

## Highly Resolved Spectra of Local Modes of Benzene

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Rotational cooling by supersonic expansion and laser labeling spectroscopy were used to obtain high-resolution fundamental and first- and second-overtone spectra of C-H stretches of benzene in a molecular beam. Rich fine structure in the spectra has been observed. Transformation from the "normal-mode" picture to the "local-mode" picture seems to occur between  $v=2$  and  $v=3$ . Vibrational lifetimes in local-mode bands exceed  $\approx 0.5$  psec.

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The familiar normal-mode (NM) picture describes well the small-amplitude molecular vibrations at low vibrational excitations. But as the vibrational energy is raised, the density of vibrational states increases rapidly, and anharmonic couplings between normal modes become important; the normal-mode picture then ceases to provide a good description of the vibrational motion. It was found, however, that for some molecules even at relatively high vibrational energies (10 000–25 000  $\text{cm}^{-1}$ ), there still exist well-defined peaks in the vibrational spectrum. They were identified as overtone vibrations confined largely to single bonds—for example, a C-H stretch. Such vibrations localized to single bonds are often known as local modes.<sup>1,2</sup>

Treated as diatomic vibrations, the energy levels of a local mode (LM) can be easily calculated.<sup>1,2</sup> Couplings between the LM and other modes, however, add fine structure to the LM spectrum. For a better understanding of high excited molecular vibrations, we would like to know how the vibrational spectrum changes from the NM to the LM picture as the vibrational energy increases. For small molecules, such as methane,<sup>3</sup> the spectra remain well resolved in the transformation from NM to LM. A few combination states of NM are nearly degenerate with the LM states; the couplings are weak and the spectral lines in a LM manifold are very sharp, corresponding to a lifetime more than 1 nsec. Larger molecules, with a much larger density of NM combination states interacting with the LM states, appear to have much broader LM spectral lines. Reported measurements on the C-H stretches of benzene showed that even in the transformation from NM to LM, the successive overtones seem to be always fairly broad, with widths in the tens of inverse centimeters.<sup>4</sup> We wonder whether the observed widths were the results of poor spectral resolution or actual lifetime broadening. In the former case, we could hope to improve the resolution and observe the fine structure; we could then obtain more information on the transition behavior from NM to LM.

In this Letter, we show that with the help of supersonic cooling of molecules and the nonlinear labeling spec-

troscopic technique,<sup>5</sup> it is indeed possible to obtain high-resolution spectra for the C-H stretches of benzene from  $v=1$  to  $v=3$ . Fine structures with a resolution of  $\sim 1$   $\text{cm}^{-1}$  have been observed in the spectra.

The normal vibrational modes of benzene in the ground electronic state are fairly well known.<sup>6</sup> There is a famous case of Fermi resonance between the C-H stretch  $\nu_{20}$  and the combination modes  $\nu_8 + \nu_{19}$  and  $\nu_1 + \nu_6 + \nu_{19}$ . This should yield three peaks around  $\nu_{20}$  in the  $v=1$  spectrum. At finite temperatures, however, hot-band transitions and rotational sidebands smear the peaks and make the spectral lines appear much broader. For higher overtones ( $v \geq 2$ ), more combination states are supposed to be nearly degenerate with the C-H stretch, and one expects to find more peaks in the spectrum sharing the oscillator strength of the C-H vibration. But if the LM character of the C-H stretch now dominates, the coupling between the C-H stretch and the nearly degenerate combination states will diminish, and the spread of oscillator strength to those combination states will be limited. In either case, the overtone spectrum can also be significantly broadened by the hot-band transitions and rotational sidebands at finite temperatures.

In order to reduce spectral congestion due to rotational sidebands and hot-band transitions, we used in our experiment the state-selective labeling spectroscopic technique<sup>5</sup> on a supersonic beam of benzene. The supersonic expansion of the benzene-seeded argon gas resulted in a rotational cooling of benzene to  $T_{\text{rot}} \approx 5$  K. This reduced the width of the rotational envelope of each vibrational transition ( $\propto \sqrt{T_{\text{rot}}}$ ) from the room-temperature value of 30  $\text{cm}^{-1}$  to 4  $\text{cm}^{-1}$ . The remaining hot-band transitions were further removed by the use of three-level state-selective spectroscopy, schematically shown in Fig. 1(a). Resonant two-photon ionization (R2PI) via the 38 608- $\text{cm}^{-1}$   $\tilde{A} \leftarrow \tilde{X} 6_0^1$  transition<sup>7</sup> was used to monitor the population of a particular rotational state (or a set of a few rotational states) of the ground vibrational state. If a certain excitation depleted this population, the ionization signal would drop. Thus, by scanning the ir pump laser



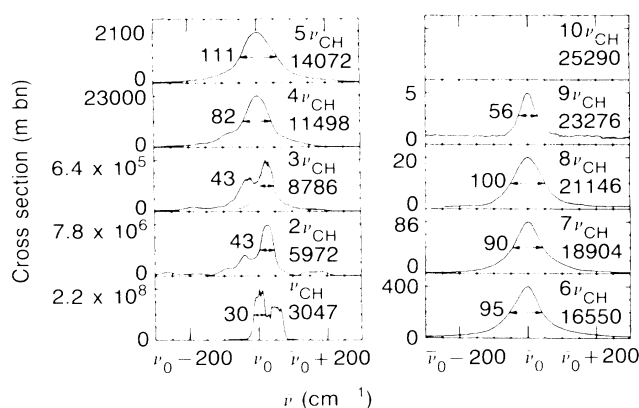


FIG. 3. Local-mode absorption spectra of room-temperature benzene gas, obtained with  $\approx 1\text{-cm}^{-1}$  resolution by Reddy, Heller, and Berry in Ref. 4. In each panel, the C-H stretching quantum number and band-center frequency appear at the upper right-hand side, and horizontal arrows mark FWHM linewidths.

peaks can be discerned, but the one at  $8827\text{ cm}^{-1}$  clearly dominates. Two characteristic features are noted in this spectrum. First, the peaks spread over a spectral range appreciably narrower than that of  $v=2$ . Second, the strong peak at  $8827\text{ cm}^{-1}$  has a width of  $10\text{ cm}^{-1}$  instead of  $4\text{ cm}^{-1}$ , suggesting either an overlap of several vibrational transitions or an appreciable increase of the homogeneous broadening. Our more detailed spectra<sup>8</sup> show that the former is the case.

The results of Fig. 2 indicate a characteristic change in the nature of the vibrational spectra between  $v=2$  and  $v=3$ , presumably due to the change from NM to LM in the description of the overtone vibrational states. With increasing vibrational excitation, the density of combination states grows rapidly. If the coupling of the C-H stretch with the combination modes remained unchanged (i.e., the C-H stretch did not become more localized), then with increasing  $v$ , the C-H stretching overtone spectrum would turn into a band with a rapidly growing overall width and number of peaks. While the  $v=2$  spectrum relative to the  $v=1$  spectrum in Fig. 2 does indeed appear this way, the  $v=3$  spectrum certainly behaves differently. It has clearly a narrower frequency spread with far fewer significant peaks than the  $v=2$  spectrum. Most of the oscillator strength shows up in a single peak. All these are indications that the C-H stretch has become "localized" at  $v=3$ ; the coupling between the C-H stretch and other modes has decreased significantly.

We can use a simple perturbation calculation to estimate the average coupling strength  $S$  between the C-H stretch and the nearly degenerate combination states. From the separations of the three peaks in Fig. 2(a), we find  $S \approx 25\text{ cm}^{-1}$  for  $v=1$ . For C-H vibrations at  $v=2$

and 3, the nearly degenerate combination states form a quasicontinuum with a density of states  $\rho$  that can be estimated by, for example, the Whitten-Rabinovitch (WR) approximation.<sup>9</sup> The overall spectral widths of the overtone bands are given by  $\Gamma \approx (2\pi/\hbar^2) |S|^2 \rho$ . For  $v=2$ , we obtain  $\Gamma \approx 30\text{ cm}^{-1}$  from Fig. 2(b),  $\rho \approx 10^3/\text{cm}^{-1}$ , and, hence,  $S \approx 0.07\text{ cm}^{-1}$ . For  $v=3$ , we have  $\Gamma \approx 10\text{ cm}^{-1}$ ,  $\rho \approx 10^5/\text{cm}^{-1}$ ,<sup>10</sup> and  $S \approx 0.004\text{ cm}^{-1}$ . The result here shows that the coupling strength  $S$  indeed decreases very rapidly as  $v$  changes from 1 to 3.

The picture deduced from our spectra differs from that of Ref. 4: We find that the LM bands contain many fine structures and the LM band envelopes are much narrower than was previously thought.

We expect that the C-H stretch would become increasingly localized with larger  $v$  so that the overtone bandwidth for  $v > 3$  is not likely to be significantly larger than the  $10\text{-cm}^{-1}$  width of the  $v=3$  band. Unfortunately, because of laser limitations, our state-selective spectroscopic technique is not sensitive enough to obtain overtone spectra with  $v > 3$ . Sibert, Reinhardt, and Hynes<sup>11</sup> have calculated higher C-H overtone spectra ( $v=5-9$ ) of benzene, and found an apparent bandwidth of  $\approx 50\text{ cm}^{-1}$ , in agreement with the room-temperature experimental result of Ref. 4. This is, however, much larger than the  $\approx 10\text{-cm}^{-1}$  width we would expect. It would certainly be interesting if the same calculation on the  $v=1-4$  bands could be done.

We have reported here a high-resolution study of how a vibrational mode of a typical large molecule changes its character from NM to LM with increasing excitation energy. This was made possible by the use of a state-selective nonlinear spectroscopic technique on a rotationally cooled molecular beam. The results indicate that the LM feature of the C-H stretch of benzene begins to prevail at vibrational excitations between  $v=2$  and  $v=3$ . The homogeneous linewidth of the LM spectra is not likely to exceed  $10\text{ cm}^{-1}$ , suggesting a vibrational lifetime longer than  $0.5\text{ psec}$ .

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