

## LETTERS TO THE EDITOR

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## COMMUNICATIONS

### Eigenstate resolved infrared–infrared double-resonance study of intramolecular vibrational relaxation in benzene: First overtone of the CH stretch

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The first eigenstate resolved, near the infrared spectrum of benzene in the region of the first C–H stretch overtone ( $6000\text{ cm}^{-1}$ ) has been obtained with an IR–IR double-resonance molecular beam optothermal spectrometer. Using a hierarchical tree analysis and level spacing statistics, we show that the intramolecular vibrational relaxation occurs nonergodically over at least seven different time scales ranging from 100 fs to 2 ns. © 1997 American Institute of Physics.

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#### I. INTRODUCTION

Since the pioneering work of M. Berry and co-workers,<sup>1</sup> benzene has been one of the most important model systems for the study of intramolecular vibrational relaxation (IVR) (see Refs. 2–4, and references therein). Recent experimental work has focused on jet-cooled samples in the region of the first and second overtones, near  $6000$  and  $8900\text{ cm}^{-1}$ , respectively.<sup>3,5</sup> Because of the linewidth of the lasers employed, the effective resolution of these experiments was a few  $\text{cm}^{-1}$ , allowing the study of IVR dynamics of  $2\nu_{\text{CH}}$  on time scales of  $\sim 1$  ps or less. The spectrum reported by Page *et al.*<sup>5</sup> shows the presence of at least 30 vibrational bands spread over a range of  $300\text{ cm}^{-1}$ . The bright state is believed to consist of a CH stretching excitation intermediate between local and normal mode motion.<sup>6</sup> Each peak in the spectrum represents a resonance in the early time dynamics which arises from the mixing of this vibration with a manifold of states produced by other in-plane vibrational modes. The survival probability calculated from this spectrum, reveals an IVR “lifetime” for the bright state of 100 fs. The qualitative features of the experimental spectra have been reproduced in theoretical models by Jung and Wyatt,<sup>2</sup> Zhang and Marcus,<sup>7</sup> and Iachello and Oss.<sup>8</sup>

Thanks to recent improvements in our molecular beam spectrometer,<sup>9</sup> we now have the sensitivity and the resolution to obtain an eigenstate resolved spectrum of the first overtone band of benzene, which allows us to extend the time interval over which IVR has been studied in this molecule by more than 4 orders of magnitude. To solve the spectral congestion problem we have used near-IR/mid-IR double resonance. This gives a spectrum originating from a single, assigned, lower rotational level of the ground vibrational state,

thus completely eliminating the inhomogeneous rotational contribution.

#### II. EXPERIMENT

The experiment has been carried out using an optothermal molecular beam laser spectrometer which has been described in detail in a previous paper.<sup>10</sup> Briefly, a 1% mixture of benzene in helium is expanded through a  $50\text{ }\mu\text{m}$  nozzle at a backing pressure of 60 psi (410 kPa). A molecular beam, formed by collimating the expansion with a 0.5 mm conical skimmer, impinges on a liquid He cooled bolometer which senses the change in the energy content of the beam. A few cm downstream from the skimmer, the beam is pumped with about 1 W of  $^{13}\text{CO}_2$  laser radiation at  $9.6\text{ }\mu\text{m}$  in a single, almost orthogonal, crossing. This is enough IR power to strongly saturate the  $\nu_{14} \text{ }^rQ_0(2)$  transition which is only 17 MHz from the center of the  $R_{30}$  line of the  $^{13}\text{CO}_2$  laser,<sup>11</sup> giving about  $10\text{ }\mu\text{V}$  of signal when the laser is chopped at 280 Hz. Further downstream, the beam interacts with  $1.67\text{ }\mu\text{m}$  radiation from a commercial F-Center laser<sup>12</sup> that probes the C–H stretch overtone. The interaction region is located inside a resonant cavity which enhances the circulating power by a factor of 100 in this wavelength region. A detailed description of the cavity is reported in Ref. 9. A V-type double-resonance signal is seen as a dip in the  $10\text{ }\mu\text{V}$  baseline generated by the  $\text{CO}_2$  laser only when the transitions pumped by the two lasers share the same lower level. The average  $\text{CO}_2$  laser frequency is locked to the peak of the bolometer absorption signal, yet some excess noise due to frequency fluctuations of the laser is still present. A special problem is posed by the fact that occasionally large frequency excursions of the  $\text{CO}_2$  laser occur, putting the laser off resonance with the molecular transition. This causes the

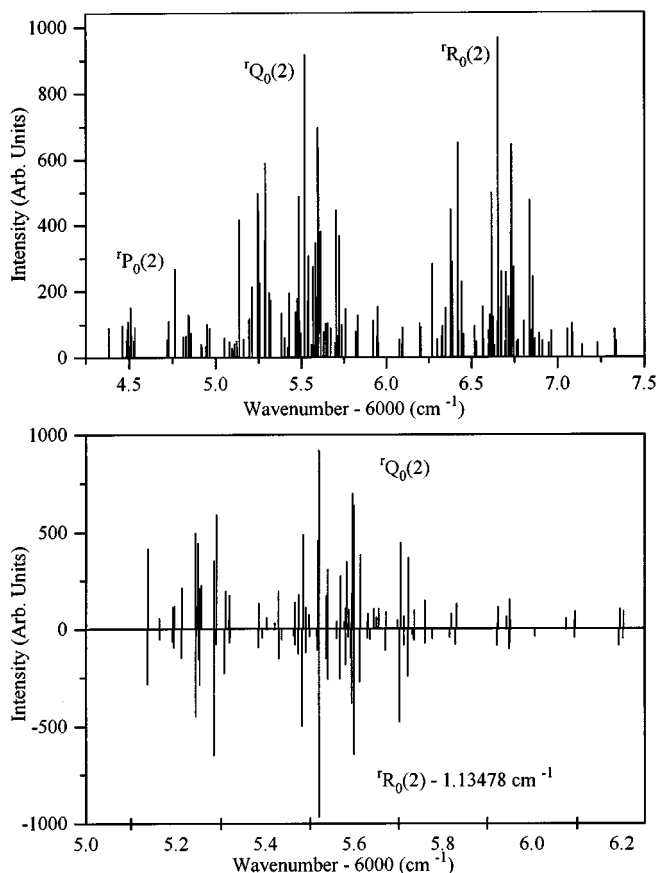


FIG. 1. Top panel: stick spectrum with all the observed double resonance transition from the  $J=2, K=0$  level. Bottom panel: the  $Q$  and  $R$  transitions enlarged and superimposed top-to-bottom for comparison.

baseline to shift down briefly, which could be mistaken for a double-resonance signal. Given the highly non-Gaussian character of this noise, two scans of the same spectrum were collected under the same experimental conditions, retaining only those features which appear in both spectra. For calibration purposes, the absorption spectrum of iodomethane has been collected in a White-type gas cell simultaneously with the benzene beam spectrum. A scanning 150 MHz confocal etalon is used to linearize the spectrum. Estimated absolute and relative accuracy of the calibrated spectrum based on the literature value of the iodomethane lines<sup>13</sup> are 5 and 1 MHz, respectively.

### III. RESULTS

In the top panel of Fig. 1 the double-resonance C–H stretch overtone spectrum of the feature centered at 6005  $\text{cm}^{-1}$  is shown. All the transitions originate from the  $J=2, K=0$  ground state. The  ${}^1R_0(2)$ ,  ${}^1Q_0(2)$ , transitions and the weaker  ${}^1P_0(2)$  are recognizable as separated clumps of about 60, 70, and 40 lines, respectively. Assignment of each spectral line to one of the three clumps has been made based on visual inspection of relative intensities and line positions, except for the regions where two clumps overlap. In the latter case, direct comparison between  $P$ ,  $Q$ , and  $R$  branches has been made by superposition of the strongest feature of each

branch, as shown in the bottom panel of Fig. 1 for the  $Q$  and  $R$  branches. Although this procedure is rigorously correct only if the IVR and rotational dynamics are separable, the observed spectra show striking similarities between the lines in each branch. This in turn means that, at least for these low  $J$  states, anharmonic coupling strongly dominates over Coriolis coupling, and that the relative shifts between the bright state and the bath states coupled to it do not significantly change with  $J$ . The standard deviation of the separation between corresponding lines in the  $Q$  and  $R$  branches ( $1\text{--}5 \times 10^{-3} \text{ cm}^{-1}$ , depending upon the criterion used to match those lines that do not have an immediately evident counterpart) is reasonably close to the value of  $2.5 \times 10^{-3}$  expected based upon the spread in  $\Delta B$  for the 20 perturbations observed by Pliva and Pine<sup>14</sup> in the  $\nu_{12}$  fundamental.

The observed density of coupled states for the central portions of the  $R$  and  $Q$  branches is very close to the value calculated (based on a harmonic Hamiltonian approximation<sup>15</sup>) for the density of bath states with the same symmetry as the bright state: 100 and 133 states per  $\text{cm}^{-1}$ , respectively. The same is not true for the  $P$  branch, which is about three times less intense due to the Hönl–London factor, nor for the wings where the intensity fades. When a significant fraction of the lines disappears into the noise, erroneous conclusions about the underlying dynamics may be derived. Therefore most of the observations reported below are based on the appearance of the  $R$  and  $Q$  branch portions mentioned above, where we are confident that almost all the coupled states are observed.

### IV. TREE ANALYSIS

The clustering of lines evident in Fig. 1, makes this spectrum a good candidate for a hierarchical analysis, which was developed in Ref. 16 and applied to an overtone spectrum of propyne in Ref. 17. The idea behind such an analysis is to artificially degrade the resolution of the observed spectrum by convoluting it with a Gaussian of large enough width ( $\Gamma$ ) such that no structure is resolved, and then to see how unresolved features split as  $\Gamma$  is decreased. This gives a quantitative assessment of the amount of clustering, and an estimate of the number of distinct time scales present in a spectrum. In terms of the standard tier model of IVR,<sup>18,19</sup> this analysis estimates the number of coupled tiers present in a spectrum. The graphical representation of such a tree, generated from the  $Q$ -branch of the spectrum in Fig. 1, is presented in the bottom panel of Fig. 2. For comparison, a tree from the spectrum of Ref. 5 is shown in the top panel. The time scales for the two panels range from approximately 150 fs (the top split of the tree in the top panel) down to approximately 40 ns (the last node on the tree in the bottom panel).

There is a direct correspondence between (i) large gaps between the nodes of a tree, the presence of distinct time scales in the spectrum, and the presence of tiers sequentially coupled to the bright state, (ii) the number of such gaps, the number of distinct time scales, and the number of successive tiers, (iii) the position of each gap, the magnitude of the corresponding time scale, and the effective coupling to the

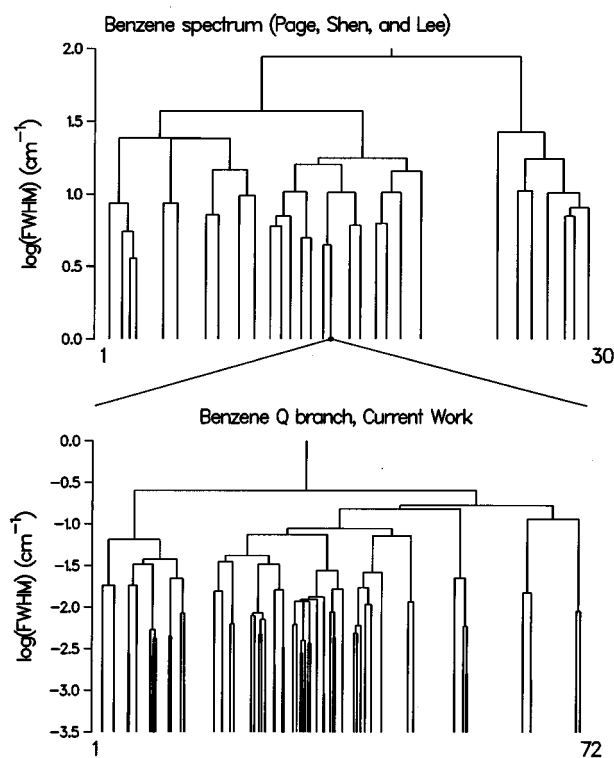


FIG. 2. Top panel: hierarchical trees generated for the spectrum of Page, Shen, and Lee (Ref. 5). ( $\nu=2$ ). Bottom panel: the tree for the  $Q$ -branch of the spectrum of Fig. 1. The dot near the bottom of the top tree and the lines emanating from it indicate where the tree of the bottom panel should be attached.

corresponding tier. Also, the number of states coupled to the bright state up to a certain tier is approximately equal to the number of nodes above the corresponding gap. Visual inspection of the trees in Fig. 2 reveals the following. There is a large gap between the top node and subsequent nodes for both trees. There are also significant gaps below the second and fifth nodes of the top tree indicating that there are roughly three and then six states in subsequent tiers. These numbers are close to those quoted in Ref. 5 for the number of IR active modes: 3 and 7 neglecting and including Fermi resonances, respectively. The tree for the present spectrum, which is shown in the bottom panel of Fig. 2, indicates that besides the two distinct groups discussed above, there are distinct gaps below nodes 3, 4, and 8 which in turn indicate a clumping of the spectrum into 4, 5, and then 9 groups. The results of the visual inspection can be quantified using the techniques discussed in Ref. 16. The rest of the analysis will focus on the region of the  $Q$ -branch where the density of observed states is close to the calculated value, as explained at the end of the previous section. This region includes lines 19 to 61, as measured from low to high energy.

Parsimonious tree analysis<sup>16,20</sup> has been used to find the number of distinct time scales present in the spectrum. A parsimonious tree replaces a particular tree with one where nodes can occur only at a fixed number of specified widths whose values minimize a suitably chosen error function.<sup>16,20</sup> The error function measures the “distance” between the par-

simonious tree and the actual tree. An elbow in the curve obtained from plotting the absolute error vs the number of allowed widths is expected when the number of time scales is properly identified.<sup>16</sup> A parsimonious tree analysis shows that there are *approximately* four distinct time scales in the middle portion of the  $Q$ -branch, indicating roughly four coupled tiers of states. These widths, 0.087, 0.042, 0.017, and 0.0063  $\text{cm}^{-1}$  from the bottom panel of Fig. 2, can be converted into the time domain to 0.17, 0.35, 0.85, and 2.3 ns. The longest time scale can be observed in the Fourier transform of this portion of the  $Q$ -branch where there is a set of distinct, somewhat weak recurrences at 2 ns.

## V. DISCUSSION

We have performed a number of statistical tests on the spectrum in order to extract information about the dynamics of benzene. Fourier transformation of the spectral autocorrelation function yields lifetimes which are about the same for all three observed  $J$  states ( $\approx 25$  ps), almost one order of magnitude longer than the estimate given by Page *et al.*<sup>5</sup> However a more careful inspection of the autocorrelation function reveals that two other time scales (about 100 ps and 1 ns) are involved. One very important question is whether any approximately good quantum numbers are still preserved on the time scale corresponding to the average level spacing ( $\approx 20$  ns). Classically, this corresponds to incomplete randomization of the vibrational energy into the bath of symmetry-allowed dark states, as opposed to the complete randomization expected for chaotic dynamics. In the case where no good quantum numbers except energy and angular momentum are left, level repulsion is expected according to the Gaussian orthogonal ensemble model (GOE) of Dyson.<sup>21</sup> Conversely, if there is a set of one or more hidden quantum numbers, a Poisson distribution of the energy levels is expected. We have observed that the spacing distribution in our case is reasonably well fit by a Poisson distribution, and even more so by a slightly modified version of it due to Brody<sup>22</sup>

$$P(S) = aS^\beta \exp(-bS^{\beta+1}), \quad (1)$$

where the additional parameter  $\beta$  is introduced in order to account for attraction/repulsion between the energy levels. The  $Q$  branch exhibits weak attraction (clustering) between the levels, as can be inferred from the small negative  $\beta$  parameter ( $-0.2$  overall,  $-0.1$  center portion) obtained in the fit, whereas the  $R$  branch follows overall a Poisson distribution, with some weak repulsion in the center portion ( $\beta = 0.2$ ). These observations are confirmed by the  $\Delta_3$  statistics<sup>23</sup> which also tests for remnants of long range order in the spectrum that could originate from GOE-type statistics. As shown in Fig. 3, the result is consistent with an almost perfect Poisson distribution for the  $R$  branch and a weak clustering for the  $Q$  branch. The deviation from a perfect Poisson distribution at long range allows us to estimate the number of sequences present in the spectrum to be about five, each one corresponding to different values of some set of quantum numbers whose nature and identity are at present unknown to us. In general, it's not surprising to observe that

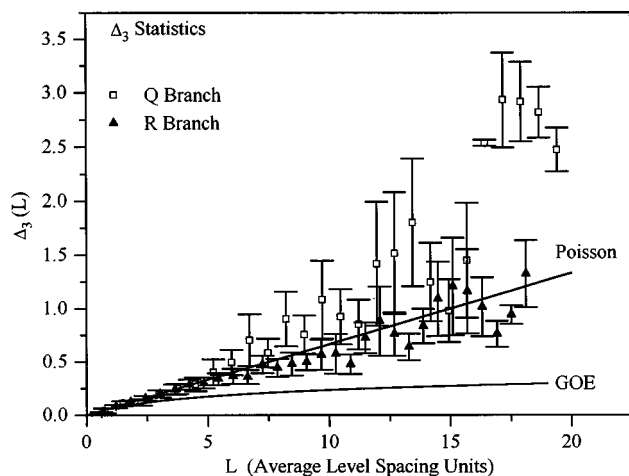


FIG. 3.  $\Delta_3$  statistics for the center portion of the  $Q$  and  $R$  branches of the spectrum of Fig. 1. The limiting cases of Poisson and GOE level distributions are also plotted.

the dynamics still exhibit some remnants of order. Indeed this has been previously observed for other molecules, such as  $\text{NO}_2$ , at a time scale on the order of 200 ps.<sup>24</sup> What is surprising in this case is that this happens for such a, comparatively speaking, big molecule as benzene, on a very long time scale (20 ns).

In summary, we have observed and rotationally assigned an eigenstate resolved spectrum of benzene in the region of the first C–H stretching overtone. Analysis of both this, and a previously observed<sup>5</sup> lower resolution spectrum reveals highly hierarchical dynamics with at least seven distinct time scales spanning 100 fs to 2 ns. The dynamics produce a highly mixed, but not statistical even at infinite time, distribution of vibrational excitation. These results may have important consequences for the assumptions made by Rice–Ramsperger–Kassel–Marcus and other statistical approaches to chemical reactions in large polyatomic molecules.

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