Disentanglement of triplet and singlet states of azobenzene: direct EELS detection and QMC modeling

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Singlet and triplet excited states of trans-azobenzene have been measured in the gas phase by electron energy loss spectroscopy (EELS). In order to interpret the strongly overlapping singlet and triplet bands in the spectra a set of large-scale correlated quantum Monte-Carlo (QMC) simulations was performed. The EELS/QMC combination of methods yields an excellent agreement between theory and experiment and for the two low-lying excited singlet and two low-lying triplet states permitted their unambiguous assignment. In addition, EELS revealed two overlapping electronic states in the band commonly assigned as $S_2$, the lower one with a pronounced vibrational structure, the upper one structureless. Finally, the agreement between theory and experiment was shown to further increase by taking computationally into account the finite temperature effects.

I. Introduction

Azobenzene (AB), C$_{12}$H$_{10}$N$_2$, is perhaps the most prominent photoswitchable molecule with a relatively simple molecular structure. AB exists in the two structural isomers shown in Fig. 1, the energetically more stable trans (E) isomer and the metastable cis (Z) isomer, which have different physical, electronic, and transport properties. The E isomer is markedly longer compared to the $Z$ isomer, by $\approx$2.4 Å, and has a dramatically higher conductance, by two orders of magnitude, with respect to the $Z$ isomer. Laser light of appropriate wavelength induces $E \rightarrow Z$ photoswitching in AB. In the ground state, $S_0$, $Z \rightarrow E$ isomerization can take place also thermally. The two isomers exhibit different absorption bands which make AB a good candidate for light-triggered switches, image storage devices, and materials with photo-modulable properties. The isomerization is generally tacitly assumed to proceed in the singlet state. As shown below, triplet states can be involved and play an important role in thermal isomerization. The neglect of the role of the triplet states is presumably in part a consequence of the scarcity of experimental studies of the triplet states—existing experiments reported only absorption into singlet states. The main goal of this manuscript is to fill the gap and to provide the most complete characterization of the electronic structure of AB by a joint experimental/theory study.

![Structure of trans (E) and cis (Z) isomers of azobenzene featuring different CNNC dihedral angles.](Fig. 1)

Low-energy absorption spectra of AB have been measured for both isomers in gas phase and inert solvents. They show peaks attributed to the lowest $n\pi^*$ ($S_1$) and $\pi\pi^*$ ($S_2$) singlet states. The experiments were performed at temperatures from room temperature to temperatures in excess of 500 K, in some cases different parts of the same spectra were measured at different temperatures.

Experimental information on low-energy triplet states ($T_1, T_2, \ldots$) of AB is scarce, despite the fact that the $S_0 \rightarrow T_1$ spin-orbit coupling is an order of magnitude larger than values typical for aromatic compounds. No phosphorescence spectrum has been detected to date, and absorption spectra failed to reveal any band attributable to the singlet–triplet absorption or to triplet–triplet transient absorption upon laser excitation. To the best of our knowledge to date only two brief reports on triplet states of AB exist. Shashoua attributed to $T_1$ a state at $\sim$2.3 eV determined by magneto-optical rotary dispersion. Indirect information on $T_1$ was obtained by Monti et al. by analyzing the rate constant for energy transfer from a number of energy donors with different triplet energies. Adiabatic energies of 1.52 eV and 1.78 eV were determined for the $T_1$ states of the $E$ and $Z$ isomers, respectively. The fact that so far the $T_1$ state escaped direct...
observation points to its very short lifetime.\textsuperscript{12} DFT calculation revealed a $T_1$ state at the energy of 1.48 eV.\textsuperscript{12} Using CAS-SCF/CAS-PT2 techniques this energy was later refined to 1.83 eV.\textsuperscript{9} Four triplet states were calculated by Hättig and Hald\textsuperscript{13} using the CC2 and CCSD methods. However, as we show below, these computed energies vary considerably with the method used as do those calculated for singlets. These facts indicate that despite numerous experimental\textsuperscript{4,5,10,11} and theoretical\textsuperscript{9,12-24} studies, photochemistry of AB is far from adequately understood, both in terms of availability of complete and accurate spectral data and of theoretical description of the quantum effects involved.

In this paper we fill the gap in our understanding of the photochemistry of AB by presenting fully correlated quantum Monte Carlo (QMC)\textsuperscript{25,26} simulations, transcending our previous study of the lowest singlet states ($S_0$, $S_1$)\textsuperscript{24} to a higher singlet state ($S_2$) and adding triplet states ($T_1$, $T_2$, ...), and by validating the theoretical predictions by comparison with electron energy loss (EEL) spectra of gas phase trans AB taken at a range of residual electron energies permitting the observation of both singlet and triplet states.

The QMC method is superior for the present task because short-range correlations are treated exactly and do not limit the accuracy of the results. The present calculations are a formidable task, as we deal with ground- and excited states of a large molecule with almost hundred electrons deemed until recently beyond practical computational feasibility. Due to its favorable low-order polynomial scaling with the system size,\textsuperscript{25,26} the QMC method provides a practical route to achieving chemical accuracy ($\approx 0.04$ eV) for this system. In addition, we use a combination of different methods to provide lower bound estimates of thermal effects which affect the experimental spectra. Our final QMC results reduce residual errors to $\sim 0.1$ eV, an outstanding achievement for a system of this size. The accuracy is enough to provide guidance in disentangling the host of overlapping singlet and triplet bands in the EEL spectra and in understanding the photochemistry of AB.

Concerning alternatives to QMC, the simplest approach is based on the DFT and generalized restricted open shell Kohn–Sham (gROKS) description of the lowest excited singlet state $S_1$\textsuperscript{14–17} and triplet state $T_1$.\textsuperscript{12} The best quantum chemistry results up to date use CC2\textsuperscript{13,18} CCSD,\textsuperscript{13} and CAS-SCF/CAS-PT2 description.\textsuperscript{9,12,19} While the use of these methods allows exploration of the potential hypersurface and thus provides very useful insights into dynamics of AB\textsuperscript{14–17,20} or possible conical intersections, photo-isomerization pathways, quantum yields, \textit{etc.},\textsuperscript{9,12,19,22,23} the insufficient accuracy of electronic correlation treatments by all these methods significantly limits the predictive power of the results. In contrast, the accuracy of the QMC method is limited only by the accuracy of the nodal hypersurfaces of the trial many-body wave function, fixed by CAS-SCF wave function in present simulations.\textsuperscript{24} Short-range correlations, treated only perturbatively at the CAS-PT2 level, are exact in QMC. Most of the QMC applications up to date are restricted to ground states of fairly small molecular systems, with excited states still representing a direction with fairly little expertise.\textsuperscript{27–30} Only recently truly large-scale QMC photochemical calculations started to appear.\textsuperscript{24,31–33}

The main initial goal of this study was to shed light on the low-energy triplet states of trans AB by a joint experimental/theory study. In doing so we revealed complete electronic structure of trans AB, including also singlets where new gas phase results are also needed. In particular, we unambiguously assign the first two triplet and singlet states, identify three higher-lying triplet states and a host of singlet and triplet states in the 6–8 eV range. The accurate correlated QMC simulations turned out indispensable in disentanglement of the triplet and singlet states and in understanding the measured EEL spectra.

\section{Methods}
\subsection{A. Experiment}

The trochoidal electron spectrometer used in the present study was described in detail previously.\textsuperscript{34} It uses magnetic collimation of the electron beams, trochoidal monochromators as electron energy filters, and a collision chamber with small apertures for the incident and scattered electron beams. The experiment involves intercepting the sample vapor at low pressure ($\sim 10^{-4}$ mbar) with a beam of electrons of varying incident energy $E_i$ and detecting electrons scattered at a fixed residual energy $E_r$. The incident electrons can excite the target molecules, thereby loosing an amount of kinetic energy $\Delta E = E_i - E_r$ equal to the excitation energy. A spectrum of excited states is obtained by plotting the scattered electron current $I_r$ against the electron energy loss $\Delta E$. The collision chamber was kept at about 80 $^\circ$C during the measurement, the resolution was about 0.05 eV. The energy scale, calibrated on high vibrational overtones of N$_2$ in AB/N$_2$ mixtures, is accurate to within 0.03 eV. This instrument detects electrons scattered into forward (0$^\circ$) and backward (180$^\circ$) directions.\textsuperscript{35} Forward scattering dominates and dipole selection rules apply approximately at $E_r = 20$ eV—the spectrum recorded with $E_r = 20$ eV is consequently similar to the UV/VIS absorption spectrum. Triplet bands appear in the spectra recorded with low residual energies, but the dipole allowed bands do not completely disappear. The cross sections for excitation of the triplet states are often backward peaked, so that the capacity of the present instrument to detect the backward scattered electrons is very helpful for the detection of the triplet states.\textsuperscript{35} Spin allowed but dipole forbidden transitions may also appear in the spectra recorded with low $E_r$.

\subsection{B. Theory}

Simulation of the excitation energies used a five-level modeling: (1) geometry was obtained from DFT optimization, (2) trial wave function was constructed from a truncated CAS-SCF expansion, (3) trial wave function was optimized using VMC (variational Monte-Carlo) techniques, (4) excitation energies were computed from DMC (diffusion Monte-Carlo) simulation, and (5) \textit{ab initio} Car–Parrinello dynamics simulations\textsuperscript{36} at various temperatures were used to estimate the finite temperature corrections for various transitions. For static DFT and CAS-SCF we used the GAMESS suite of codes,\textsuperscript{37,38} all VMC and DMC calculations used the QWalk code,\textsuperscript{39} while for dynamical DFT simulations we used the CPMD planewave pseudopotential code.\textsuperscript{40}

As in the EELS experiment, vertical excitation energies were calculated for the trans isomer, with the exception of the lowest singlet states, where energies along the torsion
coordinate (CNNC dihedral angle), including barrier heights, were calculated. The reason is that rotation along the CNNC dihedral angle is the preferred pathway for both photo and thermal isomerization processes.\(^9,19\) The ground-state geometries were calculated using DFT techniques with B3LYP exchange-correlation functional\(^{41}\) with the Greeff–Lester type effective core pseudopotential\(^{42,43}\) for all species and cc-pVTZ basis set.\(^{44}\) The use of DFT-optimized ground-state atomic structure in QMC-determined energies may lead to bias. Nevertheless for the \(E\) isomer, where electron diffraction experiments exist, our B3LYP geometry lies within experimental error bars of the most recent gas-phase electron diffraction experiment.\(^{45}\)

Importance of geometry on the excitation energies of AB has been emphasized by Hättig and Hald,\(^{13}\) who found effects of 0.2–1.0 eV, depending on the state. The balanced active space in singlet CAS-SCF calculations consisted of 14 electrons in 12 orbitals (14/12)\(^9,12,19,24\) initially constructed from DFT orbitals.\(^{24}\) In some tests a (16/14) orbital space was used. For the triplets the orbital space was (14/14) constructed from state-averaged CISD calculations.

The natural orbitals and expansion coefficients were generated from CAS-SCF calculations, with orbital space optimized for each state. Subsequently a truncated CAS-SCF expansion was used retaining all symmetry adapted configuration state functions (CSFs) with weights \(\geq 0.01\) optimized together with variational parameters of the spin-dependent Schmidt–Moskowitz Jastrow correlation factor\(^{26,46}\) including electron–electron, electron–nucleus, and electron–electron–nucleus terms. The expansions consist of between 107 and 1228 Slater determinants or 38 and 322 CSFs. In VMC, the trial wave functions\(^{47}\) and their nodes were optimized by minimizing a linear combination of energy and variance.\(^{47}\) Final results were obtained by DMC runs. In order to estimate thermal corrections, see Section III, we ran finite temperature (300 to 500 K) dynamics simulations ~50 ps long.

The selection of states for the VMC/DMC simulation was based on the CAS-SCF energies. However, as discussed in Section III, dynamical correlations, absent at the CAS-SCF level, often change the ordering of states in energy, causing shifts in energy between states of \(\sim 1\) eV. In total the first three CAS singlet and the first five CAS triplet states were considered for further QMC treatment. Due to the energy shifts such a procedure does not necessarily yield the lowest energy states. These triplet states are labeled \(T_m\), \(T_n\), \(T_l\).

### III. Results and discussion

Fig. 2 shows the EEL spectra as they were recorded. The interpretation of these spectra is hampered by the fact that dipole-allowed and forbidden transitions overlap in the spectra recorded at low \(E_r\), and by the overlap of the triplet bands. In addition, a background due to excitation of a quasicontinuum of high vibrational overtones occurs at low energy-losses, particularly at low \(E_r\).\(^{34}\)

To facilitate the interpretation we therefore processed the spectra as shown in Fig. 3. First, the low energy-loss background was fitted to the tail of a broad Gaussian profile centered near \(\Delta E = 0\) eV and subtracted to obtain a flat baseline below the lowest electronically excited states. The \(E_r = 20\) eV spectrum in the top panel is now very similar to gas-phase VIS/UV absorption spectra and characteristic for dipole-allowed transitions. To obtain spectra of the forbidden transitions, we then subtracted the \(E_r = 20\) eV spectrum from the \(E_r = 3\) eV
and the $E_r = 1.25$ eV spectra, multiplying it first by a factor chosen to make the 5.64 eV band, which must be due to an allowed transition, disappear in the difference spectra.

The transition energies (the 2.78, 4.10 and 5.64 eV bands) and the general shape of the spectrum recorded with $E_r = 20$ eV agree well with published gas phase absorption spectra.\(^4,4^8\) The only difference is that the $S_1$ band is only 18× weaker than the 4.10 eV band, whereas in the quantitative absorption spectra it is about 60× weaker.\(^4,4^8\) This is because the residual energy of $E_r = 20$ eV is still too low for the high energy limit where the dipole transition intensities apply, and the nominally dipole-forbidden transition to the $S_1$ state is consequently enhanced. Like in the absorption spectra, the 4.10 eV band has a faint structure, assigned to the N=N stretch vibration—it appears weaker in the EEL spectra because of the inferior resolution. Its visibility is improved in the small (gray) insert under the 4.10 eV band of the $E_r = 20$ eV spectrum, obtained by subtracting an arbitrary smooth background from the experimental 4.10 eV band. The resolution of EELS is not sufficient to resolve the 220 cm\(^{-1}\) structure observed in the absorption spectra.\(^4\)

The 4.10 eV band has a profoundly different shape in the spectrum with $E_r = 3$ eV in Fig. 3. The low-energy part is strongly enhanced and appears as a band with clear vibrational structures at 3.77, 3.91 and 4.06 eV,\(i.e.,\) with an average spacing of 0.145 eV (1170 ± 200 cm\(^{-1}\), presumably N=N stretch). Similar observation is made in the $E_r = 1.25$ eV spectrum. This means that the 4.10 eV band corresponds to two electronic states, one structured peaking at 3.91 eV, the other structureless, peaking at 4.10 eV. It is unlikely that the 3.91 eV band is due to a triplet state, because the same vibrational structure appears also in the $E_r = 20$ eV EEL and the UV absorption spectra where triplet states are not visible. The observation of two states within the 4 eV band is consistent with the relatively recent evidence of two different decay times (170 and 420 fs) reported across the 4.10 eV band, interpreted as lifetimes of partly overlapping $S_1$ and $S_{1,2}$ states,\(20\) and with theoretical predictions.\(^1^3,1^6,1^8,2^0\) There is a subtle point, however. It is the 3.91 eV band which is enhanced at low $E_r$ in the present experiment, indicating a higher degree of ‘forbiddenness’ than the 4.10 eV band. In contrast, the calculations\(^1^8\) indicate the lowest oscillator strength (0.85) for the lowest (S1) of the three overlapping states, whereas $S_1$ has an oscillator strength of only 0.02, and $S_2$ is dark. This represents an indication that the $S_2$, $S_3$ ordering may be reversed. This is why we compare the 4.10 eV band, and not the 3.91 eV band, to the calculated $S_1$ energy. The evidence is not very strong, however, because the calculated oscillator strength of the $S_1$ ($S_2$ in ref. 20) is reported to strongly depend on geometry and varies with the theoretical model.\(^1^8,2^0\) The EEL spectrum recorded with $E_r = 1.25$ eV has a very weak narrow shoulder at around 3.55 eV, which is probably a ‘hot band’ of the 3.91 eV band.

The two low-lying triplet bands overlap and were fitted to Gaussian profiles to determine the peak positions. The fit is only approximate because the experimental Franck-Condon profile is slightly asymmetrical (the high energy side is more gradual than the onset), and because the fitting Gaussian profiles are slightly wider and shifted (by −0.04 and −0.02 eV for $T_1$ and $T_2$, respectively) in the $E_r = 1.25$ eV spectrum when compared to the $E_r = 3$ eV spectrum. The average values are given in Table 3 and the shifts are absorbed in the confidence limit which is taken as ±0.05 eV. The shifts are likely to be a consequence of resonant excitation, whereby the incident electron can, at a suitable incident energy, be trapped in the vicinity of the target molecule for a short time (shorter than a vibrational period), and the positions of the nuclei relax slightly during the lifetime of this ‘negative ion resonance’.

The consequence of the relaxation is a small deviation from the Franck-Condon profile. The resonance is more likely to affect the lower $E_r$ spectrum. Finally, the 4.2–4.8 eV spectral region is more ‘filled’ in the $E_r = 1.25$ eV spectrum than in the $E_r = 3$ eV spectrum and we interpret this as an evidence for two higher-lying triplet states. Their energies are only estimated to be around 4.3 and 4.6 eV.

We now proceed to comparison of our experimental transition energies derived from the EEL spectra as described above to the QMC theory and to other experiments. In Table 1 results of the present experiment are compared to gas phase absorption experiment,\(^4,1^2,1^3,1^6,1^7,1^9,2^4\) and with the present QMC theory. Validation of QMC potential energy surface (PES) in $S_0$ and $S_1$ along the CNNC dihedral angle as well as of the transition energies against present and previous\(^4\) gas phase experiments is shown in Fig. 4. For completeness and direct comparison the present QMC results and results of the “CCSD extrapolated” calculation of ref. 13 are also shown graphically in the EEL spectra in Fig. 3.

Both Table 1 and Fig. 3 indicate a very good agreement of the present QMC results with the experimental values for the $T_1$, $S_1$, $T_2$, and $S_2$ states. The most important novel information from our QMC calculation comes from the study of triplet states. We confirm the presence of the $T_1$ state by computationally locating it at 1.89 eV, which agrees nicely with the experimental shoulder position at 2.04 eV. Other calculations find $T_1$ at energies spread between 1.48 and 2.4 eV\(^1^2,1^3\) depending on the method used. Our calculated value of 2.55 eV for the $T_2$ state compares favorably with the experimental value of 2.70 eV. The earlier theoretical study, the CC2/CCSD calculations,\(^1^3\) yielded energies of 1.75 eV (CCSD), 2.83 eV (CC2), and 2.64 (CCSDS\(_{\text{ref}}\))—see Table 1.

The calculated $T_m$ and $T_n$ energies are also well consistent with the EEL spectrum recorded with $E_r = 1.25$ eV, although an accurate comparison is not possible because of severe band overlap in the experimental spectrum. More precise assignment of these states is hampered by the fact that the CAS wave functions provide a poor initial guess for QMC, see Fig. 5 for more details. More triplet states at energies around ~4 eV are expected theoretically, but cannot be assigned by our current computation, as more CAS states would have to be considered because of massive energy shifts due to dynamical correlation. We therefore do not assign any specific values to the indexes $m, n, l$ in $T_m$, $T_n$, and $T_l$ in Table 1.

The first state above $S_2$ having an appreciable oscillator strength is calculated to be $S_0$,\(^1^3,1^8\) and we assign it to the 5.64 eV EEL and UV bands. It appears substantially too high in the “CCSD extrapolated” calculation shown in Table 1, but other calculations place it closer to the observed value. Its photochemistry has recently been studied (at 6 eV) and found to yield excitation-specific photochemistry with C–N bond scission instead of isomerization.\(^3^9\)
Table 1 Vertical excitation energies from the $S_1(A_2)$ ground state to various singlet and triplet final states for the trans isomer of AB, energy differences between the ground states of the $E$ and $Z$ isomers $\Delta E_{E-Z}$, and energies of the transition state on the $S_0(T_1)$ surface $\Delta E_{S_0}^{TS}(\Delta E_{S_0}^{TS})$. Values calculated using various methods and experimental results are compared for all quantities. All energies are in eV, relative to the $E$ isomer. The experimental data are when not otherwise noted, the present results, with a confidence limit of $\pm 0.05$ eV.

<table>
<thead>
<tr>
<th>Final state</th>
<th>DFT$^a$/gROKS$^d$</th>
<th>CCSD$^d$</th>
<th>RI-CC2$^c$</th>
<th>CCSDexp$^a$</th>
<th>CAS-SCF$^b$</th>
<th>CAS-PT2$^b$</th>
<th>DMC</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1(A_2)$ ($\pi^+\pi^-$)</td>
<td>2.17$^e$</td>
<td>2.94$^f$</td>
<td>2.84$^{f}$</td>
<td>2.95$^{g}$</td>
<td>3.18$^{m,n}$</td>
<td>2.53$^{m,n}$</td>
<td>2.82(6)$^{p}$</td>
<td>2.78</td>
</tr>
<tr>
<td>$S_1(A_2)$ ($\pi^+\pi^-$)</td>
<td>3.85$^{f}$</td>
<td>4.04$^{f}$</td>
<td>4.36$^{f}$</td>
<td>6.35$^{m,n}$</td>
<td>4.23$^{m,n}$</td>
<td>4.35(6)/4.23(6)$^{p}$</td>
<td>4.10</td>
<td>4.12$^p$</td>
</tr>
<tr>
<td>$S_1(A_2)$ ($\pi^+\pi^-$)</td>
<td>4.31$^{f}$</td>
<td>4.44$^{f}$</td>
<td>4.63$^{f}$</td>
<td>5.71$^{m,n}$</td>
<td>4.46$^{m,n}$</td>
<td>4.46$^{m,n}$</td>
<td>3.91$^e$</td>
<td>—</td>
</tr>
<tr>
<td>$\Delta E_{E-Z}^f$</td>
<td>0.52$^j$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.71$^{m,n}$</td>
<td>0.52$^{m,n}$</td>
<td>0.50(6)$^{p}$</td>
<td>0.55$^e$</td>
</tr>
<tr>
<td>$\Delta E_{S_0}^{TS}$</td>
<td>1.73$^i$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.80$^{m,n}$</td>
<td>1.65$^{m,n}$</td>
<td>1.80(6)$^{p}$</td>
<td>1.73$^{m,p}$</td>
</tr>
</tbody>
</table>

$^a$ Assuming $\Delta E_{S_0}^{TS} = 0.5$ eV.$^b$ 6-31G* basis. $^c$ Plane-wave basis. $^d$ cc-pVTZ basis. $^e$ aug-cc-pVTZ basis. $^f$ Adiabatic. $^g$ Ordering uncertain, see text. $^h$ After finite temperature correction. $^i$ Ref. 16. $^j$ Ref. 17. $^k$ Ref. 12. $^l$ Ref. 13. $^m$ Ref. 9. $^n$ Ref. 19. $^o$ Ref. 24. $^p$ Ref. 4.

Finally we wish to discuss the relation of our QMC results with those from other theoretical models. As the results represent excitations from ground state $S_0$ PES we start by discussing the quality of description of the $S_0$ surface along the CNCN dihedral angle. We find, see Table 1, that all methods, except for CAS-SCF, describe well the energy difference $\Delta E_{E-Z}^f$ between the minima corresponding to trans and cis isomers. At the barrier ($\Delta E_{S_0}^{TS}$) this PES involves a complicated state formed by cleavage of a $\pi$-bond in the N=O group to form a biradical intermediate and correspondingly the computed barrier height varies between 1.65 (CAS-PT2) and 1.80 eV (DMC). The DMC barrier $\Delta E_{S_0}^{TS}$ shows only a marginal difference of $0.07$ eV compared to the gas phase experiment.$^4$ There are two possible sources for this difference. In our calculations the transition state has been fixed to a dihedral angle of 90°, whereas the real value may be slightly different. More importantly, a non-adiabatic $S_0 \rightarrow T_1 \rightarrow S_0$ torsion pathway via the first excited triplet state, $T_1$, which crosses the $S_0$ PES, was proposed.$^9,19$ consistent with large $S_0 \rightleftharpoons T_1$ spin-orbit coupling found for AB.$^3$ Indeed, our $T_1$ DMC adiabatic energy of 1.40 eV computed at the transition state, $\Delta E_{S_0}^{TS}$ corroborates this scenario.

Substantial differences are found between the various theoretical methods for excited state energies. The gROKS method underestimates the $S_1$ excitations by as much as $0.7$ eV,$^{16,17}$ CAS-SCF results$^9,19$ significantly overestimates the excitations by $0.4$ eV, while CAS-PT2 results$^9,19$ underestimate the excitations by up to 0.3 eV with respect to the gas phase experiments. A somewhat better estimate is provided by the CCSD$_{\text{exp}}$$^{13}$ overestimating the $S_1$ excitation by $0.2$ eV. The accuracy achieved with QMC methods can clearly be seen in Table 1 and Fig. 4. Most of the studied transitions are either symmetry or spin forbidden. The exception being $S_0 \rightarrow S_2$, which is indeed dominating the EEL spectrum in the top panel of Fig. 3. Our estimated oscillator strength of this transition at the CAS-SCF level is 0.84. The DMC energy of $S_0 \rightarrow S_1$ of 4.35 eV appears to be higher than both experimental values of 4.10 and 4.12 eV$^4$ where the CAS-PT2 result of 4.23 eV appears to be in better agreement with experiments. However, CCSD$_{\text{exp}}$$^{13}$ yields an excitation energy very similar to our QMC result. To test the robustness of our results we have enlarged our orbital space in constructing the trial wave function to (16/14) to arrive at exactly the same excitation
energy of 4.35 eV. We argue below that the agreement with experiments improves by inclusion of thermal effects.

As for triplets, our QMC estimate of the T1 is in much better agreement with the experiment than the CC2/CCSD predictions and in slightly better agreement than CAS-PT2 and CCSD estimate of T1 energies clearly demonstrates the basis set dependence of the traditional quantum chemistry methods. At the aug-cc-pVTZ level, CCSD yields a wrong ordering of the energies which is only corrected in CCSD$_{\text{exp}}$ after basis set effect correction. Our DMC energies are free of such an error, as they use â€”functions as a basis set. QMC estimates of the excitation energies of the higher triplet states are also in better agreement with experiments than the CC2/CCSD energies.

We investigated the question whether the remaining difference between the DMC and the experimental transition energies could be, at least in part, due to temperature effects. The experiment measures excitation energies averaged over a range of configurations which the target molecule can reach thermally. In contrast, the theoretical excitation energies are computed for a single (ground-state) optimized geometry. In order to provide results more directly comparable to the measured values, the excitation energies would have to be sampled along a finite-temperature trajectory. In a preliminary study we attempted to estimate the finite temperate effects by taking into account the CNNC dihedral angle distribution sampled at the Sn DFT PES by Car–Parrinello dynamics using the somewhat cheaper CAS-PT2 energies to estimate the excitation energies. This yielded a prediction that the finite temperature corrected transition energies at 500 K should be lower than the vertical values by 0.12, 0.02, and 0.01 eV for the S2, S1, and T1 states, respectively, thus improving the agreement between QMC theory and experiment, in particular for the S2 state where the difference is currently the largest. Adding finite temperature corrections also to the other transitions and/or extending the model beyond the CNNC dihedral is expected to further improve the agreement with experiment.

IV. Conclusions

We present a complete electronic structure measurement of trans-azobenzene in the gas phase, including both singlet and triplet excited states, by electron energy loss spectroscopy (EELS) supported by a set of large-scale correlated quantum Monte-Carlo (QMC) simulations. The calculated vertical excitation energies into the lowest two singlet and triplet states are in excellent agreement with the energies of the band maxima in the EEL spectra, the differences being $-0.14$ eV for the T1 and T2 states, and 0.04 eV and 0.25 eV (0.13 eV after finite temperature correction) for S1 and S2 states, respectively. We further report three higher-lying triplet states, with energies again in very good agreement with the observed triplet bands. We suggest that most of the remaining bias in our DMC energies can be removed by finite-temperature corrections. Finally, we report experimental high-lying singlet and triplet EEL bands in the 6–8 eV range, outside of the common range of UV spectrometers. This provides the most complete characterization of electronic structure of AB to date by a joint experimental/theory study.

The EEL spectra reveal two close-lying states in the band around 4 eV, which has long been assigned to only one (S2) state. The lower of these two states has a pronounced vibrational structure with a spacing of 0.145 ± 0.025 eV and peaks (r = 1) at 3.91 eV. The upper is structureless and peaks at 4.10 eV. The lower state is more pronounced in EEL spectra recorded with a low residual energy, indicating a “partly forbidden” nature. These findings are consistent with the observation of two distinct decay times across the “S2-band” by Schultz et al., interpreted as due to partly overlapping S2 and S3,4 states. These findings are also consistent with the more recent calculations, predicting three closely-lying states around this energy, one with a large oscillator strength (S3), one with a small oscillator strength, and one forbidden (the latter two, S3,4, are nearly degenerate and their ordering depends on model). The assignment of the experimental bands to these close-lying calculated states is not quite resolved—their ordering is not certain and it is puzzling why many theories predict the S2 state slightly too high. We suggest that the latter problem could be due, at least in part, to the effect of finite temperature which lowers the experimental band maximum. We note that calculating the Franck-Condon profiles for the S2, S1 and S0 states would be helpful in resolving the problem of ordering, since the observed bands have markedly different profiles.

Finally, we expect that with advent of QMC force methods fully dynamical QMC simulations on ground- and excited-state PESs of accuracy similar to the one achieved here for the single-point energies will become feasible. This will make a consistent QMC treatment of electronic and atomic structure possible and open up novel unconventional alternative routes to high-accuracy modeling of finite-temperature effects, conical intersections, statistical sampling of PESs, etc. Work along that line is now under way.

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References