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Electronic Excitation Spectrum of *s*-Tetrazine: An Extended-STEOM-CCSD Study

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The theoretical vertical electronic excitation spectrum of 1,2,4,5-tetrazine is obtained using the extended similarity transformed equation-of-motion coupled cluster method and is compared to previous CASPT2 and MRCI results. In extended-STEOM-CCSD, all types of excitations that occur in *s*-tetrazine, notably n → π*, π → π*, Rydberg transitions and doubly excited states are obtained from a single calculation, and in a balanced way. All features in the experimental vacuum UV spectrum up to about 11 eV are assigned to calculated dipole-allowed transitions. Additional features found in the electron energy loss spectrum are assigned to dipole-forbidden singlet and triplet transitions of ungerade symmetry. An interesting convoluted feature in the experimental vacuum-UV spectrum that extends between about 8.15 and 8.6 eV is assigned to a pair of states of B_{2u} symmetry, calculated at 8.28 and 8.54 eV, that are essentially the plus and minus combination of a singly excited π → π* and a doubly excited n,n → π*,π* configuration that can be expected to exhibit extensive vibronic interaction.

I. Introduction

In a recent experimental study, high-quality vacuum-UV and electron energy loss (EEL) spectra of *s*-tetrazine were reported and a tentative assignment was made based on multireference CI calculations.[26] The recent experiment agrees well with the previous work by Fridh et al.[10] that focused on the Rydberg states, and also with the data presented by Innes in his comprehensive review on the azabenzenes.[14] Despite its high symmetry (D_{2h}), the *s*-tetrazine molecule shows a host of dipole-allowed transitions that have very diverse characteristics. The four nitrogen lone-pair orbitals in *s*-tetrazine lead to a variety of low-lying n → π* transitions and n → R Rydberg states. The nitrogen atoms are also accountable for a very low-lying π* orbital (of a_u symmetry) that can actually bind an electron, although the negative anion is found to dissociate upon electron attachment.[26] Due to the rather low-lying π* orbitals and the presence of a quartet of nitrogen lone-pair orbitals, the *s*-tetrazine molecule has a number of low-lying excited states that either have substantial n,n → $\pi^*\pi^*$ double excitation character or are almost purely doubly excited states. The *s*-tetrazine molecule also exhibits the π → π* transitions that are typical of benzene and the azabenzenes, and there are some low-lying π → *R* Rydberg states. Nature, of course, does not distinguish according to this classification of states and a substantial mixing of the above categories may occur. The triplet states are accessible through low-energy EEL spectroscopy and are somewhat easier to describe theoretically. Less valence−Rydberg mixing occurs in the triplet states, while also mixing with low-lying doubly excited states configurations is less important since most of these are necessarily singlets as they involve the α and β component of the same spatial orbital.

The theoretical description of the singlet part of the electronic spectrum of *s*-tetrazine is a challenge that requires a balanced treatment of n → π*, π → π*, Rydberg states, and n,n → $\pi^*\pi^*$ double excitations. The first excited singlet state at 2.35 eV has been studied in detail using accurate ab initio methods which included the geometrical relaxation of the S_1 state upon excitation.[30,33] Presently, a number of theoretical studies on *s*-tetrazine have appeared that allow at least a partial interpretation of the recent experimental data.[9,18,26,28,34] In the paper by Palmer et al., the reported experimental data are interpreted using the results of MRCI calculations (see Table 4 of ref 26). However, the theoretical MRCI results are rather erratic and typically deviate by about 0.5−1.0 eV from the experimental data. This kind of accuracy is insufficient to reliably interpret the complex spectrum of *s*-tetrazine. In the MRCI calculations, a different set of reference configurations was selected for the states in each symmetry block and it may be hard to obtain a balanced description of the spectrum in such a way.

Rubio and Roos[28] have presented a recent CASPT2 study on the spectrum of *s*-tetrazine. Their work is a tour de force, as different reference spaces are required for different types of excitations, while the level shift technique is used extensively to improve the convergence of the perturbation expansion and to avoid intruder states. Moreover, the B_{1u} states were obtained from a diagonalization over the CASPT2 wave functions using a so-called multistate CASPT2 calculation. Rubio and Roos have made the interesting observation that doubly excited configurations are highly important in *s*-tetrazine. This includes both a strong mixing of n,n → $\pi^*\pi^*$ double excitations in some of the n → π* states and the existence of very low-lying purely doubly excited states, predicted to lie at 4.37 and 5.16 eV in the CASPT2 calculation. Below, we will show that an important mixing of doubly excited states also occurs in the π → π* states of B_{2u} symmetry, which is crucial to understand some details of the spectrum. However, this aspect was not observed in the CASPT2 calculations, presumably because no n-type orbitals were included in the active space that is used to describe the π → π* excitations.

A very recent paper[34] showed a comparison of a time-dependent DFT approach that includes a strategy to describe Rydberg excited states[12] to CASPT2 results and experimental data for a number of unsaturated organic systems. The test cases included *s*-tetrazine, and the agreement for the various transitions

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in this molecule with CASPT2 results was quite good in general, with the DFT results often falling slightly (∼0.2−0.4 eV) below the CASPT2 results. We will not explicitly include the TDDFT results in our discussions, but note that, in general, CASPT2 results are found to be low compared to the present extended-STEOM results, and the agreement with TDDFT tends to be worse therefore and is also more erratic.

The above assessment of the multiconfigurational CASPT2 and MRCI calculations shows that there are a number of computational parameters that have to be chosen judiciously, and it can be very hard to obtain fully converged results. Without a doubt the final CASPT2 results for the dipole-allowed n → π^* and $\pi \rightarrow \pi^*$ transitions appear to compare well with experiment but this in itself does not prove convergence of the calculations. In order to interpret complicated experimental spectroscopic data it is highly desirable to employ theoretical methods that can be expected to provide accurate results, and which do not require an elaborate choice of user-determined calculational parameters.

During the past years it has been shown that the closely related CC3 and EOM-CCSD($\tilde{\mathrm{T}}$) methods are reliable tools to obtain theoretical vertical excitation energies for states that are dominated by single excitations, provided the ground state is reasonably well described by single reference CC theory.[5−7,9,16,35,36] The errors are expected to be less than 0.1 eV for such states, provided the atomic basis set is adequate, and this is presumably the main source of error. This claim is based on extensive comparisons with full CI results for small molecules[7,16,35,36] and comparisons with unambiguous experimental results. This is a moot point as in many theoretical investigations calculated vertical excitation energies are compared to the experimental band maxima. However, a number of assumptions enter this approximation that need not be satisfied.[8] A far better comparison is to compare directly to the 0−0 transition, which can often be fairly easily identified experimentally. The calculation of the 0−0 band requires a geometry optimization of ground and excited state and an estimate of the zero-point frequencies. This is a difficult task, but a small number of such calculations have been performed, proving the accuracy of CC3.[5,6] An even better comparison would be to calculate the complete Franck−Condon profile, and its temperature dependence, which also only requires the force constants in ground and excited states, at least in the harmonic approximation.[2,3]

In a recent EOM-CCSD($\tilde{\mathrm{T}}$) study on vertical excitations in the azabenzenes by Del Bene et al.[9] also *s*-tetrazine was included, and their results can be compared to the recent experimental data.[26] The calculated vertical $\pi \rightarrow \pi^*$ transitions as well as the dipole-allowed n → π^* transitions compare well to experiment, while also the lowest Rydberg state is in very good agreement with the experimental 0−0 transition (3.19 vs 3.17 eV). Due to the expense of these calculations, only a limited number of states were obtained in the EOM-CCSD($\tilde{\mathrm{T}}$) study and a full comparison to the experimental spectrum is not possible. Moreover, the finding by Rubio and Roos[28] that doubly excited configurations are very important for some states in *s*-tetrazine leads to some controversy. It has been established that EOM-CCSD($\tilde{\mathrm{T}}$) and similarly CC3 can have difficulties to describe doubly excited states (typical errors are 0.3−0.5 eV), as demonstrated by calculations on small molecules and comparisons to full CI.[7,16,35,36] It is of interest, therefore, to further investigate the importance of doubly excited states in *s*-tetrazine and also to obtain the higher lying Rydberg states.

In recent years, we have developed an alternative to the EOM-CCSD, EOM-CCSD($\tilde{\mathrm{T}}$), and CC3 methods, which is also rooted in CC theory and which provides remarkable accuracy for highly reduced computational expense. In the similarity transformed equation of motion coupled cluster method (STEOM-CC[21−23]), one first performs a double similarity transform of the many-body Hamiltonian using calculated information on the ground state from a CCSD calculation, important ionized states from an IP-EOM-CCSD calculation,[1] and finally electron attached states and virtual orbitals from an EA-EOM-CCSD calculation.[1,20] As a result of the transformations, the various excitation blocks (singles, doubles, etc.) are decoupled to a large extent in the final transformed Hamiltonian, although the eigenvalues have not changed, of course. In the original STEOM-CCSD method the transformed Hamiltonian is diagonalized over singly excited configurations to obtain approximate eigenvalues, which are comparable in accuracy to EOM-CCSD($\tilde{\mathrm{T}}$) and CC3 results. The STEOM method has been tested against full CI, CC3, and EOM-CCSD($\tilde{\mathrm{T}}$) benchmarks,[23,18] while a comparison has also been made to various experimental 0−0 transitions in the azabenzenes, using CIS to obtain the optimized geometries for the excited states.[18] The accuracy of these latter combined STEOM/CIS calculations was found to be about 0.1 eV for the states considered, unambiguously demonstrating the accuracy of the approach. The STEOM study on the azabenzenes also included the vertical excitations in *s*-tetrazine, and results were very similar to the EOM-CCSD($\tilde{\mathrm{T}}$) results mentioned before. However, the controversy is also the same: STEOM cannot be expected to give an adequate description of significantly doubly excited states, and further study is warranted therefore.

To overcome the problems to describe doubly excited states we very recently implemented the direct diagonalization of the doubly transformed STEOM effective Hamiltonian over both singly and doubly excited configurations. In benchmark applications to small molecules for which Full CI results are available the so-called extended-STEOM approach was found to describe singly and doubly excited states equally accurate (about 0.1 eV errors). Moreover, for states that are dominated by singly excited configurations STEOM and extended-STEOM typically differ by less than 0.05 eV, demonstrating that STEOM is essentially converged for such states. Compared to STEOM the extended-STEOM approach is rather expensive computationally, although the method can be applied with ease to a molecule the size of *s*-tetrazine, and we only require a single calculation to obtain a balanced description of all singlet excited states.

The purpose of this study is to describe the complete manifold of low-lying vertical excitations in *s*-tetrazine using methodology that is capable of describing excited states of very different character in an inherently balanced way, free of any computational bias beyond the choice of atomic basis set. At this moment we do not aim to resolve the 0−0 transitions in the spectrum, but we wish to unambiguously identify the features in the spectrum that mark the presence and importance of doubly excited states. The paper is organized as follows. In the next section we give a more elaborate discussion of the extended-STEOM aproach, while in section III we discuss results for the excited states in *s*-tetrazine, focusing in sequence on the n → π^* excitations, the $\pi \rightarrow \pi^*$ transitions, the Rydberg series, the doubly excited states, and the triplet states. We will compare to the available experimental data and also make extensive comparisons to the recent CASPT2 and MRCI calculations.

II. Theory

In STEOM-CCSD the Hamiltonian expressed in the language of second quantization is transformed twice to yield

$$\hat G = \{e^{\hat S}\}^{-1}\, e^{-\hat T}\, \hat H e^{\hat T}\{e^{\hat S}\} \tag{1}$$

The operator

$$\hat T = \hat T_1 + \hat T_2 = \sum_{i,a} t_i^a \{\hat a^\dagger \hat\imath\} + \frac{1}{4}\sum_{i,a} t_{ij}^{ab}\{\hat a^\dagger \hat\imath \hat b^\dagger \hat\jmath\} \tag{2}$$

is the standard single reference CCSD operator, and the transformed Hamiltonian $\hat H = e^{-\hat T}\hat H e^{\hat T}$ is used in equation of motion coupled cluster theory.[1,20,32] According to common convention, *a*,*b*,*c* label virtual spin-orbitals, while *i*,*j*,*k* indicate occupied spin-orbitals in the Hartree−Fock determinant that describes the zeroth-order ground state. The operator $\hat S$ consists of two components: a detachment or ionization component

$$\hat S^- = \hat S_1^- + \hat S_2^- = \sum_{i',m} s_{i'}^{m}\{\hat m^\dagger \hat\imath'\} + \frac{1}{2}\sum_{i,j,a,m} s_{ij}^{am}\{\hat a^\dagger \hat\imath \hat m^\dagger \hat\jmath\} \tag{3}$$

where *m*,*n* label active holes, while a prime on an index indicates an explicitly inactive orbital. Braces indicate that operators act in normal order, as defined with respect to the vacuum $|\Phi_0\rangle$. In addition $\hat S$ contains an attachment component

$$\hat S^+ = \hat S_1^+ + \hat S_2^+ = \sum_{a',e} s_e^{a'}\{\hat a'^\dagger \hat e\} + \frac{1}{2}\sum_{a,b,e,i} s_{ie}^{ab}\{\hat a^\dagger \hat\imath \hat b^\dagger \hat e\} \tag{4}$$

where *e*,*f* will indicate active virtual indices. Using the definition of the operators, the transformed Hamiltonian can be expressed as

$$\begin{aligned}\hat G &= \{e^{\hat S}\}^{-1} e^{-\hat T}\hat H e^{\hat T}\{e^{\hat S}\} \\ &= g_0 + \sum_{p,q} g_q^p\{\hat p^\dagger \hat q\} + \sum_{p,q,r,s} g_{rs}^{pq}\{\hat p^\dagger \hat r \hat q^\dagger \hat s\} + ...\end{aligned} \tag{5}$$

where given the operators $\hat S$ and $\hat T$ the normal ordered matrix elements of $\hat G$ can be obtained using Wick's theorem.[17] The defining equations for the amplitudes are given by

$$g_i^a = g_i^{ab} = 0 \tag{6}$$

$$g_{ij}^{am} = g_{i'}^{m} = 0 \tag{7}$$

$$g_{ie}^{ab} = g_e^{a'} = 0 \tag{8}$$

The first equations (6) are identical to the CCSD equations. The second set of equations (7) determine the operator $\hat S^-$, and in practice we obtain the amplitudes by solving the IP-EOMCC eigenvalue problem[1,24,25] and a specific normalization.[23] Likewise the third set of equations (8) defines $\hat S^+$ and is solved by finding suitable eigenvectors of the EA-EOMCC equations.[1,20] As a result of the transformations the new Hamiltonian takes the following form over singly, doubly, triply excited determinants and so forth.

$$\mathbf{G} \rightarrow \begin{array}{c} \\ \begin{pmatrix} 0 \\ S \\ D \\ T \end{pmatrix} \end{array} \begin{array}{c} \begin{pmatrix} 0 & S & D & T \end{pmatrix} \\ \begin{pmatrix} X & X & X & 0 \\ 0 & X & X & X \\ 0 & \sim & X & X \\ \sim & \sim & \sim & X \end{pmatrix} \end{array} \tag{9}$$

In this picture *X* indicates "large" modified matrix elements, while ∼ indicates matrix elements that tend to be small in magnitude: The original coupling elements are transformed to zero, and the residual matrix element corresponds to three-body interactions that are introduced by the transformation. In practice, $\hat S_1$ is not included in the final transformation, as it does not affect the eigenvalues in any of the (truncated) equations, only the eigenvectors. The appeal of the many-body transformation strategy is that each excitation block is approximately decoupled from higher excitations. In EE-STEOM[21−23] the Hamiltonian is diagonalized therefore over singly excited states only, and this efficient approach is found to be comparable in accuracy to EOM-CCSD($\hat T$) or CC3 that require a perturbative inclusion of triples.[18] A formally straightforward extension of EE-STEOM would be to diagonalize $\hat G$ over both single and double excitations, and this provides access to doubly excited states, and states that have a mixed character. In practice, it is more convenient to start directly from the parametrization for the excited states in extended-STEOM as given by

$$|\Psi\rangle = e^{\hat T}\{e^{\hat S}\}\hat C|\Phi_0\rangle \tag{10}$$

where the operator $\hat C = \hat C_1 + \hat C_2$ contains one-and two-particle excitation operators with respect to $|\Phi_0\rangle$, while $\hat T$ and $\hat S$ are predetermined as discussed above. The accuracy of extended-STEOM in this picture derives because triple excitations are included implicitly through

$$[\{\hat S_2^+ \hat S_2^-\}\hat C_1 + \hat S_2 \hat C_2]|\Phi_0\rangle \tag{11}$$

In principle, eq 10 also includes implicit quadruples, but these contributions are discarded in extended-STEOM as they are rather costly to evaluate and have been shown to be of little significance.[19] After some suitable manipulations we end up with the eigenvalue equation

$$\sum_\lambda \langle\Phi_\mu|(1-\hat S)\bar H\{e^{\hat S}\}|\Phi_\lambda\rangle c_\lambda = E c_\mu \tag{12}$$

and the actual diagonalization is achieved in direct fashion by considering eq 12 as an elementary matrix-vector multiplication. The evaluation of a single multiplication proceeds through a sequence of one- and two-body intermediates that is defined to minimize floating point operations and storage requirements. The extended-STEOM approach in our implementation therefore scales as n^6, but the prefactor is rather steep. In practice, each excited state in an extended-STEOM calculation takes about twice the time of a CCSD calculation for the ground state. For more details on extended-STEOM we refer to our earlier paper.[19] The biggest advantage of the approach is that it is essentially a black box, one-shot calculation. Valence excited states, Rydberg states, and predominantly doubly excited states all emerge from a diagonalization of the transformed Hamiltonian.

To quantitatively characterize the excitation character of a state we will use the so-called %C1 criterion, which is defined as the percent singles in a state that is transformed from the STEOM picture back to the EOM-CCSD picture, and which is normalized over singles and doubles. The accuracy of extended-STEOM for small well-behaved Hartree−Fock molecules is about 0.1 eV compared to full CI. The same level of accuracy is obtained for both singly and for doubly excited states. For singly excited states (%C1 > 90%) we find that the results are typically converged already at the STEOM level, and upon

TABLE 1: Correlated Ionization Potentials and Electron Affinities (eV) for *s*-Tetrazine

orbital	character	MR−CI[a]	IP-EOM-CCSD	experiment[a]
$3b_{3g}$	*n*	9.55	9.69	9.7
$1b_{2g}$	π	12.29	12.05	11.9
$5b_{1u}$	*n*	12.20	12.22	12.1
$6a_g$	*n*	13.13	12.67	12.8
$4b_{2u}$	*n*	13.35	12.89	12.8
$1b_{1g}$	π	13.80	13.26	13.3
$1b_{3u}$	σ	16.46	16.16	15.8
$4b_{1u}$	σ	17.88	17.41	17.1
$5a_g$	σ	18.48	17.84	17.5
$3b_{2u}$	σ	20.57	19.16	19.3

attachment	energies	MR−CI	EA-EOM-CCSD
1 a_u	π^*	−0.31	−0.84
2 b_{3u}	π^*	0.62	0.35
7 a_g	σ^*	3.36	0.69
6 b_{1u}	σ^*	3.77	0.93
5 b_{2u}	σ^*		1.97

[a] MRCI results and experimental data from ref 26.

extending the diagonalization manifold to include doubly excited configurations results do not change by more than about 0.05 eV.[19]

III. Results

In the STEOM, extended-STEOM, and EOM-CCSD calculations discussed below we use the molecular geometry for *s*-tetrazine as used in previous EOM-CCSD($\hat{\mathrm{T}}$)[9] and STEOM-CCSD studies.[18] The molecule has D_{2h} symmetry and is oriented in the *yz*-plane with the CH groups lying on the *z*-axis. This determines the irreducible representations of the molecular orbitals, as discussed in ref 26. The basis set is a standard polarized basis set (PBS) designed by Sadlej[29] to obtain molecular properties and which is also quite suitable to describe excitation energies. We cannot expect to obtain an accurate description of very diffuse Rydberg states using this basis set, and to describe these states we have performed an additional STEOM calculation, augmenting the PBS basis set by a 2s2ps2d set of diffuse basis functions[31] located in the center of the molecule. In the STEOM and extended-STEOM calculations the occupied orbitals above −23 eV are taken to be active, while in addition all virtual orbitals below 8 eV are included in the active space. In total we have 10 occupied and 28 virtual orbitals in the active space. The energy cutoff for the active space is to some extent abitrary and is located at positions where there is a significant energy gap in the Hartree−Fock orbital energies. The results are not very sensitive to the precise size of the active space, and moreover computational cost does not depend critically on the number of active orbitals.

Frontier Orbitals in *s*-Tetrazine. In Table 1 we present correlated ionization potentials and electron affinities as obtained by the IP-EOM-CCSD and EA-EOM-CCSD approaches, which are part of a STEOM calculation. A comparison is made with a recent experimental photoelectron spectrum and MRCI interpretation.[26] As seen from Table 1, the agreement between IP-EOM-CCSD and experiment is quite good (<0.15 eV deviation). The MRCI results are similar for the highest lying orbitals but deteriorate somewhat for the deeper lying orbitals. The ionization manifold is characterized by an isolated lone-pair orbital at 9.7 eV, a π orbital at 11.9 eV, a second π-orbital at 13.3 eV, and three orbitals between 12 and 13 eV that have primarily nitrogen lone-pair character. The other occupied orbitals have σ character and do not play a significant role in the excitation spectrum. The EA-EOM-CCSD electron attachment energies indicate that *s*-tetrazine can bind an extra electron (EA = 0.84 eV) in its first π^* orbital, having a_u symmetry. Another low-lying π^* orbital has b_{3u} symmetry, while the other virtual orbitals comprise a set of Rydberg orbitals. The a_g orbital defines an s-type Rydberg orbital, the b_{1u}, b_{2u}, and b_{3u} orbitals represent a set of p-orbitals, while d-type Rydberg orbitals are characterized by b_{1g}, b_{2g}, b_{3g}, and a_g symmetries.

n → π^* Excitations. To discuss the excitation spectra of *s*-tetrazine and to facilitate the comparison to experiment and the recent CASPT2 and MRCI calculations, the excited states are classified as n → π^*, $\pi \rightarrow \pi^*$, Rydberg, and doubly excited states, although states of mixed character occur. The n → π^* excitations are collected in Table 2, and each of them can be fairly well characterized as a single configuration involving the excitation from one of four possible nitrogen lone-pair orbitals into one of two valence π^* orbitals, eight excitations in total. Comparing STEOM, extended-STEOM, and EOM-CCSD, we see quite consistent results. STEOM results are typically 0.1−0.2 eV higher than extended-STEOM results, while EOM-CCSD results are substantially higher, between 0.4 and 0.6 eV. The potential difficulties for EOM-CCSD are indicated by the %C1 character which is usually below the critical value of about 90%. This also explains the somewhat larger deviations between STEOM and extended-STEOM, which for states that are completely dominated by singly excited configurations tend to be less than about 0.05 eV. We note that also EOM-CCSD($\hat{\mathrm{T}}$) results[9] are in very good agreement with the present extended-STEOM results. The agreement between extended-STEOM and MRCI is reasonable, although substantial deviations occur for certain states as indicated by exclamation marks in Table 2. Unfortunately, it is precisely the experimentally accessible states that appear to be described rather poorly in the MRCI calculation. The comparison of CASPT2 with extended-STEOM also shows some deviations as indicated by exclamation marks in Table 2. In ref 28 two sets of calculations are reported for the n → π^* excitations, and we are comparing to the CASPT2 results that are obtained using a second set of n orbitals in the active space ($6\pi + 8n$), possibly including some Rydberg orbitals, which are indicated B or C in Table 1 of ref 28. It has been noted before[9,18,27] that the description of excitations from nitrogen lone-pair orbitals in aromatic rings can be problematic in CASPT2, and the inclusion of a second set of n-type orbitals may be a general recipe to overcome these difficulties. Only the B_{3u} states are dipole-allowed transitions and we find that results compare fairly well with the experimental data in both CASPT2 and extended-STEOM. The feature at 3.4 eV listed among the experimental data in Table 2 is a theoretical estimate from an analysis of vibronic coupling effects.[13] In the CASPT2 paper some additional very weak features in the experimental vacuum-UV spectrum are identified, but we see little evidence for the proposed assignments[28] that would depend on vibronic coupling mechanisms to gain some intensity.

There are features in the electron energy loss (EEL) spectrum that we can identify with singlet n → π^* transitions of ungerade symmetry as indicated in Table 2. Most of the features in the EEL spectrum will be associated with triplet excited states of ungerade symmetry (see Table 7 below). The ungerade representations include both the three B_{1u} representations and the A_u representation, and we note that singlet A_u transitions are dipole-forbidden in optical spectroscopy. The comparison of experimental and theoretical results indicates that all ungerade transitions are observed in EEL spectroscopy while gerade transitions are forbidden. We will return to a discussion of the

TABLE 2: *s*-Tetrazine Excitation Energies for the n → π* Excitations: Comparison of EOM-CCSD, STEOM-CCSD, and Extended-STEOM-CCSD Calculations in PBS Basis Set with CASPT2 and MRCI Results and Experimental Vacuum-UV and EEL Data

state	character	EOM CCSD	STEOM CCSD	Ext- STEOM	%C1	CAS PT2[a]	MR-CI[b]	vac-UV	EEL[b]
B_{3u}[e]	$3b_{3g} \rightarrow 1a_u$	2.68	2.38	2.22	90	1.96	2.86 !	2.25[c]	2.35
A_u	$3b_{3g} \rightarrow 2b_{3u}$	4.03	3.74	3.62	88	3.06 !	3.78	3.4[d]	3.6
B_{1g}	$5b_{1u} \rightarrow 1a_u$	5.29	4.91	4.73	88	4.51	5.09		
B_{2g}	$4b_{2u} \rightarrow 1a_u$	5.70	5.33	5.09	85	5.05	5.21		
A_u	$6a_g \rightarrow 1a_u$	5.69	5.38	5.23	88	5.28	5.93 !		5.0
B_{2g}	$5b_{1u} \rightarrow 2b_{3u}$	6.69	6.38	6.16	82	5.48 !	6.31		
B_{3u}[e]	$6a_g \rightarrow 2b_{3u}$	6.95	6.67	6.53	88	6.37	7.14 !	6.34[b]	6.4
B_{1g}	$4b_{2u} \rightarrow 2b_{3u}$	7.20	6.86	6.73	87	6.20 !	6.57		

[a] CASPT2 results from ref 28. [b] MRCI results and experimental vacuum-UV and EEL data from ref 26. [c] Reference 14. [d] Reference 13. [e] Dipole-allowed transition.

selection rules in low-energy EEL spectroscopy when we discuss the triplet states in *s*-tetrazine.

***π* → *π** Transitions**. The low-lying $\pi \rightarrow \pi^*$ excitations, collected in Table 3, are all dipole-allowed transitions and compare fairly well between different methods and with experiment. STEOM results deviate somewhat erratically from extended-STEOM results, but not by more than about 0.2 eV. EOM-CCSD results consistently fall 0.2−0.3 eV higher than extended-STEOM, except for the second $\pi \rightarrow \pi^*$ excitation of B_{2u} symmetry which has significant double excitation character: %C1 = 70%. This behavior is completely consistent with previous results which show typical shifts of this magnitude for valence excited states. Interestingly, EOM-CCSD($\hat{T}$) results[9] tend to fall about 0.2 eV below extended-STEOM and they appear to lie at or below the 0−0 band for the excitations at 4.70 and 7.60 eV. The adiabatic electronic excitation energy will be lower still, while also the vibrational correction to the 0−0 transition will be negative,[18] which appears to indicate that the perturbative triples correction in EOM-CCSD($\hat{T}$) is overshooting somewhat. On the other hand, from a theoretical perspective we would consider the EOM-CCSD($\hat{T}$) to be the most accurate method, and there are experimental uncertainties: The 0−0 band assigned to the feature at 4.70 eV emerges at lower energy, and the first clearly identifiable transition may not be the 0−0 band. Similarly, the band located at 7.60 eV is part of a very complicated feature and the precise location of the 0−0 band is uncertain therefore.

The comparison of CASPT2 and extended-STEOM is excellent for the first three states, but we note that disentangling the B_{1u} states takes substantial effort in the CASPT2 calculation and requires inclusion of a Rydberg state in the active space and a final diagonalization of the perturbatively corrected states in a so-called multistate CASPT2 calculation (see Tables 4 and 5 in ref 28). The $\pi \rightarrow \pi^*$ transitions are calculated at far too high energies in the MRCI calculation,[26] and a comparison does not seem meaningful.

A very interesting phenomenon occurs in the second and third state of B_{2u} symmetry. In extended-STEOM we find a very strong mixing of essentially the singly excited $\pi \rightarrow \pi^*$ ($1b_{1g} \rightarrow 2b_{3u}$) and a doubly excited n,n → π^*,π^* ($5b_{1u}3b_{3g} \rightarrow 1a_u^2$) configuration. This leads to two close-lying states at 8.28 and 8.54 eV that are qualitatively the plus and minus combination of the above two configurations. Within the regular STEOM approximation we can only determine one of these states, but also in the EOM-CCSD calculations only one state is found that is essentially singly excited (%C1 = 91%). This can be understood because implicit triple excitations are needed to accomplish the near-degeneracy of the “dressed” singly and doubly excited configurations in extended-STEOM, while this dressing is absent in EOM-CCSD. In the CASPT2 calculations three states are found using a ($6\pi + 4n + Ry$) active space, at 7.27, 8.16, and 8.32 eV (extracted from Table 2 in ref 28), while only one state at 7.94 eV is found using a 12π active space (Table 4 in ref 28). The CASPT2 calculations therefore confirm the existence of close-lying states, although the details are perhaps not correct. In order to describe both the $\pi \rightarrow \pi^*$ and the n,n → π^*,π^* configurations and their coupling, it appears that a ($12\pi + 8n$) active space is needed in CASPT2, which is beyond current computational capabilities. The splitting between the two states is minor at the extended-STEOM level, indicating that the interaction element between the dominant configurations is rather small, which also explains the satisfactory accuracy of the excitation energy for the other approaches. However, at least two states are needed to explain the experimental data. In the experimental vacuum-UV absorption spectrum there is a complicated feature at around 8.3 eV (Figure 2b of ref 26), which appears to be composed of two about equally intense transitions. In the assignment based on the MRCI calculation these states are thought to be a Rydberg and a $\pi \rightarrow \pi^*$ excited state. The extended-STEOM calculations predict two intense, close-lying $\pi \rightarrow \pi^*$ states of the same symmetry, which should give rise to an intricate vibronic structure, if one transcends the Born−Oppenheimer approximation. We do not think a Rydberg state contributes to this feature, as will be discussed below. It seems to be very interesting to completely resolve this part of the spectrum, but this is well beyond the scope of this paper. In any case, the complexity of the experimental feature appears to be in agreement with the above assessment of the situation based on the extended-STEOM calculation.

Rydberg States. In Table 4 we have listed Rydberg states up to about 10.5 eV. The first set of Rydberg states all involve excitation from the highest lying $3b_{3g}$ lone-pair orbital, and this series will converge to the ionization potential at 9.7 eV. We have only included the first s,p,d set of Rydberg states as excitations into more diffuse orbitals will require a more specialized basis set. In Table 4 we also include the lowest Rydberg states that arise from excitations from other occupied orbitals. These transitions explain the higher energy region of the experimental spectrum. As seen from Table 4 the difference between STEOM and extended-STEOM is usually less than 0.1 eV, while EOM-CCSD results consistently fall slightly above the STEOM results. Some of the states have a quite low %C1 character, and the difference between calculated results may be slightly larger then. The consistency of results between STEOM, EOM-CCSD, and extended-STEOM for Rydberg states has been observed before[18] and lends a high degree of credibility to our calculated results. In order to estimate the effect of additional diffuse basis functions on the Rydberg states, we repeated the STEOM calculation augmenting the basis set with an additional set of diffuse 2s2p2d functions[31] positioned in the center of the molecule. Most transitions were hardly affected, but three of the states did shift by almost 0.3 eV. These levels are indicated

TABLE 3: Excitation Energies for $\pi \rightarrow \pi^*$ Transitions in *s*-Tetrazine: Comparison of EOM-CCSD, STEOM-CCSD, Extended-STEOM, and EOM-CCSD($\hat{T}$) Calculations in PBS Basis Set with CASPT2 Results and Experimental Data

state	character	EOM CCSD	STEOM CCSD	Ext- STEOM	EOM CCSD($\hat{T}$)	%C1	CAS PT2[a]	exptl (vac-UV[b]) 0−0 (max)
B_{2u}	$1b_{2g} \rightarrow 1a_u$	5.24	4.72	4.90	4.71	88	4.89	4.70 (5.0)
B_{1u}	$1b_{1g} \rightarrow 1a_u$	7.41	7.31	7.14	6.95	92	7.13	6.85 (7.1)
B_{1u}	$1b_{2g} \rightarrow 2b_{3u}$	7.87	7.65	7.64	7.46	91	7.54	7.60 (7.6)
B_{2u}	$1b_{1g} \rightarrow 2b_{3u}$	8.70	8.44	8.28	8.20	70	8.16	8.15[c](8.3)
	$\pm\, 5b_{1u}3b_{3g} \rightarrow 1a_u^2$			8.54		60	8.32	

[a] Reference 28. [b] Reference 26. [c] The experimental 0−0 band is reassigned to 8.15 instead of 8.29 as reported in ref 26 (see text).

in brackets in the STEOM-CCSD column of Table 4, and these values are to be considered the more accurate.

All of the dipole-allowed transitions of B_{1u}, B_{2u}, and B_{3u} symmetry obtained from STEOM, EOM-CCSD, or extended-STEOM calculations compare quite well to the experimental features, and we believe therefore that the assignment as shown in Table 4 is correct. The first Rydberg state has B_{3g} symmetry and is reported as a very weak feature in the experimental spectrum at 5.92 eV. It has to gain its intensity through a vibronic coupling mechanism. There is some uncertainty concerning the position of the second dipole-allowed Rydberg state, which has B_{1u} symmetry. From the calculation in the diffuse basis set it appears that the vertical transition is around or below 7.79 eV, and it would therefore be part of a large feature in the spectrum that involves $\pi \rightarrow \pi$ transitions, as well as the vibrational progression that corresponds to the first dipole-allowed Rydberg state. If this is the case, the transition might be very hard to identify experimentally. On the other hand, in ref 26 the onset of a 0−0 transition is seen at 8.15 eV, which is claimed to be a Rydberg state. This does not agree with our calculations, and we think the 8.15 eV peak is the onset of a convoluted feature that involves a mixture of $\pi \rightarrow \pi^*$ and doubly exited configurations, as discussed above.

Surprisingly, the agreement between extended-STEOM and CASPT2 is not very good at all for the Rydberg states. For the $3b_{3g}$ Rydberg series the results are about 0.5−1.0 eV lower in CASPT2. The comparison for the b_{2g} Rydberg series (corresponding to the highest π-orbital) is better and CASPT2 agrees well with our results. In the CASPT2 calculations for the Rydberg states arising from excitation from the nitrogen lone-pair orbitals, only the four occupied n-orbitals are included in the active space ($6\pi + 4n + \mathrm{Ry}$). The calculations on the $n \rightarrow \pi^*$ transitions indicated that another set of lone-pair orbitals is required, and this may explain the rather large discrepancies. The MRCI results are fairly consistent with the STEOM and extended-STEOM results, usually falling about 0.3 eV below. There are some very notable exceptions, however, as indicated by exclamation marks in Table 4. They typically involve crucial dipole-allowed excited Rydberg states which makes it very hard to reliably assign the experimental spectrum using the MRCI results.

Doubly Excited States. While discussing the primarily singly excited states of $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and Rydberg character, we frequently encountered evidence of a strong mixing with doubly excited configurations. In Table 5 we focus on all of the low-lying states that have substantial double excitation character, and include results from extended-STEOM and CASPT2 calculations. It is seen that there are two very low-lying doubly excited states at 5.06 (A_g) and 6.30 eV (B_{3g}) that involve a double excitation from the HOMO nitrogen lone-pair orbital into the π^* orbitals. There is a corresponding third state, having A_g symmetry at 8.43 eV. At energies above 7 eV a host of doubly excited states develop that involve excitations from other occupied orbitals, while also double excitations arise that involve excitation into a Rydberg virtual orbital (The A_u state at 9.02 eV listed in Table 5 is the lowest state of this kind.) All of the states mentioned above are essentially purely doubly excited states (%C1 < 10%). Interestingly, there are a number of other states that exhibit a strong mixing between singly and doubly excited configurations. The %C1 is a very revealing criterion in these calculations, as it typically falls between 30% and 70% in such cases. Sometimes, such a mixing leads to a pair of states that are close in energy. The second and third states of B_{3g} symmetry at 7.78 and 7.81 eV are a prime example of such a mixing involving a singly excited Rydberg transition, and not surprisingly the splitting of the states is very small. Another example is the pair of B_{2u} states at 8.28 and 8.54 eV, which involves the mixing of a $\pi \rightarrow \pi^*$ and a π^*,π^* double excitation, and which gives rise to the interesting experimental spectral feature around 8.3 eV, mentioned before. In the B_{1g} states at 7.06 and 8.07 eV the splitting is appreciable and the low-lying state involves significantly more $n \rightarrow \pi^*$ character. Similarly, in the pair of B_{2g} states at 8.06 and 6.16 eV that involve mixing of a $n \rightarrow \pi^*$ configuration and $n,n \rightarrow \pi^*,\pi^*$ double excitation the splitting is much larger, and also the assumed pairing of the states is less evident. Both of the dipole-allowed transitions that involve doubly excited configurations and that have B_{1u} and B_{2u} symmetry overlap with an experimental feature. The B_{1u} state is almost purely a doubly excited state and presumably has a low oscillator strength, which we are not yet able to calculate within extended-STEOM. The onset of a transition at 8.15 eV may correspond to this state, which is calculated to lie at 8.18 eV. We think it is more likely, however, that the feature at 8.15 eV is the onset of the transition into the pair of intense B_{2u} states, which is then expected to show complicated vibrational progressions up to about 8.66 eV.[26] The location of the B_{2u} pair of states is precisely right to explain this convoluted experimental feature that has a maximum around 8.3 eV. In conclusion, the present calculations appear to corroborate the previous findings[19] that extended-STEOM is an accurate tool to describe doubly excited states or mixtures of singly and doubly excited configurations.

If we compare extended-STEOM results to CASPT2 results for the doubly excited states, we find qualitative but certainly not quantitative agreement. As seen from Table 5, the CASPT2 results are consistently about 1 eV lower than the extended-STEOM results, while various doubly excited states appear to be missing in the CASPT2 calculation. Let us emphasize however, that the CASPT2 calculation was the first to draw attention to the importance of doubly excited configurations in *s*-tetrazine, which was not observed in previous STEOM,[18] EOM-CCSD($\hat{T}$)[9] and MRCI calculations.[26]

Summary of Dipole-Allowed Transitions. Combining the data in Tables 2−5, we can assign all clearly identified features in the experimental vacuum-UV spectrum to computed dipole-allowed transitions, and there should be little doubt concerning the present assignment. In Table 6 we summarize all dipole-allowed transitions and also include the results from the STEOM

TABLE 4: Excited Rydberg States in *s*-Tetrazine: Comparison of EOM-CCSD, STEOM-CCSD, and Extended-STEOM-CCSD Calculations in PBS Basis Set with CASPT2 and MRCI Results and Experimental Vacuum-UV Data. STEOM Results Obtained in a PBS + Diffuse Basis Set Listed in Parentheses in the STEOM-CCSD Column If Substantially Different

state	character	EOM CCSD	STEOM CCSD	Ext- STEOM	%C1	CAS PT2[a]	MRCI[b]	exptl (vac-UV) band origins[b]
				$3b_{3g}$ Rydberg Series				
B_{3g}	$3b_{3g} \rightarrow 7a_g$	6.59	6.51	6.47	91	6.02	6.15	5.92 (vib)
B_{2u}*	$3b_{3g} \rightarrow 6b_{1u}$	7.37	7.31	7.29	91	6.75	7.73 !	7.19
A_u	$3b_{3g} \rightarrow 3b_{3u}$	7.70	7.64 (7.36)	7.62	91	6.80	7.34	
B_{3g}	$3b_{3g} \rightarrow 8a_g$	7.92	7.82	7.81	66	7.36	7.48	
B_{1u}*	$3b_{3g} \rightarrow 5b_{2u}$	8.13	8.06 (7.79)	7.99	92	6.96	7.62	7.6
B_{1g}	$3b_{3g} \rightarrow 2b_{2g}$	8.14	7.90	8.07	68	7.55	7.86	
A_g	$3b_{3g} \rightarrow 4b_{3g}$	8.28	8.20	8.11	90	7.62	8.05	
				Other Rydberg States				
B_{2g}	$1b_{2g} \rightarrow 7a_g$	8.85	8.82	8.76	93	8.80	8.96	
B_{1u}*	$5b_{1u} \rightarrow 7_{ag}$	9.18	9.09		89		8.98	8.79
A_g	$6a_g \rightarrow 7a_g$	9.52	9.43				9.36	
B_{3u}*	$1b_{2g} \rightarrow 6b_{1u}$	9.61	9.60	9.55	88	9.48	10.03	9.6
B_{2u}*	$4b_{2u} \rightarrow 7a_g$		9.71		90		11.00 !	9.7
B_{1u}*	$1b_{2g} \rightarrow 2a_u$		10.03 (9.76)		94	9.45	10.24	9.7
B_{3u}*	$5b_{1u} \rightarrow 2b_{2g}$		10.27		86		10.14	10.2
B_{3u}*	$6a_g \rightarrow 5b_{3u}$	10.54	10.58		90		10.56	10.2

[a] Reference 28. [b] Reference 26.

TABLE 5: Excitations in *s*-Tetrazine Having Significant Double Excitation Character (%C1 <70%): Comparison of Extended-STEOM-CCSD and CASPT2 Results

state	character	Ext-STEOM	%C1	CASPT2[a]	exptl (vac-UV) band origins[b]
A_g	$3b_{3g}{}^2 \rightarrow 1_{au}{}^2$	5.06	0	4.37	
B_{3g}	$3b_{3g}{}^2 \rightarrow 1a_u\ 2b_{3u}$	6.30	2	5.16	
B_{1g}	$4b_{2u} \rightarrow 2b_{3u}$	7.06	52	5.99	
	$3b_{3g} \rightarrow 2b_{2g}$				
	$3b_{3g}1b_{2g} \rightarrow 1a_u{}^2$				
B_{3g}	$3b_{3g} \rightarrow 8a_g$	7.78	39		
	$3b_{3g}\ 6\ a_g \rightarrow 1a_u{}^2$	7.81	66		
B_{2g}	$5b_{1u} \rightarrow 2b_{3u}$	8.06	30		
	$3b_{3g}1b_{1g} \rightarrow 1a_u{}^2$				
	$3b_{3g}1b_{2g} \rightarrow 1a_u\ 2b_{3u}$	6.16	82		
B_{1g}	$3b_{3g} \rightarrow 2b_{2g}$	8.07	68		
	$3b_{3g}1b_{2g} \rightarrow 1a_u{}^2$				
B_{1u}[c]	$4b_{2u}\ 3b_{3g} \rightarrow 1a_u{}^2$	8.18	2	6.94 7.31	8.15
B_{2u}[c]	$1b_{1g} \rightarrow 2b_{3u}$	8.28	70	7.27	8.15
	$5b_{1u}\ 3b_{3g} \rightarrow 1a_u{}^2$	8.54	60	8.16, 8.32	
A_g	$3b_{3g}{}^2 \rightarrow 2b_{3u}{}^2$	8.43	8	7.20	
A_u	$3b_{3g}{}^2 \rightarrow 1a_u 7a_g$	9.02	1		
B_{2g}	$3b_{3g}1b_{1g} \rightarrow 1a_u{}^2$	9.25	12		
	$5b_{1u} \rightarrow 2b_{3u}$				

[a] Reference 28. [b] Reference 26. [c] Dipole-allowed transition.

calculation in the extended basis set. As seen, the diffuse basis functions have little effect on the low-energy part of the spectrum, but we do find some additional transitions from the HOMO b_{3g} orbital into higher-lying Rydberg orbitals. Overall, we see quite good agreement between STEOM and extended-STEOM. The maximum deviation is less than 0.2 eV, and the assignment of the spectrum is well possible using the STEOM data only. However, in doing so we would miss a number of doubly excited states, and in particular the feature around 8.3 eV would be misrepresented. As mentioned before, in the CASPT2 paper some other features are listed, notably at 5.5 and 5.9 eV, but they are very weak. It is possible that these features correspond to forbidden n → π* transitions, that are borrowing intensity from a vibronic coupling mechanism, but the evidence is not very strong.

Triplet States. Besides the vacuum-UV absorption spectrum, an electron energy-loss EEL spectrum was also provided in ref 26. This type of spectroscopy provides access to both singlet and triplet states, and in Table 7 we report STEOM excitation energies for the triplet states and compare to CASPT2 and MRCI theoretical results and the experimental EEL data. Agreement between STEOM and CASPT2 for excitations into the lowest π* orbital of a_u symmetry is quite good; however, the CASPT2 results deviate by about 0.5 eV from STEOM for triplet excitations into the b_{3u} π* orbitals. The MRCI calculation shows qualitative agreement with STEOM, at least for the n → π* excitations, although MRCI energies typically lie about 0.5 eV above the STEOM results. The first A_u state is a clear exception and it appears that STEOM might be overshooting the excitation energy for this state. The $\pi \rightarrow \pi$* triplet excitations in MRCI are described significantly worse, as is the case for the singlet $\pi \rightarrow \pi$* transitions. Comparing STEOM results to experiment, it appears that all states of ungerade symmetry (including the A_u states that are dipole-forbidden) are allowed transitions in the EEL experiment. Besides the triplet states this also includes the n → π* singlet states that we assigned to additional features in the EEL spectra in Table 2. Using this selection rule we obtain very satisfactory agreement with the experimental data. The selection rules for electron energy loss spectroscopy are rather complicated[4,11,15] and depend on the energy of the electron beam. At high scattering energies, EEL intensities follow the dipole-selection rules of photoabsorption spectroscopy, as the electron beam essentially creates an oscillating electric field. Triplet transitions as observed in the described experiment require low-energy scattering as an electron exchange mechanism is required to excite into the triplet states. We do not know of an empirical selection rule that reduces the intensity of gerade transitions for low-energy scattering electrons, but the comparison of experimentally observed and calculated transitions strongly suggests that such a mechanism exists. The presence of A_u transitions in *s*-tetrazine indicates an even−odd symmetry in the problem, but also shows that low-order moment expansions should not enter a discussion of EEL transition strengths. At present we will have to consider the low-energy EEL selection

TABLE 6: Compilation of Ungerade Singlet Transitions in *s*-Tetrazine: STEOM, Extended-STEOM in PBS Basis,[29] and STEOM Results in a PBS + Diffuse Basis[31] Compared with Experimental Vacuum-UV Data.[26] Oscillator Strengths Correspond to the STEOM-CCSD Calculation in the Diffuse Basis Set

state	character	PBS basis		PBS + diffuse	osc strength	exptl band origins[a]
		STEOM CCSD	Ext-STEOM	STEOM CCSD		
B_{3u}	$3b_{3g} \rightarrow 1a_u$	2.38	2.22	2.35	0.70 (−2)	2.25[b]
A_u	$3b_{3g} \rightarrow 2b_{3u}$	3.74	3.62	3.74		3.4 (vib[c])
B_{2u}	$1b_{2g} \rightarrow 1a_u$	4.72	4.90	4.73	0.52(−1)	4.70
A_u	$6a_g \rightarrow 1a_u$	5.38	5.23	5.36		5.0[d]
B_{3u}	$6a_g \rightarrow 2b_{3u}$	6.67	6.53	6.68	0.14 (−1)	6.34
B_{1u}	$1b_{1g} \rightarrow 1a_u$	7.31	7.14	7.24	0.29 (−1)	6.85
B_{2u}	$3b_{3g} \rightarrow 6b_{1u}$	7.31	7.29	7.27	0.37 (−1)	7.19
A_u	$3b_{3g} \rightarrow 3b_{3u}$	7.64	7.62	7.36 !		
B_{1u}	$1b_{2g} \rightarrow 2b_{3u}$	7.65	7.64	7.67	0.39 (0)	7.60
B_{1u}	$3b_{3g} \rightarrow 5b_{2u}$	8.06	7.99	7.79 !	0.59 (−1)	
B_{1u}	$4b_{2u}\,3b_{3g} \rightarrow 1a_u^2$		8.18			8.15
B_{2u}	$1b_{1g} \rightarrow 2b_{3u}$	8.44	8.28	8.43	0.51 (0)	8.15
	$5b_{1u}3b_{3g} \rightarrow 1a_u^2$		8.54			
B_{1u}	$5b_{1u} \rightarrow 7a_g$	9.09		9.00	0.94 (−2)	8.79
B_{2u}	$3b_{3g} \rightarrow 7b_{1u}$			9.00	?	8.79
B_{2u}	$3b_{3g} \rightarrow 8b_{1u}$	9.42		9.39	0.31 (−1)	
B_{1u}	$3b_{3g} \rightarrow 6b_{2u}$	9.69		9.50	0.37 (−1)	9.6
B_{3u}	$1b_{2g} \rightarrow 6b_{1u}$	9.60	9.55	9.56	0.29 (−1)	9.6
B_{2u}	$4b_{2u} \rightarrow 7a_g$	9.71		9.70	0.47 (−1)	9.7
B_{1u}	$1b_{2g} \rightarrow 3b_{3u}$	10.03		9.74 !	0.13 (−2)	9.7
B_{1u}	$6a_g \rightarrow 6b_{1u}$			10.12	0.12 (−1)	
B_{3u}	$6a_g \rightarrow 3b_{3u}$	10.58		10.26 !	0.16 (−1)	10.2
B_{2u}	$5b_{1u} \rightarrow 4b_{3g}$			10.27	0.23 (−1)	10.2
B_{3u}	$5b_{1u} \rightarrow 2b_{2g}$	10.27		10.54 !	0.88 (−3)	
B_{2u}	$6a_g \rightarrow 5b_{2u}$			10.69	0.81 (−2)	
	$5b_{1u} \rightarrow 5b_{3g}$					
B_{3u}	$1b_{1g} \rightarrow 5b_{2u}$			11.21	0.32 (−1)	11.1

[a] Vacuum-UV data from ref 26. [b] Reference 14. [c] Reference 13. [d] EEL data 26.

TABLE 7: Triplet Excited States in *s*-Tetrazine: Comparison of STEOM, CASPT2, MRCI, and EEL Experimental Data

state	character		STEOM	CASPT2[a]	MRCI[b]	expt[b]
$^3B_{3u}$	$3b_{3g} \rightarrow 1a_u$	$n \rightarrow \pi^*$	1.71	1.45	2.24	1.68
^3A_u	$3b_{3g} \rightarrow 2b_{3u}$	$n \rightarrow \pi^*$	3.47	2.81 !	3.14	2.9
$^3B_{1u}$	$1b_{1g} \rightarrow 1a_u$	$\pi \rightarrow \pi^*$	3.67	4.25 !	4.68 !	3.6
$^3B_{1g}$	$5b_{1u} \rightarrow 1a_u$	$n \rightarrow \pi^*$	3.97	3.76	4.36	
$^3B_{2u}$	$1b_{2g} \rightarrow 1a_u$	$\pi \rightarrow \pi^*$	4.35	4.29	4.67	4.2
$^3B_{2g}$	$4b_{2u} \rightarrow 1a_u$	$n \rightarrow \pi^*$	4.78	4.67	4.59	
^3A_u	$6a_g \rightarrow 1a_u$	$n \rightarrow \pi^*$	4.89	4.85	5.38	4.6
$^3B_{1u}$	$1b_{1g} \rightarrow 1a_u$	$\pi \rightarrow \pi^*$	5.31	5.09	4.68	5.2
$^3B_{2g}$	$b_{1u} \rightarrow 2b_{3u}$	$n \rightarrow \pi^*$	6.16	5.30 !	6.42	
$^3B_{3g}$	$3b_{3g} \rightarrow 7a_g$	$n \rightarrow R$	6.48		4.84, 6.97	
$^3B_{3u}$	$6a_g \rightarrow 2b_{3u}$	$n \rightarrow \pi^*$	6.54	6.14 !	6.78	6.4
$^3B_{1g}$	$b_{2u} \rightarrow 2b_{3u}$	$n \rightarrow \pi^*$	6.77	5.68 !	6.72	
$^3B_{2u}$	$3b_{3g} \rightarrow 6b_{1u}$	$n \rightarrow R$	7.29		7.54	6.9
$^3B_{2u}$	$1b_{1g} \rightarrow 2b_{3u}$	$\pi \rightarrow \pi^*$	7.36	6.81 !	8.46 !	6.9

[a] CASPT2 results from ref 28. [b] MRCI and experimental EEL data from ref 26.

rules for transitions of ungerade symmetry an empirical finding that awaits a more complete theoretical understanding.

IV. Conclusions

The present study of the electronic excitation spectrum of *s*-tetrazine builds a strong case for the extended-STEOM-CCSD approach. Whereas CASPT2 and MRCI calculations require a judicious choice of active space and other user-determined computational choices to describe specific excited states, in extended-STEOM the complete excitation spectrum is obtained from a single essentially blackbox calculation that provides an inherently balanced description of singly and doubly excited states. Moreover, as a side product of an extended-STEOM calculation one obtains correlated ionization potentials at the IP-EOM-CCSD level, which can be compared directly to the experimental photoelectron spectrum and this provides an independent gauge for the accuracy of the calculations. Convergence of the methodology is monitored by comparison to a preliminary regular STEOM calculation that is performed at negligible additional computational costs.

In the present case of *s*-tetrazine most of the spectral features are described fairly well already by a regular STEOM calculation, and extended-STEOM results are usually quite close (within 0.2 eV). For comparison purposes we have also performed an EOM-CCSD calculation, which yields excitation energies that are often substantially larger (0.2−0.6 eV), depending on the particular type of excitation. A STEOM calculation in an extended basis set provides access to some higher lying Rydberg states but overall results are found to change only slightly upon inclusion of additional diffuse basis functions.

All observed features in the vacuum-UV and EEL experimental spectra are easily assigned to calculated transitions in the STEOM or extended-STEOM approaches, and their consistency lends a high degree of credibility to our results. All of the accumulated evidence appears to support the accuracy of the present calculations and the validity of the assignments. There are some features in the spectrum related to doubly excited configurations that are only described correctly using the more elaborate extended-STEOM approach. The %C1 criterion is found to provide a very useful diagnostic of the character of an excitation and it can be used to indicate that an extended-STEOM description is warranted based on results from a standard STEOM calculation.

The extended-STEOM calculation predicts that the convoluted experimental feature located between 8.15 and about 8.6 eV involves a pair of close-lying states of B_{2u} symmetry, calculated to lie at 8.28 and 8.54 eV, that are a mix of a singly excited $\pi \rightarrow \pi^*$ transition and a doubly excited $n^2 \rightarrow \pi^{*2}$ configuration.

The experimental feature may involve another purely doubly excited state of B_{1u} symmetry at 8.18 eV, which is expected to carry a low oscillator strength, however. Intricate vibronic coupling is expected to occur involving the pair of B_{2u} states that would lead to the complicated structure that is observed in the experimental spectrum and that is yet to be understood in detail.

From a comparison of calculated and experimental electron energy-loss data we have conjectured a selection rule that only transitions to ungerade symmetry are allowed in low-energy EEL spectroscopy, but this hypothesis demands a better theoretical understanding.

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