OVERVIEW

Neat fluorobenzene and mixed benzene-fluorobenzene clusters have been studied via resonant two photon ionization (R2PI) spectroscopy to measure ultraviolet spectra through fluorobenzene’s B2 → A1, 0̃0 vibrational transition at 37813 cm⁻¹. In separate experiments, the clusters were scanned from -200 cm⁻¹ to +80 cm⁻¹ relative to 37813 cm⁻¹. Spectra reveal reproducible sharp features for all dimers and trimers. Initial efforts have focused on interpretation of the spectra in terms of rigid structures and isomerization.

EXPERIMENTAL

• Resonant Two-Photon Ionization (R2PI) Spectroscopy
• Sources: C6H5F; 50 mol% C6H6/C6H5F
• Background pressure: 10⁻⁷ torr
• Carrier gas: He (10 atm)
• Resolution (C6H5F and C6H6/C6H5F): 0.11 cm⁻¹ (step-size limited)
• Transition (C6H5F and C6H6/C6H5F): C6H5F; B2 → A1, 0̃0; 37813 cm⁻¹

Similar to experiments reported in Ref. 1

RESULTS: Neat (C6H5F)n Clusters

Fig. A: Mass spectrum of neat Fm [(C6H5F)m] clusters at 528.915 nm, using Coumarin 540A dye.

Fig. B: R2PI spectra of the neat fluorobenzene monomer, dimer, and trimer at a resolution of 0.11 cm⁻¹. Sharp features are reproducible and distinct. The dimer peak at -18.6 cm⁻¹ is an artifact of trimer fragmentation.

Fig. C: Lower resolution spectra (0.60 cm⁻¹) of neat fluorobenzene clusters through (C6H5F)13. Spectra of clusters larger than the trimer tend to be broad and lacking in significant sharp features.

Peak positions and relative intensities of sharp features in the neat fluorobenzene dimer (above) and trimer (below). *The dimer peak at -18.6 cm⁻¹ shift originates from fragmentation of the trimer.

Fig. D: A cleaned C6H5F dimer spectrum. Cleaning was accomplished by subtracting ~1/3 times the raw trimer spectrum from the raw dimer spectrum (Fig B); it removed artifacts originating from fragmentation of the trimer. The spectrum can be interpreted as a superposition of four van der Waals progressions, with the origins and fundamental wavenumbers tabulated below. Standard errors are in parentheses.

<table>
<thead>
<tr>
<th>peak (cm⁻¹)</th>
<th>label</th>
<th>origin</th>
<th>% intensity</th>
</tr>
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<tbody>
<tr>
<td>-37.2 (1.4)</td>
<td>1</td>
<td>3.7</td>
<td>100</td>
</tr>
<tr>
<td>16.2 (0.6)</td>
<td>2</td>
<td>15.2</td>
<td>98</td>
</tr>
<tr>
<td>-7.1 (0.3)</td>
<td>3</td>
<td>6.2</td>
<td>94</td>
</tr>
<tr>
<td>4.1 (0.2)</td>
<td>4</td>
<td>3.2</td>
<td>92</td>
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</table>

Fig. D

Analyses: van der Waals Modes in the C6H5F Dimer

ANALYSIS: Representative Dimer Structures

Fig. H: One of the BF dimer local minimum energy structures identified via electronic structure MP2 calculations. The structure is viewed from the x axis (left) and z-axis (right).

Fig. I: One FF dimer local minimum energy structure based on MP2 calculations. Experimental results suggest the possibility of as many as four distinct FF isomers in the cluster beam.

RESULTS: Mixed (C6H6)m(C6H5F)n Clusters

Fig. E: Mass spectrum of mixed benzene-fluorobenzene clusters at 528.915 nm. In order, Fm, Bn, and F2 are labeled with asterisks. The small peak between “3” and “4” is F3.

Fig. F: R2PI spectra of the neat fluorobenzene benzene dimer and trimer at a resolution of 0.11 cm⁻¹. Clusters are excited and ionized through fluorobenzene’s B2 → A1 transition.

Fig. G: Lower resolution spectra (0.88 cm⁻¹) of mixed fluorobenzene benzene through seven-molecule clusters.

BETWEEN:

Peak positions (cm⁻¹) and relative intensities of sharp features in BF, BF2, and BF3. *Peaks marked with asterisks may provide evidence of fragmentation.

<table>
<thead>
<tr>
<th>peak (cm⁻¹)</th>
<th>label</th>
<th>origin</th>
<th>% intensity</th>
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<td>95</td>
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<td>-5.0 0.2</td>
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<td>0.4</td>
<td>38</td>
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<tr>
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<td>8</td>
<td>10.5</td>
<td>30</td>
</tr>
<tr>
<td>10.5 25.6</td>
<td>9</td>
<td>13.5</td>
<td>20</td>
</tr>
</tbody>
</table>

Fig. H

Fig. I

ADDITIONAL ANALYSIS:

Still in Progress

Still in Progress

• Sharp, reproducible features in the dimer and trimer spectra suggest that few isomers of these clusters are present. The F2 dimer spectrum has four van der Waals modes, indicating no more than four isomers.

• These features should be interpretable, given reliable structures and frequency data.

• Mixed BF2 spectra show evidence of fragmentation, which requires further analysis and corrections.

• A set of atom pair-pair potential energy parameters has been derived for a 12-9-6-4-1 potential on the basis of more than 150 MP2 single-point structure calculations. The minimum-energy dimer structures derived from these PES parameters do not appear to be realistic, but are useful as starting structures for MP2 calculations.

ONGOING WORK

Minimum-energy structures of the dimers and trimers are in the process of being identified.

Electronic structure calculations will explore the nature and fundamental frequencies of van der Waals modes in the dimers.

After correcting for fragmentation, BT dimer spectra will be analyzed in terms of the number of isomers present, their structures, and their van der Waals progressions.

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REFERENCES