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π -Stacking, C–H/ π , and Halogen Bonding Interactions in Bromobenzene and Mixed Bromobenzene–Benzene Clusters

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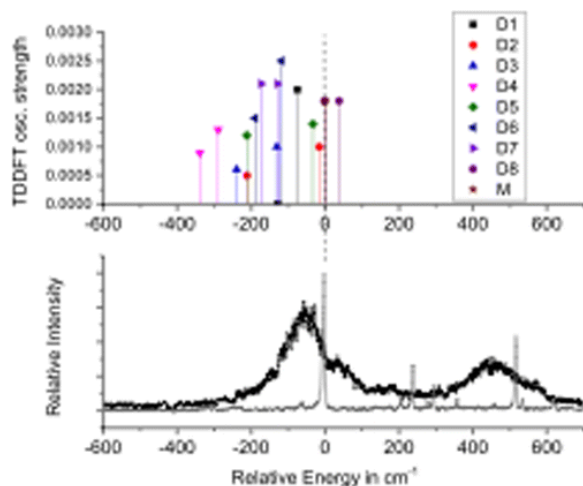
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Abstract



Noncovalent interactions play an important role in many chemical and biochemical processes. Building upon our recent study of the homoclusters of chlorobenzene, where π - π stacking and CH/ π interactions were identified as the most important binding motifs, in this work we present a study of bromobenzene (PhBr) and mixed bromobenzene-benzene clusters. Electronic spectra in the region of the PhBr monomer S_0 - S_1 ($\pi\pi^*$) transition were obtained using resonant two-photon ionization (R2PI) methods combined with time-of-flight mass analysis. As previously found for related systems, the PhBr cluster spectra show a broad feature whose center is red-shifted from the monomer absorption, and electronic structure calculations indicate the presence of multiple isomers and Franck-Condon activity in low-frequency intermolecular modes. Calculations at the M06-2X/aug-cc-pVDZ level find in total eight minimum energy structures for the PhBr dimer: four π -stacked structures differing in the relative orientation of the Br atoms (denoted D1-D4), one T-shaped structure (D5), and three halogen bonded structures (D6-D8). The calculated binding energies of these complexes, corrected for basis set superposition error (BSSE) and zero-point energy (ZPE), are in the range of -6 to -24 kJ/mol. Time-dependent density functional theory (TDDFT) calculations predict that these isomers absorb over a range that is roughly consistent with the breadth of the experimental spectrum. To examine the influence of dipole-dipole interaction, R2PI spectra were also obtained for the mixed PhBr...benzene dimer, where the spectral congestion is reduced and clear vibrational structure is observed. This structure is well-simulated by Franck-Condon calculations that incorporate the lowest frequency intermolecular modes. Calculations find four minimum energy structures for the mixed dimer and predict that the binding energy of the global minimum is reduced by ~30% relative to the global minimum PhBr dimer structure.

SPECIAL ISSUE

This article is part of the Terry A. Miller Festschrift special issue.

I Introduction

Noncovalent interactions are crucially important in a wide array of chemical and biochemical processes, influencing chemical reactivity and molecular structure,(1-10) molecular recognition and binding,(11-16) and the structure and function of biomolecules.(17-22) Important noncovalent interactions fall into a general class of donor-acceptor interactions and include hydrogen bonding, π - π stacking, CH/ π interactions, and halogen bonding. As these may exist in cooperation or competition,(23-27) probing the relative strength of these interactions has been the target of much effort from both experiment and theory.(17, 28-40) From our perspective, phenyl halide clusters are prototypical systems, where noncovalent interactions of different types are operative, including π - π stacking,(30, 38, 39, 41-48) CH/ π ,(18, 38, 49) and halogen bonding interactions.(3,

15, 49-56) The latter involves a halogen (X) atom as acceptor and arises from the polarized electron distribution around the halogen, which gives rise to a region of positive electrostatic potential on the axis of the C–X bond referred to as the “ σ -hole”.(33-35)

Clusters of aromatics have long been considered as model systems for understanding π – π stacking and CH/ π interactions.(57, 58) For example, Bernstein and co-workers conducted seminal studies of the R2PI spectra of toluene dimer through the S_1 state, which showed two features that were significantly broadened with respect to the monomer absorption.(28, 29, 59) These two features were attributed to different isomers, and this was confirmed using UV–UV hole-burning spectroscopy.(60) Wright and co-workers later examined larger toluene clusters using R2PI methods and found that the spectra were similar to that of the dimer, leading them to the suggestion that the favored (π –stacked) binding motif of the dimer formed the core of larger clusters.(59) Similar studies using R2PI and zero-kinetic energy (ZEKE) spectroscopy have been reported on substituted benzene dimers, including dimers of fluorobenzene,(61-68) chlorobenzene,(56, 69, 70) phenol, aniline,(71-74) and others.(37, 75)

The S_0 – S_1 spectroscopy and dissociation dynamics of the halobenzenes has been extensively studied,(76-81) and it is well-appreciated that the S_1 state is predissociative, being crossed by repulsive $n\sigma^*$ states that correlate with ground state products. In their early studies, Smalley and co-workers found that chloro- and bromobenzene could be detected using ns-scale R2PI methods through the S_1 state—however, iodobenzene dissociated too rapidly to be detected.(82) The measured lifetime of the S_1 state of PhCl is ~ 1 ns,(83) while that of PhBr is ~ 30 ps.(84) Recent ultrafast studies of chlorobenzene clusters (PhCl) $_n$ with $n = 2$ –4 found biexponential kinetics, with a fast (~ 170 fs) component that shortened with increasing cluster size, attributed to rapid internal conversion to the S_0 state, and a slow component (~ 1 ns) that lengthened with increasing cluster size, attributed to subsequent dissociation of the hot S_0 molecules.

We recently examined noncovalent interactions in clusters of chlorobenzene (PhCl) using resonant two-photon ionization (R2PI) spectroscopy in the origin region of the S_0 – S_1 ($\pi\pi^*$) state of the monomer. The R2PI spectra of PhCl clusters exhibited a broadened spectrum whose center was red-shifted from the monomer absorption, and was similar for all cluster sizes examined (up to the tetramer). For the dimer, electronic structure calculations at the M06-2X/aug-cc-pVDZ level found five minimum energy structures, four π -stacked structures and one T-shaped structure bound through CH/ π interaction; no minima corresponding to halogen bonded structures were identified. The calculated Time Dependent Density Functional Theory (TDDFT) spectra revealed that these isomers absorb over a broad range, and the calculated absorptions were red-shifted with respect to the monomer transition. Additional spectral broadening was found to arise from Franck–Condon activity as a result of the significant geometry change in the two electronic states, where electronic excitation induces a transition from a parallel displaced to sandwich structure with a reduced separation of the two monomers.

Building upon our previous study of chlorobenzene clusters,(70) the present work highlights the study of noncovalent forces in bromobenzene and mixed bromobenzene–benzene clusters, using R2PI spectroscopy. Due in part to the short lifetime of the S_1 state of the PhBr monomer, we are not aware of any prior studies have examined the spectroscopy of clusters of PhBr. Our experimental results are supported by electronic structure calculations based upon density functional theory (DFT) and post-Hartree–Fock (e.g., CCSD(T)) methods in concert with correlation-consistent basis sets. In comparison with chlorobenzene, we expect halogen bonding to become more important in bromobenzene clusters, due to the increased depth of the σ -hole on bromine.

II Experimental and Computational Methods

Our experiments utilized a linear time-of-flight mass spectrometer (TOFMS) coupled with a supersonic molecular beam source, which has previously been described in detail.(85) A mixture of bromobenzene in He, generated

by passing the high-purity gas at a pressure of typically $\sim 1\text{--}2$ bar over a sample of bromobenzene held in a temperature-controlled bath, was expanded from the 1.0 mm diameter nozzle of the pulsed valve and passed through a 1.0 mm diameter skimmer into the differentially pumped flight tube of a one-meter linear TOFMS. The flight tube was evacuated by a 250 L/s turbomolecular pump, with a gate valve used to isolate the detector, which was kept under vacuum at all times. The main chamber was evacuated with a water-baffled diffusion pump (Varian VHS-4). With the nozzle on, typical pressures were $\sim 5 \times 10^{-5}$ mbar (main chamber) and $\sim 1 \times 10^{-6}$ mbar (flight tube).

Ionization was initiated by a 1 + 1 R2PI scheme, with laser light near 270 nm generated from frequency doubling in a BBO crystal the output of a dye laser (Lambda-Physik, Scanmate 2E), pumped by the third harmonic of an Nd:YAG laser (Continuum NY-61). The laser was operated on a C540A dye, giving typical output pulse energies of ~ 1 mJ in the doubled beam, which was loosely focused with a 1.0 m plano-convex lens into the chamber.

Ions were extracted and accelerated using a conventional three-plate stack, with the repeller plate typically held at +2100 V, the extractor plate at +1950 V, and the third plate at ground potential.(85) The ions traversed a path of 1 m prior to striking a dual chevron Microchannel Plate (MCP) detector. The detector signal was amplified ($\times 25$) using a fast preamplifier (Stanford Research SRS445A), and integrated using a boxcar system (Stanford Research SRS250) interfaced to a personal computer. An in-house LABVIEW program controlled data acquisition and stepped the laser wavelength; typically, the signal from 20 laser shots was averaged at each step in wavelength.

To support our experimental findings, electronic structure calculations were performed using the Gaussian 09 software package on the MU Pere high speed cluster.(86) Full geometry optimizations were carried out using DFT (M06-2X) with an aug-cc-pVDZ basis set, with single point CCSD(T) energies obtained for selected structures. Prior computational studies on related systems(17, 32, 37) have extensively benchmarked the performance of DFT methods against high level post-Hartree–Fock ab initio single reference methods. The Minnesota meta-GGA (generalized gradient approximation) hybrid functional M06-2x, among other methods, provides a good cost-to-performance ratio,(32) and the aug-cc-pVDZ basis set performs well in calculating the counterpoise correction.(32) Our calculated binding energies were corrected for zero point energy (ZPE), with the counterpoise method used to correct for basis set superposition error (BSSE).

Time-dependent DFT (TDDFT) methods based on range-separated hybrid and meta-GGA hybrid functionals were used to calculate the electronic spectra of the clusters and the optimized geometry of the S_1 states. Methods employed included the range-separated hybrid functional ω B97X-D,(87) the meta-GGA hybrid functionals M06 and M06-2X,(88) and CAM-B3LYP,(89, 90) all with an aug-cc-pVDZ basis set. The performance of the ω B97X-D and M06-2X methods for electronic excitations, including Rydberg and charge transfer excitations, have previously been benchmarked.(91)

III Results and Discussion

Representative R2PI spectra of the bromobenzene monomer, dimer, and trimer in the region of the origin band of the monomer $S_0\text{--}S_1$ ($\pi\pi^*$) transition are displayed in Figure 1. Note that the electronic spectroscopy of the monomer has previously been studied.(69, 92-95) Focusing on the region of the origin band, the spectra for the clusters show a broad absorption which peaks to lower energy as compared to the monomer. This finding is similar to that observed for chlorobenzene(70) and related systems, including toluene and fluorobenzene.(28, 29, 69, 75) Based upon the previous work, we attribute this broadness primarily to the presence of different isomers and unresolved vibrational structure in Franck–Condon active modes. Other contributing factors should include the presence of multiple isotopomers (^{79}Br , ^{81}Br), transitions arising from vibrational excited levels (“hot bands”), and lifetime broadening. We rule out cracking of larger clusters as a source of this broadening, as

spectra of the dimer obtained at lower seed ratios, where the signal associated with the trimer and higher clusters has disappeared, still retains the same appearance (Figure S1).

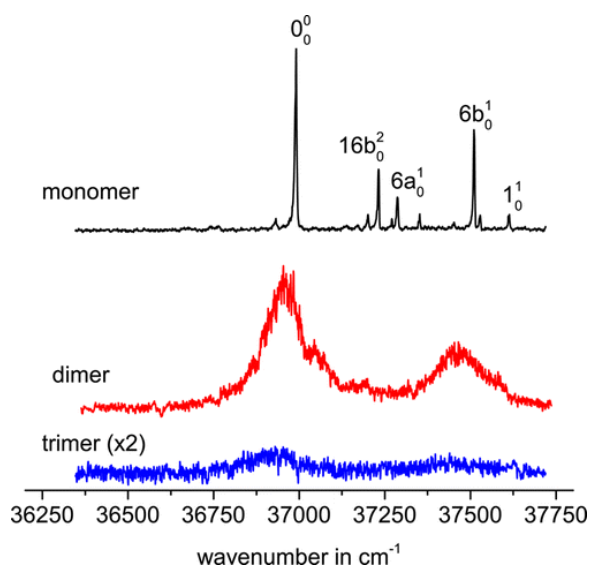


Figure 1. Resonant two-photon ionization (R2PI) spectra of mass-selected bromobenzene monomer, dimer, and trimer in the region of the origin band of the S_0-S_1 ($\pi\pi^*$) transition of the monomer. Monomer assignments are taken from ref 82

As an aid in characterizing the expected isomers, we employed DFT calculations at the M06-2X/aug-cc-pVDZ level, with geometry optimizations initiated from a variety of starting geometries that loosely corresponded to π -stacked, C–H/ π , and halogen–bonded structures. Eight minimum energy structures (D1–D8) were found for the bromobenzene dimer, and these are shown in Figure 2; noted are the calculated binding energies, counterpoise and ZPE corrected. Dimers D1–D4 are π -stacked with a parallel–displaced structure.^(17, 32, 39, 40) As the planes of the two monomers are separated by ~ 3.3 Å, the two Br atoms are not in close van der Waals contact, and these four π -stacked isomers differing in the relative orientation of the Br atoms have calculated binding energies between roughly -19 and -23 kJ/mol. D5 is a T-shaped isomer reflecting interactions of the C–H groups of one monomer with the π -system and Br atom of the other, and this dimer has a calculated binding energy roughly one-half that of the π -stacked isomers. In all, D1–D5 are similar to those identified for chlorobenzene; however, a key difference is the existence of the halogen bonded structures D6–D8. D6 and D7 correspond to above-atom and above-bond structures, respectively, where the σ -hole of the Br atom of one monomer interacts with the π -system of the other. These exhibit binding energies similar to that of D5. Finally, D8 corresponds to a side-on interaction of the 2 Br atoms—according to our calculations, this dimer exhibits the weakest binding.

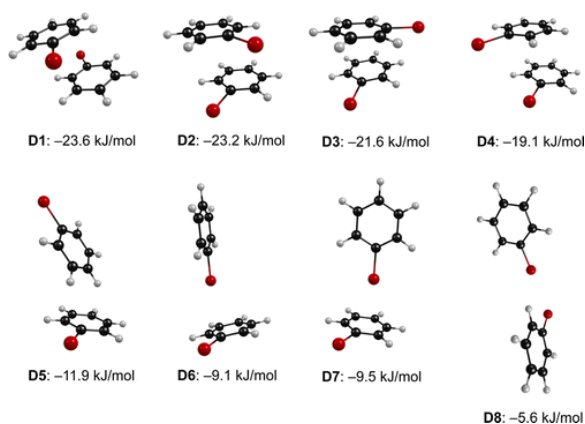


Figure 2. Optimized structures (D1–D8) and binding energy for the bromobenzene dimer, calculated at the M06-2X/aug-cc-pVDZ level of theory. The binding energies are counterpoise and ZPE corrected.

In prior studies of chlorobenzene dimers, we found that the M06-2X/aug-cc-pVDZ binding energies were overestimated with respect to high level single reference ab initio benchmarks, which in turn were in good agreement with available experimental data. Here, a counterpoise corrected CCSD(T)//M06-2X/aug-cc-pVDZ calculation of representative π -stacked (D1) and halogen-bonded (D6) dimers using ZPE corrections at the M06-2X/aug-cc-pVDZ level yielded binding energies of -16.7 (D1) and -6.9 (D6) kJ/mol, indicating that the M06-2X binding energies are too large by ~ 25 – 30% . To compare among different DFT methods, we carried out calculations of a representative dimer, D1, at the B97D and M05-2X levels of theory, which were previously benchmarked for similar systems.⁽³²⁾ The calculated (CP and ZPE corrected) binding energy at the M05-2X/aug-cc-pVDZ level was identical to that calculated with M06-2X (Figure 2), while the B97D/aug-cc-pVDZ calculation yielded a binding energy of 19.9 kJ/mol, roughly 15% smaller.

Representative calculated TDDFT (TDCAM-B3LYP/aug-cc-pVDZ) spectra of the bromobenzene dimers D1–D8 and monomer are shown in Figure 3, along with the experimental spectra of the monomer (gray) and dimer (black). The TDDFT spectra are shown as stick spectra, and the calculated energies have been scaled to match the experimental energy of the S_1 state of the monomer—the zero of the energy scale shown is thus referenced to the monomer origin transition. Note that the unscaled TDDFT vertical excitation energies and oscillator strengths are provided in Table S1 in the Supporting Information. The calculated spectra of the dimers show two absorptions split by an exciton splitting that is isomer dependent. In all dimers except D8, the calculated electron transitions are predicted to lie to lower energy (i.e., are red-shifted) compared to the monomer absorption. For the π -stacked dimers, the red-shift changes systematically with the relative alignment of the monomer dipoles, being largest for D4. The calculated spectra of the global minimum, dimer D1, lies closest to the peak in the experimental spectrum, and the absorptions of various isomers occur over a range that, when scaled, is roughly similar to that observed experimentally. We carried out additional TDDFT calculations on the bromobenzene monomer and dimer D1, using the ω B97X-D,⁽⁸⁷⁾ M06,⁽⁸⁸⁾ and M06-2X functionals,⁽⁸⁸⁾ and the results are shown in Figure S2. With the exception of the M06 method, there is little variation in the relative calculated oscillator strengths, exciton splitting, and red-shift.

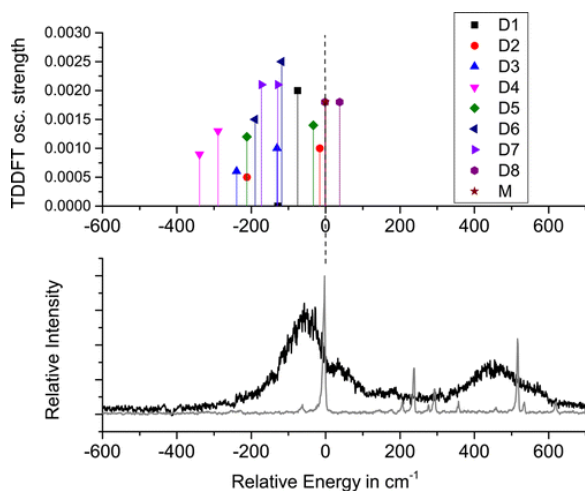


Figure 3. Calculated TDDFT (TDCAM-B3LYP/aug-cc-pVDZ) spectra of the bromobenzene dimers shown in Figure 2. The calculated energy has been scaled and referenced to the observed position of the origin band of the monomer. The lower panel shows an expanded view of the experimental R2PI spectra of the bromobenzene monomer (gray) and dimer (black).

As a validation of the TDDFT calculations, we consider results for a simpler but related system, $\text{PhCl}\cdots\text{NH}_3$. Here it is well-known from several R2PI studies that the complex displays a sharp origin band shifted by 76 cm^{-1} to the blue of the monomer origin.⁽⁹⁶⁾ Scaled TDM06-2X calculations of the two possible σ -ortho complexes, which cannot be distinguished on the basis of electronic spectroscopy, reproduce this shift to within 10 cm^{-1} , as shown in Figure S3 in the Supporting Information.

The TDDFT optimizations shed light on Franck–Condon (FC) activity expected in the electronic transitions. The optimized structures of the lowest lying excited electronic state of dimers D1, D5, and D6 at the TDM06-2X/aug-cc-pVDZ level are shown in Figure S4. For dimer D1, calculations predict that electronic excitation induces a rearrangement from a parallel-displaced structure to a sandwich structure, with the distance between the monomers decreasing from ~ 3.3 to $\sim 3.0\text{ \AA}$. This is similar to previous findings for related systems.^(97, 98) As a consequence of this geometry change, significant FC activity is expected in low frequency torsional modes that involve displacement of the two monomer subunits. Dimer D5 also undergoes a large geometry change, from a T-shaped to more parallel structure, due to the weakening of the C–H/ π interaction in the excited ($\pi\pi^*$) state. In contrast, halogen-bonded structure D6 undergoes a relatively small geometry change upon electronic excitation. These points are discussed in more detail below in calculations on the mixed bromobenzene–benzene dimer.

In addition to inhomogeneous structure in the S_0 – S_1 spectrum arising from the presence of multiple isomers and FC activity, homogeneous broadening must also be present. While ultrafast studies of bromobenzene clusters have not been reported, ultrafast experiments on chlorobenzene clusters show a biexponential decay with a short lifetime component of $\sim 200\text{ fs}$.⁽⁵⁶⁾ As discussed above, it is known that the S_1 lifetime of bare bromobenzene is of order 30 ps , some 30-fold shorter than isolated chlorobenzene.⁽⁸⁴⁾ To model the effects of homogeneous broadening, we have simulated the rotational structure of the S_0 – S_1 transition of one ($^{79}\text{Br}, ^{79}\text{Br}$) isotopomer a representative dimer (D1) using the calculated (TD)DFT rotational constants. Figure S5 (Supporting Information) shows a stick spectrum of the predicted band (upper panel) and a spectrum convolved with a 0.2 cm^{-1} Lorentzian line width (lower panel). Clearly, the expected level of homogeneous broadening in this system is sufficient to wipe out the vestiges of rotational structure.

To gain additional insight into noncovalent interactions and the origins of spectral broadening in this system, we carried out experiments on mixed bromobenzene–benzene clusters. Figure 4 shows representative R2PI spectra

of the bromobenzene monomer, bromobenzene–benzene (PhBr⋯Bz) dimer, and PhBr⋯(Bz)₂ trimer in the region of the origin band of the monomer S₀–S₁ (ππ*) transition. In comparison with the bromobenzene dimer, the mixed PhBr⋯Bz dimer displays a broadened feature that peaks slightly to higher energy (blue-shifted) with respect to the monomer origin band and displays some structure (lower panel of Figure 4). Calculations reveal four minimum energy structures for the mixed dimer, and these are shown in Figure 5, while Figure 6 displays the calculated and scaled TDDFT spectra of these complexes at the TDCAM-B3LYP/aug-cc-pVDZ level, using the protocol described above. The unscaled TDDFT vertical excitation energies and oscillator strengths are provided in Table S2 in the Supporting Information.

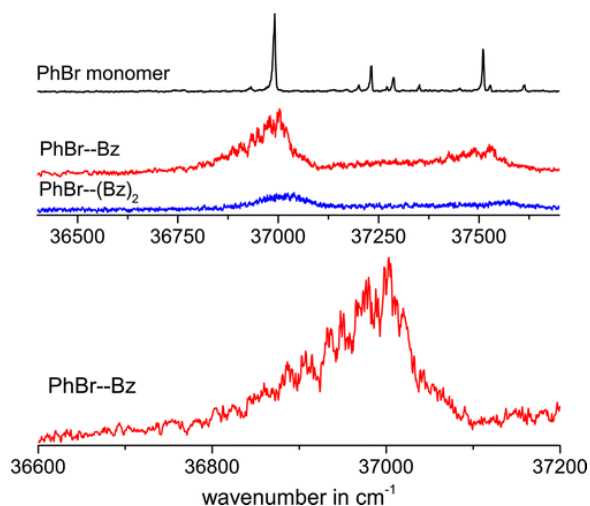


Figure 4. Resonant R2PI spectra of mass-selected bromobenzene monomer and mixed bromobenzene–benzene dimer and trimer in the region of the origin band of the S₀–S₁ (ππ*) transition of the monomer.

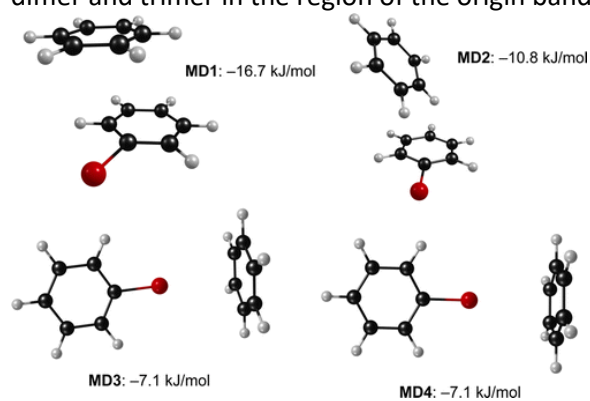


Figure 5. Optimized structures (MD1–MD4) and binding energy for the mixed bromobenzene–benzene dimer, calculated at the M06-2X/aug-cc-pVDZ level of theory. The binding energies are counterpoise and ZPE corrected.

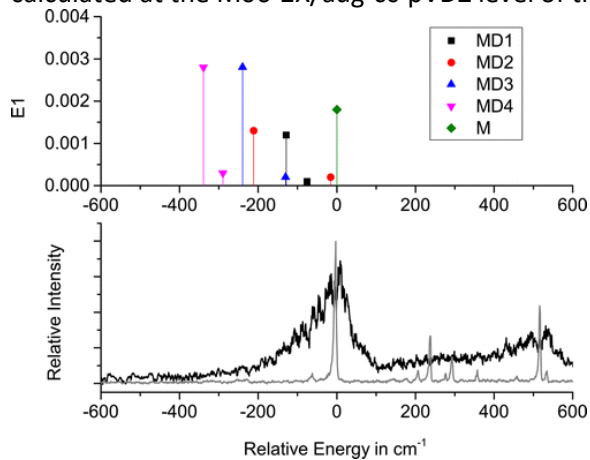


Figure 6. Calculated TDDFT (TDCAM-B3LYP/aug-cc-pVDZ) spectra of the mixed bromobenzene–benzene dimers shown in Figure 5. The calculated energy has been scaled and referenced to the observed position of the origin band of the monomer. The lower panel shows an expanded view of the experimental R2PI spectra of the bromobenzene monomer (gray) and mixed dimer (black).

Consistent with our findings for the bromobenzene homodimer, the four minimum energy structures of the mixed PhBr⋯Bz dimer correspond to a parallel-displaced π -stacked structure (MD1; mixed dimer 1), which is the global minimum, a T-shaped isomer bound by C–H/ π interaction (MD2), and two halogen bonded structures (MD3, MD4). The binding energies of MD2–MD4 are similar to those in the homodimers; however, the binding energy of MD1 is decreased roughly 30% with respect to D1. This indicates the important role of dipole–dipole coupling in these systems. The calculated and scaled TDDFT spectra of the mixed dimers (Figure 6 and Table S2) are similar to those of the homodimers, reflecting red-shifts with respect to the monomer transition. The smallest mean red-shift, and smallest exciton splitting, is found for the global minimum structure, dimer MD1.

To model the structure observed in the R2PI spectra of the bromobenzene–benzene mixed dimer, we optimized the structure of the S_0 and S_1 states of MD1 at the (TD) M06-2X/aug-cc-pVDZ level of theory. The calculated structures and mass-weighted normal mode displacements were used in a Franck–Condon simulation of the spectra that incorporated the full effects of Duschinsky mixing, using the PGOPHER program suite.(99) The two lowest frequency intermolecular modes were included, and only transitions originating from the vibrationless level of the ground state were included. The full parameter list of the simulations is provided in Table S3 in the Supporting Information. Figure 7 shows a comparison of experimental and simulated spectra in the region of the origin transition, where the stick spectrum has been convolved with a Gaussian function of 4 cm^{-1} full width at half-maximum. Clearly, the simulated spectrum captures the salient features of the experiment. This suggests that FC activity in the lowest energy intermolecular modes of this dimer is largely responsible for the broad appearance of the spectrum. This is understandable, since for the π -stacked dimer MD1 S_0 – S_1 excitation induces a significant geometry change from a parallel-displaced to sandwich structure, as noted above. The slight blue shift in the peak of the spectrum relative to the monomer likely arises from the build-up of transitions. Given the spectral complexity predicted for this single isomer, and the expected presence of not only multiple isomers but multiple isotopomers (^{79}Br , ^{81}Br) and homogeneous broadening, it is unlikely that higher resolution or UV–UV hole-burning experiments would be informative.

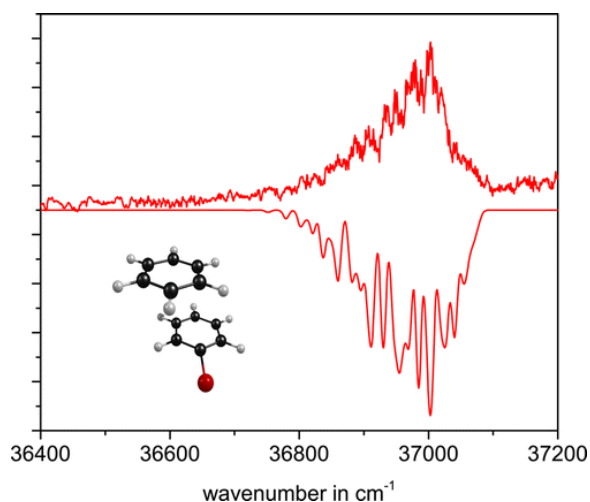


Figure 7. Experimental and simulated spectra of the origin band of the mixed bromobenzene–benzene dimer. The simulation is based on a two-mode Franck–Condon simulation as described in the text.

With respect to the chlorobenzene system, the primary difference for bromobenzene is the presence of the halogen-bonded dimers, where the σ -hole on Br interacts with the π -cloud of the aromatic partner, or alternatively, with the halogen atom of that partner. Calculations predict that in this system the halogen bonding interactions are weaker than π -stacking interactions, but of the same order of magnitude as CH/ π interactions. Thus, they are probably quite important in larger clusters,⁽⁶⁹⁾ where multiple binding motifs are the norm.

IV Conclusions

To understand the nature of noncovalent interactions in a prototypical system, we have examined bromobenzene and mixed bromobenzene–benzene clusters using R2PI spectroscopy in concert with electronic structure calculations. As found previously for chlorobenzene and related systems, the R2PI spectra of the bromobenzene dimer and trimer, obtained in the origin region of the S_0 – S_1 ($\pi\pi^*$) state of the monomer, show a broad spectrum that is red-shifted with respect to the monomer transition. For the mixed bromobenzene–benzene dimer, this feature peaks slightly to the blue of the monomer origin band and displays some vibrational structure.

Our observations are examined in the light of electronic structure calculations. For the bromobenzene dimer, calculations find eight minimum energy structures; four π -stacked structures, one T-shaped structure bound through CH/ π interaction, and three halogen bonded structures. The π -stacked structures are the most strongly bound (between -19 and -24 kJ/mol), and the halogen bonded isomers the weakest (between -6 and -9 kJ/mol). Calculated TDDFT spectra of these isomers show that these absorb over a range consistent with the breadth of the experimental spectrum, and with the exception of one halogen bonded dimer, the calculated absorptions are red-shifted with respect to the monomer transition. The TDDFT calculations were validated on a known and related system, the PhCl \cdots NH₃ dimer. Optimization of the S_1 state of three characteristic PhBr dimers reveals that the π -stacked and T-shaped structures undergo significant changes in geometry in the electronic excitation, suggesting significant FC activity in low-frequency intermolecular modes of the complex.

For the mixed bromobenzene–benzene dimer, four minimum energy structures were found. Calculated TDDFT spectra show similar trends to those observed for the PhBr homodimer. A two-mode Franck–Condon simulation of π -stacked mixed dimer MD1 captures the salient features of the experimental spectrum and demonstrates that the spectral broadening arises in large part from Franck–Condon activity associated with geometrical changes (from parallel-displaced to sandwich structure) induced by electronic excitation.

Future studies could include the study of halobenzene clusters with other donors including N atom and O atom donors. However, due to the difficulty in ionizing the halobenzenes as a result of the short S_1 lifetime, we plan to use N atom and O atom containing chromophores such as aniline and phenol to further investigate halogen-bonding interactions. Such an approach will greatly expand the range of systems that can be examined.

Supporting Information

Five figures and three tables of additional experimental and computational data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Acknowledgment

Support of this research by the National Science Foundation (CHE-1057951) is gratefully acknowledged. This research was also supported in part by National Science Foundation awards OCI-0923037 "MRI: Acquisition of a Parallel Computing Cluster and Storage for the Marquette University Grid (MUGrid)" and CBET-0521602 "Acquisition of a Linux Cluster to Support College-Wide Research & Teaching Activities".

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