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REGULAR ARTICLE

A multireference *n*-electron Valence State Perturbation Theory study of the electronic spectrum of *s*-tetrazine

Celestino Angeli · Renzo Cimiraglia · Mirko Cestari

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Abstract This paper addresses the study of the electronic spectrum of the *s*-tetrazine molecule in the ab initio frame making use of the multireference *n*-electron Valence State Perturbation Theory (NEVPT2). The theoretical description of the excited states of this molecule is complex, because of the different computational requirements of the low-lying excited states which must be treated on an equal footing. More than forty electronic excited states of various nature ($n \rightarrow \pi^*$, $nn \rightarrow \pi^*\pi^*$, $\pi \rightarrow \pi^*$, $n\pi \rightarrow \pi^*\pi^*$, and Rydberg) are considered here. Various active spaces are used to reach a good quality zero order description, needed to avoid unrealistic results in the perturbation treatment. The quasi-degenerate perturbation theory must be used in most of the cases, given the presence of a marked mixing among various states. The results here presented have been used to add new information to the interpretation of the experimental spectra. While in many cases previous assignments of the experimental features are confirmed, in various cases they are questioned and new assignments are proposed. With the new assignments, a good agreement is found between experiments and NEVPT2. The comparison with other high level ab initio methods shows that NEVPT2 performs well, being in general in close agreement with Extended-STEOM-CCSD and CC3, while the agreement with CASPT2 and GVVPT2 is less satisfactory (the CASPT2 excitation energies being lower than the NEVPT2 ones by $\simeq$0.4 eV). Finally, comparing NEVPT2 with TD-DFT, a reasonable accordance with the values obtained with the PBE0 functional is observed, while the agreement with those computed with the HCTH functional is lower.

Keywords Multireference Perturbation Theory · NEVPT · *s*-tetrazine · Electronic spectrum · Excited states · Quasi-degenerate Perturbation Theory

1 Introduction

The theoretical description of excited states of heteroaromatic molecules has a long history and continues to be an active research field. Over the last years, our group has been active on this subject, reporting the study of pyrrole [1, 2], furan [3], thiophene [4], and free base porphin [5]. This paper further pursues this project and addresses the *s*-tetrazine molecule.

From a general point of view, *s*-tetrazine (1,2,4,5-tetrazine) and other azabenzenes have attracted the attention given their possible uses in spectral hole burning. This group of molecules is a good candidate for permanent hole burning [6]: indeed, after excitation to the S_1 state, one of the possible relaxation mechanisms is the dissociation to HCN and N_2. Derivatives of *s*-tetrazine have also been shown to posses potential antitumor activity [7].

From the theoretical point of view, the study of the spectrum of *s*-tetrazine presents, besides a set of difficulties in common with all conjugated molecules [8], some peculiarities. Indeed, with respect to other azines and to benzene the presence of four nitrogen lone pairs makes the

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C. Angeli (✉) · R. Cimiraglia
Dipartimento di Chimica, Università di Ferrara,
Via Borsari 46, 44100 Ferrara, Italy
e-mail: anc@unife.it

M. Cestari
Dipartimento di Scienze Chimiche,
Università di Padova, via Marzolo 1, 35131 Padova, Italy

electronic spectrum of *s*-tetrazine more complex. The nitrogen atoms account for high energy σ (non-bonding lone pairs, indicated hereafter as n) and for low energy (virtual) π^* orbitals, doubly occupied and empty, respectively, in the simplest description of the ground states. This leads to a number of low-lying $n \rightarrow \pi^*$ and Rydberg (with an excitation from the n or π orbitals) transitions. Moreover, the states falling in the region of the dipole allowed $\pi \rightarrow \pi^*$ states can show a large (or even dominant) component on $nn \rightarrow \pi^*\pi^*$ doubly excited determinants (the first doubly excited state is supposed to have an excitation energy of $\simeq$4.5 eV, see for instance Ref. [9]). For these reasons, the lowest part of the electronic spectrum of *s*-tetrazine is dense, with more than 500 strong peaks describing four vibrational progressions, as reported by Mason [10]. To accurately describe all these states, it is necessary to have a theoretical method able to treat in a balanced way different electron correlation effects (valence/Rydberg states, lone pair/singly occupied orbitals, σ–π correlation, singly/doubly excited states), and this is a challenge for any ab inito method. For this reason, *s*-tetrazine has also been considered as a test molecule to validate new theoretical methods.

Another reason for the large interest on azabenzene compounds is related to the fact that the excited $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states usually show a strong charge rearrangement with respect to the ground state, thus a solvatochromic behavior is expected. The accurate description of the electronic spectrum of *s*-tetrazine in gas-phase is, therefore, important for a correct calculation of the energy shift due to its interaction with the solvent molecules and for the comprehension of the nature of such an interaction [11]. These studies are of particular interest for understanding the structure and function of biological systems, where azines and their derivatives are involved in the formation of hydrogen bonds [11].

The *s*-tetrazine molecule has also been considered for theoretical studies concerning excited state properties, as for instance nuclear geometry of the first excited state [6], static [6] and dynamic polarizabilites [12], and excited state absorption [13].

The accurate description of the experimental studies on *s*-tetrazine is out of the scope of this paper (the reader is referred to the key publications [14–16]). A summary of the previously published theoretical and experimental studies on *s*-tetrazine can be found in Refs. [17, 18]. Here we only recall that the S_1 excited state of *s*-tetrazine has B_{3u} symmetry and it can be qualitatively described as a promotion of one electron of the N lone pairs (n) from the b_{3g} non-bonding orbital to an antibonding π^* orbital of a_u symmetry ($n \rightarrow \pi^*$ transition). This transition is dipole allowed and its vertical excitation is close to 2 eV: for these reasons, *s*-tetrazine has a deep reddish-purple color. For the other azabenzenes, the S_1 excited state is higher in energy and falls outside the visible region.

Despite the large theoretical efforts devoted to this molecule, the vertical excitation energy of some excited states and their nature in *s*-tetrazine remain unclear. This study aims to contribute new information and to clarify the interpretation of the experimental results, by adopting the multireference n-electron Valence State Perturbation Theory (NEVPT) [5, 19–22] as a computational tool.

The remainder of this paper is organized as follows: in Sect. 2 the computational details are described, in Sect. 3 the results of the NEVPT2 calculation are reported and finally, Sect. 4 contains some concluding remarks.

2 Computational details

The *s*-tetrazine molecule lies in the yz plane with the two carbon atoms on the z axis and all calculations are performed in the D_{2h} symmetry group. The atomic natural orbital (ANO) basis set [23] is used with the contraction $14s9p4d/4s3p2d$ for the C and N atoms and $8s4p/3s2p$ for the H atoms. To describe the Rydberg states, this basis is modified adding a set of molecular-centered diffuse functions ($8s8p8d$). The exponents of such functions are generated using the procedure proposed by Kaufmann et al. [24] and are kept uncontracted. The ANO basis has been used in Ref. [6] (without diffuse functions) and in Ref. [9] (with diffuse functions) in a CASPT2 study. Unlike this study, the diffuse functions considered in Ref. [9] were contracted to $1s1p1d$ to partially reduce the appearance of intruder states, a problem upon which CASPT2 shows a marked dependence. As NEVPT2 is exempt from such a problem, the full set of diffuse functions is used, to allow for the maximum flexibility. The zero order wavefunctions are computed at the complete active space self consistent field (CASSCF) level using the Molcas package [25]. Different types of active spaces have been considered. The first, called in the following CAS A, contains the four lone pairs of the N atoms and the six valence π orbitals (14 electrons in 10 orbitals). The symmetry and the numbering of these orbitals are reported in Table 1 to facilitate the analysis of the wavefunctions discussed in the next section.

This space is the smallest able to describe the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ valence transitions. To describe also the

Table 1 Symmetry, numbering, and nature of the orbitals defining the minimal valence active space

n	$3b_{3g}$, $4b_{2u}$, $5b_{1u}$, $6a_g$
π	$1b_{1g}$, $1b_{2g}$, $1b_{3u}$
π^*	$1a_u$, $2b_{2g}$, $2b_{3u}$

Rydberg states, the active space has been enlarged adding orbitals in the appropriate irrep. For instance, two Rydberg states belong to the A_g symmetry ($n \rightarrow 3d_{yz}$ and $\pi \rightarrow 3d_{xz}$): for the calculations performed in this symmetry, one b_{3g} ($3d_{yz}$) and one b_{2g} ($3d_{xz}$) orbitals have been added to the active space to allow for the description of these states. The number of states considered for each symmetry changes accordingly.

The resulting active space is therefore different for each symmetry considered in the CASSCF procedure, see Table 2. A second type of active space has been considered for a better description of the $\pi \rightarrow \pi^*$ transitions. This space, indicated with CAS B, contains the six π orbitals and electrons supplemented with a second set of six π virtual orbitals (6 electrons in 12 orbitals). Finally, the third type of active space, indicated with CAS C, has been used to improve the description of the $n \rightarrow \pi^*$ transitions. This space contains the n and π orbitals and electrons plus a second set of four virtual orbitals of the same symmetry of the n lone pairs (14 electrons in 14 orbitals). When more than one state is considered for a given irrep, the wavefunctions are computed with a state average procedure (SA-CASSCF).

The geometry used in this study has been calculated by Schütz et al. [6] at the CASSCF (14,14) + CASPT2 level using the ANO basis [23] set with the same contraction scheme considered here. For the sake of clarity, the relevant geometrical parameters are reported: r(N–N) = 1.3253 Å, r(C–N) = 1.3385 Å, r(C–H) = 1.0735 Å, ∠(N–C–N) = 126.6°.

The CASSCF zero order description is perturbatively corrected applying the state-specific (SS) [19–21] and the quasi-degenerate (QD) [26] versions of NEVPT to the second order in the energy, using both the strongly contracted (SC) and partially contracted (PC) variants. For more details concerning the NEVPT2 approach, the reader is referred to the original papers [19–21] and to a more recent article [5]. Here it is worth remembering that the PC-NEVPT2 variant is expected to give results of higher quality than the SC-NEVPT2 one, given that it has a larger number of perturber functions and a greater flexibility (a lower contraction) in their construction. The excitation energies computed at the ground state equilibrium geometry (vertical excitation energies) are in the following compared with the energies corresponding to the maximum of the experimental bands: it is known that such a simplified approach, neglecting the vibrational effects, introduces an error which is normally of the order of 0.1–0.2 eV. This aspect must be kept in mind when considering the results reported in Sect. 3.

Table 2 The active spaces of type A used for each irrep

Irrep	a_g	b_{3u}	b_{2u}	b_{1g}	b_{1u}	b_{2g}	b_{3g}	a_u	# MO	# States
A_g	1	2	1	1	1	3	2	1	12	6
B_{3u}	1	2	1	1	2	2	1	1	11	4
B_{2u}	1	2	1	1	2	2	1	1	11	6
B_{1g}	1	2	1	1	1	3	2	1	12	6
B_{1u}	1	3	2	1	1	2	1	1	12	6
B_{2g}	4	2	1	2	1	2	1	1	14	6
B_{3g}	4	2	1	2	1	2	1	1	14	6
A_u	1	3	2	1	1	2	1	1	12	5

An indication on the nature of the states (valence or Rydberg) can be obtained by the calculation of their spatial extent along x (the axis orthogonal to the molecular plane) measured by $\langle x^2 \rangle$, the expectation value of $\sum_{i=1}^{N} x^2(i)$ (N number of electrons). The values of $\langle x^2 \rangle$ computed at the QD-NEVPT2 level are obtained by the transformation of the matrix representing $\langle x^2 \rangle$ in the model space with the CASSCF vectors, to the basis of the eigenvectors of the second order corrected effective Hamiltonian.

It is worth noticing that NEVPT is free from the intruder state problem, while other MRPT methods strongly suffer from this drawback. Indeed, as an example, in the CASPT2 study on s-tetrazine [9] an extensive use of the level shift technique was carried out with the aim to avoid the intruder state divergences. As noted by the authors, the introduction of the level shift technique produces a sizeable modification (0.15 eV) of the excitation energies also for the states which are not exposed to the intruder state problem.

3 Results

3.1 State-specific and quasi-degenerate NEVPT2

The results reported in this section have been obtained using both SS-NEVPT2 and QD-NEVPT2. In certain cases, the application of QD-NEVPT2 has produced a strongly diagonal effective Hamiltonian, whose eigenvectors and eigenvalues are essentially identical to the starting CASSCF wavefunctions and SS-NEVPT2 energies. In particular this happens for the A_g, B_{2g}, and B_{3g} symmetries, for which the results are reported in Table 3, where, for the sake of conciseness, only the SS-NEVPT2 values are reported.

For the other five symmetries the results are shown in Table 4, where both the SS-NEVPT2 and the QD-NEVPT2 results are reported.

A modest variation is observed for the first two states of A_u symmetry passing from SS-NEVPT2 to QD-NEVPT2 (differences in the excitation energy lower than 0.15 eV) and this symmetry has been considered among the cases for which the QD approach is relevant, even if the SS approach can be considered rather satisfactory.

Table 3 CASSCF, state-specific NEVPT2 (SC and PC) vertical transition energies (eV), and CASSCF diffuseness ($\langle x^2 \rangle$ in a_0^2, within parentheses) for the ^1A_g, $^1B_{2g}$, and $^1B_{3g}$ states

State	Character	CASSCF	NEVPT2 SC	NEVPT2 PC
A_g symmetry				
1	GS	0.00 (24.3)	0.00	0.00
2	$nn \rightarrow \pi^*\pi^{*a}$	5.84 (26.0)	4.76	4.66
3	$3b_{3g} \rightarrow 3d_{yz}$	7.95 (44.6)	7.91	7.88
4	$nn \rightarrow \pi^*\pi^{*b}$	9.49 (26.6)	8.24	8.15
5	$\pi \rightarrow \pi^{*c}$	8.70 (24.3)	9.40	9.37
6	$1b_{2g} \rightarrow 3d_{xz}$	10.15 (79.3)	10.40	10.38
B_{2g} symmetry				
1	$n \rightarrow \pi^{*d}$	5.65 (24.7)	5.65	5.59
2	$n \rightarrow \pi^{*e}$	7.09 (24.9)	6.17	6.05
3	$3b_{3g} \rightarrow 3d_{xy}$	7.83 (92.1)	8.07	8.05
4	$1b_{2g} \rightarrow 3s$	8.42 (47.0)	8.82	8.78
5	$1b_{2g} \rightarrow 3d_{z^2}$	9.55 (41.8)	10.07	10.04
6	$1b_{2g} \rightarrow 3d_{x^2-y^2}$	9.92 (73.2)	10.58	10.57
B_{3g} symmetry				
1	$nn \rightarrow \pi^*\pi^{*f}$	7.10 (25.8)	6.13	6.01
2	$3b_{3g} \rightarrow 3s$	6.31 (48.1)	6.34	6.29
3	$3b_{3g} \rightarrow 3d_{z^2}$	7.40 (43.5)	7.56	7.52
4	$3b_{3g} \rightarrow 3d_{x^2-y^2}$	7.69 (49.6)	7.99	7.96
5	$\pi \rightarrow \pi^{*g}$	8.30 (23.6)	8.91	8.86
6	$1b_{2g} \rightarrow 3d_{xy}$	10.05 (91.7)	10.56	10.55

[a] Double excitation $3b_{3g}3b_{3g} \rightarrow 1a_u1a_u(71\%)$

[b] Double excitation $3b_{3g}3b_{3g} \rightarrow 2b_{3u}2b_{3u}(47\%)$

[c] Mixed nature: double excitation $1b_{2g}1b_{2g} \rightarrow 2b_{3u}2b_{3u}(16\%)$ + single excitations $1b_{2g} \rightarrow 2b_{2g}(13\%)$ and $1b_{3u} \rightarrow 2b_{3u}(21\%)$

[d] Single excitation $4b_{2u} \rightarrow 1a_u(54\%)$ + double excitation $1b_{1g}3b_{3g} \rightarrow 1a_u1a_u(30\%)$

[e] Single excitation $5b_{1u} \rightarrow 2b_{3u}(48\%)$ + double excitation $1b_{2g}3b_{3g} \rightarrow 2b_{3u}1a_u(30\%)$

[f] Double excitation $3b_{3g}3b_{3g} \rightarrow 2b_{3u}1a_u(59\%)$

[g] Single excitations $1b_{3u} \rightarrow 1a_u(30\%)$ + $1b_{1g} \rightarrow 2b_{2g}(12\%)$ + double excitations $1b_{1g}1b_{2g} \rightarrow 1a_u1a_u(26\%)$ + $1b_{1g}1b_{1g} \rightarrow 2b_{3u}1a_u(13\%)$

In the B_{3u} symmetry only two states (the third and the fourth) are affected by the use of QD-NEVPT2, leaving the first two states almost unchanged. From Table 4 it is apparent that these two states result from a mixing of a valence $n \rightarrow \pi^*$ and a Rydberg state at the CASSCF level. Such mixing is removed after the diagonalization of the second order effective Hamiltonian matrix, leading to two pure states, the lowest (the third state of this symmetry) being the Rydberg one at the QD–SC level and the valence one with QD–PC. This difference between SC and PC is due to the fact that the off diagonal element of the effective matrix is small and of opposite sign in the two variants of NEVPT2.

For the B_{1g} symmetry, the situation for the fourth and sixth states is similar to what is found for the B_{3u} symmetry. In this case, the two states are well separated both at the CASSCF and NEVPT2 level (2.0 and 0.5–0.6 eV, respectively), but a substantial off diagonal element of the effective Hamiltonian matrix (of the order of 0.8 eV) leads to a mixing of these two states. Moreover, the fourth state becomes almost degenerate with the Rydberg $3b_{3g} \rightarrow 3d_{xz}$ state if the electron correlation is taken into account with SC-NEVPT2 (with PC-NEVPT2 they are quite far from each other). This quasi degeneracy is the origin of a moderate mixing of the two states at the QD–SC NEVPT2 level (as indicated by the increase of the $\langle x^2 \rangle$ value for the fifth state from $\simeq 26\ a_0^2$ to $\simeq 29\ a_0^2$ passing from CASSCF to NEVPT2). Finally, another effect is a partial mixing of the first and fifth states which leads, for the first state, to a sizeable difference between the SS-NEVPT2 energies and the QD-NEVPT2 ones. Let us note, in passing, that in the CASSCF/CASPT2 study of Ref. [9] only five states have been considered, given that the $1b_{2g} \rightarrow 3d_{yz}$ was found to be the fifth state, while here it is the sixth.

For the other two symmetries (B_{2u} and B_{1u}), the situation is more complex and the application of QD-NEVPT2 leads in general to a mixing of different CASSCF wavefunctions.

One can note that, apart from the A_u and B_{3u} symmetries where the results are easily interpretable, in the symmetries where the QD approach affects the final results, at least one state shows a drastic reduction of the excitation energy passing from the CASSCF to the SS-NEVPT2 level. Such differential correlation energy, which is as large as 2.2–2.7 eV for the 5 $^1B_{1g}$, 2 $^1B_{1u}$, and 5 $^1B_{1u}$ states and reaches the anomalous values of 3.4 (SC) and 4.0 (PC) eV for the 3 $^1B_{2u}$ state, is a clear indication of the poor quality of the zero order description for these states. As previously found [2–5, 8, 27], in such situation a marked difference between the SC and PC variants of NEVPT2 is also observed. While the results for the B_{1g} symmetry can be considered reasonable, for the B_{1u} and B_{2u} symmetries the low quality of the zero order wavefunctions leads to a complete upsetting of the description when the perturbation corrections are taken into account. In these cases the perturbation approach cannot be trusted, as clearly indicated also by the disagreement of SC and PC NEVPT2, and the interpretation of the results for these symmetries with the CAS A space is rather ambiguous. Moreover, it is worth noticing that, while in the B_{2u} symmetry the QD approach substantially modifies only the first and third states (the others remaining almost unchanged with respect to the single state approach), in the B_{1u} symmetry all states are affected by the application of the QD formalism. For these reasons, these special cases are studied in the next sections also with other active spaces, as firstly suggested

Table 4 CASSCF, state-specific and quasi-degenerate NEVPT2 (SC and PC) vertical transition energies (eV) and CASSCF, QD–SC, and QD–PC diffuseness ($\langle x^2 \rangle$ in a_0^2, within parentheses) for the B_{3u}, B_{2u}, B_{1g}, B_{1u}, and A_u symmetries

State	Character	CASSCF	SC	QD–SC	PC	QD–PC
B_{3u} symmetry						
1	$n \rightarrow \pi^{*a}$	3.23 (25.2)	2.36	2.34 (25.2)	2.32	2.29 (25.2)
2	$n \rightarrow \pi^{*b}$	7.79 (25.4)	7.20	7.22 (25.4)	7.14	7.17 (25.4)
3	$n \rightarrow \pi^{*c}$	9.54 (30.8)	9.53	9.62 (25.0)	9.49	9.39 (25.6)
4	$1b_{2g} \rightarrow 3p_z$	9.50 (33.9)	9.50	9.41 (39.6)	9.46	9.56 (39.3)
B_{2u} symmetry						
1	$\pi \rightarrow \pi^{*d}$	4.98 (24.2)	5.60	5.38 (24.1)	5.59	5.10 (24.1)
2	$3b_{3g} \rightarrow 3p_z$	7.51 (41.9)	7.04	7.04 (42.0)	7.01	7.01 (42.0)
3	$\pi \rightarrow \pi^{*d}$	11.21 (24.3)	7.80	7.94 (24.5)	7.16	7.57 (24.5)
4	$nn \rightarrow \pi^{*}\pi^{*e}$	8.75 (26.2)	8.39	8.42 (26.1)	8.33	8.35 (26.2)
5	$nn \rightarrow \pi^{*}\pi^{*e}$	10.01 (26.4)	9.28	9.26 (26.4)	9.21	9.17 (26.3)
6	$nn \rightarrow \pi^{*}\pi^{*e}$	9.69 (26.3)	9.64	9.72 (26.3)	9.59	9.71 (26.3)
B_{1g} symmetry						
1	$n \rightarrow \pi^{*f}$	5.45 (25.1)	5.13	4.83 (25.1)	5.08	4.53 (25.1)
2	$n\pi \rightarrow \pi^{*}\pi^{*e}$	7.15 (26.0)	6.87	6.75 (26.6)	6.81	6.62 (26.0)
3	$n \rightarrow \pi^{*f}$	7.64 (28.5)	7.15	6.98 (25.4)	7.07	6.92 (28.5)
4	$3b_{3g} \rightarrow 3d_{xz}$	8.01 (79.3)	7.89	7.87 (78.7)	7.86	7.93 (79.3)
5	$n\pi \rightarrow \pi^{*}\pi^{*e}$	10.02 (25.9)	7.80	8.38 (29.0)	7.54	8.29 (25.9)
6	$1b_{2g} \rightarrow 3d_{yz}$	10.25 (41.9)	10.34	10.37 (42.3)	10.31	10.38 (41.9)
B_{1u} symmetry						
1	$\pi \rightarrow \pi^{*d}$	9.47 (42.1)	7.33	6.77 (25.1)	7.25	6.15 (25.0)
2	$\pi \rightarrow \pi^{*d}$	10.40 (32.5)	7.82	7.34 (34.0)	7.66	6.76 (25.3)
3	$3b_{3g} \rightarrow 3p_y$	7.70 (42.4)	7.81	7.43 (34.7)	7.71	7.35 (42.8)
4	$nn \rightarrow \pi^{*}\pi^{*e}$	9.24 (27.0)	7.86	7.73 (26.8)	7.64	7.47 (27.2)
5	$nn \rightarrow \pi^{*}\pi^{*e}$	10.66 (27.5)	7.92	8.27 (27.0)	7.54	8.19 (27.0)
6	$1b_{2g} \rightarrow 3p_x$	9.01 (43.3)	8.13	9.34 (68.0)	7.82	9.72 (68.2)
A_u symmetry						
1	$n \rightarrow \pi^{*g}$	4.61 (25.5)	3.63	3.53 (25.5)	3.55	3.41 (25.4)
2	$n \rightarrow \pi^{*h}$	6.46 (25.2)	5.95	6.01 (25.1)	5.87	5.95 (25.1)
3	$3b_{3g} \rightarrow 3p_x$	7.25 (72.0)	7.08	7.09 (72.1)	7.05	7.06 (72.2)
4	$n\pi \rightarrow \pi^{*}\pi^{*i}$	9.67 (25.0)	9.85	9.89 (26.1)	9.78	9.85 (25.6)
5	$1b_{2g} \rightarrow 3p_y$	9.76 (44.3)	9.94	9.95 (41.2)	9.91	9.91 (43.6)

The analysis of the wavefunction is presented for the QD–PC calculations

[a] Single excitation $3b_{3g} \rightarrow 1a_u(80\%)$

[b] Single excitation $6a_g \rightarrow 2b_{3u}(62\%)$

[c] Mixed nature: single excitation $5b_{1u} \rightarrow 2b_{2g}(22\%)$ + double excitation $5b_{1u}1b_{2g} \rightarrow 1a_u1a_u(20\%)$

[d] Almost pure $\pi \rightarrow \pi^*$ single excitation nature with CAS B (excitation energies in Table 8)

[e] The analysis of the wavefunction is in Table 7 for the CAS C active space

[f] The analysis of the wavefunction is in Table 6 for the CAS C active space

[g] Single excitation $3b_{3g} \rightarrow 2b_{3u}(74\%)$

[h] Single excitation $6a_g \rightarrow 1a_u(67\%)$

[i] Double excitations $4b_{2u}1b_{2g} \rightarrow 1a_u1a_u(21\%)$ and $1b_{3u}3b_{3g} \rightarrow 1a_u1a_u(17\%)$ + single excitation $4b_{2u} \rightarrow 2b_{2g}(18\%)$

by Rubio and Roos [9]. A special care will be devoted to the B_{1u} symmetry, which contains states for which the electronic transition from the ground state is dipole allowed.

The results for all the studied states are commented and compared with previously published values and with experimental findings in the next subsections, considering separately the Rydberg, the $n \rightarrow \pi^*$, and the $\pi \rightarrow \pi^*$ states.

Table 5 CASSCF, state-specific NEVPT2 (SC and PC) vertical transition energies (eV), and diffuseness ($\langle x^2 \rangle$ in a_0^2, within parentheses) for the $n \rightarrow$ Ryd and $\pi \rightarrow$ Ryd states

State	Character	CASSCF	NEVPT2 SC	NEVPT2 PC	CASPT2[a]	STEOM CCSD[b]	Extended STEOM	TD-DFT PBE0[c]	TD-DFT HCTH[d]	Exp.
$n \rightarrow$ Ryd series										
$2\ ^1B_{3g}$	$3b_{3g} \rightarrow 3s$	6.31 (48.1)	6.34	6.29	6.02	6.51	6.47	6.23	6.00	
$3\ ^1A_u$	$3b_{3g} \rightarrow 3p_x$	7.25 (72.0)	7.08	7.05	6.80	7.36	7.62	7.35	6.84	
$3\ ^1B_{1u}$	$3b_{3g} \rightarrow 3p_y$	7.70 (42.4)	7.81	7.71	6.96	7.79	7.99	7.86	7.19	7.6[e]
$2\ ^1B_{2u}$	$3b_{3g} \rightarrow 3p_z$	7.51 (41.9)	7.04	7.01	6.75	7.31	7.29	6.77	6.70	7.19[e], 7.12[f]
$3\ ^1B_{3g}$	$3b_{3g} \rightarrow 3d_{z^2}$	7.40 (43.5)	7.56	7.52	7.36	7.82	7.81	7.44	7.15	
$4\ ^1B_{1g}$	$3b_{3g} \rightarrow 3d_{xz}$[c]	8.01 (79.3)	7.89	7.86	7.55	7.90	8.07	8.44	7.65	
$3\ ^1A_g$	$3b_{3g} \rightarrow 3d_{yz}$	7.95 (44.6)	7.91	7.88	7.62	8.20	8.11	7.86	7.56	
$4\ ^1B_{3g}$	$3b_{3g} \rightarrow 3d_{x^2-y^2}$	7.69 (49.6)	7.99	7.96	7.72			8.51	7.71	
$3\ ^1B_{2g}$	$3b_{3g} \rightarrow 3d_{xy}$	7.83 (92.1)	8.07	8.05	7.77			8.81	7.75	
$\pi \rightarrow$ Ryd series										
$4\ ^1B_{2g}$	$1b_{2g} \rightarrow 3s$	8.42 (47.0)	8.82	8.78	8.80	8.82	8.76			
$6\ ^1B_{1u}$[g]	$1b_{2g} \rightarrow 3p_x$	9.96 (54.6)	9.70 (78.4)	9.91 (78.6)	9.45	9.76				
$5\ ^1A_u$	$1b_{2g} \rightarrow 3p_y$	9.76 (44.3)	9.95	9.91	10.01					
$4\ ^1B_{3u}$	$1b_{2g} \rightarrow 3p_z$	9.50 (33.9)	9.50	9.46	9.48	9.60	9.55			9.7[e], 9.6[f]
$5\ ^1B_{2g}$	$1b_{2g} \rightarrow 3d_{z^2}$	9.55 (41.8)	10.07	10.04	10.17					
$6\ ^1B_{1g}$	$1b_{2g} \rightarrow 3d_{yz}$	10.25 (41.9)	10.34	10.31	10.36					
$6\ ^1A_g$	$1b_{2g} \rightarrow 3d_{xz}$	10.15 (79.3)	10.40	10.38	10.41				>9	
$6\ ^1B_{3g}$	$1b_{2g} \rightarrow 3d_{xy}$	10.05 (91.7)	10.56	10.55	10.59					
$6\ ^1B_{2g}$	$1b_{2g} \rightarrow 3d_{x^2-y^2}$	9.92 (73.2)	10.58	10.57	10.60					

All states computed with the active space A (see text). Comparisons with previously published results and with experimental data are presented

[a] Ref. [9]

[b] Ref. [28]

[c] Ref. [29]

[d] Ref. [30]

[e] VUV absorption spectrum, Ref. [16]

[f] Electron impact energy loss spectrum, Ref. [31]

[g] Computed with the CAS B space at the QD-NEVPT2 level using three states (the other two having $\pi \rightarrow \pi^*$ nature, see Table 8)

3.2 The Rydberg states

Following the work of Rubio and Roos [9], the Rydberg states, where an electron is excited from the n $3b_{3g}$ (HOMO) and the π $1b_{2g}$ orbital to the $3s$, $3p$, and $3d$ Rydberg orbitals, are considered. These two Rydberg series converge to the two ionization potentials relative to the B_{3g} and B_{2g} states of the ion, experimentally found to be 9.7 and 12.1 eV [16]. The vertical excitation energies and the diffuseness at different levels of calculation are reported for these states in Table 5, together with a selection of previously published results and the known experimental values.

As a first general consideration, one can note that the NEVPT2 excitation energies are higher than the CASPT2 ones. Nooijen [28] has pointed out that for these states the agreement between CASPT2 and Extended-STEOM is quite poor, with differences in the range 0.5–1.0 eV. NEVPT2 is in a closer agreement with STEOM-CCSD and Extended-STEOM, the differences being not larger than 0.2–0.3 eV. A relevant exception is the 3^1A_u state, for which the Extended-STEOM value (7.62 eV) differs from the NEVPT2 ones by 0.5–0.6 eV. However, for this state the STEOM-CCSD excitation energy is lowered by 0.28 eV (from 7.64 to 7.36 eV, see Ref. [28]) using a basis set larger than the one used in the Extended-STEOM calculation. Thus also in this case, the difference between NEVPT2 and Extended-STEOM can be estimated to be lower than 0.4 eV.

In more detail, the lowest Rydberg state, $2\ ^1B_{3g}$, originates from the excitation $3b_{3g} \rightarrow 3s$. In the experimental spectrum, a weak absorption has been detected at 5.92 eV. In Ref. [9] two candidates were identified for this transition based on the CASPT2 results: the $3b_{3g} \rightarrow 3s$ state and one of the $n \rightarrow \pi^*$ states ($2\ ^1B_{1g}$), located at 6.02 and 5.99 eV, respectively. In a TD-DFT(HCTH) calculation [30], the excitation energy for the 2 $^1B_{3g}$ Rydberg state has also been found to be 6.00 eV. Later on, a STEOM-CCSD and Extended-STEOM study has suggested higher values (6.51 and 6.47 eV), a result confirmed by TD-DFT(PBE0) [29] (6.34 eV) and CC3 [13] (6.38 eV). The NEVPT2 values for the $3b_{3g} \rightarrow 3s$ excitation, 6.34 (SC) and 6.29 (PC) eV, are in between the two limiting values and indicate that the experimental feature at 5.92 eV cannot conclusively be attributed to this state.

For the $3b_{3g} \rightarrow 3p$ transitions, the NEVPT2 values allow to confirm the attribution of these transitions to the intense and structured band experimentally observed around 7.2 eV. In particular, we assign this transition to the $3b_{3g} \rightarrow 3p_z$ state, in agreement with the assignment of Nooijen [28] (based on STEOM-CCSD and Extended-STEOM) and in disagreement with the assignment of Rubio and Roos [9] (based on CASPT2), who have proposed the $3b_{3g} \rightarrow 3p_y$ state. NEVPT2, STEOM-CCSD, and Extended-STEOM predict the $3b_{3g} \rightarrow 3p_y$ state much higher in energy (in the range 7.71–7.99 eV) suggesting to assign to this state the experimentally observed [16] transition at 7.6 eV, while in the CASPT2 study it has been assigned to one of the $^1B_{1u}$ $\pi \rightarrow \pi^*$ states. However, at the higher level (CAS C for the $nn \rightarrow \pi^*\pi^*$ states and CAS B for the $\pi \rightarrow \pi^*$ ones), NEVPT2 indicates a high density of states of B_{1u} symmetry in this region: a $nn \rightarrow \pi^*\pi^*$ state at 7.6–7.8 eV (see Table 7), two $\pi \rightarrow \pi^*$ states between 7.2 and 8.0 eV (see Table 8), and the $3b_{3g} \rightarrow 3p_y$ Rydberg state. For these reasons the assignment of the experimental transition at 7.6 eV is complex. Moreover, the numbering of the $^1B_{1u}$ states is also difficult, because it strongly depends on the level of calculation. In the following, the numbering reported in Table 4 has been maintained.

The $3b_{3g} \rightarrow 3d$ transitions are computed at the NEVPT2 level in the interval 7.56–8.07 eV (SC) and 7.52–8.05 eV (PC), slightly above the CASPT2 values (7.36–7.77 eV), a trend shown also by the STEOM-CCSD and Extended-STEOM methods, while TD-DFT gives quite different values according to the functional employed, with TD-DFT(HCTH) in close agreement with CASPT2. The $3b_{3g} \rightarrow 3d_{yz}$ transition has been computed as 7.94 eV with CC3 [13], a value very close to the NEVPT2 ones (7.91 and 7.88 eV for SC and PC, respectively).

NEVPT2 locates the first Rydberg state originated from the excitation out of the $\pi 1b_{2g}$ orbital at 8.82 (SC) and 8.78 (PC) eV, in excellent agreement with CASPT2, STEOM-CCSD, and Extended-STEOM. This agreement between different methods is found also for the other states, with the only relevant exception of the $1b_{2g} \rightarrow 3p_x$ state, for which a marked difference is observed with CASPT2, while the STEOM-CCSD estimation is rather close to the two NEVPT2 values. This state has B_{1u} symmetry, for which, as described in Sect. 1, the use of the CAS A space presents problems. The values reported in Table 5 have been obtained by considering three states with the CAS B space (two $\pi \rightarrow \pi^*$ states and the Rydberg one). In this calculation a clear valence/Rydberg mixing is present at the CASSCF level, as indicated by $\langle x^2 \rangle$ (see also Table 8, where the two $\pi \rightarrow \pi^*$ states with the same active space are reported): such a mixing is effectively treated by QD-NEVPT2, leading to three pure states after the introduction of the dynamical electron correlation.

The comparison of NEVPT2 with CASPT2 is particularly relevant, given that they have been applied on a common set of states. The results of this study confirm the assignment of Rubio and Roos to the $1b_{2g} \rightarrow 3p_z$ transition of the narrow peak observed at 9.6 eV in the EEL spectrum [31] and at 9.7 eV in the VUV spectrum [16].

3.3 The $n \rightarrow \pi^*$, $nn \rightarrow \pi^*\pi^*$, and $n\pi \rightarrow \pi^*\pi^*$ states

In this section we consider the states with $n \rightarrow \pi^*$, $nn \rightarrow \pi^*\pi^*$, and $n\pi \rightarrow \pi^*\pi^*$ nature. They belong to all the symmetries and the results for the excitation energy and for the diffuseness are reported in Tables 6 and 7.

As a difference with the CASPT2 study [9], where the use of the CAS C active space for the study of the $nn \rightarrow \pi^*\pi^*$ states was not possible, all states are here computed with both CAS A and CAS C.

The lowest excited state of *s*-tetrazine is of $n \rightarrow \pi^*$ type and has B_{3u} symmetry. It has been shown that after Franck–Condon excitation, it does not show strong structural relaxation [6, 34] and, therefore, the vertical and adiabatic experimental excitation energies are quite close, amounting to 2.35 and 2.25 eV, respectively [10]. The NEVPT2 values (both the SC and PC variants and with both the CAS A and CAS C active spaces, see Table 6) agree well with the experimental finding, and with the previously published values computed with high level methods, the largest discrepancy being met with CASPT2 [9] and TD-DFT(HCTH) [30], which underestimate the vertical excitation energy of this transition by roughly 0.4 eV.

The excitation energy to the second excited state (1 ^1A_u, a transition optically forbidden) has been experimentally estimated to be 3.4 eV by Innes [14] by means of an analysis of the experimental vibronic coupling with the first excited singlet. This result is in partial agreement with the observation of a weak feature at 3.6 eV in the electron energy-loss spectrum [16]. From the theoretical point of view, CASPT2, GVVPT2, and TD-DFT(HCTH) give too low values, 3.06, 3.09, and 2.90 eV, respectively, while Extended-STEOM (3.62 eV) and TD-DFT(PBE0) (3.47 eV) are closer to the experimental data. Two CC3 values have been published (3.68 [13] and 3.79 [33] eV): the first is obtained with the same basis set used in the CASPT2 study [9], while the second uses a basis set less

Table 6 CASSCF, state-specific and quasi-degenerate NEVPT2 (SC and PC) vertical transition energies (eV), and diffuseness ($\langle x^2 \rangle$ in a_0^2, within parentheses) for the $n \rightarrow \pi^*$ states

State	Active space	CASSCF	NEVPT2 SC	NEVPT2 PC	CASPT2[a]	GVVPT2[b]	Extended STEOM[c]	CC3[d]	CC3[e]	TD-DFT PBE0[f]	TD-DFT HCTH[g]	Exp.
1^1B_{3u}	CAS A	3.23 (25.2)	2.34 (25.2)	2.29 (25.2)	1.96	2.01	2.22	2.41	2.53	2.25	1.90	2.25[k], 2.35[l]
	CAS C	3.86 (25.4)	2.36 (25.4)	2.21 (25.4)								
$1\ {}^1A_u$	CAS A	4.61 (25.5)	3.53 (25.5)	3.41 (25.4)	3.06	3.09	3.62	3.68	3.79	3.47	2.90	3.4,3.6[l]
	CAS C	5.00 (25.7)	3.64 (25.7)	3.46 (25.7)								
$1\ {}^1B_{1g}^{\mathrm{h}}$	CAS A	5.45 (25.1)	4.83 (25.1)	4.53 (25.1)	4.51	4.47	4.73	4.85	4.97	4.85	4.23	
	CAS C	5.86 (25.4)	4.85 (25.4)	4.67 (25.4)								
$2\ {}^1A_u$	CAS A	6.46 (25.2)	6.01 (25.1)	5.95 (25.1)	5.28	5.32	5.23		5.46	5.34	4.82	5.5[l]
	CAS C	6.94 (25.5)	5.95 (25.5)	5.81 (25.5)								
$1\ {}^1B_{2g}$	CAS A	5.65 (24.7)	5.65	5.59	5.05	4.92	5.09		5.34	5.67	4.97	5.5[l]
	CAS C	5.87 (25.4)	5.49 (25.4)	5.42 (25.4)								
$2\ {}^1B_{2g}$	CAS A	7.09 (24.9)	6.17	6.05	5.48	5.78	6.16		6.23	6.07	5.33	5.9[l]
	CAS C	7.12 (25.6)	6.11 (25.6)	6.00 (25.6)								
$3\ {}^1B_{1g}^{\mathrm{i}}$	CAS A	7.64 (28.5)	6.98 (25.4)	6.92 (28.5)	6.20	6.60	6.73		7.08	6.95	6.65	
	CAS C	8.08 (25.6)	6.97 (25.6)	6.81 (25.6)								
2^1B_{3u}	CAS A	7.79 (25.4)	7.22 (25.4)	7.17 (25.4)	6.37		6.53		6.67	6.50	5.84	6.6[m], 6.34[l]
	CAS C	8.05 (25.6)	6.98 (25.6)	6.85 (25.6)								
$3\ {}^1B_{3u}^{\mathrm{j}}$	CAS A	9.54 (30.8)	9.62 (25.0)	9.39 (25.6)	8.10							
	CAS C	10.29 (25.2)	9.24 (25.2)	9.08 (25.2)								

The NEVPT2 values are computed at the QD level if the diffuseness is reported, and at the SS level otherwise. The wavefunction analysis is reported at the the QD–PC level with the CAS C active space. Comparisons with previously published results and with experimental data are presented

[a] Ref. [9]

[b] Ref. [32]

[c] Ref. [28]

[d] Ref. [13], with the same basis set used in Ref. [9]

[e] Ref. [33], with the TZVP basis set [37]

[f] Ref. [29]

[g] Ref. [30]

[h] Single excitation $5b_{1u} \rightarrow\ 1a_u(68\%)$ + double excitation $1b_{2g}\ 3b_{3g} \rightarrow\ 1a_u\ 1a_u(12\%)$

[i] Single excitation $4b_{2u} \rightarrow\ 2b_{3u}(68\%)$

[j] Mixed $n \rightarrow \pi^*$ and $n\pi \rightarrow \pi^*\pi^*$ nature, see Table 4

[k] Gas phase absorption spectrum at room temperature, Ref. [10]

[l] VUV absorption spectrum, Ref. [16]

[m] EEL spectrum, Ref. [16]

suited for the correct description of Rydberg states. The NEVPT2 excitation energies with CAS A (3.53 and 3.41 eV) are in excellent accordance with the experimental values. The use of the larger CAS C active space leads to modest variations (in particular at the PC level), thus confirming the good quality of the results.

In the EEL spectrum [16], three features are observed at 4.2, 4.6, and 5.2 eV. They are not found in the VUV spectrum, thus suggesting that they are due to triplet states or optically forbidden singlet states. In the CASPT2 study, six optically forbidden singlet transitions were found between 4.0 and 5.5 eV. Here only three transitions fall in this range, only two of them below 5.0 eV (1 $^1B_{1g}$ and 2 ^1A_g), both close to 4.6 eV. The assignment of these transitions is made complex also by the presence of triplet states in this energy interval (seven states found in the CASPT2 [9] study).

Palmer et al. [16] attributed the very weak band observed at 5.5 eV to the 2 ^1A_u state. This assignment was questioned by Rubio and Roos [9] who indicate the 2 $^1B_{2g}$ state as an alternative candidate for this transition, even if the 2 ^1A_u state was not ruled out. Our calculations position the 2 $^1B_{2g}$ above 6 eV (confirmed by Extended-STEOM [28] and by CC3 [33] calculation) and therefore exclude it for this transition. The NEVPT2 values for the 2 ^1A_u are close to 6 eV with the CAS A space, while they become 5.95 (SC)

Table 7 CASSCF, state-specific and quasi-degenerate NEVPT2 (SC and PC) vertical transition energies (eV), and diffuseness ($\langle x^2 \rangle$ in a_0^2, within parentheses) for the $nn \rightarrow \pi^*\pi^*$ and $n\pi \rightarrow \pi^*\pi^*$ states

State	Active space	CASSCF	NEVPT2 SC	NEVPT2 PC	CASPT2[a]	GVVPT2[b]	Extended STEOM[c]	CC3[d]	TD-DFT PBE0[e]	TD-DFT HCTH[f]	Exp.
$2\ ^1A_g$	CAS A	5.84 (26.0)	4.76	4.66	4.37	4.34	5.06				
	CAS C	6.35 (26.3)	4.78	4.62							
$1\ ^1B_{3g}$	CAS A	7.10 (25.8)	6.13	6.01	5.16	5.26	6.30				5.9[n]
	CAS C	7.65 (26.4)	6.15	6.00							
$2\ ^1B_{1g}^{\mathrm{g}}$	CAS A	7.15 (26.0)	6.75 (26.6)	6.62 (26.0)	5.99	6.20	7.06	6.87	7.61	6.04	
	CAS C	7.55 (25.3)	6.67 (25.3)	6.55 (25.3)							
$4\ ^1B_{1u}^{\mathrm{h}}$	CAS A	9.24 (27.0)	7.73 (26.8)	7.47 (27.2)	6.94						7.6[n]
	CAS C	10.43 (27.1)	7.81 (26.9)	7.60 (27.0)							
$4\ ^1A_g$	CAS A	9.49 (26.6)	8.24	8.15	7.20		8.43				
	CAS C	10.10 (26.9)	8.28	8.08							
$5\ ^1B_{1u}^{\mathrm{i}}$	CAS A	10.66 (27.5)	8.27 (27.0)	8.19 (27.0)	7.13						
	CAS C	11.25 (26.7)	8.70 (26.7)	8.50 (26.7)							
$5\ ^1B_{1g}^{\mathrm{j}}$	CAS A	10.02 (25.9)	8.38 (29.0)	8.29 (25.9)							
	CAS C	10.13 (25.3)	8.33 (25.3)	8.15 (25.3)							
$4\ ^1B_{2u}^{\mathrm{k}}$	CAS A	8.75 (26.2)	8.42 (26.1)	8.35 (26.2)	7.27		8.28				
	CAS C	9.43 (26.3)	8.10 (26.2)	7.96 (26.0)							
$5\ ^1B_{2u}^{\mathrm{l}}$	CAS A	10.01 (26.4)	9.26 (26.4)	9.17 (26.3)	8.16		8.54				8.3[n]
	CAS C	10.20 (24.9)	8.48 (25.0)	8.26 (25.5)							
$6\ ^1B_{2u}^{\mathrm{m}}$	CAS A	9.69 (26.3)	9.72 (26.3)	9.71 (26.3)	8.32						
	CAS C	10.58 (26.6)	9.13 (26.6)	9.01 (26.6)							
$4\ ^1A_u$	CAS A	9.67 (25.0)	9.89 (26.1)	9.85 (25.6)							
	CAS C	10.31 (25.3)	9.60 (25.3)	9.49 (25.3)							

The NEVPT2 values are computed at the QD level if the diffuseness is reported, at the SS level otherwise. The wavefunction analysis is reported at the the QD–PC level with the CAS C active space. Comparisons with previously published results and with experimental data are presented

[a] Ref. [9]

[b] Ref. [32]

[c] Ref. [28]

[d] Ref. [33]

[e] Ref. [29]

[f] Ref. [30]

[g] Double excitation $1b_{2g}3b_{3g} \rightarrow 1a_u1a_u$(33%) + single excitation $3b_{3g} \rightarrow 2b_{2g}$(29%)

[h] Double excitation $5b_{1u}3b_{3g} \rightarrow 2b_{3u}1a_u$(70%)

[i] Double excitations $4b_{2u}3b_{3g} \rightarrow 1a_u1a_u$(51%) + $6a_g5b_{1u} \rightarrow 1a_u1a_u$(20%) + $5b_{1u}3b_{3g} \rightarrow 2b_{3u}1a_u$(10%)

[j] Double excitations $1b_{1g}3b_{3g} \rightarrow 2b_{3u}1a_u$(26%) and $1b_{2g}3b_{3g} \rightarrow 1a_u1a_u$(17%) + single excitation $3b_{3g} \rightarrow 2b_{2g}$(17%)

[k] Double excitations $5b_{1u}3b_{3g} \rightarrow 1a_u1a_u$(35%) and + $3b_{3g}3b_{3g} \rightarrow 2b_{2g}1a_u$(12%) + single excitation $1b_{1g} \rightarrow 2b_{3u}$(14%)

[l] Double excitation $5b_{1u}3b_{3g} \rightarrow 1a_u1a_u$(16%) + single excitations $1b_{2g} \rightarrow 1a_u$(15%) and $1b_{1g} \rightarrow 2b_{3u}$(28%)

[m] Double excitation $4b_{2u}3b_{3g} \rightarrow 2b_{3u}1a_u$(58%)

[n] VUV absorption spectrum, Ref. [16]

and 5.81 (PC) eV by enlarging the active space (CAS C). The PC-NEVPT2 excitation energy is 0.35 eV higher than the CC3 value (5.46 eV) and appreciably higher than those computed with CASPT2, GVVPT2, Extended-STEOM, and TD-DFT(HCTH). The NEVPT2 results do not bear out the assignment of the transition at 5.5 eV to the 2 ^1A_u state, but it must be noted that for this state NEVPT2 gives results quite far from all other methods and this study does not give a definitive indication. On the other hand, the transition to the 1 $^1B_{2g}$ state is close to 5.5 eV (all NEVPT2 values are in the range 5.42–5.65 eV).

In the VUV spectrum [16], a weak band has been observed at $\simeq$5.9 eV. This band has been attributed to the transition to the 2 $^1B_{1g}$ state computed at 5.99 eV in the CASPT2 study [9]. The NEVPT2 results are in disagreement with such an attribution: the 2 $^1B_{1g}$ is found at $\simeq$6.6–

Table 8 CASSCF, quasi degenerate NEVPT2 (SC and PC) vertical transition energies (eV), and diffuseness ($\langle x^2 \rangle$ in a_0^2, within parentheses) for the $\pi \rightarrow \pi^*$ states

State	Active space	CASSCF	NEVPT2 SC	NEVPT2 PC	CASPT2[a]	Extended STEOM[b]	CC3[c]	CC3[d]	TD-DFT PBE0[e]	TD-DFT HCTH[f]	Exp.
1 $^1B_{2u}$	CAS A	4.98 (24.2)	5.38 (24.1)	5.10 (24.1)	4.89	4.90	5.20	5.12	5.81	5.54	4.97[g], 5.0[h]
	CAS B	5.07 (24.4)	5.29 (24.5)	5.32 (24.5)							
1 $^1B_{1u}$	CAS A	9.47 (42.1)	6.77 (25.1)	6.15 (25.0)	7.13	7.14	7.28	7.45	7.06	6.84	7.1[g,h]
	CAS B	8.81 (31.2)	7.36 (26.3)	7.20 (26.0)							
2 $^1B_{1u}$	CAS A	10.40 (32.5)	7.34 (34.0)	6.76 (25.3)	7.54	7.64		7.79	7.57	7.51	7.6[g,h]
	CAS B	9.28 (45.8)	8.06 (26.9)	7.81 (27.0)							
3 $^1B_{2u}$	CAS A	11.21 (24.3)	7.94 (24.5)	7.57 (24.5)	7.94	8.28		8.51	8.50	8.19	8.3[g,h]
	CAS B	10.45 (25.5)	8.71 (25.4)	8.55 (25.4)							
5 ^1A_g	CAS A	8.70 (24.3)	9.40	9.37	8.55						
	CAS B	8.64 (24.6)	9.07	9.13							
5 $^1B_{3g}$	CAS A	8.30 (23.6)	8.91	8.86	8.08			8.47		8.86	
	CAS B	8.00 (24.3)	8.56	8.59							

The NEVPT2 values are computed at the QD level if the diffuseness is reported, at the SS level otherwise. Comparisons with previously published results and with experimental data are presented

[a] Ref. [9]

[b] Ref. [28]

[c] Ref. [13], with the same basis set used in Ref. [37]

[d] Ref. [33], with the TZVP basis set [37]

[e] Ref. [29]

[f] Ref. [30]

[g] VUV absorption spectrum, Ref. [16]

[h] Electron impact energy loss spectrum, Ref. [31]

6.7 eV (the SC or PC variants, with CAS A or CAS C, showing small variations). Two other states are indicated by NEVPT as possible candidates for this band: the 2 $^1B_{2g}$ and the 1 $^1B_{3g}$ states, both with an excitation energy close to 6.0 eV (at PC-NEVPT2 level with both active spaces, SC-NEVPT2 giving only slightly higher values).

The VUV band observed at 6.34 eV in the VUV spectrum [16] and at 6.6 eV in the EEL spectrum [31] has been assigned [9] to the dipole allowed transition to the 2 $^1B_{3u}$ state. NEVPT2 gives for this state higher values (6.85 eV with the PC variants and CAS C). The reduction in the excitation energy passing from the CAS A to the CAS C active space (0.32 eV at the PC level) indicates the low quality of the zero description given by the CAS A active space. Moreover, the comparison with the CC3 and Extended-STEOM values (0.2–0.3 eV lower) suggests that NEVPT2 gives in this case, as found for the 2 ^1A_u state, slightly too high values. However, the assignment of this experimental band to the 2 $^1B_{3u}$ state is confirmed by NEVPT2, given that only the optically forbidden 2 $^1B_{1g}$ state has an excitation energy in the range 6.3–6.6 eV.

As reported by Nooijen [28], the complicated experimental feature observed [16] around 8.3 eV is explained only by the assumption that two transitions are responsible for it. In Ref. [16], these two states have been identified in a $\pi \rightarrow \pi^*$ of B_{2u} symmetry and a Rydberg transition on the basis of MRDCI calculations. Nooijen has excluded the contribution of the Rydberg states to this feature and suggested that the two states have both B_{2u} symmetry and a mixed $\pi \rightarrow \pi^*$ and $nn \rightarrow \pi^*\pi^*$ nature. The presence of two close-lying states of the same symmetry is expected to originate a complex vibronic structure [28]. The NEVPT2 results support this interpretation: transitions to two states, one with a relevant $nn \rightarrow \pi^*\pi^*$ nature (5 $^1B_{2u}$, see Table 7) and a second one with a pure $\pi \rightarrow \pi^*$ nature (3 $^1B_{2u}$, see Table 8), are found to be close to 8.30 eV.

3.4 The $\pi \rightarrow \pi^*$ states

Among the $\pi \rightarrow \pi^*$ states, two different families can be identified: the neutral and the ionic states. Both of them do not show a net charge separation, but a valence bond (VB) analysis of the wavefunction shows that, while the neutral states are well represented by a superposition of neutral VB structures, the ionic states are described by a mixing of VB structures with a charge separation. As recently pointed out on the basis of an orthogonal VB analysis (see for instance Refs. [35, 36]) of the V state of ethene [8], the accurate calculation of the two types of states presents very different requirements: the neutral states are normally well described by the most accurate ab initio methods which often give results in good agreement among themselves and with the available experimental data. On the contrary the ionic states present peculiar difficulties, with different theoretical approaches giving in most cases contradictory results. Such peculiarities of the ionic states originate from the fact that the charge separation of the ionic VB structures induces a response of the σ network which is different for each VB structure (dynamic σ polarization) and that such a polarization induces, in its turn, a modification of the effective atomic charge felt by the π electrons, leading to a relaxation of the π orbitals (p contraction, see Ref. [8]). Taking correctly into account these two physical effects is not straightforward and different methods behave differently in this respect.

To alleviate these difficulties, Rubio and Roos [9] propose to study the ionic states excluding from the active space the n orbitals and electrons and doubling the π orbitals. The results with such and active space (CAS B) are reported in Table 8 along with those with the CAS A active space.

The excitation energy for the 1 $^1B_{2u}$ state is 5.38 (QD–SC) and 5.10 (QD–PC) eV with CAS A. Remembering that this state is neutral, such a large difference between the two variants of NEVPT2 is not expected. Actually, such difference is a consequence of the anomalous behavior of SC and PC-NEVPT2 for the 3 $^1B_{2u}$ state, with a very large effect of the electron correlation on the excitation energy and a difference for this quantity of 0.8 eV between the two variants, see Table 4. This has an impact on the 1 $^1B_{2u}$ state through the off-diagonal elements of the effective Hamiltonian. The use of the CAS B active space improves the zero order description of the 3 $^1B_{2u}$ state, reducing the effect of the electron correlation on the excitation energy (from 3.4–4.0 to < 2.0 eV) and increasing the agreement between SC and PC (difference of 0.16 eV, see Table 8). With this active space, the NEVPT2 values for the 3 $^1B_{2u}$ state are in accordance (in particular the PC variant) with CC3 [33] (8.51 eV) and with the experimental findings, while CASPT2 is $\simeq$0.6 eV lower. Moreover, the values of the excitation energy for the 1 $^1B_{2u}$ state become 5.29 (QD–SC) and 5.32 (QD–PC) eV, in good agreement with one another, and with the values obtained with the CAS A active space, as expected for a neutral state. Moreover, they agree with the CC3 values, are relatively close to the experimental data, and are slightly higher than that of CASPT2 and Extended-STEOM.

For the other two neutral $\pi \rightarrow \pi^*$ states, 5 ^1A_g and 5 $^1B_{3g}$, passing from the CAS A active space to the CAS B one, bring about a small, but perceptible, variation of the CASSCF and NEVPT2 excitation energies, of the order of 0.2–0.3 eV, with the NEVPT2 CAS B values in agreement with CC3 (not available for 5 ^1A_g) and, as found in other cases, $\simeq$0.5 eV higher than CASPT2.

As regards the ionic states, the values computed with the CAS A active space are not worthy of interest, as explained in Sect. 1. Indeed, the low quality of the zero order description makes the effect of the electron dynamic correlation on the excitation energy exceedingly large. With the CAS B active space, following the improvement of the zero order description, the CASSCF excitation energies are reduced and the impact of the electron dynamic correlation on the excitation energy is attenuated, but remains considerable: 1.5–1.6 eV for the 1 $^1B_{1u}$ state, 1.2–1.5 eV for the 2 $^1B_{1u}$, and 1.7–1.9 eV for the 3 $^1B_{2u}$. The difficulty to reach a high quality description of these states is also pointed out by the difference between the SC and PC values, which is as large as 0.25 eV for the 2 $^1B_{1u}$ state, even with the large CAS B active space.

The first transition to a $\pi \rightarrow \pi^*$ ionic state, 1 $^1B_{1u}$, is computed with the active space B at 7.36 (SC) and 7.20 (PC) eV. Rubio and Roos [9] have found that this transition has an intensity close to zero and have assigned it the experimental feature at 7.1 eV. The NEVPT2 results are slightly higher than this value and than the CASPT2, Extended-STEOM, and TD-DFT(PBE0) results (all close to 7.1 eV). The two CC3 studies give values in agreement with (7.28 eV, Ref. [13]) and slightly higher than (7.45 eV, Ref. [33]) the NEVPT2 ones. In the first CC3 study, this state has been found to have a mixed valence/Rydberg nature (see Table 4 of the electronic supplementary information of Ref. [13]) and it is worth noticing that it has been computed with a basis set better suited for the Rydberg states than the basis set used in the second study.

By comparing s-tetrazine with benzene, one notes that the dipole allowed (doubly degenerate) 1 $^1A_{1g} \rightarrow$ 1 ^1E_u transitions in benzene, experimentally found at 6.94 eV, are blue-shifted in s-tetrazine leading to an intense band in the region 7–9 eV. The degeneracy is removed in s-tetrazine leading to two distinct peaks, observed at 7.6 and 8.3 eV and assigned [9] to the 2 $^1B_{1u}$ and 3 $^1B_{2u}$ states (see the end of Sect. 3 for a comment of the experimental feature observed at 8.3 eV). The NEVPT2 calculations confirm these assignments, even if, as in the case of the 1 $^1B_{1u}$ state, the NEVPT2 values are slightly higher than the experimental values ($\simeq$0.2 eV for the PC variant) and than that of CASPT2, Extended-STEOM, and TD-DFT (HCTC). However, unlike the 1 $^1B_{1u}$ case, the agreement with CC3 is excellent for these states.

4 Conclusions

In this paper, a comprehensive survey of the lowest singlet states of the s-tetrazine molecule has been presented. The accurate description of the vertical excitation energies for this system is complicated by the nature of the various states which show an unusual wide variety. Indeed, two series of Rydberg states (converging to two different ionization potentials), two different types of single excitations ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$), and two different types of double excitations ($nn \rightarrow \pi^*\pi^*$ and $n\pi \rightarrow \pi^*\pi^*$) must be described simultaneously on an equal footing. Additionally, it is crucial to allow for a possible mixing of the wavefunctions under the effect of the dynamic electron correlation, which affects the states of different nature in a different manner.

Such a demanding task has been conducted using the NEVPT2 approach, making use of the quasi-degenerate formulation to correctly account for the possible mixing among the states in each symmetry. On the basis of the NEVPT2 computed vertical excitation energies, some experimental features have been reassigned, questioning previously published considerations, while in the other cases the accepted assignments have been confirmed. The results are in general in good agreement with the experimental available data and with those obtained with high level ab initio methods. In particular, considering for NEVPT2 the PC variant with the largest active space used for each state, the average deviation of the NEVPT2 values from the CC3 ones is of the order of 0.2 eV (Ref. [33], with a basis set not well suited for the Rydberg states) and close to 0.1 eV (only seven states, Ref. [13], with a basis set able to describe Rydberg states), while it is $\simeq$0.35 eV with Extended-STEOM and larger than 0.4 eV with CASPT2 (CASPT2 always giving lower excitation energies, with very few exceptions).

As far as the comparison of NEVPT2 and TD-DFT is concerned, one notes a reasonable agreement of NEVPT2 with TD-DFT(PBE0), with an average difference of 0.3 eV (the largest difference being >1 eV), but with a close agreement for the lowest states. On the contrary, with TD-DFT(HCTH) the agreement is less satisfactory even for the lowest states, although the average difference (0.4 eV) is not very far from that found with TD-DFT(PBE0). In particular, as in the case of CASPT2, TD-DFT(HCTH) always gives lower excitation energies than NEVPT2, with the only exceptions of the 1 $^1B_{2u}$, 3 $^1B_{2u}$, and 5 $^1B_{3g}$ $\pi \rightarrow \pi^*$ states. This general trend has been first reported by Nooijen [28], who noted that both CASPT2 and TD-DFT(HCTH) give in general too low excitation energies.

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