Theor Chem Acc (2007) 118:35–46
DOI 10.1007/s00214-006-0239-5

REGULAR ARTICLE

A multireference perturbation theory study on the vertical electronic spectrum of thiophene

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Received: 25 October 2006 / Accepted: 6 December 2006 / Published online: 9 January 2007

Abstract The vertical electronic spectrum of the thiophene molecule is investigated by means of second and third order multireference perturbation theory (NEVPT). Single-state and quasi-degenerate NEVPT calculations of more than 25 singlet excited states have been performed. The study is addressed to the theoretical characterization of the four lowest-energy $\pi \rightarrow \pi^*$ valence states, as well as the $3s$, $3p$ and $3d$ Rydberg states. In addition, the excitation energies of two $\pi \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ valence states are also reported. For almost all the excited states, coupled cluster calculations (CCSD and CCSDR(3)) have been also carried out, using the same geometry and basis set used for the NEVPT ones, in order to make the comparison between the results of the two methods meaningful. A remarkable accordance between the NEVPT and CC excitation energies is found. The present results, over all, confirm the experimental assignments but, above all, represent an important contribution to the assignments of some low-energy $\pi \rightarrow \sigma^*$ states, valence and Rydberg, for which a firm interpretation is not available in the literature.

Keywords Multireference perturbation theory · Quasi-degenerate multireference perturbation theory · NEVPT · Thiophene · Five–membered hetero–cycles

1 Introduction

The experimental and theoretical investigation of the electronic absorption spectra of the five–membered six π–electrons compounds has received a particular attention since the beginning of the last century. The ongoing interest in the physical chemistry properties and spectroscopical features of pyrrole, furan and thiophene is certainly motivated by the prominent rôle they play in the biological and Pharmaceutical chemistry, as well as in the modern material science. However, despite the large number of joint experimental and theoretical efforts, a detailed interpretation of the absorption spectra of these molecules still remains to be reached and, by now, they are regarded as prototypic examples for the theoretical studies of excited states. The VUV spectra of these systems show a complex profile because of the appearance of rich series of Rydberg transitions, that overlap the valence bands and make the identification of the states quite a difficult task.

Within a project addressed to the theoretical characterization of the electronic spectra of the hetero–cyclopentadienes, we have elsewhere [1,2] presented the application of the n-electron valence state perturbation theory (NEVPT) approach [3–8] to the study of the low-lying valence and Rydberg states of pyrrole [1] and furan [2]. As shown in Refs. [1,2], the NEVPT excitation energies were in good accordance with experiment and, above all, with the results of the most accurate ab initio techniques, providing a reliable description of many valence and Rydberg states. In particular, in the presence of a good zero order wavefunction, the most accurate NEVPT results showed an excellent agreement ($\simeq$0.1–0.2 eV) with the results obtained at the highest levels of the coupled cluster hierarchy (CC3, CCSD(T), etc. . .).

Here we briefly recall that NEVPT is a form of multireference perturbation theory, which is based upon a CAS-CI (usually CASSCF) reference wavefunction

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and that it is characterized by the use of perturbation functions still of multiconfigurational type. The distinguishing mark of NEVPT with respect to other MRPT approaches (as for instance CASPT2 [9]), where a projected generalized Fock-like operator is used, lies in the usage of a two-electron model operator (Dyall's Hamiltonian [10]) in order to define $\hat{\mathcal{H}}_0$. Dyall's Hamiltonian is mono-electronic in the inactive orbitals but fully bielectronic in the active ones. Such a choice, properly taking into account the interactions occurring among the active electrons, ensures the complete absence of intruder states in the NEVPT calculations.

According to the degree of contraction of the outer space zero order wavefunctions, different formulations of NEVPT2 can be defined, going from the simplest "strongly contracted" one to the "totally uncontracted" one, passing through the "partially contracted" scheme, having exactly the same degree of contraction of the CASPT2 method [9]. Up to now, at the second order level, both in the single-state [4,5] and quasi-degenerate [7] formulations, both the "strongly contracted" (SC-NEVPT2) and "partially contracted" (PC-NEVPT2) variants have been efficiently implemented in our laboratory. Finally, the recent development of the third order correction to the energy in the "strongly contracted" scheme (SC-NEVPT3) [8] surely represents an important advance in the NEVPT technique, whose relevance has already been shown in several interesting applications [8,1,2,11].

In the present work, as a conclusion of this series of studies on the hetero-cyclopentadienes, we consider the electronic spectrum of thiophene. The four low-lying $\pi \rightarrow \pi^*$ valence states, the lowest-energy $n \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ states, as well as the $3s$, $3p$ and $3d$-type Rydberg states are computed. As we shall discuss later, no large attention has been paid in the literature to the theoretical investigation of the electronic spectrum of thiophene and therefore its interpretation is still far from being complete, since consistent discrepancies (i.e. up to 0.7–0.8 eV) among the various ab initio results exist. The main objective of the present work is to reduce such ambiguities, providing a wide and accurate theoretical study on the vertical spectrum of thiophene by means of second and third order multiconfigurational perturbation theory. For almost all the excited states under consideration, the accuracy of the NEVPT results is also judged with respect to some reference coupled cluster calculations [12,13], expressly performed for this study.

The article is organized as follows: in Sect. 2 the computational details are illustrated; the results are presented in Sect. 3, where the valence-Rydberg mixing (Sect. 3.1) and the spectral assignments (Sect. 3.2) are discussed.

2 Computational details

The calculation of the vertical excitation energies was performed at the experimental equilibrium geometry [14] and, as in the two previous works [1,2] and in Ref. [15], a contracted ANO-L [16] basis set was used, with a contraction scheme S[$5s4p2d$], C[$4s3p1d$], and H[$2s1p$]. In order to get an accurate description of the the $3s$, $3p$ and $3d$ Rydberg states, the original ANO basis set was supplemented with a set of molecule-centered $1s1p1d$ functions, obtained by contraction of a set of $8s8p8d$ diffuse functions. The exponents of the Rydberg functions were optimized as described by Kaufmann et al. [17] and the contraction coefficients were determined following the methodology developed by Roos and coworkers [18]. In the labelling of the Rydberg states, for analogy with pyrrole and furan, we have adopted the convention of choosing 3 as the lowest value of n, instead of 4, that would be the appropriate choice for molecules, such as thiophene, containing atoms belonging to the third row (see Ref. [19]).

The molecule belongs to the C_{2v} point group and in the present calculations, adopting the convention used in most previous studies, it is placed in the yz plane with the z axis as C_2 axis. So, at the single Slater determinant level, the ground state electronic configuration of thiophene can be written as $(\sigma\text{-core})(1b_1)^2(2b_1)^2(3b_1)^2(1a_2)^2$, from which four low-lying singlet $\pi \rightarrow \pi^*$ states are expected: two $^1B_2$ states principally dominated by the $1a_2 \rightarrow 4b_1$ and $3b_1 \rightarrow 2a_2$ excitations respectively and two $^1A_1$ states arising from the antisymmetric ($^1A_1(V)$) and symmetric ($^1A_1(V')$) linear combination of the two $1a_2 \rightarrow 2a_2$ and $3b_1 \rightarrow 4b_1$ configurations. Moreover, since the experimental ionization potential of the $11a_1$ lone pair amounts to 12.1 eV [20], two $n \rightarrow \pi^*$ valence states (A_2 and B_1 symmetries) are expected near 9–10 eV.

Since we were interested in $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ excited states, the six π-electrons and the two lone pair electrons were active in all the calculations (note that the $1b_1$ π orbital, localized on the sulfur atom, was included into the inactive core). Two different types of active spaces were employed: one to compute the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ states and one for the $\pi \rightarrow \sigma^*$ states. For the calculations of the π-type excited states, the minimum active space should include the five π valence orbitals, the lone pair orbital and the three π Rydberg orbitals, giving a space 1503, where the notation indicates the number of orbitals for each symmetry species of the C_{2v} point group (a_1, b_1, b_2, a_2 in order). Nevertheless, as we have shown and discussed in the preceding studies [1,2], the use of the smallest space (1503) does not allow for a satisfactory description of the

$\pi \rightarrow \pi^*$ valence states, giving rise to consistent divergencies in the perturbative series. The quality of the results was shown to be remarkably improved by the extension of the active space with one set of π-type virtual orbitals (see Ref. [1]). Since, on the basis of some preliminary calculations, this behaviour has also been observed for the thiophene molecule, in the present study we shall present only the results obtained with a larger space, composed of 12 active orbitals (1704) and 8 active electrons.

On the other hand, for the calculations of the $\pi \rightarrow \sigma^*$ states one need not include in the active space π-type Rydberg orbitals (b_1 and a_2 symmetries), and the smallest active space is a 5322 space, composed of the lone pair orbital, the five π valence orbitals and of the six Rydberg σ-type orbitals. However, as we shall discuss later (Sect. 3.1), in order to treat the effects of the mixing occurring among a low-energy $\pi \rightarrow \sigma^*$ valence state and some $3p$ and $3d$ Rydberg states, the use of an extended active space, including one more orbital of b_2 symmetry (5332), was necessary.

The molecular orbitals were obtained from state-averaged CASSCF calculations, using the Molcas 5.4 package [21], where the average process was carried out over all the states of interest of a given symmetry; the number of states considered in the CASSCF calculations for each active space is reported in detail in Table 1. The excitation energy of each state was determined with respect to the corresponding ground state $^1A_1$, computed for both the 1704 and 5332 spaces, taking into account that, while a state-averaged CASSCF calculation was performed in the former case, a single-root optimization was carried out in the latter. Then, as in the previous CASPT2 study [15], the five $1s$ orbitals were kept frozen during the perturbative treatment. Finally, the CCSD and CCSDR(3) calculations, reported in the present study, were carried out with the DALTON program [22], using the same geometry [14] and ANO+$1s1p1d$ basis set employed for the NEVPT ones. The oscillator strengths for the excited states were calculated with the CASSCF state interaction (CASSI) method [23], using the NEVPT2 and NEVPT3 energy differences. Moreover, for those states subjected to quasi-degenerate NEVPT2 treatment, the transition dipole moments were recomputed using the corrected linear combinations obtained by diagonalization of the QD-NEVPT2 matrix.

Table 1 Summary of the active spaces and number of states included in the CASSCF calculations

Nature	Symmetry	Active space	Number of states
$\pi \rightarrow \pi^*$	A_1	(1704)	6
	B_2		5
$n \rightarrow \pi^*$	A_2	(1704)	2
	B_1		1
$\pi \rightarrow \sigma^*$	B_1	(5332)	7
	A_2		7

3 Results and discussion

3.1 Valence–Rydberg mixing

A well-known complication in the MRPT calculations of the excited states of small and medium size molecules is the possible mixing occurring among the zero order wavefunctions of valence and low-lying Rydberg excited states. When at CASSCF level such valence–Rydberg mixing takes place, the application of a single-state perturbative correction, leaving the coefficients of the zero order wavefunction unchanged, is unreliable. On the other hand, it is also possible that two or more states, which are not mixed in the zero order description, become very close in energy after the perturbative correction in such a way that a mixing is liable to occur. As we shall discuss in the following, both these effects play a crucial rôle in the treatment the singlet excited states of thiophene, not only for the π-type states but, above all, for the σ-type excited states, where a low-energy $\pi \rightarrow \sigma^*$ valence state, strongly mixed with the $3p$ and $3d$-type Rydberg states, appears. In such cases, a quasi-degenerate approach, taking into account the coupling among the states and allowing for a decontraction of the zero order wavefunctions, is needed for an accurate evaluation of the dynamical correlation energy. Since, as mention in Sect. 1, the NEVPT approach was implemented up to the third order in the single-state formalism and up to the second order in the more complex quasi-degenerate variant, in the following discussion, the SC-NEVPT3 results will be presented only for those states not involved in the mixing processes.

3.1.1 *$\pi \rightarrow \pi^*$ singlet excited states*

As can be seen in Table 2, where the CASSCF, QD-NEVPT2 and CCSD values of the $\langle x^2 \rangle$ component of the second moment of the charge distribution are collected, at the zero order level, the more consistent mixing effects take place among the states of the B_2 and A_2 symmetries. In fact, both the lower-energy $\pi \rightarrow \pi^*$ valence state ($4^1B_2(V)$) and the $n \rightarrow \pi^*$ (2^1A_2) state show too diffuse a character for pure valence states, with values of $\langle x^2 \rangle$ amounting roughly to 39 and 42 a.u. respectively; indeed, the ground state of thiophene has a value of $\langle x^2 \rangle$ of about 30 a.u. Then, a minor

Table 2 CASSCF, QDNEVPT2 and CCSD $\langle x^2\rangle$ component of the second moment of the charge distribution (a.u.) for the $\pi \to \pi^*$ and $n \to \pi^*$ excited states of thiophene

		$\langle x^2\rangle$			
State	Assignment	CASSCF	SC-QDNEVPT2	PC-QDNEVPT2	CCSD
$2^1A_1(V)$	$\pi \to \pi^*$	33.57	31.19	30.65	31.26
3^1A_1	$3b_1 \to 3p_x$	90.13	91.79	91.03	88.12
4^1A_1	$1a_2 \to 3d_{xy}$	89.02	90.36	90.45	87.01
5^1A_1	$3b_1 \to 3d_{xz}$	89.80	89.52	69.48	85.15
$6^1A_1(V')$	$\pi \to \pi^*$	32.65	32.56	63.43	40.91
1^1B_2	$1a_2 \to 3p_x$	93.17	93.12	93.42	89.91
2^1B_2	$1a_2 \to 3d_{xz}$	86.76	89.52	89.38	88.06
3^1B_2	$3b_1 \to 3d_{xy}$	83.88	86.69	81.71	85.34
$4^1B_2(V)$	$\pi \to \pi^*$	38.81	32.85	32.62	31.55
$5^1B_2(V')$	$\pi \to \pi^*$	33.85	34.15	40.04	35.99
1^1A_2	$n \to 3d_{xy}$	81.52	90.89	90.67	
2^1A_2	$n \to \pi^*$	41.81	32.32	32.89	

Table 3 NEVPT, CCSD and CCSDR(3) vertical transition energies (eV) of the $^1A_1$ excited states of thiophene

Method	$\pi \to \pi^*$	$3b_1 \to 3p_x$	$1a_2 \to 3d_{xy}$	$3b_1 \to 3d_{xz}$	$\pi \to \pi^*$
CASSCF	5.71	6.36	6.88	7.02	8.06
SC-NEVPT2	5.94	7.17	7.56	7.89	8.00
PC-NEVPT2	5.89	7.18	7.56	7.90	7.86
SC-NEVPT3	5.78	6.97	7.41	7.69	7.94
SC-QDNEVPT2	5.88	7.18	7.55	7.89	8.04
PC-QDNEVPT2	5.80	7.20	7.56	7.89	7.94
CCSD	5.78	7.11	7.53	7.83	7.93
CCSDR(3)	5.70	7.10	7.50	7.81	7.71

Table 4 NEVPT, CCSD and CCSDR(3) vertical transition energies (eV) of the $^1B_2$ excited states of thiophene

Method	$1a_2 \to 3p_x$	$1a_2 \to 3d_{xz}$	$3b_1 \to 3d_{xy}$	$\pi \to \pi^*$	$\pi \to \pi^*$
CASSCF	6.17	6.83	7.01	7.16	8.88
SC-NEVPT2	6.94	7.58	7.85	6.47	8.30
PC-NEVPT2	6.95	7.59	7.86	6.37	8.12
SC-NEVPT3	6.70				8.36
SC-QDNEVPT2	6.94	7.64	7.92	6.34	8.31
PC-QDNEVPT2	6.95	7.69	7.97	6.14	8.14
CCSD	6.84	7.56	7.81	6.23	7.96
CCSDR(3)	6.81	7.54	7.80	6.10	7.85

valence–Rydberg mixing can also be detected among the $2^1A_1(V)$ valence state and the $3b_1 \to 3p_x$ (3^1A_1) and $1a_2 \to 3d_{xy}$ (4^1A_1) Rydberg states.

The single-state and quasi-degenerate NEVPT excitation energies of the $^1A_1$, $^1B_2$ states, together with the CCSD and CCSDR(3) ones, are reported in Tables 3 and 4, respectively. Instead, in Table 5 are shown the NEVPT results for the states of A_2 symmetry.

As is apparent in Table 3, the application of the QD approach leads to a slight lowering ($\leq$0.1 eV) of the single-state NEVPT2 excitation energy of the $2^1A_1(V)$ state, in agreement with the slight reduction observed in its value of $\langle x^2\rangle$, passing from $\simeq$33 (CASSCF) to $\simeq$30 a.u. (PC-QDNEVPT2). However, as the CASSCF mixing can be regarded as negligible, the trend of the single-state NEVPT results appears coherent, with the SC-NEVPT3 calculation locating this state at 5.78 eV. A value of 5.80 eV is obtained from the PC-QDNEVPT2 calculation. A good agreement is also achieved with

Table 5 Single-state and quasi-degenerate NEVPT2 vertical transition energies (eV) of the π-type $^1A_2$ excited states of thiophene

Method	$n \to 3d_{xy}$	$n \to \pi^*$
CASSCF	9.77	10.07
SC-NEVPT2	10.49	10.13
PC-NEVPT2	10.45	10.04
SC-QDNEVPT2	10.61	10.01
PC-QDNEVPT2	10.64	9.86

the CC results, where this transition is predicted at 5.78 (CCSD) and 5.70 eV (CCSDR(3)). As can be seen from the results in Table 3 and from the values of $\langle x^2 \rangle$ reported in Table 2, the description of the other $^1A_1$ states is essentially not influenced by the application of the QD formalism, with the only exception of the $6^1A_1(V')$ state at the PC level. Concerning this issue some remarks are needed. Similarly to what we found for pyrrole [1] and furan [2], the ionic character of the higher-energy $^1A_1$ valence state, in addition to its partial nature of double excitation, makes the calculation of this state rather problematic. The difficulties are clearly shown by the difference (0.15–0.2 eV) between the strongly contracted and the partially contracted results. Note that for this state, a remarkable difference, amounting roughly to 0.2 eV, is also obtained from CCSD and CCSDR(3) calculations. So, at the partially contracted level, where the $6^1A_1(V')$ state is computed at significantly lower energy, a quasi degeneracy with the $3b_1 \rightarrow 3d_{xz}$ Rydberg state occurs, with the two states being separated by less than 0.04 eV. The QD formalism, applied at the PC-NEVPT2 level, gives rise to a strong mixing between the two wavefunctions, in such a way that the resulting roots have values of $\langle x^2 \rangle$ amounting to $\simeq$69 and $\simeq$63 a.u. (values in Table 2). A similar mixing, even if less pronounced, was also found in the CCSD calculations, where the computed $\langle x^2 \rangle$ are $\simeq$85 and $\simeq$41 a.u. for the Rydberg and valence state, respectively. The SC-NEVPT3 excitation energy of the $6^1A_1(V')$ state is 7.94 eV, in excellent accordance with the value of 7.93 eV obtained from the CCSD calculation.

As above mentioned and shown by the results in Tables 2 and 4, the valence-Rydberg mixing effects are more prominent among the $^1B_2$ states. The $4^1B_2(V)$ valence state, mixed at CASSCF level with the 2^1B_2 and 3^1B_2 Rydberg states, after the QD calculation, shows a remarkable reduction ($\simeq$6 a.u.) in the value of its $\langle x^2 \rangle$; the recovery of the valence nature is, obviously, followed by the lowering in its excitation energy, that, at the more accurate PC level, reduces from 6.37 to 6.14 eV. In accordance with the PC-QDNEVPT2 result, the CCSDR(3) transition energy of this state is 6.10 eV ($\langle x^2 \rangle \simeq$31 a.u.), whereas a value of 6.23 eV is attained at CCSD level. Obviously, the opposite behaviour is observed for the two Rydberg states, whose transition energies slightly increase ($\simeq$0.1 eV). However, the second moments of the charge distribution, reported in Table 2, indicate that at the PC level, where the two states are more close in energy, a small mixing occurs between the $3b_1 \rightarrow 3d_{xy}$ Rydberg state and the $5^1B_2(V')$ valence state; as can be seen in Table 4, however, the effects on the excitation energies are negligible. A small mixing is also found at CCSD level, where the computed values of $\langle x^2 \rangle$ are $\simeq$36 and $\simeq$85 a.u. for the valence and Rydberg state, respectively.

Finally, the QD approach was proved to be important also for the calculation of the two π-type $^1A_2$ states, which appear mixed in the CASSCF description. At the PC level, where the correction is more efficient, the QDNEVPT2 excitation energy (Table 5) for the valence (Rydberg) state turns out to be about 0.2 eV lower (higher) than that obtained from the single-state calculations. Also, the values of $\langle x^2 \rangle$ recomputed in the correct zero order space (Table 2) are in accordance with those typical for pure valence and Rydberg states, being $\simeq$32 and $\simeq$90 a.u.

3.1.2 *$\pi \rightarrow \sigma^*$ singlet excited states*

An important difference in the spectroscopical features of thiophene with respect to the analogous hetero–cycles, pyrrole [1] and furan [2], is the presence of two low-energy $\pi \rightarrow \sigma^*$ states, one of B_1 symmetry and one of A_2 symmetry, strongly interacting with $3p$ and $3d$ type Rydberg states.

In Table 6 the values of $\langle x^2 \rangle$, the zero order assignments, the CASSCF and single-state NEVPT excitation energies of the first seven excited states of B_1 and A_2 symmetry are listed.

As can be seen, for the $^1B_1$ states, apart from a slight mixing between the $3b_1 \rightarrow 3s$ and $1a_2 \rightarrow 3p_y$ as well as the $3b_1 \rightarrow 3p_z$ and $1a_2 \rightarrow 3d_{yz}$ Rydberg states, the most significant valence–Rydberg interaction takes place between the $1a_2 \rightarrow \sigma^*$ and the $1a_2 \rightarrow 3d_{yz}$ states; moreover, also the $1a_2 \rightarrow 3p_y$ state exhibits a partial valence character. The CASSCF second moments for the Rydberg states are $\simeq$48 ($3p$) and $\simeq$45 a.u ($3d_{yz}$), where a value of $\simeq$34 a.u. is attained for the 7^1B_1 state.

An analogous situation occurs among the states of A_2 symmetry, where the three states which mix are again the 7^1A_2, having a σ^* dominant character, and the two $3b_1 \rightarrow 3d_{yz}$ and $3b_1 \rightarrow 3p_y$ Rydberg states; the computed $\langle x^2 \rangle$ are 38.20, 46.72 and 43.48 a.u., respectively.

The QDNEVPT2 calculations were carried out on five states of B_1 symmetry (1-4^1B_1 and 7^1B_1) and on three states of A_2 symmetry (3^1A_2, 6^1A_2 and 7^1A_2). As already pointed out, the third order computations were performed only for those states not involved in the valence–Rydberg mixing.

After the application of the QD formalism, the interpretation of the states in terms of Rydberg $3p_y$, $3d_{yz}$ and valence σ^* states turn out to be rather problematic. However, on the basis of the evaluation of the values of $\langle x^2 \rangle$ in the corrected zero order space, some considerations, concerning the valence or Rydberg nature,

Table 6 CASSCF and single-state NEVPT excitation energies (eV) for the σ-type excited states of thiophene

	CASSCF			SC-NEVPT2, ΔE	PC-NEVPT2, ΔE	SC-NEVPT3, ΔE
State	Assignment	$\langle x^2 \rangle$	ΔE			
1^1B_1	$3b_1 \rightarrow 3s + 1a_2 \rightarrow 3p_y$	51.12	6.76	6.45	6.51	6.24
2^1B_1	$(1a_2 \rightarrow 3p_y + \sigma^*) + 3b_1 \rightarrow 3s$	47.99	6.90	6.50	6.54	
3^1B_1	$3b_1 \rightarrow 3p_z + 1a_2 \rightarrow 3d_{yz}$	49.30	7.27	7.06	7.11	6.82
4^1B_1	$1a_2 \rightarrow 3d_{yz} + \sigma^*$	45.64	7.44	6.97	7.00	
5^1B_1	$3b_1 \rightarrow 3d_{a_1}$	54.23	7.88	7.60	7.64	7.38
6^1B_1	$3b_1 \rightarrow 3d_{a_1}$	72.12	7.96	7.50	7.48	7.34
7^1B_1	$1a_2 \rightarrow \sigma^* + 3d_{yz}$	34.53	8.53	7.16	7.12	
1^1A_2	$1a_2 \rightarrow 3s$	51.26	6.48	6.10	6.15	5.90
2^1A_2	$1a_2 \rightarrow 3p_z$	50.18	7.03	6.77	6.82	6.55
3^1A_2	$3b_1 \rightarrow 3p_y + 3d_{yz} + \sigma^*$	43.48	7.12	6.64	6.65	
4^1A_2	$1a_2 \rightarrow 3d_{a_1}$	63.22	7.49	7.22	7.27	7.01
5^1A_2	$1a_2 \rightarrow 3d_{a_1}$	63.33	7.54	7.17	7.20	6.99
6^1A_2	$3b_1 \rightarrow 3d_{yz} + 3p_y + \sigma^*$	46.72	7.69	7.23	7.24	
7^1A_2	$3b_1 \rightarrow \sigma^* + 3d_{yz}$	38.20	8.48	7.53	7.50	

The CASSCF values of the $\langle x^2 \rangle$ component of the second moment of the charge distribution and the nature of the states are also reported

Table 7 Values of the $\langle x^2 \rangle$ component of the second moment of the charge distribution (a.u.) and QDNEVPT2 excitation energies for some σ-type excited states of thiophene

	SC-QDNEVPT2			PC-QDNEVPT2		
State	$\langle x^2 \rangle$	Assignment	ΔE	$\langle x^2 \rangle$	Assignment	ΔE
1^1B_1	36.49	$1a_2 \rightarrow \sigma^* + 3p_y$	6.33	32.77	$1a_2 \rightarrow \sigma^* + 3p_y$	6.10
2^1B_1	44.48	$1a_2 \rightarrow 3p_y + \sigma^* + 3d_{yz}$	6.38	51.66	$3b_1 \rightarrow 3s$	6.52
3^1B_1	51.15	$3b_1 \rightarrow 3s$	6.47	48.17	$1a_2 \rightarrow 3p_y$	6.86
4^1B_1	49.34	$3b_1 \rightarrow 3p_z$	7.07	49.30	$3b_1 \rightarrow 3p_z$	7.14
5^1B_1	45.19	$1a_2 \rightarrow 3d_{yz} + \sigma^*$	7.45	46.61	$1a_2 \rightarrow 3d_{yz}$	7.65
1^1A_2	33.75	$3b_1 \rightarrow \sigma^*$	6.46	31.14	$3b_1 \rightarrow \sigma^*$	6.22
2^1A_2	48.02	$3b_1 \rightarrow 3p_y + 3d_{yz}$	7.19	49.79	$3b_1 \rightarrow 3p_y$	7.25
3^1A_2	46.27	$3b_1 \rightarrow 3d_{yz} + 3p_y + \sigma^*$	7.75	47.58	$3b_1 \rightarrow 3d_{yz}$	7.94

are possible. In addition, further information has been obtained by computing the natural orbitals for each eigenstate of the QD-PT matrix in order to build the CAS-CI molecular orbitals in the corrected zero order space. In Table 7 the recomputed values of $\langle x^2 \rangle$ and the QDNEVPT2 excitation energies are reported. The CC results for all the σ-type states are, instead, listed in Table 8.

First of all, some important remarks concern the different behaviour of the two QDNEVPT2 variants. Indeed, as can be observed in Table 7, while the mixing among the $3p_y, 3d_{yz}$ and σ^* states persists at the strongly contracted level, the nature of the states appears to be in good measure pure after the PC calculations; only the ${}^1B_1$ ($1a_2 \rightarrow \sigma^*$) state shows a slight Rydberg character. The different nature of the states obtained from the SC and PC calculations is, obviously, the reason for the remarkable deviations observed between the SC-QDNEVPT2 and PC-QDNEVPT2 excitation energies. Note that these deviations can be, instead, regarded

Table 8 CCSD and CCSDR(3) excitation energies (eV) for the σ-type excited states of thiophene

		CCSD		CCSDR(3)
State	Assignment	$\langle x^2 \rangle$	ΔE	ΔE
1^1B_1	$1a_2 \rightarrow \sigma^*$ mix.	36.41	6.28	6.20
2^1B_1	$3b_1 \rightarrow 3s$	48.84	6.40	6.36
3^1B_1	$1a_2 \rightarrow 3p_y$ mix.	44.94	6.85	6.81
4^1B_1	$3b_1 \rightarrow 3p_z$	47.79	7.01	6.99
5^1B_1	$3b_1 \rightarrow 3d_{a_1}$	55.68	7.46	7.43
6^1B_1	$3b_1 \rightarrow 3d_{a_1}$	61.64	7.52	7.50
7^1B_1	$1a_2 \rightarrow 3d_{yz}$ mix.	45.06	7.60	7.55
1^1A_2	$1a_2 \rightarrow 3s$	49.15	6.10	6.05
2^1A_2	$3b_1 \rightarrow \sigma^*$ mix.	32.11	6.31	6.26
3^1A_2	$1a_2 \rightarrow 3p_z$	48.97	6.78	6.74
4^1A_2	$3b_1 \rightarrow 3p_y$	53.47	7.14	7.11
5^1A_2	$1a_2 \rightarrow 3d_{a_1}$	46.94	7.18	7.14
6^1A_2	$1a_2 \rightarrow 3d_{a_1}$	63.73	7.23	7.19
7^1A_2	$3b_1 \rightarrow 3d_{yz}$ mix.	46.14	7.81	7.80

The $\langle x^2 \rangle$ component of the second moment of the charge distribution and the nature of the states are also reported as negligible (0.07 eV at most) for the $3b_1 \rightarrow 3s$ and $3b_1 \rightarrow 3p_z$ Rydberg states. At the SC level, the excitation energies of the Rydberg states, which still have a partial valence character, are significantly lower (even ≃0.3 eV for the $1a_2 \rightarrow 3p_y$ state) than those computed at PC level; obviously, too high excitation energies are, instead, obtained for the two valence states.

Although the $1a_2 \rightarrow \sigma^*$ state still shows a small $3p$ character, the PC-QDNEVPT2 approach brings about a remarkable decrease (≃1 eV) with respect to the single-state excitation energy of the 7^1B_1 state, that, at the CASSCF level, is the state with the strongest valence nature (see Table 6); indeed, the transition energy changes from 7.12 to 6.10 eV. At the strongly contracted level as well as at CCSD level, this state is computed with a value of $\langle x^2 \rangle$ of ≃36 a.u., that is somewhat diffuse for a pure valence state. As a consequence of this partial Rydberg character the SC-QDNEVPT2 and CC excitation energies turn out to be higher than the PC one, being 6.33 and 6.30 eV (CCSDR(3)), respectively. On the contrary, both the $3b_1 \rightarrow 3s$ and $3b_1 \rightarrow 3p_z$ Rydberg states are essentially not affected by the application of the QD approach: their values of $\langle x^2 \rangle$ remain the same as computed at CASSCF level and hence the single-state and quasi-degenerate excitation energies are very similar. As shown in Table 6, the third order calculations, for both these states, bring about a lowering in the excitation energies slightly less than 0.3 eV, locating the states at 6.24 eV ($3s$) and 6.82 eV ($3p_z$). For these two states, a good accordance is also attained with the CC results (Table 8), that turn out to be only ≃0.15 eV higher than the SC-NEVPT3 ones. At PC-QDNEVPT2 level, the $1a_2 \rightarrow 3p_y$ is computed at 6.86 eV, in remarkable accordance with the CC results, that locate this state at 6.85 (CCSD) and 6.81 eV (CCSDR(3)). Then, at the PC level, the $1a_2 \rightarrow 3d_{yz}$ is calculated to lie at 7.65 eV, about 0.7 eV above the value computed in the single–state approach for the 4^1B_1 state (see Table 6). Very similar transition energies were provided by the CC calculations, where the state is located at 7.60 and 7.55 eV (respectively CCSD and CCSDR(3) values in Table 8).

Similar remarks can be made for the three $^1A_2$ states, which, after the PC-QDNEVPT2 treatment, result in a pure valence state ($\langle x^2 \rangle \simeq 31$ a.u.) and two pure Rydberg $3p_y$ and $3d_{yz}$ states. At PC-QDNEVPT2 level, the $3b_1 \rightarrow \sigma^*$ transition is predicted at 6.22 eV in very good agreement with the CC values (see Table 8), where the state is located at 6.31 (CCSD) 6.26 eV (CCSDR(3)), with a value of $\langle x^2 \rangle$ of 32.11 a.u. Instead, the two Rydberg states are shifted at higher energy with respect to single-state excitation energies: the $3b_1 \rightarrow 3p_y$ state is computed at 7.25 eV (PC-QDNEVPT2), with an $\langle x^2 \rangle$ of ≃49 a.u. and the $3b_1 \rightarrow 3d_{yz}$ excitation is predicted at 7.94 eV (PC-QDNEVPT2) with an $\langle x^2 \rangle$ of ≃47 a.u. The CC excitation energies, reported in Table 8, are only slightly lower (≃0.15) than the PC-QDNEVPT2 ones. Note that at the single–state level, the two states were calculated at 6.65 and 7.50 eV, respectively (PC-NEVPT2 values in Table 6). Finally, as can be seen in Table 6, for the other four Rydberg states, not involved in the CASSCF mixing, the application of the SC-NEVPT3 correction produces a small (0.15–0.25 eV) and regular lowering in the second order excitation energies. Comparable transition energies, even if always slightly higher than the SC-NEVPT3 ones, were obtained from the CC calculations (see values in Table 8).

3.2 The VUV absorption spectrum

In contrast to the large number of theoretical works dedicated to the absorption spectra of pyrrole and furan, surprisingly few ab initio studies on the electronic spectrum of thiophene have been published. Indeed, the first CI study by Bendazzoli et al. [24], published in 1978, was followed only by three high-level ab initio studies, namely, a single–state CASPT2 study in 1993 [15], a MRCI investigation in 1999 [19] and, finally, a SAC-CI work in 2001 [25]. In addition, some TD-DFT [26] and ADC(2) [27] results have also been presented. Although there is, over all, a good agreement in the assignments of the four lowest-energy $\pi \rightarrow \pi^*$ states, a number of inconsistencies still exists in the interpretation of some Rydberg states.

The most accurate NEVPT excitation energies and the corresponding oscillator strengths, which are used to discuss the interpretation of the spectrum, are shown in Table 9, together with the CCSDR(3) results and those of the previous theoretical studies [15,19,25,26].

3.2.1 Energy range 5–6.5 eV

In this energy range is located the first absorption region, which is composed of the two historical A and B bands. The first system (A band), whose valence $\pi \rightarrow \pi^*$ nature was experimentally assessed on the basis of the comparison of gas phase results with condensed-phase measurements [24,28–30], begins at 5.16 eV with the maximum at 5.39 eV. Furthermore, in the magnetic circular dichroism spectrum (MCD) of thiophene in hexane, two bands with opposite signs in their B-values [31–33] were detected at 5.27 and 5.64 eV, confirming the presence of two $\pi \rightarrow \pi^*$ transitions in the low-energy tail of the first VUV band. On the basis of PPP calculations [31] and ab initio prediction of the B-values [24], the lower-energy peak was attributed to the $^1A_1(V)$ state.

Table 9 NEVPT and CC vertical transition energies (eV) and oscillator strengths (within parentheses) of the singlet excited states of thiophene compared with the previous theoretical results

		NEVPT[a]							
State	Nature	SC3	PC-QD	CCSDR(3)[a,b]	SAC-CI [25]	MRCI [19]	CASPT2 [15]	TD-DFT [26]	Exp.[d]
$^1A_1(V)$	$\pi \to \pi^*$	5.78 (0.130)	5.80 (0.153)	5.70 (0.082)	5.41 (0.091)	5.69 (0.119)	5.33 (0.089)	5.64 (0.058)	5.39
$^1A_2$	$1a_2 \to 3s$	5.90		6.05	5.70	5.78	5.93	5.94	5.93
$^1B_1$	$1a_2 \to \sigma^*$		6.10 (0.004)	6.30 (0.015)	5.87 (0.011)	6.41	6.20[c] (0.002)[c]	5.67 (0.005)	
$^1B_2(V)$	$\pi \to \pi^*$		6.14 (0.107)	6.10 (0.080)	5.72 (0.113)	6.00 (0.154)	5.72 (0.070)	5.65 (0.074)	5.64
$^1A_2$	$3b_1 \to \sigma^*$		6.22	6.28	6.03	6.85	6.26[c]	6.04	
$^1B_1$	$3b_1 \to 3s$	6.24 (0.000)	6.52 (0.001)	6.36 (0.002)	6.12 (0.000)	6.33 (0.000)	6.23 (0.000)	6.32 (0.002)	
$^1A_2$	$1a_2 \to 3p_z$	6.55		6.74	6.41	7.03	6.58	6.59	6.60
$^1B_2$	$1a_2 \to 3p_x$	6.70 (0.040)	6.95 (0.045)	6.81 (0.032)	6.41 (0.038)	7.02 (0.034)	6.56 (0.030)	6.74 (0.023)	6.60
$^1B_1$	$1a_2 \to 3p_y$		6.86 (0.021)	6.81 (0.022)	6.47 (0.016)	6.39 (0.000)	6.30 (0.030)	6.72 (0.017)	6.60
$^1B_1$	$3b_1 \to 3p_z$	6.82 (0.025)	7.14 (0.024)	6.99 (0.024)	7.17 (0.019)	6.73 (0.029)	6.83 (0.020)		6.7–7.0
$^1A_1$	$3b_1 \to 3p_x$	6.97 (0.022)	7.20 (0.051)	7.10 (0.041)	6.73 (0.065)	7.31 (0.021)	6.76 (0.015)		6.7–7.0
$^1A_2$	$3b_1 \to 3p_y$		7.25	7.11	6.89	6.39	6.35		6.7–7.0
$^1A_2$	$1a_2 \to 3d_{a_1}$	6.99		7.14	6.73	7.93	6.97	6.91	
$^1A_2$	$1a_2 \to 3d_{a_1}$	7.01		7.19	6.75	7.85	7.08	7.07	
$^1A_1$	$1a_2 \to 3d_{xy}$	7.41 (0.002)	7.55 (0.000)	7.50 (0.013)	7.08 (0.018)	7.93 (0.001)	7.23 (0.001)	7.45 (0.037)	7.33
$^1B_1$	$1a_2 \to 3d_{yz}$		6.65 (0.000)	7.55 (0.000)	7.15 (0.000)		7.24 (0.001)	7.32 (0.000)	
$^1B_2$	$1a_2 \to 3d_{xz}$		7.69 (0.001)	7.54 (0.002)	7.12 (0.003)	8.11 (0.000)	7.28 (0.001)	7.43 (0.014)	
$^1B_1$	$3b_1 \to 3d_{a_1}$	7.34 (0.001)		7.43 (0.000)	7.21 (0.000)	8.18	7.37 (0.000)		
$^1B_1$	$3b_1 \to 3d_{a_1}$	7.38 (0.001)		7.50 (0.000)	7.14 (0.000)	8.26	7.67 (0.001)		
$^1A_1$	$3b_1 \to 3d_{xz}$	7.69 (0.000)	7.89 (0.077)	7.81 (0.017)	7.47 (0.034)	8.05	7.57 (0.000)		
$^1A_2$	$3b_1 \to 3d_{yz}$		7.94	7.80		7.59	7.64		7.95

Table 9 continued

		NEVPT[a]							
State	Nature	SC3	PC-QD	CCSDR(3)[a,b]	SAC-CI [25]	MRCI [19]	CASPT2 [15]	TD-DFT [26]	Exp.[d]
$^1B_2$	$3b_1 \rightarrow 3d_{xy}$		7.97 (0.129)	7.80 (0.007)	7.46 (0.024)	7.92	7.53 (0.002)		7.95
$^1A_1(V')$	$\pi \rightarrow \pi^*$	7.94 (0.238)	7.94 (0.069)	7.71 (0.294)	7.32 (0.361)	7.91 (0.429)	6.69 (0.185)	7.35 (0.121)	7.05
$^1B_1$	$n \rightarrow \pi^*$	8.26 (0.034)			7.86 (0.000)	8.83	7.77 (0.033)		
$^1B_2(V')$	$\pi \rightarrow \pi^*$	8.36 (0.412)	8.14 (0.276)	7.85 (0.105)	7.40 (0.120)	8.10 (0.131)	7.32 (0.392)	7.34 (0.071)	7.50
$^1A_2$	$n \rightarrow \pi^*$		9.86			10.34	9.69		
$^1A_2$	$n \rightarrow 3d_{xy}$		10.64			10.75	10.27		

[a] This work
[b] The reported oscillator strengths were computed at CCSD level
[c] Values from Ref. [26]
[d] Values from Refs. [19,40–44]

Our most accurate results predict the vertical transitions to the $^1A_1(V)$ and $^1B_2(V)$ states to be 5.78 (SC-NEVPT3) and 6.14 eV (PC-QDNEVPT2) respectively; the computed oscillator strengths are 0.130 ($^1A_1(V)$) and 0.107 ($^1B_2(V)$). Taking into account that for these aromatic molecules, the vertical transition and the observed maximum of the band may differ significantly, with the former being even 0.2 eV [34–36] above the latter, our present results confirm the traditional valence interpretation of the A band. The CCSDR(3) excitation energies are in remarkable accordance with the NEVPT ones, locating the $^1A_1(V)$ state at 5.70 eV and the $^1B_2(V)$ transition at 6.10 eV, with very similar intensities (0.082 and 0.080, respectively). The present results also agree with those computed in the MRCI study by Palmer et al. [19], whereas larger deviations ($\simeq$0.4 eV) are observed with the CASPT2 [15] and SAC-CI [25] values.

Then, the weak fine structure near 6 eV[19,37–39], known as the B band, is interpreted as Rydberg in nature, principally arising from the symmetry forbidden $1a_2 \rightarrow 3s$ state; this system indeed does not appear in the condensed-phase spectrum [24,28,29], where the Rydberg states are thought to play a negligible rôle. The $1a_2 \rightarrow 3s$ state ($^1A_2$) is computed, at SC-NEVPT3 level, at 5.90 eV, in perfect accordance with experiments and with the CASPT2 result [15] (5.93 eV); slightly lower excitation energies were instead obtained from the MRCI [19] (5.78 eV) and SAC-CI [25] (5.70 eV) calculations. In the CCSDR(3) computations this transition is instead obtained at 6.10 eV. Our results, in accordance with the SAC-CI [25], MRCI [19], CASPT2 [15] and TD-DFT [26], also predict the $3b_1 \rightarrow 3s$ Rydberg state to belong to the B band, with a SC-NEVPT3 vertical excitation energy of 6.24 eV. Moreover, on the basis of the present calculations, two other valence $\pi \rightarrow \sigma^*$ states, partially mixed with the $3p_y$ and $3d_{yz}$ states, should be attributed to this band: the $1a_2 \rightarrow \sigma^*$ state ($^1B_1$) is computed at 6.10 eV (PC-QDNEVPT2) with an $\langle x^2 \rangle$ of $\simeq$32.5 a.u. and a small oscillator strength (0.004) and the $3b_1 \rightarrow \sigma^*$ state ($^1A_2$) is instead located at 6.22 eV (PC-QDNEVPT2) with an $\langle x^2 \rangle$ of $\simeq$31 a.u. Very similar excitation energies were obtained from the CC calculations, where the states are computed at slightly higher energy (6.30 and 6.28 eV, respectively) and with a slightly more diffuse character (36.41 and 32.11 a.u. respectively). This partial Rydberg ($3p$) nature of the $^1B_1$ state justifies the greater oscillator strength (0.015) computed at CC level. In the SAC-CI study[25] these two states are calculated at 5.87 ($^1B_1$) and 6.03 eV ($^1A_2$) and the corresponding values of second moments of the charge distribution are $\simeq$35 and $\simeq$32 a.u. Values of 6.41 ($^1B_1$) and 7.85 eV ($^1A_2$) are reported in the MRCI work [19] and, finally, excitation energies of 6.20 ($^1B_1$) and 6.26 eV ($^1A_2$) have been obtained at CASPT2 level [26].

3.2.2 Energy range 6.5–7.8 eV

This spectral region, known as C Band, is considered as principally originated by the couple of higher-energy $\pi \rightarrow \pi^*$ states [19,20]: $^1A_1(V')$ and $^1B_2(V')$ in increasing energetical order. However, the shape of the spectrum in this region is complicated by a number of Rydberg states, which are expected to appear both at the low and high energy tails of the C band. In the electron energy loss (EEL) spectrum the maximum appears at 7.05 eV and it was attributed to Rydberg ($3b_1 \rightarrow 3p$) and/or to valence ($^1B_2(V')$) excitations [19]. The raising side, with a maximum detected at 6.60 eV, was, instead, assigned to a $1a_2 \rightarrow 3p$ state [19,20].

The best NEVPT results locate the vertical transitions to the two higher-energy $\pi \rightarrow \pi^*$ states at 7.94 ($^1A_1(V')$) and 8.14 eV ($^1B_2(V')$), whereas excitation energies of 7.71 and 7.85 were obtained from the CCSDR(3) calculations. In comparison to the experimental assignments, the NEVPT and CCSDR(3) transition energies turn out to be slightly higher, confirming the difficulty, already discussed for the analogous hetero-cycles in Refs. [1,2], of obtaining accurate theoretical results for these ionic high-energy $\pi \rightarrow \pi^*$ states. As is apparent in Table 9, for both these valence states, dissimilar oscillator strengths were obtained at SC3 and PC-QD level; this is not surprising considering that, above all for the $^1A_1(V')$ state, a remarkable mixing with the less intense Rydberg states was found in the quasi-degenerate NEVPT2 calculations (Sect. 3.1). Very similar excitation energies are reported in the MRCI study [19], where the $^1A_1(V')$ state is computed at 7.91 eV and the $^1B_2(V')$ one at 8.10 eV. On the contrary, larger differences (up to 1 eV) are observed between the NEVPT and the CASPT2 [15] results, which locate the two states at 6.69 ($^1A_1(V')$) and 7.32 eV ($^1B_2(V')$).

The first three members of the $1a_2 \rightarrow 3p$ Rydberg series have been computed to have vertical excitation energies of 6.55 (p_z), 6.70 (p_x) and 6.86 eV (p_y), in accordance with the experimental assignments [19,20] of the structure below 7 eV to a $3p$-type state converging to IP$_1$ (8.872eV). A good agreement (within 0.2 eV) is attained with the CCSDR(3) excitation energies, whereas significant discrepancies are evident among those of the previous works. Apart from the MRCI results [19], which seem to overestimate the excitation energies of both the $3p_z$ and $3p_x$ states, the main difficulties concern the calculation of the σ-type $3p_y$ state. The SAC-CI [25], MRCI [19] and single-state CASPT2 [15] excitation energies are 6.47, 6.39 and 6.30 eV, which are remarkably lower than the best NEVPT and CC values. On the contrary, a value of 6.72 eV was obtained from the TD-DFT computations [26]. The explanation for such too low excitation energies can be attributed to the partial valence σ^* character of the $3p_y$ state. The SAC-CI $\langle x^2 \rangle$ of this state is $\simeq$43 a.u. [25], where a value of $\simeq$47 is reported in the CASPT2 work [15]. Note that the single-state PC-NEVPT2 excitation energy of this state, partially mixed with the $3d_{yz}$ and σ^* states, was 6.54 eV (Table 6 in Sect. 3.1), noticeably lower than the corresponding QD value but much more similar to the SAC-CI and single-state CASPT2 results.

On the basis of our accurate NEVPT calculations, also the $3p$ components of the second Rydberg series (R′) are expected to belong to the C Band, with vertical excitation energies of 6.82 ($3p_z$), 6.97 ($3p_x$) and 7.25 eV ($3p_y$); the CCSDR(3) computations locate the states at 6.99, 7.10 and 7.11 eV, respectively. Again, the valence–Rydberg mixing seems to be the reason for the strong differences in the computed transition energies of the $3b_1 \rightarrow 3p_y$ state.

The five members of the $1a_2 \rightarrow 3d$ Rydberg series are computed to lie in the range between $\simeq$7 and $\simeq$7.7 eV, on the high-energy tail of the C Band, with a very low intensity. The best NEVPT results are 6.99 and 7.01 eV, for the two quasi-degenerate $3d_{a_1}$ states and 7.41 ($3d_{xy}$), 7.65 ($3d_{yz}$) and 7.69 eV ($3d_{xz}$) for the others. As can be seen (Table 9), the CCSDR(3) excitation energies fully agree with the NEVPT results, with differences not exceeding 0.2 eV. On the contrary, remarkably dissimilar values (up to $\simeq$1 eV) have been obtained in the previous ab initio studies.

Finally, on the higher energy shoulder of this band, the present results locate also the first three components of the $3b_1 \rightarrow 3d$ Rydberg series, whose NEVPT excitation energies are 7.34 and 7.38 eV for the two $3d_{a_1}$ type states and 7.69 eV for the $3b_1 \rightarrow 3d_{xz}$ state; however, there are not available experimental assignments for this region of the spectrum. As already pointed out, the larger oscillator strength obtained at PC-QD level for the $3b_1 \rightarrow 3d_{xz}$ state, with respect to that computed at CC level as well as those reported in the other studies, has to be ascribed to the mixing with the strong valence transition (Sect. 3.1).

3.2.3 Energy range 7.8–10 eV

As suggested by some previous experimental [19,20,37] and theoretical works [19,25], the region between 7.8–8.8 eV is dominated by excitations to Rydberg states. Since the present study is restricted to the computations of the only $3l$ Rydberg states, the experimental assignments of the higher components of the two Rydberg series will be left out (see Refs. [19,25] for a detailed discussion).

Palmer et al. [19], on the basis of their joint experimental and theoretical work, assigned the peak at 7.95 eV to a $3b_1 \rightarrow 3d$ state. The NEVPT results fully confirm this assignment, computing two components of the $3d'$ series near 7.95 eV: the dipole-forbidden $3b_1 \rightarrow 3d_{yz}$ transition is predicted to be located at 7.94 eV and the $3b_1 \rightarrow 3d_{xy}$ state at 7.97 eV, with an oscillator strength of 0.129, due to the interaction with the strong ${}^1B_2(V')$ transition. In good agreement with the NEVPT results, both the states are calculated at 7.80 eV at CCSDR(3) level. On the contrary, significantly lower values are reported in the CASPT2 study [15], where the states are given at 7.64 ($3d_{yz}$) and 7.53 eV ($3d_{xy}$).

Up to now, there is no direct experimental evidence of excitations from the lone pair orbital on the sulfur atom to π^* orbitals. However, the two lowest-energy $n \rightarrow \pi^*$ states are expected to be located in this energy region, completely hidden by intense $\pi \rightarrow \pi^*$ transitions. Our results predict the two states at 8.26 (${}^1B_1$) and 9.86 eV (${}^1A_2$); in the MRCI study [19] they are computed at 8.83 (${}^1B_1$) and 10.34 eV (${}^1A_2$) and, finally, at 7.77 (${}^1B_1$) and 9.69 eV (${}^1A_2$) in the CASPT2 work [15]. A Rydberg state $n \rightarrow 3d_{xy}$ has also been detected at 10.64 eV; a similar excitation energy (10.75 eV) is reported by Palmer et al. [19], whereas a value of 10.27 eV was obtained by Serrano-Andrés et al. [15].

4 Concluding remarks

An accurate theoretical characterization of the lowest–energy valence excited states and of the 3*s*, 3*p* and 3*d* Rydberg series of thiophene has been carried out using second and third order multireference perturbation theory (NEVPT). The central rôle played by the valence–Rydberg mixing effects in the calculation of the excited states has been widely analyzed. In particular, the application of the quasi-degenerate variant of the NEVPT method (QDNEVPT2) has proved to be necessary in order to get an accurate description of the $\pi \rightarrow \sigma^*, \pi \rightarrow 3p_y$ and $\pi \rightarrow 3d_{yz}$ states, appearing strongly mixed in the zero order description. The interpretation provided by the NEVPT results has been corroborated by the very good accordance achieved with the results of the coupled cluster calculations (CCSD and CCSDR(3)), expressly performed for this study. The present results, over all, confirm the previous experimental assignments and suggest new assignments for the $\pi \rightarrow 3p_y$ and $\pi \rightarrow 3d_{yz}$ Rydberg states, whose excitation energies, probably due to a partial valence character, seem to be underestimated by most of all the previous theoretical studies. However, in the light of the consistent discrepancies (even $\simeq$1 eV) existing among the results of the various ab initio methods, further experimental and theoretical studies on the spectrum of thiophene, in the region between 7 and 10 eV, seem to be needed.

Acknowledgments This research has been financed by local funds of the University of Ferrara (*nano & nano* project) and by the Italian MIUR through its PRIN funds.

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