

produces no emission,⁶ it is highly *unlikely* that the continuum results from an aluminum mono-hydroxide system. The combination of single and multiple collision studies suggests that the continuum emitter is a complex species which may be a metal hydrate or a compound formed in the complex metathetical oxidation of a hydrate precursor. In combination with recent matrix isolation studies of metal hydration,¹² the current work suggests formation of a complex involving an aluminum atom and several molecules of water or the rearrangement of a 1:1 aluminum-water collision complex which leads to the formation of both a metal-hydroxyl and metal-hydrogen bond.

Unfortunately, we find no evidence that previous laboratory researchers have considered or carefully eliminated the presence of water vapor in their systems.^{8,9} A survey of studies monitoring atmospheric concentrations indicates that the vast majority of water vapor present in the upper atmosphere is carried there by the payload rockets used in the seeding studies.⁶ It is also possible that the aluminum trimethyl experiments are plagued by water vapor produced in methyl group oxidation.

Finally, we should note that both the intensity distributions observed in multifarious seeding studies⁴ and theory¹³ suggest that the reaction of a weakly bound aluminum-water adduct with oxygen atoms may be the source of AlO formed in the upper atmosphere.⁶

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Observation of high-energy vibrational overtones of molecules in solids: Local modes and intramolecular relaxations

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In the last few years, the spectra of vibrational overtones¹ (at ~15–20,000 cm⁻¹) in large molecules have received considerable attention. The focus is on three problems dealing with the origin of relaxation at such high energies, the association of spectral band positions with the local modes (LM) in molecules, and the relevance of these spectra to possible selectivity in laser-induced chemistry.

Albrecht and co-workers^{2–4} using the technique of thermal lensing has identified overtones in *liquid* benzene and in several other aromatic liquids. Typically, the fifth overtone is around 6000 Å and the width (FWHM) is ~300 cm⁻¹. A similar transition has been found in *gaseous* benzene by Bray and Berry⁵ but with a width of 90 cm⁻¹ ascribed to broadening by intramolecular relaxation.⁶

We report here on the observation of CH-stretch-

ing overtones ($\nu = 2 - 6$) in *solid* naphthalene. The experiments offer the following: (a) the molecules can be frozen to low temperatures (1.3 K) so that the contribution of rotational states to the width of the resonance may be eliminated; (b) at 1.3 K the excitation is from $\nu = 0$ and hence spectral congestion can be avoided; (c) unlike gases and liquids polarization spectroscopy in solids assigns the bands; and finally (d) the inhomogeneous broadening may be realized by comparing the width of the overtone to that of nearby crystal electronic states.

Naphthalene (Aldrich Gold label) was extensively zone refined,⁷ and crystals (2–70 mm) were grown in a Bridgman furnace. The crystals were cooled carefully from room temperature to 1.3 K. The optical spectrometer used in these experiments is a home-built double beam apparatus¹⁰ whose photomultiplier output

was phase sensitive detected and digitally processed in order to obtain accurate line shape functions.

Figure 1 shows the overtone spectrum at 300 °K together with the least squares fit for the anharmonic relationship: $\Delta E(v)v^{-1} = A + Bv$, where $A = X_1 + B$. X_1 is the fundamental frequency and B is the anharmonicity. Using this relationship, we obtain $A = 3086 \pm 6 \text{ cm}^{-1}$ and $B = -55.8 \pm 1.4 \text{ cm}^{-1}$ for crystalline naphthalene, thus establishing good agreement with the liquid phase work.

The linewidth of the 0-5 transition at 300 K is 220 cm^{-1} , much narrower than the liquid line, but still broader than that of the CH overtone in benzene gas. At 1.3 K, however, the line shows a new feature; a splitting into two peaks whose apparent relative intensity is temperature dependent. The question now: Is the resonance homogeneously or inhomogeneously broadened (IB)?

To answer this question we must first eliminate two effects; the inhomogeneous crystal broadening and intermolecular vibrational splittings (IB). To disentangle the contribution of the former, we have located the triplet state in the same crystal (see Fig. 2). The 0,0 which exhibits a Davydov splitting of 10 cm^{-1} , is in excellent agreement with previous photoexcitation experiments.⁹ The first vibrational band shows a smaller ($\sim 5 \text{ cm}^{-1}$) splitting. If this picture applies to the overtone progression we can then neglect the IB due to crystal "irregularities" and vibrational resonance interactions. The splitting shown in Fig. 2, we therefore ascribe as due to different CH oscillators (say the two inequivalent sets of naphthalene).¹¹ The broadening (99 ± 7 and $147 \pm 5 \text{ cm}^{-1}$ from the computer fit results, Fig. 2) must have the contribution of both dephasing and energy relaxation processes. At room temperature the broadening increases and masks the splitting. To confirm that this temperature dependence is real and that the splitting is not due to different "local" crystallites in the long crystal used, we have taken room temperature spectra, 1.3 K spectra and then room temperature spectra again. No differences between the first and the last scan were detectable. The splittings will undoubtedly

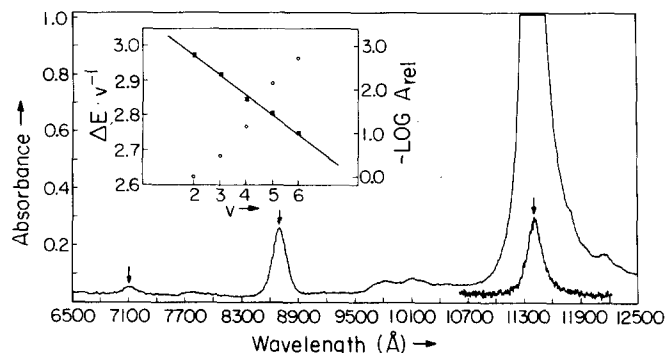


FIG. 1. Vibrational overtones of crystalline naphthalene. Only $v = 0 \rightarrow 3, 4$, and 5 are shown. Absorbance scale is relative to the background and the scan is of low resolution. The actual background absorption cannot be separated from scattering which in turn makes the absorbances reported here relative and dependent on the quality of the crystal. The repeat trace of $v = 0 \rightarrow 3$ was obtained with a thin crystal. In the insert, the relative absorbance is based on the absorbance at λ_{max} and $\Delta E v^{-1}$ is in $\text{cm}^{-1} \times 10^{-3}$.

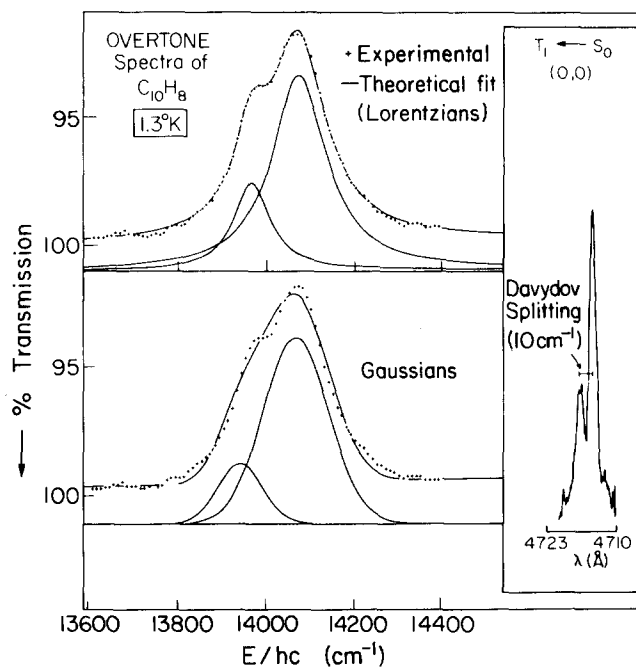


FIG. 2. The low-temperature, 0-5 overtone spectra, and the $T_1 \leftarrow S_0$ direct absorption of crystalline naphthalene. The temperature (measured from the vapor pressure of He) is 1.3°K and the resolution is 2 \AA for the overtone and $< 1 \text{ \AA}$ for the triplet-singlet absorption. The solid lines are the best computer fits, and the crosses are the digitized experimental data with a stepping resolution of 5 \AA . Transmission is relative to background.

edly contribute to the linewidth in the liquid and in the gas also. One must therefore be cautious about spectral changes in bandwidth as a function of v simply because the splitting might become smaller for higher v 's due to the difference in anharmonicity between modes.

The line shape (Fig. 2) at 1.3 K can be fit near perfectly to Lorentzians and not to Gaussians. The width of the Lorentzians compares very well with the benzene data.⁵ However, in the gas and liquid, there might be some low frequency molecular or reservoir vibrations that are populated at room temperature and will contribute to the width. In benzene, there are no very low frequency molecular modes, but the reservoir modes (e.g., librations) might heavily influence the liquid band contour, making it broader.^{4,12} In the solid at 1.3 K the ground state crystal modes will not contribute to the width, while those built on overtones will. Thus the line will be narrower than the liquid as is evident in Fig. 2. We have made preliminary analysis on the effect of crystal modes on these line shapes and find that although the line will narrow at 1.3 K relative to 300 K, the asymmetry of the line is a measure of the homogeneous width $(\pi T_2)^{-1}$, where T_2 is the total dephasing time. If T_2 is "long" ($\approx 10 \text{ ps}$) the line is asymmetric, while if T_2 is short ($\approx 0.3 \text{ ps}$), the line¹³ is essentially symmetric. With this in mind we infer that $T_2 \approx 0.1 \text{ ps}$ and that the overtone transition in the solid (no rotation!) is a limiting intrinsic one, resembling the equivalent CH modes of benzene in the gas phase. What we do not know at the moment is the contribution of T_1 to T_2 . Theoretically¹⁴ this contribution has been estimated classically to be negligible on the psec time

scale and on the order of 10^{-11} s by Robinson.¹⁵ The contribution of T_1 to T_2 is now experimentally under investigation.

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NOTES

A function for testing the reliability of long-range electron^a density in atoms

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The electron density in the outer region of ground-state two-electron atoms is found empirically to satisfy the equation

$$\ln \rho + 2(2\epsilon)^{1/2} r = m \ln r + b, \quad (1)$$

where ρ is electron density, ϵ is the first ionization energy, and b and m are adjustable parameters. Table I gives for representative two-electron atoms the range of radii for which graphs of $[\ln \rho + 2(2\epsilon)^{1/2} r]$ vs $\ln r$ are linear. (All subsequent references to graphs refer to ones of this type.) The density for each atom is computed from the most accurate scheme- P wave function of Thakkar and Smith.¹

In the range over which such a graph is linear the electron density satisfies the equation

$$\rho = C r^m \exp[-2(2\epsilon)^{1/2} r], \quad (2)$$

where C is an adjustable parameter. The graph is a very demanding test of Eq. (2), since the r -dependence of $\ln \rho$ is largely cancelled by that of $2(2\epsilon)^{1/2} r$. Nevertheless the standard deviations σ in Table I are small. The standard deviation is a statistical measure of the

fractional discrepancy between $\rho/\exp[-2(2\epsilon)^{1/2} r]$ and $C r^m$ in the linear region.

Recently Hoffmann-Ostenhof and Hoffmann-Ostenhof have proved that an upper bound to the long-range electron density is a function like that of Eq. (2), with m equal to $2Z/(2\epsilon)^{1/2} - 2$, where Z is the nuclear charge and ϵ is the ionization energy.² On the basis of a plausible physical argument they also suggest that when the screened nuclear charge $Z - n + 1$ (where n is the number of electrons) is used in place of Z , the resulting function describes the asymptotic behavior of the electron density.³ Table I compares the empirical value of m with that of $[2(Z - 1)/(2\epsilon)^{1/2} - 2]$, the expression for m in the Hoffmann-Ostenhof asymptotic density function for the case of two-electron atoms. The empirical m is 7% to 12% more negative than m for the Hoffmann-Ostenhof asymptotic function except in the case of $Z = 1$, for which the two values agree to within half a percent. By contrast the m values for all the upper-bound functions are positive numbers.

By appropriate choice of C' it is possible to make