Toward the Experimental Structure Determination of Larger Molecular Clusters: Application and Limitations of the Weak Interaction Model to the \((C_6H_6)_{13}^2 B_{2u} \leftarrow A_{1g}^0\) Spectrum

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The experimental \(B_{2u} \leftarrow A_{1g}^0\) spectrum of \((C_6H_6)_{13}^2\) was analyzed within the weak-interaction model using minimum energy structures calculated from six different potential energy surfaces. The coexistence of two isomers—both of \(C_3\) symmetry and with nearly equal populations—is supported. Structures predicted by two of the six potential energy surfaces are strongly favored. The transition dipole of benzene moieties within the cluster has a magnitude of \(~0.23\) Debye. Weak transition dipole–dipole interactions fall between \(-1.95\) and \(+2.24\) cm\(^{-1}\) and site shifts of ligand molecules range from \(-160.3\) to \(-153.8\) cm\(^{-1}\). Although the weak-interaction transition dipole–dipole model falls short of unambiguously determining isomeric structures of benzene-13, it establishes a solid foundation on which modeling can be based for determining structures of larger, high-symmetry, molecular clusters.

KEY WORDS: Molecular clusters; benzene clusters; weak-interaction model; structure determination; modeling.

INTRODUCTION

Two important motivations for studying neutral molecular cluster systems include determination of cluster structures and elucidation of intermolecular van der Waals (vdW) interactions. Benzene clusters have been the focus of both experimental [1–12] and computational [13–18] studies for a number of reasons. (1) Because benzene is the aromatic prototype, many
results from benzene cluster studies are applicable to general aromatic systems. (2) Benzene’s first excited electronic state is situated barely above 50% of the molecule’s ionization energy, making two-color resonance enhanced two photon ionization (R2PI) spectroscopy of the larger clusters possible (using a 308-nm ionizing photon) with minimum fragmentation [3, 4]. (3) Several 12-site atom-atom potential energy parameter sets applicable to benzene clusters have been developed, enabling correlation of experimental data with theoretical predictions [13, 16, 18–22].

Ultraviolet spectra of small benzene clusters, \((C_6H_6)_n, n \leq 4\), have been interpreted within the weak interaction model to determine underlying physical structures [7–12]; the model has also been applied to naphthalene clusters [23]. Despite these successes, prospects of determining larger cluster structures have been regarded as remote because the expected proliferation of isomers and of intermolecular interactions with increasing cluster size could result in congested spectra. Nevertheless, in special cases — i.e., when a specific cluster has few isomers all of which have high symmetry — experimental structure determination may be achievable.

The benzene-13 cluster represents the special case. Experimental spectra consistently support the conclusion that few (i.e., two) stable isomers exist within the cluster beam and that those isomers have high symmetry [3, 4]. Monte Carlo computations confirm these conclusions. Simulations using seven different potential energy surfaces (PES’s) consistently identify two stable isomers; the first has \(C_3\) symmetry and the second has \(S_6, C_3\), or \(C_i\) symmetry [13, 14].

Previously measured \(B_{2u} \leftarrow A_{1g}\) spectra of benzene-13 are shown in Fig. 1 [6, 24]; the two-color spectra were recorded on different days. The lower resolution (0.63 cm\(^{-1}\)) spectrum envelopes the sharper features of the higher resolution (0.20 cm\(^{-1}\)) spectrum. Four comments are in order. (1) Feature A of the higher resolution spectrum is represented by only a shoulder in the lower resolution spectrum. (2) It is believed that Features A, B, C, and D originate from surface ligands of a high-symmetry structure [3–6]. (3) The analog of Feature E is found in all \((C_6H_6)_{13}\) \(0_0^0\) and \(6_1^0\) spectra; its relative intensity is much more sensitive to expansion conditions (temperature) than Features A–D [3–6]. (4) The intensity maximum and width of Feature C are dependent on experimental resolution.

In this paper we report results of modeling both spectra in Fig. 1 within the weak interaction model. Computed structures derived from Monte Carlo simulations were used as initial configurations [13, 14]. Results support specific computational structures but fall short of precise structural characterization. Extensions to this work involving simultaneous modeling of the \(0_0^0\) and \(6_1^0\) spectra could result in unambiguous determination of benzene-13’s experimental structure.