Hierarchical structure in the $3\nu_1$ band of propyne

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Several recent papers have investigated high resolution spectra of the fundamental and the first two overtones of the $\nu_1$ mode of propyne (the acetylenic CH stretch). These studies have provided important information about the nature of intramolecular vibrational redistribution (IVR), in particular, the role of anharmonic vs rotational coupling in the onset of IVR, a subject of a good deal of interest for many years. The most recent of these studies investigated the $3\nu_1$ band, which is at an excitation energy of 9700 cm$^{-1}$, with a calculated density of vibrational states of $\sim$150/cm$^{-1}$, putting this molecule well into the intermediate regime of IVR.

Reference 5 concentrated on the study of clumps of lines designated by $J'$ and the zeroth order quantum number $K'$, with $K'$ either 0 or 1. Due to difficulties with signal-to-noise for higher $J'$ at $K'=0$ and for all $K'=1$ clumps, most of their detailed analyses focused on $K'=0$ and $0 \leq J' \leq 4$. The major conclusions of Ref. 5 can be summarized as follows: (1) the experimental density of vibrational states is within approximately a factor of 2 of the calculated density of states, suggesting that a large fraction of the vibrational phase space is occupied; (2) the rate of decay out of the CH stretch does not depend on $J'$ for $K'=0$ (the lifetime is $\sim$320 ps), suggesting the decay is dominated by anharmonic coupling; (3) although the $J'=0$ spectrum shows GOE statistics, other do not, suggesting clustering and the utility of further analysis of the sort undertaken here; and (4) the experimental density of states increases approximately linearly with $J'$ at $K'=0$, suggesting that most of the rotational phase space is occupied, implicating strong Coriolis and centrifugal coupling. Since $(x,y)$ Coriolis coupling mixes states with $\Delta K=\pm 1$, it is expected that this plays an important role.

The purpose of this note is to supplement the analyses of Ref. 5 with the hierarchical analysis of Ref. 8. The idea behind the hierarchical analysis is to view a spectrum at all resolutions in a systematic fashion. The aim is to look for important time scales and groupings of the energy levels which may be used to further understand the nature of a spectrum.

A hierarchical tree is shown in Fig. 1. It was generated for the $J'K'=2$ clump by convoluting the stick spectrum with a Gaussian window function. The ordinate of Fig. 1 shows the width of the window, which is changed continuously to observe how the spectrum changes with resolution. The nodes on the tree demonstrate where new peaks appear as the resolution is changed. Since peaks split off other peaks, the tree can be used to define a genealogy of the lines of a spectrum. Groups of lines associated with smooth spectral features at a given level of resolution can be discerned from the tree by making a single cut of the tree.

Large gaps in the nodes of a tree are associated with distinct time scales, which would be observed if there were coupled tiers of states, a common model for IVR. One such gap is located between 0.5 and 0.25 GHz in Fig. 1. Cutting the tree of Fig. 1 all the way across above 0.25 GHz gives rise to four groups of eigenstates (1–5, 6–10, 11–22, and 23–25), which we will refer to here as “subclumps,” and we associate these subclumps with a first tier of states which are populated after the initial decay of the acetylenic CH stretch. Based on the evidence discussed above, the initial decay is driven by anharmonic coupling, and the aim of the rest of the Note is to assess the relative role of anharmonic vs rotational couplings at longer time based on the properties of subclumps.

The $J$ dependence of properties of the subclumps is investigated in Table I. The data in Table I was generated from trees like the one shown for $2_0$ in Fig. 1. The second column of Table I shows optimal groupings based on statistics presented in Ref. 8. These groupings are based on three types of statistics presented in columns 3–5. The statistics in columns 3 and 4 measure roughly the width of the subclumps, with higher values indicating narrower average widths. Column 5 shows the error inherent in assuming there are three distinct time scales present in each clump. The stronger the coupling between tiers of states the greater the error in assuming there are fewer time scales than what is needed to resolve all the levels (for $n$ lines there is a maximum of $n-1$ time scales of...
TABLE I. Statistics for propyne spectra.

<table>
<thead>
<tr>
<th>$J'$</th>
<th>Subclumps</th>
<th>Dim.</th>
<th>Clustering</th>
<th>Time scales</th>
<th>Lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>0.86</td>
<td>19.3</td>
<td>0.032</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0.91</td>
<td>53.7</td>
<td>0.019</td>
<td>1.08</td>
</tr>
<tr>
<td>3</td>
<td>4(5)</td>
<td>0.95</td>
<td>138.6</td>
<td>0.020</td>
<td>1.20</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>0.78</td>
<td>41.5</td>
<td>0.031</td>
<td>1.08</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>0.72</td>
<td>17.9</td>
<td>0.041</td>
<td></td>
</tr>
<tr>
<td>GME</td>
<td>0.16</td>
<td>1.0</td>
<td>0.90</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1The number of subclumps, or states in the first tier based on an examination of the statistics of Ref. 8. In one instance (30) one partitioning (5) is close to the optimal, and is listed in parentheses.
2This is a dimensionality criterion, the fraction of the variance in the data contained in five subclumps, as calculated using the measure of Sec. III A of Ref. 8.
3The degree of clustering as described in Sec. III B of Ref. 8, once again for five subclumps.
4Relative error in replacing the trees generated from the spectra with ones having only three time scales (Sec. III C of Ref. 8).
5Averages of the lifetimes (in ns) weighted by the number of lines in a subclump, for all subclumps with five or more lines. The lifetimes were estimated from the number of subclumps in column 2.
6Statistics in the strong mixing limit for 32 lines, the number in the $3\_1$ clump.

The numbers in Table I suggest there are well-defined tiers of states, with a simple structure for the initial tier at $J' = 2, 3,$ and 4 (small numbers of subclumps). An analysis of the error inherent in assuming a reduced number of time scales (column 5 of Table I) shows that there are three distinct time scales, indicating two intermediate tiers of states before a decay into the bath of states (the first time scale is the initial CH stretch decay). The statistics and the lifetimes of Table I show at best a weak dependence of the subclump structure on $J'$, with the peak being at $J' = 3$ for most of the measures. This suggests to us the following interpretation. The decay out of the subclumps is still dominated by anharmonic coupling, as it was for the initial decay of the CH stretch. However, there is evidence for rotational coupling based on the decrease of the measures after $J' = 3$. These additional couplings must be weak compared to anharmonic coupling, because $(x, y)$ Coriolis, which is presumed to be the major additional coupling, would have a noticeably stronger effect on the decays of the subclumps. This is because matrix elements scale as $J$, and the lifetimes should thus go down as roughly $1/J^2$ (centrifugal coupling would be even stronger). We have also investigated the decay of the second tier of states (sub-subclumps), but the number of lines in these groups is too small for us to have confidence in any conclusions drawn from these data.

In summary, it appears that the hierarchical analysis is a useful tool to supplement other types of analyses already applied to the $3\_1$ band of propyne in Ref. 5. It has allowed us to demonstrate that the major route out of the first tier is anharmonic coupling, a result that may not be too surprising considering that the number of states in the first tier is generally less than the number of lines in the $J' = 0$ spectrum (8), in one case only half ($J' = 2$). In the same way that the various clumps of lines designated by $J'_{K'}$ take the place of single lines when there is no coupling between modes, the subclumps in the nonzero $J'$ clumps can be viewed as replacing the single lines of the $J' = 0$ clump. Our analysis (Table I) also puts a lower bound on the time scale for the onset of Coriolis and centrifugal coupling, suggesting that anharmonic coupling is still the dominant mode of energy transfer through about 1 ns.

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7See, for example, T. Uzer, Phys. Rep. 199, 73 (1991), and references cited there.