Resonant two-photon ionization spectroscopy of naphthalene clusters

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Supersonic beam sources provide a rich variety of cluster species, when operated under appropriate expansion conditions.[1–6] High resolution spectroscopy with rotational analysis has been applied with considerable success to dimer species, resulting in detailed information concerning geometrical structure and dynamical processes.[4–6] To date, the only resolved structure observed for large molecular clusters was that reported by Hopkins, Powers, and Smalley[1] and by Langridge-Smith, Brumbaugh, Haynam, and Levy[2] for benzene trimers and tetramers. Discrete spectra were obtained in the S_1---S_0 transitions of these species, however, the lack of rotational resolution precluded detailed spectroscopic interpretation. Prior to supersonic beam studies, dimer resonance (exciton) interactions were extensively investigated in low temperature crystalline media, including naphthalene.[7]

In this communication we report well-resolved vibronic structure in the S_1--S_0 transitions of naphthalene trimers (N_3) and tetramers (N_4). Dramatic differences are observed between spectral structures associated with totally symmetric and nontotally symmetric monomer vibrational modes in the S_1 excited state. This provides unique information concerning resonance interactions and geometry of the clusters. The naphthalene cluster spectra are highly informative because the monomer transition moments for the origin and totally symmetric vibrational species are aligned along the long molecular axis, whereas the strong, vibronically active b_{3g} transition moments are short axis polarized. (Transitions are abbreviated by the vibrational mode number, the number of quanta in S_1 is designated by the superscript, and a bar above the mode number identifies b_{3g} modes.)

The pulsed supersonic molecular beam apparatus and time-of-flight (TOF) mass spectrometer were described elsewhere.[8] Output from a single dye laser was frequency doubled and scanned across cluster transitions in the region of the monomer S_1---S_0 transition. Naphthalene ($C_{10}H_8$) was introduced into a supersonic nozzle heated to 70 °C and under 40 psi He. The detection electronics were gated, with time delay appropriate to select the cluster ion of the desired mass. Expansion conditions and pulse energies were adjusted to minimize fragmentation of larger clusters, which otherwise contribute to the spectra. (Excess energy imparted to clusters by resonant two-photon ionization is far less than the anticipated ion dissociation energy.)

Mass resolved two-photon ionization spectra of N_2, N_3, N_4, and N_5 species are shown in Fig. 1, and transition energies are reported in Table I. Whereas N_2 transitions are inherently broad, N_3 and N_4 transitions are relatively sharp. The N_2 bands suggest an unresolved progression in a low frequency intermolecular mode, possibly associated with excimer formation. In contrast, Jonkman and Wiersma[9] reported for jet-cooled 1,1′-binaphthyl monomer, a corresponding discrete absorption system with exciton splitting of 21 cm^{-1}. The N_3 origin consists of two resolved components, split by 17 cm^{-1}. A single component is observed for the N_4 and N_5 (pentamer) species. The $\overline{8}_0^1$ transition of N_3 consists of a single sharp feature, whereas for N_4, it splits into four discrete components. Moreover, a similar pattern of splitting is observed in N_4 for $\overline{7}_0^1$, and the combination $\overline{8}_0^1,8_0^1$

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TABLE I. Naphthalene cluster energy levels (energies in cm^{-1}).

Assignment	Monomer	Dimer	Trimer	Tetramer	Pentamer
0,0	32 020	31 883[a] (128[b])	31 953	31 860[e]	31 867[a]
$\overline{8}_0^1$	+435	432(60[b])	418(34[c])	435(82[d])	394
$\overline{7}_0^1$	+911	917	891(40[c])	914(74[d])	
$\overline{8}_0^1,8_0^1$	+1 137	1 157(109[b])	1 137	1 160(81[d])	
$\overline{8}_0^1,7_0^1$	+1 422	1 431(147[b])	1 422	1 428(80[d])	

[a] Measured to band center, the origin may be at substantially lower energy.
[b] Full width at half-maximum intensity.
[c] Estimated separation between outer resonance interaction components, derived from analysis.
[d] Separation between outer resonance components measured from spectra.
[e] This is the band center derived from analysis of resonance interactions.

(not shown), although, the origin and 8_0^1 are essentially unsplit. The unsplit $\overline{8}_0^1$ transition for N_3, and the unsplit origin transition for N_4, suggest that one geometrical configuration predominates for each cluster size, whereas for many molecules, a variety of cluster conformations are present.[6,10] The lack of splitting in these transitions suggests that the (site) inequivalent interaction between the molecules in the clusters is relatively small or nonexistent. Therefore, the observed splitting can be associated with resonance (exciton) interactions between monomer units of the clusters. The 17 cm^{-1} splitting of the N_3 origin is consistent with the range of resonant pair interactions (3–15 cm^{-1}) observed in the crystal by Hanson.[7]

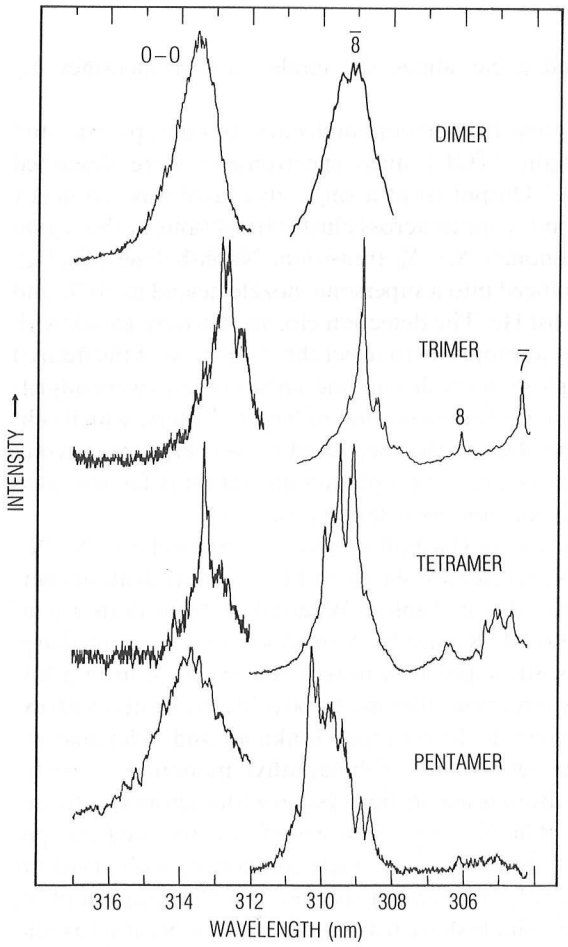

FIG. 1. Mass-resolved two-photon ionization spectra of naphthalene clusters. The weak origins and strong $\overline{8}_0^1$ transitions, which differ in intensity by a factor of 5 to 10, are normalized to about the same scale.

Each transition of the monomer should split into m components in the cluster N_m. Observation of multiplets for the origin in N_3 and for b_{3g} modes in N_4 confirms that the splittings are appreciable. Simple quantum mechanical calculations predict that only one component should be observed if all the monomer transition moments are aligned parallel. Therefore, we deduce that short axes of the naphthalene molecules are aligned parallel in N_3, whereas long axes are aligned parallel in N_4. The multiplet structure in the N_3 origin indicates that in N_3 the long axes are substantially nonparallel and the multiplet structure for short axis polarized $\overline{8}_0^1$ in N_4 indicates that the short axes are nonparallel for this molecule. These results are consistent with N_3 structures of the form, or with the triangular or pinwheel shapes suggested for benzene.[1] The N_4 cluster may have a herringbone structure, resembling crystals similar to naphthalene, however, this simple analysis is limited to information about angular orientation, exclusive of molecular position. We are currently extending investigations to isotopically mixed cluster species and to other vibronic transitions of the clusters in order to provide a quantitative interpretation of the resonance interactions and structure.

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