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

Franziska A. Balmer, Maria A. Trachsel, Ad van der Avoird, and Samuel Leutwyler
Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland
Theoretical Chemistry, Institute for Molecules and Materials, Radboud University Nijmegen, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

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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 $\sim 240$ 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 $\cdot$ (Bz)$_2$, which has a rigid triangular structure with a tipped (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.

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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 $0_0^+$ band of the (Bz)$_2$ $S_0 \rightarrow S_1$ transition at 38 046 cm$^{-1}$, red-shifted by 40 cm$^{-1}$ from the $S_0 \rightarrow S_0$ ($0_0^+$) 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 $0_0^+$ ($S_1$) 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 $S_1 \rightarrow S_1$ and the $S_0 \rightarrow S_2$ excitations of (Bz)$_2$, Schlag and co-workers subsequently...
undertook detailed spectroscopic studies of (Bz-\(h_6\))\(_2\), the (Bz-\(d_6\))(Bz-d_6)\(_2\), and of other D- and \(^{13}\)C-isotopomers of (Bz)\(_2\), attempting to determine the excitonic splitting between the \(S_0\) \(\rightarrow\) \(S_1\) and \(S_0\) \(\rightarrow\) \(S_2\) origins of (Bz)\(_2\), as well as the excited-state structure of (Bz)\(_2\).\(^{10,12}\) Combining the spectroscopic results with early high-level \textit{ab initio} calculations of (Bz)\(_2\), Schlag, Hobza, and co-workers concluded that the (Bz)\(_2\) structure is T-shaped.\(^{10,12,24,25}\) In good agreement with the later microwave structure,\(^2\) They interpreted a \(\sim 2\) cm\(^{-1}\) splitting of the \(0^0\) band of (Bz)\(_2\) as arising from the excitonic \(S_1/\tilde{S_1}\) splitting.\(^{10,12}\) Felker and co-workers performed stimulated-Raman spectroscopic measurements on (Bz)\(_2\) and its isotopomers, determined that (Bz)\(_2\) consists of two inequivalent monomers,\(^{13–16}\) and interpreted the low-frequency intermolecular and intramolecular Raman vibrational bands in terms of a T-shaped dimer.\(^{13–16}\) Erlekm et al. have recorded the IR spectrum of (Bz)\(_2\)\(^{19}\) and observed the \(b_{1u}\) stretch frequency of the stem Bz moiety, in agreement with the T-shaped structure,\(^{19,20}\) and the calculated C–H stretching frequency shift.\(^{26}\)

Felker and co-workers pointed out that the symmetry of the stem-Bz in the T-shaped dimer is lowered from \(D_{6h}\) to \(C_2\), rendering the \(S_0\) \(\rightarrow\) \(S_1\) electronic origin weakly allowed, but that the internal rotation of the cap-Bz renders its site symmetry \(C_{6v}\), in which the \(0^0\) band remains forbidden.\(^{14,16}\) Nevertheless, (Bz)\(_2\) has two excited states that correlate with the \(S_0\) \(\rightarrow\) \(S_1\) excitation of its two Bz constituents. Indeed, Henson et al. tentatively assigned a \(\tilde{6}–8\) cm\(^{-1}\) blue-shifted \(0^0_1\) band” localized on the cap-Bz moiety.\(^{14}\) As the calculations and experiments below will show, the separation between the \(S_1\) and \(S_2\) \(0^0\) transitions of the T-shaped dimer is \(\sim 200\) cm\(^{-1}\). Also, it is dominated by the “site-splitting” energy\(^{13–16}\) and not by the excitonic splitting.\(^{10,12}\)

Because benzene lacks a dipole moment, the lowest-order electrostatic interaction in (Bz)\(_2\) 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\(_2\) 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.\(^{27–33}\)

Szalewicz and co-workers, who calculated the six-dimensional intermolecular PES of Bz\(_2\) 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.\(^3\) 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.\(^4\) Below, we employ their nomenclature\(^4\) 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 \(D_e = -2.65 \pm 0.02\) kcal/mol.\(^{33}\) This value is only 0.03 kcal/mol lower than the CCSD(T)/CBS value of \(D_e = -2.62\) kcal/mol CCSD(T) value of Szalewicz and co-workers, which was not optimized for the intramolecular degrees of freedom.\(^4\)

We first concentrate on the \(C_2\)-symmetric, tipped T-shaped global minimum M2 and on the low-lying \(C_{2v}\)-symmetric index-1 saddle point S3, see Figure 1.\(^{3,4}\) We address the properties of the \(S_1\) and \(S_2\) states of (Bz)\(_2\) both spectroscopically and theoretically, with a focus on the \(S_2\) state. We present vibronic spectra of (Bz)\(_2\) and the (Bz-d_6)\(_2\) isotopomer that show weak band systems starting \(\sim 240\) cm\(^{-1}\) above the respective \(S_0\) \(\rightarrow\) \(S_1\) electronic origins. Using approximate second-order coupled-cluster CC2 calculations, we predict (1) the energetic order and the splitting between the \(S_1\) and \(S_2\) 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.,\(^{13–16}\) we find that the lowest electronic excitation of the cap-Bz—corresponding to the (Bz)\(_2\) \(S_2\) state—is extremely weak in the \(C_{2v}\)-symmetric T-shaped dimer S3. However, displacement along the \(\omega\) tipping angle from S3 towards the tipped T-shaped global minimum M2 increases both the \(f_d(S_1)\) and \(f_d(S_2)\) oscillator strengths which correspond to the stem and cap electronic transitions. (We use “tipping” for consistency with our previous work\(^34–36\) but note that the \(\omega\) coordinate was denoted “tilt” in Refs. 4–7.) We also compare the vibronic spectrum of (Bz)\(_2\) to the recently measured vibronic spectrum of the imidazole \(\cdot\) (Bz)\(_2\) cluster,\(^{37}\) which has a triangular structure with the (Bz)\(_2\) subunit bent more strongly than in (Bz)\(_2\). In Sec. IV, we extend the SCS-CC2 calculations to the \(S_1\) and \(S_2\) states of two low-lying ground-state

FIG. 1. Ground-state stationary-point structures of (benzene)\(_2\): (a) the minimum-energy \(C_3\)-symmetric structure M2 with definition of the tipping angle \(\omega\), (b) the \(C_{2v}\)-symmetric saddle-point S3 with the inertial axis system, (c) the T-shaped \(C_1\)-symmetric saddle point S3a with definition of the tilting angle \(\delta\), (d) the parallel-displaced \(C_{2h}\)-symmetric local minimum M1, and (e) the stacked-parallel \(D_{sh}\)-symmetric saddle point structure S8. The conformer nomenclature is defined in Refs. 3 and 4.
saddle-point geometries $S_{3a}, S_{8}$ and the parallel displaced local minimum $M_{1}$, see Figure 1.

II. METHODS

A. Computational methods

The $S_{1}$ excited state of B$_{2}$ has been characterized at several different levels of theory, including time-dependent DFT (TD-DFT),$^{27,29}$ complete active-space second-order perturbation theory (CASPT2),$^{28}$ linear-response coupled cluster methods [LR-CC2, LR-CCSD, and LR-CCSDR(3)],$^{30}$ and equation-of-motion CCSD,$^{31}$ but only at the stacked-parallel $S_{8}$ and parallel-displaced $M_{1}$ geometries. These structures transform as $B_{1}$ and $B_{2}$ in the $D_{3h}$ and $C_{2v}$ point groups, respectively (see Figure 1), and correspond to the “excimer” geometry of B$_{2}$. However, the stacked $S_{8}$ geometry is not a ground-state minimum, and the $M_{1}$ 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 $S_{1}$ 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 B$_{2}$ minimum in the $S_{1}$ state, we employed the spin-component scaled (SCS) CC2 method with large and diffuse basis sets.$^{38–40}$ 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.$^{40}$ Spin component scaling not only improves the CC2 excited state energies but also the dipole moments and vibrational frequencies.$^{38–40}$

We optimized the ground state of (Bz)$_{2}$ with the SCS variant of the second-order Møller-Plesset perturbation theory (MP2) method$^{40–43}$ using the Dunning augmented correlation-consistent basis sets aug-cc-pVXZ 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 Bz$_{2}$ dimer,$^{33}$ 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.$^{33}$ The SCS-CC2 vertical excitations to the $S_{1}$ and $S_{2}$ states were calculated at the respective SCS-MP2 ground-state equilibrium structures in the resolution of the identity (RI) approximation$^{43}$ employing the aVXZ basis sets. The like and unlike spin components of the MP2 and CC2 energies were scaled according to Grimme.$^{42}$ The SCS-MP2/aug-cc-pVTZ optimized Cartesian coordinates of the T-shaped M$_{2}$ minimum and the S$_{3}$ and S$_{3a}$ saddle point structures are given in Tables I–III of the supplementary material.$^{44}$

All calculations were performed using Turbomole 6.3 (RICC2 module).$^{45}$ 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 (Bz- $h_{6}$)$_{2}$ and its isotopomer (Bz- $d_{6}$)$_{2}$ were produced and cooled in a pulsed supersonic jet expansion. The Bz (Fluka, 99%) or Bz- $d_{6}$ (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)$_{2}$ (Im ⋅ Bz$_{2}$) measurements,$^{37}$ 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 Bz$_{2}$ dimers and Im ⋅ Bz$_{2}$ trimer were recorded over the 37500–39000 cm$^{-1}$ range. Electronic excitation was performed with a frequency-doubled NarrowScan dye laser (Counmarin 307 in EtOH, ∼200 μJ/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 ⋅ Bz$_{2}$ cluster fragments into the Im ⋅ Bz$^{+}$ mass channel, the true two-color R2PI spectrum of Im ⋅ Bz$_{2}$ was obtained by IR/UV holeburning measurements. The IR laser pulse (<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 ⋅ Bz$_{2}$ 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$_{s}$-symmetric M$_{2}$ 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 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$_{2v}$ (S$_{3}$) geometry, the $S_{1}$/$S_{2}$ splitting is slightly smaller, about 200–210 cm$^{-1}$ with the aVXZ basis sets. The irrep of the $S_{1}$ and $S_{2}$ states are $A'$ in the C$_{s}$ 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 ~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$_{0}$′ transition of the stem Bz is spectrally shifted by $\delta \nu = -44.4$ cm$^{-1}$ relative to the
(forbidden) electronic origin of bare Bz.8–16,18 On the other hand, the spectral shift $\delta \nu$ of the cap-Bz transition can be estimated from the spectra of X–H $\cdots$ π bonded T-shaped Bz complexes such as Cl–H $\cdots$ Bz, H$_2$O $\cdots$ Bz, and D$_2$O $\cdots$ Bz, where the Bz is in the cap position.46–49 The $S_0 \rightarrow S_1$ electronic origins of the cap-Bz become allowed due to the slight tilt of the X–H donor axis relative to the Bz surface normal and are typically shifted by $\delta \nu = +80$ to $+125$ cm$^{-1}$ above the Bz $0_0^s$ band.46–49 Combining the stem-type and cap-type spectral shifts yields a rough estimate for the site splitting of about 120–170 cm$^{-1}$, in qualitative agreement with the SCS-CC2 calculated values.

2. Electronic oscillator strengths

The SCS-CC2 calculated electronic oscillator strengths $f_{el}(S_1)$ and $f_{el}(S_2)$ depend both on the size of the basis set and geometry of the dimer. Figure 2(a) shows the calculated oscillator strengths at the $C_{2v}$-symmetric T-shaped S3 geometry and Figure 2(b) shows the analogous results at the $C_s$-symmetric M2 minimum. The $f_{el}(S_1)$ and $f_{el}(S_2)$ values are also listed in Table I.

With the diffuse aVXZ basis sets, $f_{el}(S_1)$ is about 10 times larger than $f_{el}(S_2)$ in both the $C_{2v}$ and $C_s$ geometries. With the smaller SVP basis set, $f_{el}(S_2)$ is larger than $f_{el}(S_1)$ in the S3 geometry, while in the M2 geometry, they are nearly equal, see Figures 2(a) and 2(b). While the SVP transition energies are reasonable, these electronic oscillator strengths are clearly less reliable, so they will be disregarded from now on. By contrast, the aVXZ electronic oscillator strengths change little with increasing basis set size, both at the $C_{2v}$ and $C_s$ geometries as can be seen in Figure 2. Both $f_{el}(S_1)$ and $f_{el}(S_2)$ 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 $f_{el}(S_2)$ 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 (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.44 The $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ TDM vectors are both oriented within the $c_\pi$ 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 $\sim 40^\circ$ 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 and aVQZ basis sets).

A comparison of Figures 2(a) and 2(b) reveals that both $f_{el}(S_1)$ and $f_{el}(S_2)$ are considerably smaller at the S3 than at the M2 geometry. This implies that $f_{el}$ is a function of the tipping angle $\omega$, see Figure 1(a). In Figure 6, we show the SCS-CC2/aVTZ calculated oscillator strengths $f_{el}(S_1)$ and $f_{el}(S_2)$ calculated as a function of $\omega$: both oscillator strengths indeed increase by $\sim 10$ times when $\omega$ is increased from 0° to 20°. Throughout the entire angle range shown, $f(S_1)$ is 5–10 times larger than $f(S_2)$.
on the intermolecular vibrational $\omega$ coordinate implies that there is a coordinate-dependent contribution for $\omega$ 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 M2 does not correspond to a vibrational eigenstate. The correct $\nu = 0^*/0^+$ 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

<table>
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<th>Structure</th>
<th>$f_{el}$, aug-cc-pVDZ</th>
<th>$f_{el}$, aug-cc-pVTZ</th>
<th>Fraction</th>
<th>Assignment</th>
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<td>24.6%</td>
<td>cap/stem $\pi$ $\rightarrow$ cap/stem $\pi^*$</td>
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<tr>
<td>S0 $\rightarrow$ S2</td>
<td>1.22 x 10^{-4}</td>
<td>1.15 x 10^{-4}</td>
<td>12.7%</td>
<td>stem/cap $\pi$ $\rightarrow$ cap/stem $\pi^*$ charge transfer</td>
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<tr>
<td>M2/C4v</td>
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<td>1.02 x 10^{-5}</td>
<td>20.3%</td>
<td>cap/stem $\pi$ $\rightarrow$ cap/stem $\pi^*$</td>
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<tr>
<td>S3a/C2v</td>
<td>4.39 x 10^{-6}</td>
<td>3.52 x 10^{-6}</td>
<td>10.3%</td>
<td>stem/cap $\pi$ $\rightarrow$ stem $\pi^*$</td>
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<tr>
<td>S0 $\rightarrow$ S1</td>
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<td>27.3%</td>
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<tr>
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FIG. 3. Dominant orbital excitation contributions to the S0 $\rightarrow$ S1 (red) and S0 $\rightarrow$ S2 transitions (blue) of the C2v-symmetric S3 structure of (benzene)_2 (SCS-CC2/aug-cc-pVDZ calculation).

FIG. 4. Dominant orbital excitations corresponding to the S0 $\rightarrow$ S1 (red) and S0 $\rightarrow$ S2 transitions (blue) for the C4v-symmetric M2 structure of (benzene)_2 (SCS-CC2/aug-cc-pVDZ).
SCS-CC2 transition dipole moments of the $S_0 \rightarrow S_1$ (red) and $S_0 \rightarrow S_2$ (blue) transitions of the M2 ($C_s$) structure of (Bz)$_2$, as a function of basis set size from aVDZ to aVQZ.

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-$h_6$)$_2$ and (Bz-$d_6$)$_2$. The electronic origin of (Bz-$h_6$)$_2$ lies at 38 041.7 cm$^{-1}$ and that of (Bz-$d_6$)$_2$ 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-$h_6$)$_2$ and (Bz-$d_6$)$_2$. In the (Bz-$h_6$)$_2$ 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 $v_{16}^*$ 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-$h_6$. In the (Bz-$d_6$)$_2$ spectrum, Figure 7(b), the lowest of the weak bands is observed at +208.5 cm$^{-1}$, in very good agreement with the $v_{16}^*$ = 208 cm$^{-1}$ frequency of $S_1$ state $C_3vD_{6h}$. Thus, the (Bz-$h_6$)$_2$ and (Bz-$d_6$)$_2$ spectra in Figures 7(a) and 7(b) are consistent in showing a $16_0^*$ excitation of the stem Bz moiety.

Since Bz-$h_6$ and Bz-$d_6$ have no other low-frequency vibrations in the 200–300 cm$^{-1}$ range, we assign the following

FIG. 7. Top: SCS-CC2 calculated vertical frequencies and oscillator strengths of the (benzene)$_2$ $S_0 \rightarrow S_1/S_2$ transitions with the aVXZ ($X = D,T,Q$) basis sets. The calculated frequencies are shifted by about −2000 cm$^{-1}$ to coincide with the experimental $S_1(00_0^*)$ band. Bottom: two-color resonant two-photon ionization spectra of (a) (benzene-$h_6$)$_2$ and (b) (benzene-$d_6$)$_2$. Wavenumber scales are set to zero at the respective $S_0 \rightarrow S_1$ origins; the respective wavenumbers are given next to the $00_0^*$ bands. The medium weak bands at 00$^*_{00} + 238.1$ cm$^{-1}$ in (a) and at 00$^*_{00} + 208.5$ cm$^{-1}$ in (b) are assigned to the $16_0^*$ ($e_{2u}$) out-of-plane vibrational fundamental of the “stem” Bz-$h_6$ or Bz-$d_6$ moiety. The following weak bands are attributed to the weak $S_0 \rightarrow S_2$ transition.
series of weak bands to the \( S_0 \rightarrow S_2 \) excitation. The observed ratio between the \( S_0 \rightarrow S_1 \) \( 0^{\prime}_0 \) band intensity and the integrated intensity of the weak \( S_0 \rightarrow S_2 \) bands agrees nicely with the SCS-CC2 relative oscillator strengths \( f_d(S_1) \) and \( f_d(S_2) \). The spacing between the bands is \( \sim 15 \text{ cm}^{-1} \), increasing to \( \sim 20 \text{ cm}^{-1} \) for both (Bz-\( h_0 \)) and (Bz-\( d_0 \)). The low frequency spacing between the bands implies the participation of one or several intermolecular vibrational modes, as discussed below.

C. R2PI spectrum of imidazole \( \cdot \) (benzene)\(_2\)

Figure 8(b) shows the two-color R2PI spectrum of the imidazole \( \cdot \) (benzene)\(_2\) (Im \( \cdot \) Bz\(_2\)) cluster, which has recently been observed in a spectroscopic study of the imidazole \( \cdot \) benzene dimer.\(^{37,51}\) The calculated structure of this cyclic trimer is shown in the inset of Figure 8. It involves a NH \( \cdots \) \( \pi \) interaction from the imidazole to benzene-1 followed by sequential CH \( \cdots \) \( \pi \) interactions from benzene-1 to benzene-2 and then from benzene-2 back to imidazole. The (Bz)\(_2\) moiety contained within the Im \( \cdot \) 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 \( \delta \) angle, which is defined for the S3a structure of (Bz)\(_2\) shown in Figure 1(c). Relative to the S3 structure in Figure 1(b), the symmetry descent is \( C_{2v} \rightarrow C'_v \), where the prime indicates that the mirror plane of the S3a (\( C'_v \)) structure is not the same as that in the M2 (\( C_s \)) structure.

Since the cap (or Bz-2) moiety in Im \( \cdot \) Bz\(_2\) also acts as a stem-type CH \( \cdots \) \( \pi \) donor to imidazole, it acquires a much larger \( S_0 \rightarrow S_1 \) transition dipole moment than the cap-Bz in (Bz)\(_2\). This is brought out by the SCS-CC2/aVTZ calculated transition intensities, which are \( f_d(S_1) : f_d(S_2) = 1 : 3.0 \) for the two benzene chromophores, as shown in Figure 8(a).\(^{37}\) Therefore, the Im \( \cdot \) 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 \( S_0 \rightarrow S_1 \) and \( S_0 \rightarrow S_2 \) excitations of Im \( \cdot \) Bz\(_2\) correspond to simultaneous excitations of both Bz-1 and Bz-2 moieties.\(^{37}\) The experimental ratio of the integrated band structure corresponding to the \( S_0 \rightarrow S_1 \) and \( S_0 \rightarrow S_2 \) transitions of imidazole \( \cdot \) (benzene)\(_2\) is \( f_d(S_1) : f_d(S_2) = 1 : 2.9 \), in very good agreement with the vertical SCS-CC2/aVTZ calculation, see above. Note that the \( 0^{\prime}_0 \) band of the \( S_0 \rightarrow S_2 \) transition of Im \( \cdot \) Bz\(_2\) has a width of 3.6 cm\(^{-1}\) (FWHM), which is considerably broader than the \( 0^{\prime}_0(S_1) \), which is only 0.9 cm\(^{-1}\) (FWHM) wide. This implies that the \( S_2 \) state of Im \( \cdot \) Bz\(_2\) is more strongly coupled to the \( S_1 \) state than in (Bz)\(_2\).

IV. DISCUSSION

A. Appearance of forbidden vibrational transitions

As discussed in Sec. III C, the bands at \( 0^{\prime}_0 + 238.5 \text{ cm}^{-1} \) in (Bz-\( h_0 \)) and at \( 0^{\prime}_0 + 208.5 \text{ cm}^{-1} \) in (Bz-\( d_0 \)) correspond very closely to the \( S_1 \) state \( v'_1 \) frequencies of bare benzene, which are 238 cm\(^{-1}\) in benzene-\( h_0 \) and 208 cm\(^{-1}\) in benzene-\( d_0 \).\(^{23,50}\) The \( v'_1 \) mode is degenerate (\( \epsilon_{2u} \)) and its vibrionic species in the \( S_1 \) state of Bz-\( h_0 \) and Bz-\( d_0 \) is \( B_2u \otimes \epsilon_{2u} = E_1g \). Therefore, the \( 16^0 \) fundamental transition of bare Bz-\( h_0 \) or Bz-\( d_0 \) is electric-dipole forbidden in excitation from the \( A_{1g} \) ground-state \( v'' \) = 0 level, as discussed above.\(^{21-23}\)

The SCS-CC2 calculations in Sec. II B predict that the \( S_0 \rightarrow S_1 0^{\prime}_0 \) excitation of the T-shaped M2 dimer is associated with the stem-Bz moiety. The appearance of the \( 16^0 \) band in (Bz-\( h_0 \)) and (Bz-\( d_0 \)) therefore reflects a symmetry lowering of the stem-Bz. The symmetry descents to energetically low-lying geometries\(^{3,4}\) are from \( D_{4h} \) in bare Bz to \( C_{2v} \), to \( S_3 \), or to \( C'_v \) in S3a, see Figure 1. The \( D_{4h} \rightarrow C_{2v} \) descent splits the \( \epsilon_{2u} \) vibration into \( a_2 \) and \( b_2 \) components.\(^{32}\) Since the \( S_0 \rightarrow S_1 \) TDM transforms as \( a_1 \) in \( C_{2v} \), neither component of \( v'_1 \) becomes allowed. The \( D_{4h} \rightarrow C_{2v} \) descent splits \( \epsilon_{2u} \) into \( a''_1 \) + \( a''_2 \); the electronic TDM transforms as \( a'' \) (see Figure 5), and again, neither component is allowed. The \( D_{4h} \rightarrow C'_v \) descent to S3a splits \( \epsilon_{2u} \) into \( a''_1 \) + \( a''_2 \) and the electronic TDM transforms as \( a'' \), which makes the \( v''_{16a} \) component electric-dipole allowed.

Conversely, the appearance of the \( 16^0 \) fundamental in the \( S_0 \rightarrow S_1 \) spectrum implies the existence of \( S_0 \) state levels of (Bz-\( h_0 \)) and (Bz-\( d_0 \)) that (1) have a rigid-molecule symmetry equivalent to \( C'_v \) and (2) are populated at the \( T = 3-5 \text{ K} \).
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_1 (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 cm\(^{-1}\) in (Bz-d_6)_2 and at +253 cm\(^{-1}\) in (Bz-h_6)_2, six weak bands appear further towards the blue. Since Bz-d_6 and Bz-h_6 have no low-lying vibrations other than \(\nu_{16}\), we assign these bands to the S0 \rightarrow S2 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)_2 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 S0 \rightarrow S2 electronic transition are similar to the bands that are associated with the S1(6^3_1) 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 S0 \rightarrow S2 bands are shown in Figure 9. The intermolecular vibrations involved are probably the totally symmetric modes \(\omega', \sigma', \text{ and } \chi'\), 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 \(f_{el}(S1)/f_{el}(S2)\) oscillator strengths are indicated by red/blue dots with radii that are proportional to the \(f_{el}\) values.

**TABLE II.** Benzene dimer SCS-MP2/aug-cc-pVTZ S0 state calculated and experimental intermolecular vibrational frequencies in the S1(6^3_1) and S2(0^0_0) regions (in cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Label</th>
<th>(S_{th, \text{calc.}})</th>
<th>(S_{1}(6^3_1)), exp.</th>
<th>(S_{2}(0^0_0)), exp.</th>
</tr>
</thead>
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<tr>
<td>Twist</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Tilt</td>
<td>(\delta)</td>
<td>14.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tipping</td>
<td>(\omega)</td>
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<td>23</td>
<td>21</td>
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<tr>
<td>Stretch</td>
<td>(\sigma)</td>
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<td>39</td>
<td>37</td>
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<tr>
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<td>56</td>
<td>55</td>
</tr>
<tr>
<td>Buckle</td>
<td>(\beta)</td>
<td>68.2</td>
<td></td>
<td></td>
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</table>

**FIG. 9.** Two-color R2PI spectrum of (benzene-h_6)_2 in the S1(6^3_1) region (top) and in the S2(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\(^{-1}\).

**FIG. 10.** 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 π-stacked conformers of (benzene)_2 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 \(D_{el}(S1)\) is from Ref. 4; the S1 and S2 binding energies \(D_{el}\) are discussed in the text.
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 S\(_0\) state of the M2 structure, van der Avoird et al. have calculated a CCSD(T) binding energy of \(D_g = 975\ \text{cm}^{-1}\) and a dissociation energy of \(D_h = 870\ \text{cm}^{-1}\).\(^{3,4}\) Since the S\(_0\) → S\(_1\) electronic origin of M2 lies 44 cm\(^{-1}\) below the (forbidden) S\(_0\) → S\(_1\) electronic origin of benzene at 38 086 cm\(^{-1}\), the S\(_1\) state dissociation energy of M2 is 44 cm\(^{-1}\) larger than the ground-state value, yielding \(D_h(S_0) = 914\ \text{cm}^{-1}\) and \(D_h(S_1) \sim 1020\ \text{cm}^{-1}\) for the S\(_1\) state local minimum corresponding to M2, see Figure 10.

Overall, the largest oscillator strength is \(f_{el}(S_1)\) of the M2 structure; only half of the dot is shown for clarity in Figure 10. As discussed above, the \(f_{el}(S_2)\) at the M2 geometry is \(\sim 10\) times smaller than \(f_{el}(S_1)\), in agreement with experiment. The decrease of \(\omega\) towards zero decreases both \(f_{el}(S_1)\) and \(f_{el}(S_2)\), as shown in Figure 6. This renders low-lying S\(_0\) state VRT levels that are associated with the S3 structure difficult to observe by electronic spectroscopy.

For the S3a geometry, Figure 10 shows that \(f_{el}(S_2)\) is \(\sim 10\) times larger than \(f_{el}(S_1)\) and also twice that of \(f_{el}(S_1)\) at M2. The calculated S\(_0\) → S\(_2\) transition energy is close to the S\(_0\) → S\(_2\) transition of M2. This implies that transitions from ground-state VRT levels with average geometries close to S3a might appear intermingled with the S\(_0\) → S\(_2\) 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.\(^{3,4}\) Its S\(_0\) → S\(_1\) transition is \(A_2 \rightarrow B_2\) in C\(_{2h}\) and is electric-dipole forbidden.\(^{27–30}\) However, the S\(_0\) → S\(_2\) transition of M1 is weakly allowed, and we discuss this further below.

Starting at the S\(_1\) state barrier between S3 and S3a, the S\(_1\) and S\(_2\) potentials in Figure 10 slope downwards towards M1. The S\(_1\) energy decreases by \(-1100\ \text{cm}^{-1}\) upon reaching the minimum at the stacked-parallel S8 geometry, which is shown in Figure 1(e). This S\(_1\) state well corresponds to the B\(_{1g}\) 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 \(R \sim 3.7\ \text{Å}\), longer than the optimum distance \(R_c = 3.05\ \text{Å}\) in the S\(_1\)(B\(_{1g}\)) state, thus the true B\(_{1g}\) minimum is much deeper than shown in Figure 10.\(^{27–32}\) Several theory groups have studied the B\(_{1g}\) and B\(_{2g}\) excimer states of the S8 and M1 benzene dimer, usually as a function of the interplanar distance \(R\) while maintaining the D\(_{6h}\) and D\(_{3h}\) symmetries, respectively.\(^{27–32}\) The calculated B\(_{1g}\) excimer well depths range between \(D_c = 0.46\ \text{eV} (3570\ \text{cm}^{-1})\) and \(D_c \sim 0.70\ \text{eV} (5650\ \text{cm}^{-1})\) at the TD-DFT level and \(D_c = 0.43\ \text{eV} (3470\ \text{cm}^{-1})\) at the CASPT2 level.\(^{28}\)

The S\(_0\) → S\(_1\) and S\(_0\) → S\(_2\) transitions of D\(_{6h}\)-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 C\(_{2h}\) renders the S\(_0\) → S\(_2\) transition slightly allowed. The SCS-CC2 calculated \(f_{el}(S_2)\) is \(3.40 \times 10^{-5}\), which is 35\% of that at the M2 minimum. Since the S\(_1\) state surface at the M1 geometry is strongly tipped towards S8, the S\(_0\) → S\(_2\) transition of M1 leads to levels that will couple to vibrations high up in the B\(_{1g}\) 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 S\(_0\) → S\(_2\) transition energy M1 lies near or below to the S\(_1\) origin of M2. We propose that the S\(_0\) → S\(_2\) absorption from M1-type ground-state VRT levels contributes to the weak and broad features underlying the S\(_0\) → S\(_2\) 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 \(0^0_0\), \(0^1_0\), and \(1^1_0\) vibronic bands.\(^{18}\) The corresponding S\(_1\) state levels are shown in Figure 10 as short red horizontal bars above M2. When exciting at the \(0^0_0\) 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.\(^{15}\) This process is indicated by a horizontal oscillatory line in Figure 10. Rocha-Rinza et al. have calculated the S\(_1\) state PES along the two coordinates \(R\) and \(\delta\) at the CASPT2 level with an atomic natural orbital basis set and found a 160 cm\(^{-1}\) (0.02 eV) barrier along the S\(_3\) → S3a → M1 S\(_1\) state path\(^{29}\) in qualitative agreement with Figure 10. Figure 10 indicates that the tunneling from the M2 \(\nu' = 0\) level produces the S\(_1\) state excimer in highly excited vibrations that access geometries ranging from S8 to M1 and S3a; the resulting breaking of the D\(_{6h}\) 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 B\(_{1g}\) excimer well renders back-tunneling to states near the T-shaped \(\nu' = 0\) 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 \(0^1_0\) (S\(_1\)) 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 \(\nu' = 0\) level—the \(\nu'_0\) level lies well above the S\(_1\) state barrier. While the vibrational level density corresponding to M2 is much larger at the \(\nu'_0\) vibrational energy than at the \(\nu' = 0\) 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 S\(_0\) 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 \(0^1_0\) 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 \(\nu'_0 + \nu'_1\) 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 S\(_1\) and S\(_2\) state SCS-CC2 potential energy surfaces with the CCSD(T) ground-state
binding and dissociation energies of van der Avoird et al.\textsuperscript{4} and other spectroscopic data given in Figure 10 allow to confirm and interpret the conjecture of several groups that the excited T-shaped (Bz$_2$)$_2$ dimer is only a local on the S$_1$ state surface.\textsuperscript{8,9,18} The S$_1$ and S$_2$ state surfaces are also in agreement and are consistent with the vibration-dependent fluorescence excitation/absorption results of Saigusa and co-workers.\textsuperscript{18}

V. CONCLUSIONS

Vibrionically resolved mass-selective electronic spectra of (Bz-h)$_2$ and its isotopomer (Bz-d)$_2$ are presented that show the well-known S$_0 \rightarrow$ S$_1$ transition as well as the S$_0 \rightarrow$ S$_2$ transition, which has not been reported before. The S$_0 \rightarrow$ S$_1$ transition is shifted by +253 cm$^{-1}$ for (Bz-h)$_2$ and by +223 cm$^{-1}$ for (Bz-d)$_2$ relative to the corresponding S$_0 \rightarrow$ S$_1$ 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 C$_{2h}$ level, the oscillator strengths of both transitions were nearly zero, whereas at C$_s$ symmetry, a S$_1 :$ S$_2$ ratio of roughly 10:1 was predicted by the calculations and confirmed by experiment. This conclusively shows that the $\sim 2$ cm$^{-1}$ splitting on the electronic origin of the S$_1$ state of (benzene)$_2$ does not arise from an excitonic interaction.\textsuperscript{10,12} The S$_1$/S$_2$ splitting is dominated by the structural inequivalence of the two Bz chromophores.\textsuperscript{13-15}

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 $f(\Delta S_1)$ and $f(\Delta S_2)$ oscillator strengths: the S$_0 \rightarrow$ S$_2$ 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 S$_0 \rightarrow$ S$_1$/S$_2$ 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 $f(\Delta S_1)$ and $f(\Delta S_2)$ oscillator strengths of imidazole · (benzene)$_2$ agree well with the observed spectrum.

Vertical excitation energies of the S$_1$ and S$_2$ 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,\textsuperscript{8,9,18} that the S$_0 \rightarrow$ S$_1$ 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 B$_1g$ excimer state. Since the 0$^0g_0$ band has a width of $\sim 1.3$ cm$^{-1}$,\textsuperscript{8,9,12-15,18} the lifetime for tunneling out of this minimum is $\geq 7$ ps, but it has never been directly measured.

We also interpret the state-specific fluorescence properties\textsuperscript{18} of the $\nu' = 0$, $\nu'_0$ and $\nu'_0 + \nu'_1$ levels of (Bz)$_2$ in terms of the S$_1$/S$_2$ potential energy and transition-dipole moment surfaces. The $\nu'_0$ level of (Bz)$_2$ is embedded in a huge background density of vibrations of the $B_{1g}$ excimer minimum that lies 3000–4500 cm$^{-1}$ lower. The dissociation of the (Bz)$_2$ upon excitation at the 6$^1$S$_0$ band\textsuperscript{18} agrees well with our calculations.

Combining these results with previous calculations of the S$_1$ and S$_2$ excited states at the M1 and S8 geometries,\textsuperscript{28-32} we show that the S$_0 \rightarrow$ S$_1$ and S$_0 \rightarrow$ S$_2$ transitions are optically 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 C$_i$ symmetric T-shaped dimer S3a, which has a moderately intense S$_0 \rightarrow$ S$_2$ and a weak S$_0 \rightarrow$ S$_1$ transition. This strong bias of the S$_1$ and S$_2$ 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 vibronic spectroscopic experiments on jet-cooled (Bz)$_2$ to date have indicated a T-shaped structure,\textsuperscript{8,9,12-15,17,18} although theory predicts that the parallel-displaced M1 structure is a local minimum.\textsuperscript{27-32}

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 S$_0$ state surface. An analogous bias exists against the microwave spectroscopic observation\textsuperscript{25-27} of VRT ground-state levels near the M1 parallel displaced structure, because the M1 structure has no permanent dipole moment.

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44 See supplementary material at http://dx.doi.org/10.1063/1.4922608 for the Cartesian coordinates.
52 H. Ibach, Physics of Surfaces and Interfaces (Springer-Verlag, Berlin, Heidelberg, 2006).