Cluster Growth

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Isomer-Selective Vibrational Spectroscopy of Benzene–Acetylene Aggregates: Comparison with the Structure of the Benzene–Acetylene Cocrystal**

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Cocrystals with defined molecular composition can be synthesized by co-condensation of gaseous compounds in fixed molar ratios followed by multiple heating/cooling cycles. Cocrystals with 1:1 and 1:2 ratios and with different structures have been assembled in this way.[1,2] The basic structural motifs of the unit cell are, in principle, comparable to nanocrystals (clusters) synthesized in gas jets by adiabatic cooling. However, cooperative effects may lead to isomeric crystal structures that do not necessarily represent the global minimum structures of the clusters. But since supersonic jet cooling is a non-equilibrium process, higher-energy isomers are often formed, thus opening the possibility to study unit-cell motifs directly in the form of isolated clusters. Herein, we report the structures of small benzene–acetylene clusters and compare them to the structure of the 1:1 cocrystal.

Strong C–H···π interactions ($\leq 2.5\,\mathrm{kcal\,mol^{-1}}$)[3] have found broad interest owing to their importance for the stabilization of supramolecular aggregates, crystal packing, molecular recognition, and for the folding of proteins.[4–6] A typical example of such a strong C–H···π interaction is the T-shaped benzene–acetylene (BA) dimer. We decided to investigate benzene–acetylene clusters for direct comparison with the 1:1 cocrystal.[1] Herein, we present infrared spectra of BA_2, BA_3, and B_2A clusters. BA_2 forms two isomers in supersonic jets, but only one isomer has been previously characterized by IR spectroscopy.[7,8] We now report the IR spectrum of the other isomer for the first time. It has a double T-shaped structure that is also found in the 1:1 cocrystal along the *c* axis (Figure 1). This isomer might be the seed cluster in crystal growth.

Experimentally, IR spectra of the acetylenic C–H stretching vibration of benzene–acetylene aggregates have been observed in bulk solution,[9] argon matrixes,[10] and supersonic jets.[8] NMR spectroscopy measurements point to a close CH···π contact.[11] The structure of the 1:1 benzene–acetylene cocrystal[1] has a basic packing motif of nearest neighbors consisting of T-shaped BA arrangements (Figure 1).

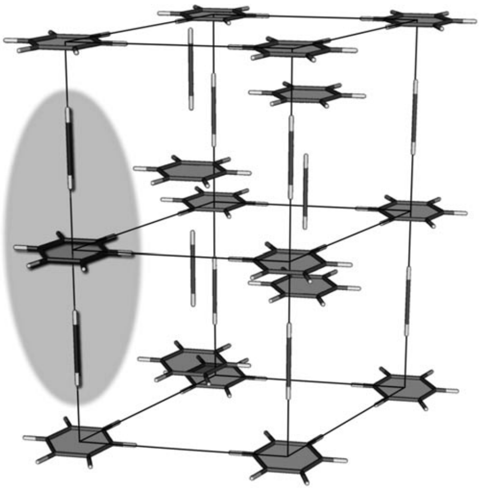

Figure 1. Solid-state structure of the benzene–acetylene 1:1 cocrystal[1] displaying the packing motif of T-shaped BA units, as determined by X-ray crystallography. Each unit cell is formed by three BA dimers.

Previous gas-phase studies have concentrated on small B_1A_m clusters ($m = 1, 2, 3$). Resonant two-photon ionization (R2PI) spectroscopy[7,8,12,13] revealed UV absorption bands at $+137\,\mathrm{cm^{-1}}$ (BA), $+127\,\mathrm{cm^{-1}}$ (BA_2, isomer 1), $+123\,\mathrm{cm^{-1}}$ (BA_2, isomer 2), and $+116\,\mathrm{cm^{-1}}$ (BA_3) relative to the 6_0^1 band of benzene[14] at $38\,606\,\mathrm{cm^{-1}}$. The blue shift indicates a reduced cluster stability in the electronically excited state owing to a lower π electron density in the benzene ring upon ππ* excitation, as in other clusters displaying hydrogen bonds to aromatic π systems.[15,16]

High-level ab initio calculations predict a T-shaped structure of BA. The acetylene molecule lies along the C_6 symmetry axis of the benzene ring and forms a π–hydrogen bond with the aromatic π system.[17–20] IR–UV double-resonance experiments support a T-shaped BA structure, whereas isomer 2 of BA_2 forms a ring-like structure.[8] Little is known about the structures of the other benzene–acetylene aggregates, which might correlate with the building blocks of the benzene–acetylene cocrystal.

Figure 2 shows the IR–UV ion-dip spectra of the two isomers of BA_2 with the UV laser tuned to $6_0^1 + 127\,\mathrm{cm^{-1}}$ (isomer 1) and $+123\,\mathrm{cm^{-1}}$ (isomer 2). Owing to fragmentation of the cluster ions, the spectra are observable only at the BA mass, but velocity map imaging allowed for an unambiguous assignment to BA_2.[9] Also shown are the calculated and scaled stick spectra of the most stable cluster structures, sorted by increasing energy from top to bottom.

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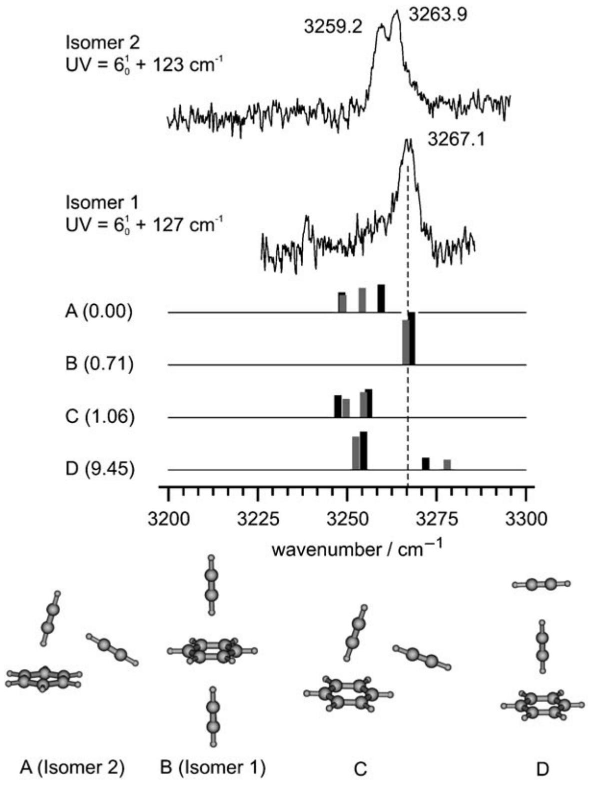

Figure 2. Isomer-selective IR–UV ion-dip spectra of isomers 1 and 2 of BA_2 (top two traces). Also shown are scaled stick spectra calculated at the RIMP2/TZVP (black) and RIMP2/TZVPP (gray) levels. Relative cluster energies (in kJ mol^{-1}) at the RIMP2/TZVPP level are given in parenthesis.

Isomer 2 shows two absorptions at 3259.2 and 3263.9 cm^{-1}. This isomer has been previously assigned to the ring structure A by comparison with quantum chemical calculations.[8] The first acetylene molecule forms a C–H···π hydrogen bond with benzene, while the second acetylene molecule binds to the π system of the C≡C bond of the first acetylene molecule and docks sideways to the C–H bonds of the benzene ring. Only structures A and C are predicted to feature two closely spaced absorptions of similar intensity, in good agreement with the experimental spectrum of isomer 2. They differ in a 30° rotation of the benzene ring. The overall spectral pattern is largely independent of the basis-set size (Figure 2).

By contrast, isomer 1 has only a single absorption at 3267.1 cm^{-1}, close to that of the T-shaped BA dimer at 3266.7 cm^{-1}.[8] This similarity points to a highly symmetric double T-shaped structure. The calculated spectra show a single absorption only for the second most stable isomer B (Figure 1), which indeed has a double T-shaped structure. The high symmetry leads to a coupling between the two antisymmetric C–H stretching vibrations of the two acetylene units, and only one IR-active vibration remains. We rule out isomer D because of its much higher energy and because of the red shift of its dominant IR band relative to the absorption of T-shaped BA. The structure of isomer 1 (B) reflects the BA_2 motif in the crystal structure (highlighted in Figure 1).

The double T-shaped arrangement is also found in the BA_3 cluster. Its IR–UV spectrum is displayed in Figure 3 and shows bands at 3252.7, at approximately 3261, and at 3268.6 cm^{-1}. In contrast to BA_2, only one isomer has been identified by UV spectroscopy.[7] The absorption at 3268.6 cm^{-1} is almost identical to that of T-shaped BA, so that one acetylene molecule is probably in a "BA-like" arrangement. Figure 3 also shows the calculated stick spectra of the most stable BA_3 isomers. Considering the agreement between calculated and experimental frequencies, only the spectra of structures A and C match the experiment reasonably well. They differ only by a 30° rotation of the benzene ring. The vibrational frequencies of structures B, D, and E are red-shifted by about 15 cm^{-1} compared to the experiment. Structure F is ruled out, as it does not predict the observed spectral pattern of three almost equally spaced absorptions of similar intensity. We therefore assign the spectrum of BA_3 to the most stable isomer A.

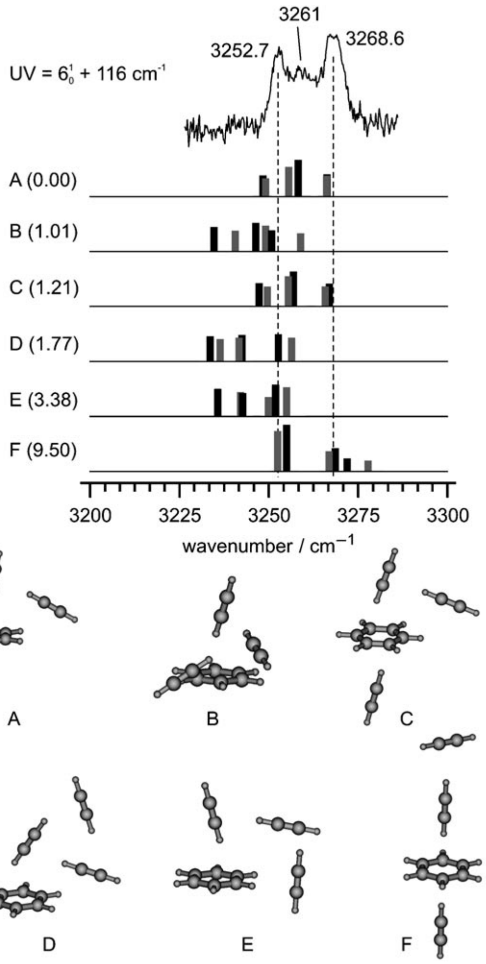

Figure 3. IR–UV ion-dip spectrum of BA_3 (top trace). Also shown are scaled stick spectra calculated at the RIMP2/TZVP (black) and RIMP2/TZVPP (gray) levels. Relative cluster energies (in kJ mol^{-1}) at the RIMP2/TZVPP level are given in parenthesis.

As mentioned above, cluster formation in supersonic jets is not strictly controlled by thermodynamics but is also influenced to a large extent by kinetics so that the cluster abundances are influenced by the formation probabilities. If we assume that BA_3 is formed by adding acetylene to an already formed BA_2 cluster, then both isomers of BA_2 are precursors to structure A of BA_3, whereas structures B and D can only be formed by adding acetylene to isomer 2 of BA_2. Therefore the formation of structure A has a higher probability, which supports our spectral assignment. The other way around, observing only structure A supports a stepwise aggregation mechanism in which acetylene is attached to preformed BA_m clusters rather than first forming acetylene clusters (e.g. the cyclic trimer) that are then attached to a benzene ring, which would exclusively lead to structure D of BA_3. We did not observe any other isomers of BA_3 even at higher acetylene concentrations of up to 10%.

Finally, Figure 4 shows the IR–UV spectrum of B_2A obtained on the B_2 mass channel and with the UV excitation laser set to $6_0^1 + 116\ \mathrm{cm}^{-1}$, together with calculated spectra of the six most stable structures. The experimental spectrum shows only a single absorption at $3259.4\ \mathrm{cm}^{-1}$. Its vibrational frequency is in good agreement with the most stable structure A. We can think of it as the combination of a T-shaped benzene dimer and a T-shaped BA cluster, that is, as a combination of the dominant B_2[21] and BA[8] structures. However, we cannot distinguish which of the moieties is formed first. We rule out structure B because of its higher energy and its higher vibrational frequency, which is close to that of the T-shaped BA cluster. All other structures are probably too high in energy.

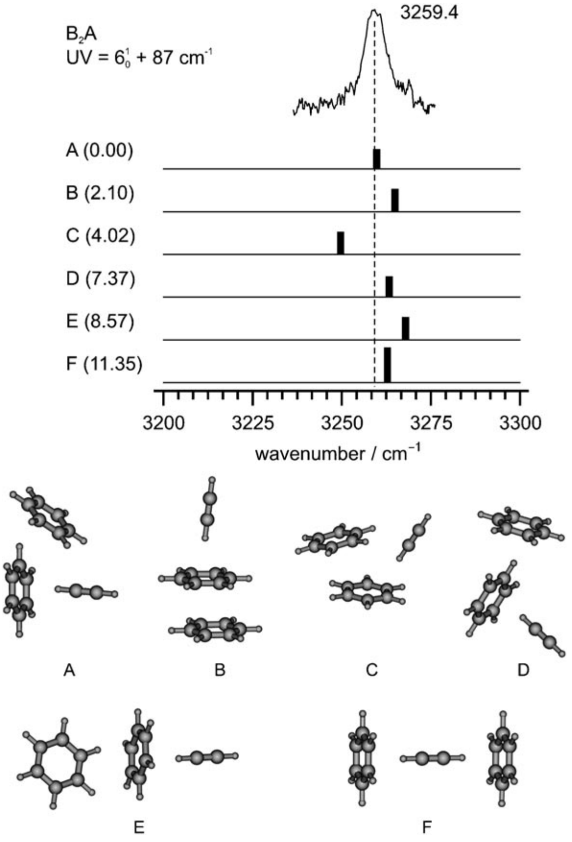

Figure 4. Isomer-selective IR–UV ion-dip spectrum of B_2A. Also shown are scaled stick spectra calculated at the RIMP2/TZVP level. Relative cluster energies (in kJ mol^{-1}) at the RIMP2/TZVPP level are given in parenthesis.

In summary, we have presented the isomer-selected infrared spectra of BA_2, BA_3, and B_2A. Isomer 1 of BA_2 has a double T-shaped structure, which is also found in the 1:1 cocrystal along the *c* axis. The structure of BA_3 points to a stepwise aggregation in which acetylene molecules are successively added to previously formed BA_m clusters. As mentioned above, the packing motif of the crystal structure is probably not the most stable structure of clusters of the same size. Therefore it is not unexpected that the most stable BA_3 and B_2A structures deviate from the arrangement of the molecules in the cocrystal. Investigations of larger clusters are required to determine whether the initial cluster structures undergo isomerization after the attachment of further molecules. The double T-shaped motif, for example, may survive in larger clusters, or it may disappear in favor of more compact structures. If it persists, then it might be the seed nucleus in the crystallization process of the BA cocrystal. By changing the expansion conditions, we are able to facilitate the formation of higher-energy isomers, such as isomer 1 of BA_2. Most importantly, we can differentiate between the various structures by our isomer-selective IR–UV double-resonance technique, assign structures on the basis of quantum chemical calculations, and compare them to the structure of the cocrystal.

Experimental Section

The basic principles of our IR–UV experimental setup were described in detail elsewhere.[22–24] A gas mixture of 0.8% benzene (Acros, >99%), 1.6% acetylene (Air Liquide, 2.6), and 97.6% helium (Air Liquide, 5.0) was expanded through the 300 μm orifice of a pulsed valve (Series 9, General Valve) at a stagnation pressure of 3 bar. The molecules cool down to a few Kelvin in the adiabatic expansion and form clusters.

The skimmed molecular beam (skimmer diameter 1 mm) crosses the UV excitation (LAS, frequency-doubled, ca. 10 μJ pulse^{-1}) and ionization lasers (FL 2002, Lambda Physics, 274 nm, ca. 120 μJ pulse^{-1}) at right angles inside the ion-extraction region of a linear time-of-flight (TOF) mass spectrometer. A pulsed IR laser beam (burn laser) is aligned collinear to the UV beams and fired 150 ns before the latter. The IR laser frequency is scanned over the vibrational transitions and removes vibrational ground-state population if resonant, while the UV excitation laser is kept at a frequency resonant with a vibronic transition of a single cluster isomer. By monitoring the ion mass signal as a function of IR frequency, cluster mass and isomer-selective infrared spectra, detected as ion dips, can be obtained.

IR laser light between 2800 and 4000 cm^{-1} is generated by difference frequency generation in a $LiNbO_3$ crystal and amplified by optical parametric amplification.[25] A spectrum of the NH stretching vibrations of ammonia was used for frequency calibration.

The RI-MP2 calculations were performed with the TURBOMOLE V5.9 program package.[26] Calculated harmonic vibrational frequencies were scaled by 0.9351 (TZVP basis set) or 0.9516 (TZVPP) to match the experimental absorption maximum of the asymmetric acetylene C–H stretching vibration of T-shaped BA.[8] All relative energies reported herein have been corrected for the zero-point energy (ZPE).

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