The elusive $S_2$ state, the $S_1/S_2$ splitting, and the excimer states of the benzene dimer

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The elusive $S_2$ state, the $S_1/S_2$ splitting, and the excimer states of the benzene dimer

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We observe the weak $S_0 \rightarrow S_2$ transitions of the T-shaped benzene dimers (Bz)$_2$ and (Bz-$d_6$)$_2$ about 250 cm$^{-1}$ and 220 cm$^{-1}$ above their respective $S_0 \rightarrow S_1$ electronic origins using two-color resonant two-photon ionization spectroscopy. Spin-component scaled (SCS) second-order approximate coupled-cluster (CC2) calculations predict that for the tipped T-shaped geometry, the $S_0 \rightarrow S_2$ electronic oscillator strength $f_{el}(S_2)$ is $\sim$10 times smaller than $f_{el}(S_1)$ and the $S_2$ state lies $\sim$40 cm$^{-1}$ above $S_1$, in excellent agreement with experiment. The $S_0 \rightarrow S_1$ ($\pi\pi^*$) transition is mainly localized on the “stem” benzene, with a minor stem $\rightarrow$ cap charge-transfer contribution; the $S_0 \rightarrow S_2$ transition is mainly localized on the “cap” benzene. The orbitals, electronic oscillator strengths $f_{el}(S_1)$ and $f_{el}(S_2)$, and transition frequencies depend strongly on the tipping angle $\omega$ between the two Bz moieties. The SCS-CC2 calculated $S_1$ and $S_2$ excitation energies at different T-shaped, stacked-parallel and parallel-displaced stationary points of the (Bz)$_2$ ground-state surface allow to construct approximate $S_1$ and $S_2$ potential energy surfaces and reveal their relation to the “excimer” states at the stacked-parallel geometry. The $f_{el}(S_1)$ and $f_{el}(S_2)$ transition dipole moments at the $C_{2v}$-symmetric T-shape, parallel-displaced and stacked-parallel geometries are either zero or $\sim$10 times smaller than at the tipped T-shaped geometry. This unusual property of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transition-dipole moment surfaces of (Bz)$_2$ restricts its observation by electronic spectroscopy to the tipped and tilted T-shaped geometries; the other ground-state geometries are impossible or extremely difficult to observe. The $S_0 \rightarrow S_1/S_2$ spectra of (Bz)$_2$ are compared to those of imidazole · (Bz)$_2$, which has a rigid triangular structure with a tilted (Bz)$_2$ subunit. The $S_0 \rightarrow S_1/S_2$ transitions of imidazole-(benzene)$_2$ lie at similar energies as those of (Bz)$_2$, confirming our assignment of the (Bz)$_2$ $S_0 \rightarrow S_2$ transition. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4922608]

I. INTRODUCTION

Molecular-beam electric-deflection measurements by Klemperer and co-workers in 1979 showed that the benzene dimer (Bz)$_2$ is polar, suggesting a T-shaped structure. In 1993, Arunan and Gutowsky measured the rotational spectrum of supersonically cooled (Bz)$_2$ by Fourier-transform microwave spectroscopy; the rotational constant $B_0 = C_0$ is compatible with a T-shaped dimer with a distance of 4.94 Å between the centers-of-mass of the “stem” and “cap” Bz moieties. The symmetric-top character of this spectrum is surprising in that any rigid T-shaped (Bz)$_2$ structure must be an asymmetric top, see Figure 1. The microwave spectrum indeed exhibits multiple splittings that reflect rapid structural interconversion processes. More recently, Szalewicz, van der Avoird, and their co-workers made great advances in the calculation of the intermolecular potential energy surface. Incorporating a detailed permutation/inversion group-theoretical treatment of the non-rigid benzene dimer, they were able to predict the low-lying internal-rotation/tunneling states of (Bz)$_2$. Schnell et al. recently re-measured and assigned the fine structure of the (Bz)$_2$ microwave spectrum in terms of vibration-rotation-tunneling (VRT) processes. The vibronic spectrum of supersonically cooled (Bz)$_2$ has been investigated since the 1980s using mass-selective resonant two-photon ionization (R2PI) spectroscopy. These experiments identified the $0^0_0^0$ band of the (Bz)$_2$ $S_0 \rightarrow S_1$ transition at 38 046 cm$^{-1}$, red-shifted by 40 cm$^{-1}$ from the $S_0 \rightarrow S_1$ $0^0_0^0$ band of Bz monomer at 38 086 cm$^{-1}$. The latter transition is strictly symmetry-forbidden as a one-photon electric-dipole transition so the question arises how the $0^0_0^0$ ($S_1$) band of (Bz)$_2$ gains intensity. Smalley and co-workers already suggested “asymmetry in the crystal field” as a cause, i.e., that symmetry lowering of one or both of the Bz monomers renders the $S_0 \rightarrow S_1$ transition slightly allowed. While the fluorescence quantum yield of (Bz)$_2$ is low, its ionization efficiency is high when compared to those of the (Bz)$_3$ and (Bz)$_4$ clusters produced in the same supersonic-jet expansion. This was interpreted in terms of vertical excitation of (Bz)$_2$ into a T-shaped $S_1$ state local minimum, followed by rapid rearrangement to a stacked-parallel structure corresponding to the lowest excimer state of $1B_1g$ symmetry.

Since the two Bz monomers in (Bz)$_2$ should give rise to two transitions corresponding to the $S_0 \rightarrow S_1$ and the $S_0 \rightarrow S_2$ excitations of (Bz)$_2$, Schlag and co-workers subsequently...
undertook detailed spectroscopic studies of (Bz-h\textsubscript{6})\textsubscript{2}, the (Bz-d\textsubscript{6})\textsubscript{2}, and of other D- and \textsuperscript{13}C-isotopomers of (Bz)\textsubscript{2}, attempting to determine the excitonic splitting between the S\textsubscript{0} → S\textsubscript{1} and S\textsubscript{0} → S\textsubscript{2} origins of (Bz)\textsubscript{2}, as well as the excited-state structure of (Bz)\textsubscript{2}.\textsuperscript{10,12} Combining the spectroscopic results with early high-level \textit{ab initio} calculations of (Bz)\textsubscript{2}, Schlag, Hobza, and co-workers concluded that the (Bz)\textsubscript{2} structure is T-shaped.\textsuperscript{10,12,24,25} In good agreement with the later microwave structure,\textsuperscript{2} they interpreted a ~2 cm\textsuperscript{-1} splitting of the 0\textsubscript{1}\textsuperscript{0} band of (Bz)\textsubscript{2} as arising from the excitonic S\textsubscript{1}/S\textsubscript{2} splitting.\textsuperscript{10,12} Felker and co-workers performed stimulated-Raman spectroscopic measurements on (Bz)\textsubscript{2} and its isotopomers, determined that (Bz)\textsubscript{2} consists of two inequivalent monomers,\textsuperscript{13–16} and interpreted the low-frequency intermolecular and intramolecular Raman vibrational bands in terms of a T-shaped dimer.\textsuperscript{13–16} Erlekam et al. have recorded the IR spectrum of (Bz)\textsubscript{2}\textsuperscript{19} and observed the 0\textsubscript{13} stretch frequency of the stem Bz moiety, in agreement with the T-shaped structure,\textsuperscript{19,20} and the calculated C–H stretching frequency shift.\textsuperscript{26}

Felker and co-workers pointed out that the symmetry of the stem-Bz in the T-shaped dimer is lowered from D\textsubscript{6h} to C\textsubscript{2v}, rendering the S\textsubscript{0} → S\textsubscript{1} electronic origin weakly allowed, but that the internal rotation of the cap-Bz renders its site symmetry C\textsubscript{6v}, in which the 0\textsubscript{13} band remains forbidden.\textsuperscript{14,16} Nevertheless, (Bz)\textsubscript{2} has two excited states that correlate with the S\textsubscript{0} → S\textsubscript{1} excitation of its two Bz constituents. Indeed, Henson et al. tentatively assigned a “6–8 cm\textsuperscript{-1} blue-shifted 1\textsuperscript{0}\textsuperscript{0} band” localized on the cap-Bz moiety.\textsuperscript{14} As the calculations and experiments below will show, the separation between the S\textsubscript{1} and S\textsubscript{0} transitions of the T-shaped dimer is ~200 cm\textsuperscript{-1}. Also, it is dominated by the “site-splitting” energy\textsuperscript{13–16} and not by the excitonic splitting.\textsuperscript{10,12}

Because benzene lacks a dipole moment, the lowest-order electrostatic interaction in (Bz)\textsubscript{2} is the relatively weak quadrupole-quadrupole interaction, the major part of the binding coming from dispersive interactions, which require high-level correlated treatments. For this reason, (Bz)\textsubscript{2} and especially the relative energies of the T-shaped, tilted T-shaped, stacked-parallel, and parallel displaced geometries have been used as a benchmark system for high-level electronic structure calculations.\textsuperscript{27–33} Szalewicz and co-workers, who calculated the six-dimensional intermolecular PES of (Bz)\textsubscript{2} using the symmetry-adapted perturbation theory (density functional theory) (SAPT(DFT)) method, located T-shaped and stacked minima as well as many index-1 saddle points.\textsuperscript{3} They later complemented this work by performing CCSD(T): coupled-cluster with singles, doubles and perturbative triples excitations calculations at three minima and nine index-1 stationary points.\textsuperscript{4} Below, we employ their nomenclature\textsuperscript{4} for the stationary points M2, S3, S3a, M1, and S8, which are shown in Figure 1. Xantheas and co-workers have recently performed a complete basis set (CBS) study of the M1 parallel-displaced dimer with the CCSD(T) method and obtained a CCSD(T)/CBS binding energy D\textsubscript{e} = −2.65 ± 0.02 kcal/mol.\textsuperscript{33} This value is only 0.03 kcal/mol lower than the CCSD(T)/CBS (D\textsubscript{e} = −2.62 kcal/mol) CCSD(T) value of Szalewicz and co-workers, which was not optimized for the intramolecular degrees of freedom.\textsuperscript{4}

We first concentrate on the C\textsubscript{2v}-symmetric, tipped T-shaped global minimum M2 and on the low-lying C\textsubscript{2v}-symmetric index-1 saddle point S3, see Figure 1.\textsuperscript{3,4} We address the properties of the S\textsubscript{1} and S\textsubscript{2} states of (Bz)\textsubscript{2} both spectroscopically and theoretically, with a focus on the S\textsubscript{2} state. We present vibronic spectra of (Bz)\textsubscript{2} and the (Bz-d\textsubscript{6})\textsubscript{2} isomer that show weak band systems starting ~240 cm\textsuperscript{-1} above the respective S\textsubscript{0} → S\textsubscript{1} electronic origins. Using approximate second-order coupled-cluster CC2 calculations, we predict (1) the energetic order and the splitting between the S\textsubscript{1} and S\textsubscript{2} excited states, (2) the electronic transition dipole moments (TDMs) and their orientations, and (3) the interpretation of the respective electronic transitions in terms of orbital excitations on the stem and cap Bz moieties. In agreement with Felker et al.,\textsuperscript{13–16} we find that the lowest electronic excitation of the cap-Bz—corresponding to the (Bz)\textsubscript{2} S\textsubscript{2} state—is extremely weak in the C\textsubscript{2v}-symmetric T-shaped dimer S3. However, displacement along the ω tilting angle from S3 towards the tipped T-shaped global minimum M2 increases both the f\textsubscript{el}(S\textsubscript{1}) and f\textsubscript{el}(S\textsubscript{2}) oscillator strengths which correspond to the stem and cap electronic transitions. (We use “tilting” for consistency with our previous work\textsuperscript{34–36} but note that the ω coordinate was denoted “tilt” in Refs. 4–7.) We also compare the vibronic spectrum of (Bz)\textsubscript{2} to the recently measured vibronic spectrum of the imidazole · (Bz)\textsubscript{2} cluster,\textsuperscript{3} which has a triangular structure with the (Bz)\textsubscript{2} subunit bent more strongly than in (Bz)\textsubscript{2}. In Sec. IV, we extend the SCS-CC2 calculations to the S\textsubscript{1} and S\textsubscript{2} states of two low-lying ground-state
saddle-point geometries S3a, S8 and the parallel displaced local minimum M1. See Figure 1.

II. METHODS

A. Computational methods

The Si excited state of Bz2 has been characterized at several different levels of theory, including time-dependent DFT (TD-DFT),\textsuperscript{27,29} complete active-space second-order perturbation theory (CASPT2),\textsuperscript{28} linear-response coupled cluster methods [LR-CC2, LR-CCSD, and LR-CCSDR(3)],\textsuperscript{30} and equation-of-motion CCSD,\textsuperscript{31} but only at the stacked-parallel S8 and parallel-displaced M1 geometries. These structures transform as $B_1g$ and $B_2g$ in the $D_{6h}$ and $C_{2v}$ point groups, respectively (see Figure 1), and correspond to the “excimer” geometry of Bz2. However, the stacked S8 geometry is not a ground-state minimum, and the M1 structure is a local minimum that has not been experimentally detected in 25 years of research. On the other hand, the excited state tipped T-shaped minimum in the Si state has not been treated by the same high-level correlated methods that allow structure optimization and normal-mode frequency calculations.

In order to study the T-shaped Bz2 minimum in the Si state, we employed the spin-component scaled (SCS) CC2 method with large and diffuse basis sets.\textsuperscript{38–40} The SCS-CC2 method has a good cost/accuracy ratio. Benchmark studies by Hättig and co-workers employing five excited-state methods (TD-B3LYP, ADC(2), CC2, SCS-CC2, and SOS-CC2) on 66 different medium-sized and large aromatic organic molecules with 10-78 atoms comparing the calculated and experimental 0-0 transition energies have shown that the SCS-CC2 gives the best performance, even better than that of the CC2 method.\textsuperscript{40} Spin component scaling not only improves the CC2 excited state energies but also the dipole moments and vibrational frequencies.\textsuperscript{38–40}

We optimized the ground state of (Bz)\textsubscript{2} with the SCS variant of the second-order Moller-Plesset perturbation theory (MP2) method using the Dunning augmented correlation-consistent basis sets aug-cc-pVQZ with X = D, T, Q, which are abbreviated as aVXZ below. In the recent CCSD(T) study of Xantheas and co-workers on the parallel displaced Bz2 dimer,\textsuperscript{33} they also employed SCS-MP2 and obtained a “best estimate” binding energy $D_e = -2.65 \pm 0.02$ kcal/mol that is identical to the CCSD(T)/CBS $D_e$ discussed above.\textsuperscript{33} The SCS-CC2 vertical excitations to the S1 and S2 states were calculated at the respective SCS-MP2 ground-state equilibrium structures in the resolution of the identity (RI) approximation\textsuperscript{43} employing the aVXZ basis sets. The like and unlike spin components of the MP2 and CC2 energies were scaled according to Grimm.\textsuperscript{42} The SCS-MP2/aug-cc-pVTZ optimized Cartesian coordinates of the T-shaped M2 minimum and the S3 and S3a saddle point structures are given in Tables I–III of the supplementary material.\textsuperscript{44}

All calculations were performed using Turbomole 6.3 (RJCC2 module).\textsuperscript{45} For this weakly bound complex, the standard Turbomole thresholds had to be lowered to the following non-standard values: SCF and one-electron density convergence, $10^{-9}$ au and $10^{-8}$ au, respectively. Geometry and force thresholds for structure optimizations were $10^{-8}$ au (energy change), $6 \times 10^{-6}$ au (maximum displacement element), $10^{-6}$ au (maximum gradient element), $4 \times 10^{-6}$ au (RMS displacement), and $10^{-6}$ au (RMS gradient).

B. Experimental methods

Benzenedimer (Bzh\textsubscript{6})\textsubscript{2} and its isotopomer (Bz-d\textsubscript{6})\textsubscript{2} were produced and cooled in a pulsed supersonic jet expansion. The Bz (Fluka, 99%) or Bz-d\textsubscript{6} (Cambridge Isotopes, 99.5% isotopic purity) sample was held at $-45$ °C to $-35$ °C, corresponding to 1-2 mbar Bz pressure, and seeded into the neon carrier gas (Linde, >99.995%) at a backing pressure of 1.3 bar. For the imidazole ⋅ (benzene)\textsubscript{2} (Im ⋅ Bz\textsubscript{2}) measurements,\textsuperscript{37} the imidazole (Sigma, >99.5%) was placed in the pulsed jet nozzle (0.4 mm diameter) and heated to 75–80 °C, corresponding to an imidazole pressure of 0.4-0.6 mbar. Mass-selective two-color (2C) R2PI spectra of the Bz2 dimers and Im ⋅ Bz2 trimer were recorded over the 37500–39000 cm$^{-1}$ range. Electronic excitation was performed with a frequency-doubled NarrowScan dye laser (Coumarin 307 in EtOH, $\sim 200 \mu$J/pulse) pumped by the 355 nm output of a Nd:YAG laser. Ionization was induced by a second frequency-doubled dye laser (FL3002, Fluorescein 27 in basic MeOH, 1 ml/pulse) at 275 nm. The ions were separated in a time-of-flight (TOF) mass spectrometer and detected by a double microchannel plate detector. As the Im ⋅ Bz2 cluster fragments into the Im ⋅ Bz$^+$ mass channel, the true two-color R2PI spectrum of Im ⋅ Bz2 was obtained by IR/UV holeburning measurements. The IR laser pulse ($\sim 8$ mJ) generated by a 10 Hz LaserVision OPO/OPA system (pumped by a Nd:YAG laser) was fixed at the NH-stretch of imidazole in the Im ⋅ Bz2 complex (3452 cm$^{-1}$). Two 2C-R2PI spectra were then measured successively in the Im ⋅ Bz$^+$ mass channel, first without and then with previous depletion of the ground state.

III. RESULTS

A. Computational results

1. Vertical excitation energies

At the $C_2$-symmetric M2 ground-state minimum geometry, the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ vertical excitation energies calculated by the SCS-CC2 method are separated by 170–260 cm$^{-1}$, corresponding to the site-splitting\textsuperscript{13–15} between the stem and cap Bz molecules. The splitting is 262 cm$^{-1}$ with the aVDZ, 250 cm$^{-1}$ with the aVTZ, and 244 cm$^{-1}$ with the aVQZ basis set, as is shown in Figure 2. At the $C_3$ (S3) geometry, the $S_1/S_2$ splitting is slightly smaller, about 200–210 cm$^{-1}$ with the aVXZ basis sets. The irreps of the $S_1$ and $S_2$ states are $A'$ in the $C_2$ geometry; in the $C_{2v}$ geometry, both excited states are $B_1$. The predictions of the aVXZ basis sets are in good mutual agreement, while the much smaller SVP basis set predicts $\sim 50 - 100$ cm$^{-1}$ smaller splittings, as shown in Figure 2.

The expected $S_1/S_2$ site splitting of the T-shaped benzene dimer can be roughly estimated from previous spectroscopic experiments: the weakly allowed $S_1 0_0^0$ transition of the stem Bz is spectrally shifted by $\delta \nu = -44.4$ cm$^{-1}$ relative to the
Larger than \( \delta \nu \) of the X–H donor axis relative to the Bz surface normal and origins of the cap-Bz become allowed due to the slight tilt 120–170 cm\(^{-1}\) shifts yields a rough estimate for the site splitting of about 2. Electronic oscillator strengths at the minimum. The Figure 2(b) shows the analogous results at the M2 geometry, as a function of basis set size, both at the C\(_2\) and C\(_4\) geometries can as be seen in Figure 2. Both \( f_{\text{el}}(S_1) \) and \( f_{\text{el}}(S_2) \) are small, 10\(^{-5}\)–10\(^{-4}\), as is expected for a nominally forbidden transition which becomes allowed via the slight distortion induced by the dimer formation. Note that \( f_{\text{el}}(S_3) \) is not equal to zero, which suggests that the \( S_0 \rightarrow S_2 \) transition might be observable for the T-shaped dimer.

3. Orbital excitations

To facilitate the discussion, we discuss the molecular orbital (MO) excitations based on the aVDZ orbitals, which are more compact than the aVTZ and aVQZ ones. Figure 3 shows that for the S3 structure, the \( S_0 \rightarrow S_1 \) transition consists of a stem-localized \( \pi \pi^* \) transition (12.6%) with small contributions from cap-\( \pi \) orbitals, a stem-\( \pi \rightarrow \) cap-\( \pi^* \) charge-transfer transition (12.5%), and a second stem-\( \pi \rightarrow \) stem-\( \pi^* \) transition (12.5%) with no contribution from cap-\( \pi \) orbitals. For the M2 structure, shown in Figure 4, the \( S_0 \rightarrow S_1 \) transition is dominated by a stem-\( \pi \rightarrow \) cap-\( \pi^* \) charge-transfer transition. Note that in the M2 geometry, the stem-\( \pi \) and cap-\( \pi \) orbitals are more strongly mixed than in the S3 structure. For both structures, the \( S_0 \rightarrow S_2 \) transition is composed of two \( \pi \pi^* \) excitations that are mainly located on the cap-Bz. The larger contribution (20.3%) also has a very small \( \pi \pi^* \) transition on the stem-Bz, while the slightly weaker transition (19.3%) is entirely located on the cap moiety.

4. Transition dipole moments

Figure 5 shows the SCS-CC2 calculated TDM vectors of (Bz)\(_2\) at the M2 geometry, as a function of basis set size for the aVXZ (X = D, T, Q) basis sets; all three calculations were done at the SCS-MP2/aVTZ optimized geometry, see the supplementary material. The \( S_0 \rightarrow S_1 \) and \( S_0 \rightarrow S_2 \) TDM vectors are both oriented within the \( \sigma_c \) symmetry plane of the dimer. The \( S_0 \rightarrow S_1 \) vector directions and lengths are similar for the three basis sets, lying at an angle of ~40° relative to the cap-Bz surface normal. The \( S_0 \rightarrow S_2 \) TDM vectors, which we have drawn at the center-of-mass of the cap Bz because they are associated with this moiety, do not lie within the cap-Bz plane, but are tipped (with the aVDZ basis set) or approximately normal to this plane (for the aVQZ basis set).

A comparison of Figures 2(a) and 2(b) reveals that both \( f_{\text{el}}(S_1) \) and \( f_{\text{el}}(S_2) \) are considerably smaller at the S3 than at the M2 geometry. This implies that \( f_{\text{el}} \) is a function of the tipping angle \( \omega \), see Figure 1(a). In Figure 6, we show the SCS-CC2/aVTZ calculated oscillator strengths \( f_{\text{el}}(S_1) \) and \( f_{\text{el}}(S_2) \) calculated as a function of \( \omega \); both oscillator strengths indeed increase by ~10 times when \( \omega \) is increased from 0° to 20°. Throughout the entire angle range shown, \( f(S_1) \) is 5–10 times larger than \( f(S_2) \). The strong dependence of \( f_{\text{el}}(S_1) \) and \( f_{\text{el}}(S_1) \)
on the intermolecular vibrational $\omega$ coordinate implies that there is a coordinate-dependent contribution for $\omega^\pi$ vibronic transitions. The vibronic transition dipole moments to levels with high $\langle \omega \rangle$ acquire intensity beyond the purely electronic transition dipole moment, equivalent to a large Herzberg-Teller effect.

At this point, we note that the tipped T-shaped structure $\mathbf{M2}$ does not correspond to a vibrational eigenstate. The correct $v = 0^1/0^2$ eigenstates in both the ground and excited electronic states are the $+ \pi$ and $- \pi$ combinations of localized wave functions in the two wells that correspond to the “left” and “right” localized minima (where Figure 1(a) shows the right-localized minimum). In the vibrational-electronic picture, the

![FIG. 3. Dominant orbital excitation contributions to the $S_0 \rightarrow S_1$ (red) and $S_0 \rightarrow S_2$ transitions (blue) of the $C_{2v}$-symmetric $\mathbf{S3}$ structure of (benzene)$_2$ (SCS-CC2/aug-cc-pVDZ calculation).](image)

![FIG. 4. Dominant orbital excitations corresponding to the $S_0 \rightarrow S_1$ (red) and $S_0 \rightarrow S_2$ transitions (blue) for the $C_{1v}$-symmetric $\mathbf{M2}$ structure of (benzene)$_2$ (SCS-CC2/aug-cc-pVDTZ).](image)

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### TABLE I. (Benzene)$_2$ oscillator strengths $f_{el}$ and fractional orbital excitation contributions to the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions, calculated with the SCS-CC2/aVTZ method (and aVDZ for the oscillator strengths) at SCS-MP2/aVTZ ground state optimized structures.

<table>
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<tr>
<th>Structure</th>
<th>$f_{el}$</th>
<th>$f_{el}$</th>
<th>Fraction</th>
<th>Assignment</th>
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<td>$S_3/C_{2v}$</td>
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<td></td>
<td></td>
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<tr>
<td>$S_0 \rightarrow S_1$</td>
<td>$6.43 \times 10^{-6}$</td>
<td>$4.65 \times 10^{-6}$</td>
<td>12.6%</td>
<td>stem/cap $\pi \rightarrow$ stem $\pi^*$</td>
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<td>$S_0 \rightarrow S_2$</td>
<td>$1.44 \times 10^{-6}$</td>
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<td>24.6%</td>
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<td>$S_0 \rightarrow S_3$</td>
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<td>$1.02 \times 10^{-5}$</td>
<td>20.3%</td>
<td>cap $\pi \rightarrow$ cap $\pi^*$</td>
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<td>$S_3a/C_s$</td>
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<td></td>
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<tr>
<td>$S_0 \rightarrow S_1$</td>
<td>$4.39 \times 10^{-6}$</td>
<td>$3.52 \times 10^{-6}$</td>
<td>10.3%</td>
<td>stem/cap $\pi \rightarrow$ stem $\pi^*$</td>
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<tr>
<td>$S_0 \rightarrow S_2$</td>
<td>$1.58 \times 10^{-5}$</td>
<td>$1.44 \times 10^{-5}$</td>
<td>27.3%</td>
<td>cap/stem $\pi \rightarrow$ cap/stem $\pi^*$</td>
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<td>$M_1/C_{2v}$</td>
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<td>0.0</td>
<td>64.6%</td>
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<td>$S_0 \rightarrow S_2$</td>
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<td>$3.50 \times 10^{-6}$</td>
<td>66.3%</td>
<td>$\pi \rightarrow \pi^*$ delocalized by symmetry</td>
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reason that the $S_0 \rightarrow S_2$ transition of (Bz)$_2$ becomes allowed is not due to symmetry-lowering or -breaking, but because it is accompanied by $v'' = 0^+ \rightarrow v' = 0^-$ or $v'' = 0^- \rightarrow v' = 0^+$ transitions between the tunneling states. These wave functions have vanishing amplitudes as the (Bz)$_2$ geometry approaches the S3 geometry.

B. Resonant two-photon ionization spectra

Figure 7 shows the 2C-R2PI spectra of (Bz-$h_0$)$_2$ and (Bz-$d_0$)$_2$. The electronic origin of (Bz-$h_0$)$_2$ lies at 38 041.7 cm$^{-1}$ and that of (Bz-$d_0$)$_2$ at 38 242.9 cm$^{-1}$, in agreement with the previous work. About 240 cm$^{-1}$ above the $S_0 \rightarrow S_1$ electronic origin, a series of weak bands is observed for both (Bz-$h_0$)$_2$ and (Bz-$d_0$)$_2$. In the (Bz-$h_0$)$_2$ spectrum, Figure 7(a), the first of these bands lies at +238 cm$^{-1}$: it is especially noticeable in the 10× magnified spectrum. In the benzene monomer $S_1$ ($B_{2u}$) state, the low-frequency $v''_1$ out-of-plane deformation mode has been inferred to lie at +237.5 cm$^{-1}$. Note, however, that this out-of-plane vibration is symmetry-forbidden in the $S_0 \rightarrow S_1$ spectrum of Bz-$h_0$. In the (Bz-$d_0$)$_2$ spectrum, Figure 7(b), the lowest of the weak bands is observed at +208.5 cm$^{-1}$, in very good agreement with the $v''_1 = 208$ cm$^{-1}$ frequency of $S_1$ state C$_6$D$_6$. Thus, the (Bz-$h_0$)$_2$ and (Bz-$d_0$)$_2$ spectra in Figures 7(a) and 7(b) are consistent in showing a $16^1_0$ excitation of the stem Bz moiety.

Since Bz-$h_0$ and Bz-$d_0$ have no other low-frequency vibrations in the 200-300 cm$^{-1}$ range, we assign the following...
C. R2PI spectrum of imidazole · (benzene)$_2$

Figure 8(b) shows the two-color R2PI spectrum of the imidazole · (benzene)$_2$ (Im · Bz$_2$) cluster, which has recently been observed in a spectroscopic study of the imidazole · benzene dimer. The calculated structure of this cyclic trimer is shown in the inset of Figure 8. It involves a NH ··· π interaction from the imidazole to benzene-1 followed by sequential CH ··· π interactions from benzene-1 to benzene-2 and then from benzene-2 back to imidazole. The (Bz)$_2$ moiety contained within the Im · Bz$_2$ trimer is roughly T-shaped, with Bz-1 acting as the stem and Bz-2 as the cap molecule. The additional interaction with imidazole tilts the stem Bz-1 along the δ angle, which is defined for the S$_3$a structure of (Bz)$_2$ shown in Figure 1(c). Relative to the S$_3$ structure in Figure 1(b), the symmetry descent is C$_2v$ → C', where the prime indicates that the mirror plane of the S$_3$a (C') structure is not the same as that in the M2 (C$_s$) structure.

Since the cap (or Bz-2) moiety in Im · Bz$_2$ also acts as a stem-type CH ··· π donor to imidazole, it acquires a much larger S$_0$ → S$_1$ transition dipole moment than the cap-Bz in (Bz)$_2$. This is brought out by the SCS-CC2/aVTZ calculated transition intensities, which are $f_{el}(S_1) : f_{el}(S_2) = 1 : 3.0$ for the two benzene chromophores, as shown in Figure 8(a). Therefore, the Im · Bz$_2$ cluster exhibits two electronic transitions corresponding to the two Bz chromophores, but with more similar intensities, as shown in Figure 8.

According to the SCS-CC2/aVTZ calculations, the S$_0$ → S$_1$ and S$_0$ → S$_2$ excitations of Im · Bz$_2$ correspond to simultaneous excitations of both Bz-1 and Bz-2 moieties. The experimental ratio of the integrated band structure corresponds very closely to the S$_1$ state $\nu'_{16}$ frequencies of bare benzene, which are 238 cm$^{-1}$ in benzene-$h_6$ and 208 cm$^{-1}$ in benzene-$d_6$. The $\nu'_{16}$ mode is degenerate ($\epsilon_{2u}$) and its vibronic species in the S$_1$ state of Bz-$h_6$ and Bz-$d_6$ is $B_{2u} \otimes \epsilon_{2u} = E_{1g}$. Therefore, the $16^1_0$ fundamental transition of bare Bz-$h_6$ or Bz-$d_6$ is electric-dipole forbidden in excitation from the $A_{1g}$ ground-state $\nu'' = 0$ level, as discussed above.

The SCS-CC2 calculations in Sec. II B predict that the S$_0$ → S$_1$ $0'_{0}(S_1)$ excitation of the T-shaped M2 dimer is associated with the stem-Bz moiety. The appearance of the $16^1_0$ band in (Bz-$h_6$)$_2$ and (Bz-$d_6$)$_2$ therefore reflects a symmetry lowering of the stem-Bz. The symmetry descents to energetically low-lying geometries are from D$_{6h}$ in bare Bz to C$_2v$ in S3, to C$_2v$ in M2, or to C'$_v$ in S3a, see Figure 1. The $D_{6h} \rightarrow C_{2v}$ descent splits the $\epsilon_{2u}$ vibration into $\alpha_2$ and $\delta_2$ components. Since the S$_0$ → S$_1$ TDM transforms as $a_1$ in C$_2v$, neither component of $\nu'_{16}$ becomes allowed. The $D_{6h} \rightarrow C_{2v}$ descent splits $\epsilon_{2u}$ into $\alpha''$; the electronic TDM transforms as $a''$ (see Figure 5), and again, neither component is allowed. The $D_{6h} \rightarrow C'_{v}$ descent to S3a splits $\epsilon_{2u}$ into $\alpha' + \alpha''$ and the electronic TDM transforms as $\alpha'$, which makes the $\nu'_{16a}$ component electric-dipole-allowed.

Conversely, the appearance of the $16^1_0$ fundamental in the S$_0$ → S$_1$ spectrum implies the existence of S$_0$ state levels of (Bz-$h_6$)$_2$ and (Bz-$d_6$)$_2$ that (1) have a rigid-molecule symmetry equivalent to $C'_v$ and (2) are populated at the T = 3–5 K
temperature of the supersonic-jet expansion. These levels must be a subset of the low-lying VRT states of (Bz)2 with an average geometry that lies close to S3a. A permutation/inversion group-theoretical treatment of the low-lying VRT states of non-rigid (Bz)2 is given in Ref. 4. In summary, the \( D_{th} \rightarrow C_s \) symmetry lowering for ground-state VRT levels whose geometries are close to the M2 minimum of the S0 surface renders the \( 0^0_0 \) (S1) band of (Bz)2 allowed. The alternative \( D_{th} \rightarrow C'_s \) symmetry lowering to different ground-state VRT levels with average geometries close to the S3a saddle point renders the \( 16^1_0 \) transition allowed.

### B. The S0 \( \rightarrow \) S2 electronic transition

Starting at \( 0^0_0 + 223 \text{ cm}^{-1} \) in (Bz\( d_6 \)) and at \( +253 \text{ cm}^{-1} \) in (Bz\( h_6 \)), six weak bands appear further towards the blue. Since Bz\( d_6 \) and Bz\( h_6 \) have no low-lying vibrations other than \( v_{16} \), we assign these bands to the \( S_0 \rightarrow S_2 \) electronic transition. This confirms the prediction of the SCS-CC2 calculations that (1) the S1 and S2 electronic excited states of (Bz)2 are spaced by approximately 250 cm\(^{-1} \) and (2) the S0 \( \rightarrow \) S2 transition is about 10 times weaker than that to the S1 state. The experimental S1 : S2 intensity ratio of the \( 0^0_0 \) bands is about 10:1. The observed splitting for (Bz)2 is 253 cm\(^{-1} \) and that of (Bz\( d_6 \)) is 223 cm\(^{-1} \). The experimental values include differential zero-point energy effects, i.e., the difference between the excited-state and ground-state total zero-point vibrational energies.

The intensities and spacings of the bands associated with the \( S_0 \rightarrow S_2 \) electronic transition are similar to the bands that are associated with the \( S_1(6^1_0) \) intramolecular excitation of (Bz)2. The ground-state van der Waals vibrational modes of (Bz)2 have been extensively discussed by Felker and coworkers\(^{14} \) and have been calculated by Hobza and co-workers\(^{25} \). Our preliminary assignments of the \( S_0 \rightarrow S_2 \) bands are shown in Figure 9. The intramolecular vibrations involved are probably the totally symmetric modes \( \omega^t \), \( \sigma^t \), and \( \chi' \), based on ground-state normal mode calculations at the SCS-CC2/aVDZ level. The calculated and experimental frequencies are given in Table II.

### C. Geometry dependence of the S0 \( \rightarrow \) S1 and S0 \( \rightarrow \) S2 electronic oscillator strengths

The SCS-CC2 calculations and Figures 2 and 6 show that the electronic oscillator strengths \( f_{el}(S1) \) and \( f_{el}(S2) \) depend on the (Bz)2 structure. Figure 10 generalizes these findings by showing the S0, S1, and S2 state SCS-CC2 electronic energies at the energetically low-lying stationary points M2, S3, S3a, M1, and S8 that have been previously localized on the S0 state CCSD(T) potential energy surface.\(^{34} \) As in Figure 6, the calculated \( f_{el}(S1) \) and \( f_{el}(S2) \) oscillator strengths are indicated by red/blue dots with radii that are proportional to the \( f_{el} \) values.

![Two-color R2PI spectrum of (benzene-h_6) in the S1(6^1_0) region (top) and in the S0(0^0_0) region (bottom), with tentative intermolecular vibrational assignments. The wavenumber scales are relative to the (Bz)2 S1 origin at 38 041.7 cm^{-1}.](image)

![SCS-CC2/aVTZ calculated vertical excitation energies and oscillator strengths \( f_{el} \) of the S0 \( \rightarrow \) S1 (red) and S0 \( \rightarrow \) S2 (blue) transitions for different T-shaped and \( \pi \)-stacked conformers of benzene2 (for the conformer abbreviations see Fig. 1). The calculated energies are connected to indicate qualitative features of the S0 (black), S1 (red), and S2 (blue) potential energy surfaces. The electronic oscillator strengths \( f_{el} \) are indicated by dot radii as in Figure 6, points labeled “x” mean that \( f_{el} < 10^{-6} \). The largest \( f_{el}(S1) = 1.2 \times 10^{-4} \) for M2 is halved for clarity. The S0 state energies of the M2, S3, S3a, M1, and S8 conformers are from Ref. 4. The energy and \( f_{el} \) values for the point between M1 and SS are from a SCS-CC2/aVTZ calculation. The S1 state binding energy \( D_b(S1) \) is from Ref. 4; the S1 and S2 binding energies \( D_b \) are discussed in the text.](image)

### Table II. Benzene dimer SCS-MP2/aug-cc-pVTZ S0 state calculated and experimental intermolecular vibrational frequencies in the S1(6^1_0) and S2(0^0_0) regions (in cm\(^{-1} \)).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Label</th>
<th>( S_{th} ) calc.</th>
<th>( S_1(6^1_0) ), exp.</th>
<th>( S_2(0^0_0) ), exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Twist</td>
<td>( \theta )</td>
<td>10.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tilting</td>
<td>( \delta )</td>
<td>14.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tipping</td>
<td>( \omega )</td>
<td>30.7</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>Stretch</td>
<td>( \sigma )</td>
<td>59.4</td>
<td>39</td>
<td>37</td>
</tr>
<tr>
<td>Shear</td>
<td>( \chi )</td>
<td>68.1</td>
<td>56</td>
<td>55</td>
</tr>
<tr>
<td>Buckle</td>
<td>( \beta )</td>
<td>68.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The ground- and excited-state dissociation energies for the (Bz)₂ → Bz + Bz and (Bz)₂ → Bz + Bz' processes are indicated at the left side of Figure 10. For the S₀ state of the M₂ structure, van der Avoird et al. have calculated a CCSD(T) binding energy of Δₑ = 975 cm⁻¹ and a dissociation energy of Δ₀ = 870 cm⁻¹.⁴ Since the S₀ → S₁ electronic origin of M₂ lies 44 cm⁻¹ below the (forbidden) S₀ → S₁ electronic origin of benzene at 38 086 cm⁻¹, the S₁ state dissociation energy of M₂ is 44 cm⁻¹ larger than the ground-state value, yielding Δ₀(S₁) = 914 cm⁻¹ and Δₑ(S₁) ∼ 1020 cm⁻¹ for the S₁ state local minimum corresponding to M₂, see Figure 10.

Overall, the largest oscillator strength is fₑ(S₁) of the M₂ structure; only half of the dot is shown for clarity in Figure 10. As discussed above, the fₑ(S₂) at the M₂ geometry is ~10 times smaller than fₑ(S₁), in agreement with experiment. The decrease of ω towards zero decreases both fₑ(S₁) and fₑ(S₂), as shown in Figure 6. This renders low-lying S₀ state VRT levels that are associated with the S₃ structure difficult to observe by electronic spectroscopy.

For the S₃a geometry, Figure 10 shows that fₑ(S₂) is ~10× larger than fₑ(S₁) and also twice that of fₑ(S₂) at M₂. The calculated S₀ → S₁ transition energy is close to the S₀ → S₂ transition of M₂. This implies that transitions from ground-state VRT levels with average geometries close to S₃a might appear intermingled with the S₀ → S₂ transition of M₂. This may explain part of the band structure observed in the S₂ region of Figures 7(a) and 7(b).

Continuing along the abscissa of Figure 10 leads to the parallel-displaced M₁ structure, see Figure 1(d), which is a ground-state local minimum. Its S₀ → S₁ transition is A₂ → B₂ in C₂ᵥ and is electric-dipole forbidden.⁷⁻⁹ However, the S₀ → S₁ transition of M₁ is weakly allowed, and we discuss this further below.

Starting at the S₁ state barrier between S₃ and S₃a, the S₁ and S₂ potentials in Figure 10 slope downwards towards M₁. The S₁ energy decreases by ~1100 cm⁻¹ upon reaching the minimum at the stack-parallel S₈ geometry, which is shown in Figure 1(e). This S₁ state well corresponds to the B₁₄₁ excimer state of (Bz)₂, which has been extensively treated by calculations at different levels of theory.²⁷⁻³¹ Note that the interplanar distance of S₈—at which the vertical electronic excitations are calculated—is R ≈ 3.7 Å, longer than the optimum distance Rₑ = 3.05 Å in the S₁(B₁₄₁) state, thus the true B₁₄₁ minimum is much deeper than shown in Figure 10.²⁷⁻³² Several theory groups have studied the ¹B₁₄₁ and ¹B₂₄₂ excimer states of the S₈ and M₁ benzene dimer, usually as a function of the interplanar distance R while maintaining the D₉₆ and D₂₉₂ symmetries, respectively.²⁷⁻³² The calculated B₁₄₁ excimer well depths range between Dₑ = 0.46 eV (3570 cm⁻¹) and Dₑ = 0.70 eV (5650 cm⁻¹) at the TD-DFT level and Dₑ = 0.43 eV (3470 cm⁻¹) at the CASPT2 level.²⁸

The S₀ → S₁ and S₀ → S₂ transitions of D₉₆-symmetric S₈ are both electric-dipole forbidden.²⁷,²⁹,³¹ However, at the M₁ geometry—which may be populated in the supersonic jet experiments—the symmetry lowering to C₂ᵥ renders the S₀ → S₂ transition slightly allowed. The SCS-CC2 calculated fₑ(S₂) is 3.40 × 10⁻⁶, which is 35% of that at the M₂ minimum. Since the S₁ state surface at the M₁ geometry is strongly tipped towards S₈, the S₀ → S₂ transition of M₁ leads to levels that will couple to vibrations high up in the B₁₄₁ excimer well, see Figure 10, and the high vibrational mode density at this energy should lead to a broad and continuous band shape. The SCS-CC2 predicted S₀ → S₁ transition energy M₁ lies near or below to the S₁ origin of M₂. We propose that the S₀ → S₂ absorption from M₁-type ground-state VRT levels contributes to the weak and broad features underlying the S₀ → S₂ origin in the R2PI spectrum, see Figure 7.

D. The excited-state T-shape ↔ excimer interconversion

Saigusa and co-workers have experimentally studied the formation and fluorescence of the (Bz)₂ excimer following electronic excitation of M₂ at its 0₁ₐ, 0₁₈, and 0₁₆₁ vibronic bands.¹⁸ The corresponding S₁ state levels are shown in Figure 10 as short red horizontal bars above M₂. When exciting at the 0₁₆₁ band, they observed only broad, red-shifted excimer fluorescence with a maximum at 32 000 cm⁻¹ and interpreted this as a tunneling-induced isomerization process leading from the initial M₂ to the S₈ excimer geometry.¹⁸ This process is indicated by a horizontal oscillatory line in Figure 10. Rocha-Rinza et al. have calculated the S₁ state PES along the two coordinates R and δ at the CASPT2 level with an atomic natural orbital basis set and found a 160 cm⁻¹ (0.02 eV) barrier along the S₃ → S₃a → M₁ S₁ state path.²⁸ in qualitative agreement with Figure 10. Figure 10 indicates that the tunneling from the M₂ ν′ = 0 level produces the S₁ state excimer in highly excited vibrations that access geometries ranging from S₈ to M₁ and S₃a; the resulting breaking of the D₉₆ symmetry of S₈ gives rise to weakly allowed fluorescence, as observed by Saigusa and co-workers.¹⁸ The high density of vibrational states in the B₁₄₁ excimer well renders back-tunneling to states near the T-shaped ν′ = 0 level exceedingly improbable, in agreement with experiment.¹⁸

Interestingly, Saigusa and co-workers observed both resonance fluorescence from the T-shaped dimer and excimer fluorescence when exciting the 6₁₆₁ (S₈) band and interpreted this in terms of an excited-state equilibrium between T-shaped and excimer geometries.¹⁸ Figure 10 shows that—in contrast to the ν′ = 0 level—the ν′₆ level lies well above the S₁ state barrier. While the vibrational level density corresponding to M₂ is much larger at the ν′₆ vibrational energy than at the ν′ = 0 level, the mode density of the excimer structures also increases, so it is not immediately obvious that the T-shape ↔ excimer equilibrium is strongly shifted toward the T-shaped structure. However, Figure 10 shows that the T-shaped structures have much larger oscillator strengths for fluorescence emission to S₀ than the excimer-type structures. This strongly biases the probability for observing resonance fluorescence in favor of the T-shaped structures. When exciting at the 6₁₆₁ band, Saigusa and co-workers observed only Bz’ monomer fluorescence and interpreted this as dimer dissociation being fast relative to excimer formation and fluorescence.¹⁸ This is in agreement with the position of the ν′₆ + ν′₇ level, which lies above the dissociation limit to Bz + Bz’. The dissociation process is schematically indicated shown in Figure 10.

In summary, the combination of the S₁ and S₂ state SCS-CC2 potential energy surfaces with the CCSD(T) ground-state
V. CONCLUSIONS

Vibrionically resolved mass-selective electronic spectra of (Bz-h2)2 and its isotopomer (Bz-d6)2 are presented that show the well-known S0 → S1 transition as well as the S0 → S2 transition, which has not been reported before. The S0 → S1 transition is shifted by +253 cm⁻¹ for (Bz-h6)2 and by +223 cm⁻¹ for (Bz-d6)2 relative to the corresponding S0 → S1 origin.

The agreement with SCS-CC2/aug-cc-pVQZ vertical excitation energies and corresponding oscillator strengths is excellent. We show that the oscillator strengths are strongly geometry dependent: at the T-shaped C2v level, the oscillator strengths of both transitions were nearly zero, whereas at C2 symmetry, a S1 : S2 ratio of roughly 10:1 was predicted by the calculations and confirmed by experiment. This conclusively shows that the ~2 cm⁻¹ splitting on the electronic origin of the S1 state of benzene does not arise from an excitonic interaction. The S1/S2 splitting is dominated by the structural inequivalence of the two Bz chromophores.

The R2Pi spectrum of the trimer imidazole · (benzene)2 is presented in comparison: the two benzene units within this trimer complex form a structure similar to the (benzene)2, although the stem benzene is tipped sideways, similar to S3a due to the interaction with the imidazole moiety. The R2Pi spectra of imidazole · (benzene)2 confirm the strong geometry dependence of the f,0(S1) and f,1(S2) oscillator strengths: the S0 → S2 transition is much stronger in imidazole · (benzene)2 than in (benzene)2 because the benzene moieties are fixed at a low-symmetry geometry and are strongly tilted compared to (benzene)2. The S0 → S1/S2 electronic origin frequencies of imidazole · (benzene)2 lie very close to those of (Bz)2, thereby confirming the interpretation of the (Bz)2 spectrum. The calculated f,0(S1) and f,1(S2) oscillator strengths of imidazole · (benzene)2 agree well with the observed spectrum.

Vertical excitation energies of the S1 and S2 states were calculated at five ground-state stationary-point geometries ranging from the T-shaped M2, S3, and S3a structures to the stacked M1 and S8 geometries. The excited-state potentials constructed from these energies agree with the proposition of earlier workers that the S0 → S1 excitation of (benzene)2 leads to a T-shaped local minimum that rapidly rearranges into a vibrationally excited excimer geometry, and that ionization takes place from the B1g excimer state. Since the 0′ 0 band has a width of ~1.3 cm⁻¹, the lifetime for tunneling out of this minimum is ≥7 ps, but it has never been directly measured.

We also interpret the state-specific fluorescence properties of the ν′ = 0, ν′, and ν′ + 1 levels of (Bz)2 in terms of the S1/S2 potential energy and transition-dipole moment surfaces. The ν′, level of (Bz)2 is embedded in a huge background density of vibrations of the B1g excimer minimum that lies 3000–4500 cm⁻¹ lower. The dissociation of the (Bz)2 upon excitation at the 0′, 0 band agrees well with our calculations.

Combining these results with previous calculations of the S1 and S2 excited states at the M1 and S8 geometries, we show that the S0 → S1 and S0 → S2 transitions are only partially forbidden for many ground-state structures that are populated in the jet-cooled (Bz)2 ground state, specifically for VRT levels near S3 and M1. The only other structure with a reasonable transition-dipole moment is the C2v symmetric T-shaped dimer S3a, which has a more intense S0 → S1 and a weak S0 → S2 transition. This strong bias of the S1 and S2 transition-dipole moment surfaces of (Bz)2 against geometries that are not T-shaped, such as M1 and S8, is the main reason why all vibrionic spectroscopic experiments on jet-cooled (Bz)2 to date have indicated a T-shaped structure, although theory predicts that the parallel-displaced M1 structure is a local minimum.

The electronic spectrum of jet-cooled (Bz)2 can only be observed through an experimental “keyhole” that strongly favors observation of the T-shaped geometry and does not allow to observe the other low-energy minima on the S0 state surface. An analogous bias exists against the microwave spectroscopic observation of VRT ground-state levels near the M1 parallel displaced structure, because the M1 structure has no permanent dipole moment.

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45. See supplementary material at http://dx.doi.org/10.1063/1.4922608 for the Cartesian coordinates.