finite amplitudes extended throughout the host crystal. In contrast, a localized excitation has not only a maximum amplitude at the guest site, but also its amplitudes at host sites decay asymptotically with increased distance from the guest. In 1965 Dettman and Ludwig<sup>3</sup> established the concept of a *rotational* (librational) localized phonon in a molecular lattice with the help of a model calculation on a linear-chain doped molecular crystal. An important result of their investigation was that localized as well as pseudolocalized guest rotations are possible in the frequency region of host translations (but not rotations). We present below an experimental verification of this concept of localized and/or pseudolocalized rotational phonons for two real, three-dimensional systems and suggest that this phenomenon should be quite general for chemically mixed molecular crystals.

A criterion for localization or pseudolocalization is

a large guest site amplitude. We have used the method of isotopic substitution to verify the presence of such an amplitude. Upon perdeuteration of the naphthalene guest we observe a reduction in the prominent phonon frequencies of 4.5% ( $-1.5\% + 3.5\%$ ) for naphthalene in biphenyl and 5.5% ( $\pm 2.5\%$ ) for naphthalene in durene. A *completely localized* harmonic guest phonon model predicts the mass effect for a naphthalene translation to be 3% (frequency reduction upon

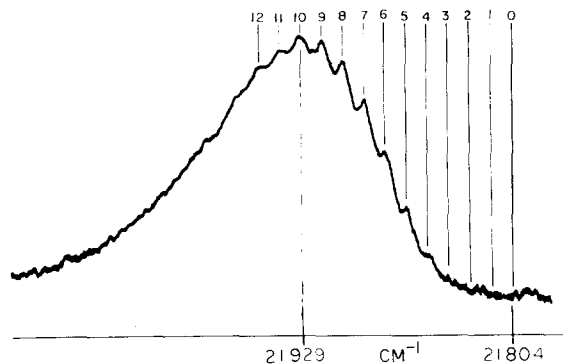


FIG. 1. Densitometer trace of the  $433\text{ cm}^{-1}$  ( $b_{3g}$ ) absorption band at  $2^\circ\text{K}$  for the first singlet-singlet transition of 0.67% (nominal) naphthalene ( $C_{10}H_8$ ) in biphenyl ( $C_{12}H_{10}$ ). The face is  $ab$  and the splitting  $12.5\text{ cm}^{-1}$ .

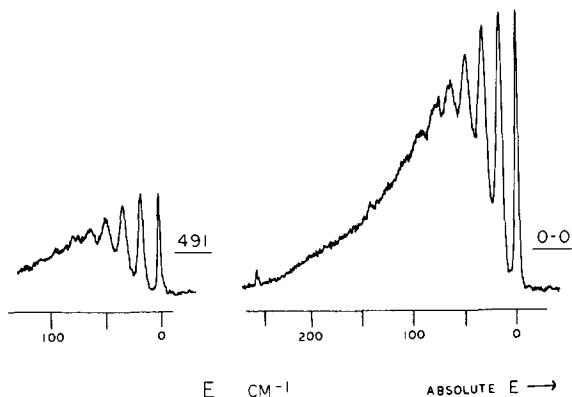


FIG. 2. Densitometer trace of the 0-0 naphthalene in durene phosphorescence band observed in a 1.1% (nominal)  $C_{10}D_8$  in  $C_{10}D_{14}$  crystal at 2°K. The origin of the reversed energy scale is at 21 441  $cm^{-1}$ . The observed major phonon spacings are: 17, 34, 51, 65, and 80  $cm^{-1}$ . A vibronic band (491  $cm^{-1}$ ) is also shown.

perdeuteration). It also predicts a 6%–9% effect for naphthalene rotation, depending on the axis of rotation. As the guest concentration is less than 1% (see below), localization or pseudolocalization is established by our observations. As guest translation and rotation do not mix in a  $C_i$  site, the localized motion must be rotational. From these and additional arguments<sup>4,5</sup> we assign the observed phonon modes to *guest rotations* having a high degree of localization at the guest site: about 80% *guest* localization of the excitation in the biphenyl host<sup>6</sup> and at least 30% *guest* localization in the durene host. It should be noted that isotopic substitution of the *host* was also investigated, resulting in a  $0\% \pm 3\%$  shift for biphenyl but about 17% for durene. These and other points such as amplitudes, barriers, symmetry, orientational relaxation, and Franck-Condon factors will be discussed in detail in forthcoming publications.<sup>4,5</sup> We only wish to point out here our belief that localized or pseudolocalized phonons are responsible for much of the spectroscopic fine structure accompanying vibronic bands in chemically (but not isotopically<sup>7,8</sup>) mixed crystals, and we suspect that rarely would this structure be entirely accounted for in terms of “anomalous” host phonons.<sup>9</sup>

In this context we note that our observed guest frequencies of 12.5 and 17  $cm^{-1}$  (Figs. 1 and 2) are well below the lowest observed rotational lattice modes of the biphenyl and durene hosts,<sup>10</sup> but well inside their translational manifolds,<sup>11,12</sup> as required by Dettman and Ludwig’s model.<sup>13</sup>

Experiments have been performed on samples immersed in supercooled helium (1.8°K). The spectra were taken at a resolution of 0.5  $cm^{-1}$  on a Jarrell-Ash 1 m double grating monochromator (photographically and photoelectrically). The sample preparation will be discussed in full separately.<sup>4,5</sup> We only point out here that the crystals were of good to perfect optical quality, that the data are reproducible and that the nominal guest concentrations of 0.5%–1% are really *upper limits*, due to segregation upon crystallization, etc.

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## Coherence Length in the Isotropic Phase of a Nematic Liquid Crystal: *p*-Methoxybenzylidene *p*-*n*-Butylaniline\*

B. CHU, C. S. BAK, AND F. L. LIN

*Chemistry Department, State University of New York at Stony Brook, Stony Brook, New York 11790*

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In this Communication we report the results of an experimental study of the angular dependence of the intensity of light scattered by fluctuations of

the order parameter  $Q^1$  in the isotropic phase of a nematic liquid crystal, *p*-methoxybenzylidene *p*-*n*-butylaniline (MBBA). The intensity and spectrum of