

# Coupled cluster calculations of the vertical excitation energies of tetracyanoethylene

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(Received 6 November 2002; accepted 14 February 2003)

Coupled cluster linear-response formalism has been used to compute the vertical spectrum of ethylene and tetracyanoethylene (TCNE). We show that for both molecules the  $\pi\pi^*$  excitation  ${}^1A_{1g} \rightarrow {}^1B_{1u}$  of the experimental spectrum is not vertical nor the 0-0 transition. For TCNE this excitation is the only experimentally observed band. We have computed vertical excitations of 5.2 eV in gas phase and 5.1 eV in acetonitrile and estimated a lower bound for the 0-0 transition in the gas phase of 4.3 eV. © 2003 American Institute of Physics. [DOI: 10.1063/1.1565999]

## I. INTRODUCTION

Tetracyanoethylene (TCNE) is a polynitrile with very strong electron acceptor character [electron affinity of 2.89 eV (Ref. 1)] due to the empty  $\pi^*$  molecular orbitals of the  $C\equiv N$  bond that allow easy ionization. TCNE forms charge-transfer complexes with electron donors. Indeed, TCNE was present not only in the first discovered bulk molecular ferromagnet  $[Fe(C_5Me_5)_2][TCNE]$ ,<sup>2</sup> but also in a variety of charge-transfer complexes as meso-tetraphenylporphyrinate salts of manganese and iron (Mn(TPP) [TCNE],<sup>3</sup> Fe (TPP) [TCNE] (Ref. 4)), phthalocyanine salts (Mn(Pc) [TCNE] (Ref. 5)), or different metallocenium salts such as  $[Co(C_5Me_5)_2][TCNE]$ ,<sup>6</sup> among others. These salts have very interesting magnetic and conductive properties and some of them present magnetic ordering temperatures  $T_c$  as high as 28 K,<sup>7</sup> and large coercive fields  $H_{cr}$  comparable to those of rare-earth commercial magnets.<sup>8</sup>

The presence of TCNE and its derivatives in charge-transfer compounds makes it worthwhile to study its excited states from both theoretical and experimental points of view. The UV-visible spectrum of TCNE is characterized by a single absorption around  $40\,000\text{ cm}^{-1}$  depending on solvent. Thus in 1,2-dimethoxyethane<sup>9</sup> the maximum appears at  $39\,000\text{ cm}^{-1}$ , while in acetonitrile<sup>6</sup> it is displaced to  $38\,300\text{ cm}^{-1}$  with molar extinction  $\varepsilon = 16\,750\text{ M}^{-1}\text{ cm}^{-1}$ . The observed band is assigned to a  $\pi \rightarrow \pi^*$  transition with some vibrational structure ( $\lambda_1 = 37\,000\text{ cm}^{-1}$ ,  $\varepsilon_1 = 15\,000\text{ M}^{-1}\text{ cm}^{-1}$ ;  $\lambda_2 = 38\,300\text{ cm}^{-1}$ ,  $\varepsilon_2 = 16\,750\text{ M}^{-1}\text{ cm}^{-1}$ ;  $\lambda_3 = 39\,200\text{ cm}^{-1}$ ,  $\varepsilon_3 = 15\,880\text{ M}^{-1}\text{ cm}^{-1}$ ;  $\lambda_4 = 40\,300\text{ cm}^{-1}$ ,  $\varepsilon_4 = 11\,800\text{ M}^{-1}\text{ cm}^{-1}$ ). The vibrational structure is probably due to the coupling of the stretching mode of the ethylenic bond that has lower energies in the excited state.<sup>6</sup>

In this context, we mention the difficulty of theoretically reproducing the equivalent transition in ethylene. Actually, the transition to the so-called  $V$  state in ethylene has been the subject of a number of theoretical contributions<sup>10-14</sup> in order to rationalize the big difference found between experiment and *ab initio* calculations in an apparently simple system. The main conclusion of these studies is the nonverticality of the above-mentioned transition.

In this paper, we have investigated the excitation ener-

gies of TCNE. Among the theoretical methods capable of delivering high-precision results for the vertical excitation energies of a molecule such as tetracyanoethylene, we have chosen to use a response function approach with a coupled cluster reference function. This wave function guarantees a size extensive treatment of dynamic correlation and this implies an accurate description of systems characterized by a single reference description and together with the subsequent linear-response calculation provides good theoretical estimations of second-order properties. In particular, the poles of the linear-response function represent the excitation energies from the reference state to an orthogonal set of excited states, while the corresponding residues are the associated transition moments.

The paper is organized as follows: In Sec. II the details of calculations are presented and Sec. III summarizes our results. Finally Sec. IV contains some concluding remarks.

## II. COMPUTATIONAL DETAILS

We have used the coupled cluster linear-response formalism using a linked triples corrected coupled cluster singles and doubles (CCSD) wave function as reference function,<sup>15-18</sup> with the effect of connected triples estimated by means of the CCSDR(3) (Ref. 19) method. In addition, solvent effects were taken into account with the method proposed by Christiansen and Mikkelsen.<sup>20</sup> In all cases,  $1s$  core orbitals were kept frozen in the coupled cluster calculation.

Calculations on TCNE were performed using two generally contracted basis sets of the atomic natural orbital (ANO) (Ref. 21) type with contractions  $5s4p1d$  and  $5s4p2d1f$ , respectively. The last was proven to be basically equivalent to Dunning's valence augmented triple zeta correlation consistent basis sets<sup>22</sup> in a previous study on urea spectrum.<sup>23</sup> The reported ethylene calculations were only carried out in the smallest of the previously mentioned basis sets, with hydrogen described by a  $4s1p$  contraction and supplementing with a  $2s2p2d$  set of Rydberg functions placed in the origin and with the exponents obtained following the scheme suggested by Dunning and Hay<sup>24</sup> in order to properly describe Rydberg excited states. Some additional calculations were

TABLE I. Calculated and averaged observed geometric parameters for TCNE.

	C=C (Å)	C-CN (Å)	C≡N (Å)	$\theta$ (C-C≡N)	$\theta$ (NO-C-CN)
CASSCF (5s4p1d) <sup>a</sup>	1.356	1.435	1.138	179.23	116.52
CCSD (5s4p1d)	1.355	1.438	1.161	179.00	117.30
B3P86 (ccpvtz)	1.362	1.420	1.151	179.02	117.10
SCF (STO-3G) <sup>b</sup>	1.344	1.460	1.158	179.80	116.60
SCF (DZ+Dc) <sup>b</sup>	1.340	1.439	1.150	179.60	116.50
X ray <sup>c</sup>	1.344	1.439	1.153		
X ray double atom <sup>c</sup>	1.358	1.431	1.166		
Neutron <sup>c</sup>	1.355	1.432	1.160	177.93	116.11

<sup>a</sup>CASSCF 10 in 10.<sup>b</sup>Reference 6.<sup>c</sup>Reference 27.

performed using the same basis sets as Peyerhoff and co-workers<sup>10</sup> and Serrano *et al.*<sup>12</sup>

The molecular geometry was fixed at  $D_{2h}$  symmetry and determined by restricted optimization at the density functional theory (DFT) level, using Becke's three-parameter functional<sup>25</sup> with the nonlocal correlation provided by the Perdew expression<sup>26</sup> and using Dunning's ccpVTZ basis.<sup>24</sup> This geometry was compared to both experimental data<sup>27</sup> and CCSD and complete active space self-consistent field (CASSCF) (10:10)  $D_{2h}$  optimized geometries with the 5s4p1d ANO basis. Results are presented in Table I. The B3P86 and CCSD geometries are very similar and in good agreement with those observed crystallographically. Major differences are found in the case of the CASSCF optimized geometry for the length of the cyanide bond, showing the importance of an adequate treatment of dynamic correlation. Since the CCSD(T) optimized geometry were not available, the optimized B3P86 geometry was used throughout the work as it is well known that this parametrization of the density functional provides fairly accurate geometries.

All coupled cluster calculations were carried out using the DALTON program,<sup>28</sup> in which the above-mentioned algorithms<sup>15–20</sup> are implemented, while DFT optimization was done by means of the GAUSSIAN 98 program.<sup>29</sup>

### III. RESULTS AND DISCUSSION

#### A. Vertical excitation energies

We have carried out CCSD and CCSDR(3) calculations to determine single excited states of TCNE below 77 000  $\text{cm}^{-1}$ . Calculated vertical excitation energies are presented in Table II (ANO basis 5s4p1d) and Table III (ANO basis 5s4p2d1f), in which the last column reports the most important excitations contributing to the excited-state wave function, even though in a very coarse approximation as important mixing occurs in several cases.

As a first point we note that all the reported excitations are clearly dominated by single excitations, and this implies a high accuracy with respect to the full configuration interaction limit of the computed values for the triples corrected energies. In this context, we mention that inclusion of linked triples corrections through the CCSDR(3) method diminishes all excitation energies for both basis sets in approximately

TABLE II. Excitation energies (eV), CCSD oscillator strengths and description for the lowest singlets of TCNE (5s4p1d ANO basis set).

Symmetry	Excitation	CCSD	CCSDR(3)	O. strength	Description
$^1A_g$	1	7.47	7.14		$1b_{2g} \rightarrow 2b_{2g}$
	2	9.29	9.10		$7a_g \rightarrow 10a_g$
	3	9.49	9.31		$8a_g \rightarrow 10a_g$ $2b_{3u} \rightarrow 3b_{3u}$ $7a_g \rightarrow 10a_g$
$^1B_{3u}$ (X)	1	6.53	6.33	0.0005	$7b_{1u} \rightarrow 2b_{2g}$
	2	7.20	6.84	0.0346	$6b_{1u} \rightarrow 2b_{2g}$
	3	7.33	7.17	0.0010	$2b_{3u} \rightarrow 9a_g$
$^1B_{2u}$ (Y)	1	6.65	6.34	0.1462	$1a_u \rightarrow 2b_{2g}$
	2	8.62	8.35	0.0199	$2b_{3u} \rightarrow 2b_{1g}$
	3	9.28	9.16	0.0001	$5b_{3g} \rightarrow 9b_{1u}$ $5b_{2u} \rightarrow 10a_g$ $6b_{3g} \rightarrow 2b_{2g}$ $5b_{3g} \rightarrow 2b_{2g}$ $2b_{3u} \rightarrow 8b_{2u}$
$^1B_{1g}$	1	5.91	5.71		$6b_{3g} \rightarrow 2b_{2g}$
	2	6.89	6.55		$5b_{3g} \rightarrow 2b_{2g}$
	3	8.12	8.04		$2b_{3u} \rightarrow 8b_{2u}$
$^1B_{1u}$ (Z)	1	5.39	5.23	0.4838	$2b_{3u} \rightarrow 2b_{2g}$
	2	8.92	8.58	0.1464	$1b_{3u} \rightarrow 2b_{2g}$
	3	9.33	9.20	0.0330	$6b_{1u} \rightarrow 10a_g$ $7a_g \rightarrow 9b_{1u}$ $8a_g \rightarrow 2b_{2g}$ $7a_g \rightarrow 2b_{2g}$
$^1B_{2g}$	1	6.32	6.13		$2b_{3u} \rightarrow 9b_{1u}$
	2	7.28	6.95		$1b_{1g} \rightarrow 2b_{2g}$
	3	7.79	7.65		$2b_{3u} \rightarrow 2a_u$ $6b_{3g} \rightarrow 10a_g$ $5b_{2u} \rightarrow 9b_{1u}$ $5b_{3g} \rightarrow 9a_g$
$^1B_{3g}$	1	6.77	6.45		$6b_{3g} \rightarrow 10a_g$
	2	9.01	8.70		$5b_{2u} \rightarrow 9a_g$
	3	9.27	9.14		$6b_{2u} \rightarrow 2b_{2g}$ $5b_{2u} \rightarrow 2b_{2g}$ $1a_u \rightarrow 10a_g$ $1b_{1g} \rightarrow 9b_{1u}$
$^1A_u$	1	6.31	6.10		$6b_{2u} \rightarrow 2b_{2g}$
	2	7.15	6.80		$5b_{2u} \rightarrow 2b_{2g}$
	3	8.57	8.49		$1a_u \rightarrow 10a_g$ $1b_{1g} \rightarrow 9b_{1u}$

0.2–0.3 eV. Nevertheless, there are some exceptions in which the change is less than 0.1 eV, but according to Bartlett,<sup>13</sup> the behavior of the  $V \pi \rightarrow \pi^*$  state in ethene may indicate that the CCSD results could be fortuitously good. Adding an extra  $d$  and  $f$  sets to the small basis decreases the excitation energies to a lesser extent. Actually, this effect accounts for no more than 0.1 eV except for the higher states in which the augmentation of basis causes a slightly larger diminution. In any case, neither the inclusion of triples nor the augmentation of the basis produces a change in the order of states showing a homogeneous description of all the states at the CCSD level with the small basis. Indeed, the chosen 5s4p1d basis is enough for a semiquantitative picture of the vertical spectrum of tetracyanoethylene. Concerning the choice of basis, we recall that given the relatively large size of the studied system, the existence of low-lying Rydberg states is not to be expected. This is contrary to the case of ethylene that will be also studied later on. In any case, we have also computed the expected value of  $\langle r^2 \rangle$  in some selected states of tetracyanoethylene. The obtained results show that there is basically no change when comparing the ground and the considered excited states. This clearly confirms that no Rydberg functions are needed in the atomic-orbital basis set.

The lowest singlet state belongs to the  $^1B_{1u}$  symmetry class and appears 5.16 eV above the  $^1A_g$  ground state using the CCSDR(3) level and the extended basis. It is assigned to

TABLE III. Excitation energies (eV), CCSD oscillator strengths and description for the lowest singlets of TCNE ( $5s4p2d1f$  ANO basis set).

Symmetry	Excitation	CCSD	CCSDR(3)	O. strength	Description
$^1A_g$	1	7.44	7.11		$1b_{2g} \rightarrow 2b_{2g}$
	2	9.20	9.02		$7a_g \rightarrow 10a_g$
	3	9.42	9.23		$6b_{1u} \rightarrow 9b_{1u}$ $2b_{3u} \rightarrow 3b_{3u}$
$^1B_{3u}$ (X)	1	6.46	6.26	0.0005	$6b_{1u} \rightarrow 9b_{1u}$ $7b_{1u} \rightarrow 2b_{2g}$
	2	7.15	6.79	0.0324	$6b_{1u} \rightarrow 2b_{2g}$
	3	7.27	7.10	0.0007	$2b_{3u} \rightarrow 9a_g$ $2b_{1u} \rightarrow 10a_g$
$^1B_{2u}$ (Y)	1	6.62	6.31	0.1446	$1a_u \rightarrow 2b_{2g}$
	2	8.53	8.25	0.0188	$2b_{3u} \rightarrow 3b_{1g}$
	3	9.18	9.05	0.0000	$5b_{3g} \rightarrow 9b_{1u}$ $5b_{2u} \rightarrow 10a_g$
$^1B_{1g}$	1	5.85	5.65		$6b_{3g} \rightarrow 2b_{2g}$
	2	6.83	6.48		$5b_{3g} \rightarrow 2b_{2g}$
	3	8.02	7.94		$2b_{3u} \rightarrow 8b_{2u}$ $2b_{3u} \rightarrow 10b_{2u}$
$^1B_{1u}$ (Z)	1	5.33	5.16	0.4711	$2b_{3u} \rightarrow 2b_{2g}$
	2	8.88	8.57	0.1533	$1b_{3u} \rightarrow 2b_{2g}$
	3	9.24	9.11	0.0335	$6b_{1u} \rightarrow 10a_g$ $7a_g \rightarrow 9b_{1u}$
$^1B_{2g}$	1	6.25	6.06		$8a_g \rightarrow 2b_{2g}$
	2	7.22	6.90		$7a_g \rightarrow 2b_{2g}$
	3	7.70	7.57		$2b_{3u} \rightarrow 9b_{1u}$
$^1B_{3g}$	1	6.74	6.42		$1b_{1g} \rightarrow 2b_{2g}$
	2	8.95	8.64		$2b_{3u} \rightarrow 3a_u$ $6b_{3g} \rightarrow 10a_g$
	3	9.18	9.03		$5b_{2u} \rightarrow 9b_{1u}$ $5b_{3g} \rightarrow 10a_g$
$^1A_u$	1	6.25	6.04		$6b_{2u} \rightarrow 2b_{2g}$
	2	7.09	6.74		$5b_{2u} \rightarrow 2b_{2g}$
	3	8.46	8.39		$1a_u \rightarrow 10a_g$ $1b_{1g} \rightarrow 9b_{1u}$

a  $\pi \rightarrow \pi^*$  transition mainly centered in the ethylenic bond, with some contribution from the cyanides moieties. There is one more transition below 6 eV, the  $1^1B_{1g}$  excitation that represents a charge donation from the  $C \equiv N$  group to the  $C=C$  double bond, but is not symmetry allowed. In general, the excitations with lower energy are those to the  $2b_{2g}$  orbital, the antibonding  $\pi$  orbital of the ethylenic bond, from the highest occupied orbitals of the cyanide groups. For instance, the second most intense transition is the  $1^1B_{2u}$  excitation at 6.31 eV from  $\pi_{CN}$  to  $\pi_{CC}^*$ . As indicated above, the

TABLE IV. Excitation energies (eV) and transition properties CCSD for the lowest singlets of TCNE with  $CH_3CN$  solvent ( $5s4p1d$  ANO basis set).

Symmetry	Excitation	Excitation energies (eV)	Oscillator strength	Direction
$^1B_{3u}$	1	6.56	0.0004	X
	2	7.31	0.0078	X
	3	7.46	0.0361	X
$^1B_{2u}$	1	6.65	0.1939	Y
	2	8.61	0.0357	Y
	3	9.32	0.1785	Y
$^1B_{1u}$	1	5.30	0.5661	Z
	2	8.86	0.2228	Z
	3	9.45	0.0608	Z

effect of the extra basis functions is more important for the states beyond 8 eV, which also appear very mixed.

To estimate the intensity of the transitions, we have calculated the oscillator strength of the dipole allowed transitions at the CCSD and these are summarized in Tables II and III. The transition to the first  $^1B_{1u}$  state with  $f=0.47$  represents the most intense one and it is also the major feature in the experimental electronic spectrum of TCNE as it is discussed below. In addition, one can find two more bands in the theoretical spectrum with a noticeable intensity, although in both cases with less than one-third of the intensity of the previous one. They correspond to transitions to the  $2^1B_{1u}$  state and to the  $1^1B_{2u}$  state with energies 8.57 and 6.31 eV, respectively, and both with an oscillator strength of 0.15. Other symmetry allowed transitions have a negligible intensity.

To the best of our knowledge, the electronic spectrum of TCNE has not been measured in the gas phase. Thus, in order to facilitate a comparison with respect to experimental data, we have also investigated solvent effects. In particular, we have calculated the coupled cluster linear response (CCLR) vertical spectrum of tetracyanoethylene in acetonitrile, one of the solvents in which the experimental spectrum is available. As a matter of fact, the polar character of acetonitrile [ $\epsilon_{st}=35.94$ ,  $\epsilon_{op}=1.798$  (Ref. 30)] is enough to expect some changes in the aspect of the spectrum. The molecular geometry was reoptimized using DFT formalism and the Onsager method,<sup>31</sup> but the encountered changes were not significant with variations in bond distances of the order of 0.001 Å.

Following Christiansen and Mikkelsen,<sup>20</sup> the molecule was placed inside a cavity in a medium of definite electrical permittivities, but contrary to them the cavity radius considering the molecular volume was defined by a contour of 0.001 electrons/bohr<sup>3</sup>. The cavity radius was then taken 0.5 Å larger, which gives finally a value of 8.09 a.u. It should be mentioned that the method used is probably not optimal for the planar TCNE molecule as the boundary of the spherical cavity is too far from the  $C=C$  double bond, where the interesting transition mainly takes place, but still it should be sufficient for giving an approximate picture. We have used CCSD linear response and the small  $5s4p1d$  ANO basis set to take into account the effect of solvent on the considered excitation energies and transition strengths. Results are presented in Table IV, where we observe that the presence of acetonitrile mainly modifies the states belonging to the  $^1B_{1u}$  and  $^1B_{3u}$  classes of symmetry. In particular, acetonitrile stabilizes the two lowest states of  $^1B_{1u}$  symmetry that are also those for which the transition is most intense. On the other hand, this solvent produces a hypsochromic displacement in the considered  $^1B_{3u}$  states as well as in the  $3^1B_{1u}$  state.

We have paid special attention to the  $1^1B_{1u}$  state as responsible for the observed  $\pi \rightarrow \pi^*$  experimental absorption. We have thus calculated the corresponding excitation energy using the larger basis  $5s4p2d1f$  and found a value of 5.24 eV to be compared with the *in vacuo* result of 5.33 eV. The oscillator strength happened to be 0.562, equal to the small basis results. The effect of triples excitations in the spectrum of dissolved TCNE could not be taken into ac-

TABLE V. Vertical electronic transition energies CCSDR(3) to several excited states of etene ( $C_2H_4$ ).

	ANO1 w/o Rydberg <sup>a,b</sup>	ANO1 <sup>a,b</sup>	ANO2 w/o Rydberg <sup>a,c</sup>	ANO2 <sup>a,c</sup>	AO 84C <sup>d</sup>	PT2F <sup>a,b</sup>	MRCI <sup>d</sup>	EOM- CCSD(T) <sup>a,b</sup>	EOM- CCSDT-3 <sup>a</sup>	Expt.
1 $^1B_{1u}$	7.98	7.86	7.97	7.92	7.90	8.40	7.96	7.74	7.89	7.66(7.8) <sup>e</sup>
1 $^1B_{3u}$	7.28	7.22	7.32	7.25	7.17	7.17	7.13	7.10	7.24	7.11
1 $^1B_{1g}$	7.94	7.88	7.99	7.90	7.85	7.85	7.86	7.76	7.91	7.80 <sup>f,g</sup>
1 $^1B_{2g}$	8.01	7.92	8.04	7.94	7.86	7.95	7.89	7.80	7.95	7.90 <sup>f</sup>
2 $^1A_g$	9.20	8.40	8.98	8.29	8.21	8.40	8.21	8.28	8.42	8.28 <sup>f</sup>
2 $^1B_{3u}$	9.89	8.73	9.70	8.76	8.75	8.66	8.73	8.61	8.75	8.62
2 $^1B_{1u}$	10.50	9.25	10.50	9.27	9.43	9.31	8.83	9.13	9.28	9.33 <sup>h</sup>
1 $^1A_u$	9.27	8.97	9.33	8.97	8.98	8.94	8.88	8.85	8.99	
3 $^1B_{3u}$	10.97	9.02	11.68	8.96	8.97	9.03	8.92	8.90	9.05	8.90
1 $^1B_{2u}$	10.44	9.21	10.45	9.01	9.07	9.18	8.98	9.08	9.23	9.05
Reference	this work	this work	this work	this work	this work	12	10	13	13	45

<sup>a</sup>Geometry  $r(C=C)=1.339$ ,  $r(C-H)=1.086$ ,  $\theta=117$ ,  $6^\circ$ . Reference 43.

<sup>b</sup>ANO1 =  $4s3p2d(C)/3s2p(H)$  basis set, Rydberg funct.  $C(2s):0.012\ 138, 0.004\ 248\ 2$ ;  $C(2p):0.008\ 015, 0.002\ 805\ 2$ ;  $C(1d):0.028\ 512$ . Ref. 12.

<sup>c</sup>ANO2 =  $5s4p1d(C)/4s1p(H)$  basis set, Rydberg functions  $C(2s):0.017\ 25, 0.0437$ ;  $C(2p):0.015\ 75, 0.0399$ ;  $C(2d):0.011\ 25, 0.028\ 25$  added at the center of the CC bond.

<sup>d</sup>84C Ref. 44:  $4s2p2d(C)2s1p(H)$  AO basis set with Rydberg functions  $C(2s):0.02, 0.01$ ;  $C(2p):0.017, 0.009$ ;  $C(2d):0.03, 0.022$  added at the center of the CC bond, geometry, Ref. 10  $rC=C=1.35$ ,  $r(O-H)=1.071$ ,  $\theta=117^\circ$ .

<sup>e</sup>Theoretical estimate, Ref. 11.

<sup>f</sup>Reference 46.

<sup>g</sup>Reference 47.

<sup>h</sup>References 48 and 49.

count, but it is reasonable to assume that it should not be very much larger than in the gas phase. Therefore the vertical excitation in acetonitrile can be estimated to be between 5.0 and 5.1 eV.

As mentioned in the introduction, the maximum of the experimental spectrum of TCNE in acetonitrile appears at  $38\ 300\ \text{cm}^{-1}$  or 4.75 eV. Of course, we have computed vertical excitations and thus the comparison is by no means direct. Anyway, the difference is still large enough to merit some comments. In principle, there are several possible sources of error in a theoretical calculation and clearly the first of them is the inadequacy of the method used. In this respect, we should recall that as shown by Christiansen *et al.*,<sup>19</sup> the employed CCSDR(3) method is correct to third order in the fluctuation potential for states dominated by single excitations. Indeed, all the computed energies correspond to states clearly dominated by this kind of excitation, in such a way that the weight of singlet excitations in the  $1\ ^1B_{1u}$  state is more than 94% for the two basis sets used. The use, then, of a nonappropriated method must be disregarded. Of course, a previous requisite is a correct description of the ground state. That this is actually the case is definitely shown by the very small contribution, less than 4%, of  $t_1$  amplitudes to the total CCSD wave function, the ground state being thus properly described by a single reference description.

A second possibility could be the lack of enough flexibility in the atomic basis set. We have already stated that for a molecular system such as tetracyanoethylene the existence of low-lying Rydberg states is not to be expected. In addition we have explicitly calculated the CCSD expectation value of the square of the distance for this state using the  $5s4p1d$  basis. The obtained value ( $\langle r^2 \rangle^{1/2} = 930.8\ \text{a.u.}$ ) shows the valence character of the considered state when compared to the ground-state value ( $\langle r^2 \rangle^{1/2} = 931.5\ \text{a.u.}$ ). In addition, the employed basis is diffuse enough to properly describe the

$1\ ^1B_{1u}$  state of TCNE as shown by Gwaltney and Bartlett in another context.<sup>32</sup> Thus Rydberg functions are not needed in the basis to correctly describe the  $1\ ^1B_{1u}$  state. On the other hand, it is nowadays well established that a correct description of valence states can be achieved by using basis sets of augmented triple zeta quality. We have already indicated that this is the case for the large basis and actually a calculation using an expanded basis  $6s5p2d1f$  gave a CCSD value for the transition to the  $1\ ^1B_{1u}$  state of 5.327 eV, less than 0.01 eV below the value computed with our large basis.

Therefore it is probable that the  $\pi \rightarrow \pi^*$  transition in TCNE is not vertical, in a similar way than what is encountered for ethene<sup>10-14</sup> and other small polyenes such as trans-butadiene.<sup>13</sup> In the following subsection we review the  $V-N$  transition in ethylene in order to completely check the quality of the method and basis set we have used and address the nonverticality of the experimental absorption.

## B. Ethylene spectrum

The largest interest of the ethylene spectrum<sup>33-36</sup> is centered in a broad band with maximum at 7.66 eV, which was interpreted by Mulliken<sup>37</sup> as resulting from a  $\pi \rightarrow \pi^*$  transition from the  $^1A_{1g}$  ground state to the  $^1B_{1u}$  state, the so-called  $V$  state. This band is partly overlapped by several Rydberg series and indeed it has demonstrated<sup>11</sup> that the  $V$  state has a quite small but significant Rydberg character. From a theoretical point of view, the main feature of this transition is that it is not vertical, while for the vertical transition several sophisticated quantum chemistry studies have arrived at a value a bit lower than 8 eV.

In order to test both the method and basis sets that we have used in our study on tetracyanoethylene, we have also carried out theoretical calculations of the vertical excitations to the lowest singlet states of ethylene. We have used several basis sets and geometries to compare our numbers with pre-



vious theoretical data. Results were collected in Table V, together with other theoretical results and experimental data, which are thought to be adiabatic and then probably somewhat lower than the true vertical excitation energies. The CC3 excitation energies have also been computed by Christiansen *et al.*,<sup>38</sup> but they have not been included in Table V because all electrons were correlated, contrary to all the coupled cluster calculations reported. Anyway, their results do not differ significantly of those collected in Table V. We have used the currently accepted geometry<sup>39,40</sup> of the ground state in the calculations with ANO basis (the first four columns), where ANO1 stands for the basis used by Serrano *et al.*,<sup>12</sup> and ANO2 represents the smallest of the basis employed in our study of TCNE modified as discussed in Sec. II. In addition, we have also carried out calculations with a different basis and in a slightly different geometry,<sup>41</sup> as used by Petrongolo *et al.*

In general terms, it can be seen in Table V that the differences found among all the calculations which share geometry and atomic basis set are not significant in most of the cases. As a matter of fact, the second largest difference between our number and complete active space to second order perturbation theory (CASPT2) excitation energies is 0.07 eV for the  $2^1B_{1u}$  state. This difference is actually inside the estimated margins of error of both approaches. The only exception to this general behavior appears in the  $1^1B_{1u}$  transition corresponding to the  $\pi \pi^*$  state. In this case the CCSDR(3) result is 7.86 eV, while the CASPT2 excitation energy is 8.40 eV with the same basis,<sup>12</sup> but in a subsequent paper<sup>42</sup> Roos and co-workers used multi-state CASPT2 to get a vertical excitation energy of 7.98 eV with a different basis. As mentioned above, the estimated vertical transition is close to 7.8 eV.

Comparing our results to those from Watts *et al.*<sup>13</sup> a good agreement is again found. In Table V we have not included triples noncorrected results because, as it is well known, the CCLR/CCSD and equation of motion CCSD (EOM-CCSD) excitation energies are the same. The effect of triples moves the CCSD results closer to the experimental values by making the CCSDR(3) computed excitation energies correct to third order in the fluctuation potential. It is important to mention that the agreement with respect to experiment of the noniterative EOM-CCSD( $\tilde{T}$ ) is usually better than that of the iterative EOM-CCSDT-3. This effect was not encountered when comparing the iterative CC3 and the noniterative CCSDR(3), but it should be kept in mind that Christiansen *et al.*<sup>37</sup> calculated the excitation energies without freezing the core contrary to what Watts *et al.*<sup>13</sup> and we did. At any rate, the value of the excitation energy that we are especially interested in, i.e., the  $1^1B_{1u}$  transition, is basically coincident in nearly all the couple cluster approaches considered: 7.86 eV in CCSDR(3), 7.87 eV in CC3, and 7.89 eV in EOM-CCSDT-3, although 7.74 eV in EOM-CCSD( $\tilde{T}$ ).

Bartlett and co-workers<sup>13</sup> also examined the convergence of the atomic basis set at the CCSD level. Their conclusion is that the EOM-CCSD excitation energy of the  $V$  state remains unaltered even with an ANO basis of double-augmented triple zeta quality. Nevertheless, we have augmented the atomic-orbital basis set until  $5s4p1d/4s1p$ /Rydberg in order

to fit with the smallest basis that we have used in the TCNE study. There are, actually, no major changes, although some excitation energies are in this way put closer to the experimental values. This is especially important for the  $1^1B_{2u}$  transition, which is computed as 9.21 eV with basis ANO1, but as 9.01 eV with basis ANO2. Once more, the  $1^1B_{1u}$  transition is basically unchanged by being increased only 0.06 eV. Indeed, also the CASPT2 result is slightly modified when changing the basis as it goes from 8.40 eV with the basis ANO1 to 8.45 with the basis used in Ref. 42.

Contrary to TCNE, there are several low-lying states in ethylene of Rydberg or mixed Rydberg valence character. Clearly this implies that a proper description can only be achieved if the appropriate basis functions are included in the basis set. However, we have also computed the vertical spectrum of ethene in absence of Rydberg functions and of course most of the results are incorrect. Anyway, the effect of Rydberg functions on the  $1^1B_{1u}$  transition is only of 0.05 eV, showing in this way the ability of the ANO2 basis to describe the  $V$  state of ethylene and its derivatives.

Our results are essentially coincident as well with those from Petrongolo *et al.*<sup>10</sup> using the same basis and geometry with the notable exception of the  $2^1B_{1u}$  state that we determine at 9.43 eV, i.e., 0.6 eV higher than Buenker and co-workers.<sup>10</sup> The experimental value is 9.33 eV.

In order to get a more direct comparison with experiment, we have also calculated the energy of the 0-0 transition to the  $1^1B_{1u}$  state. As we cannot calculate Hessians at the coupled cluster level, zero-point energies of both the  $1^1A_{1g}$  ground state and the  $1^1B_{1u}$  excited state were determined inside the Hartree-Fock formalism. Geometries were numerically optimized only at the CCSD level and restricting to  $D_2$  symmetry, but the excitation energies were triples corrected via the CCSDR(3) approach. In this way, we estimate the value of the 0-0 transition to be 5.42 eV, in very good agreement with the experimental value of 5.50 eV extrapolated from the experimental spectra by Foo and Innes.<sup>43</sup> The 0-0 transition has also been computed by Mebel *et al.*,<sup>14</sup> at  $D_2$  geometry who proposed a value of 5.45 eV combining CASSCF(2/11) and MRCI calculations. However, recently Ben-Nun and Martínez studied the conical intersections between electronic states of ethylene and found a pyramidalized structure for the  $V$  state from both CASSCF(2/6) and MRCI calculations<sup>44</sup> and *ab initio* multielectronic state molecular dynamics.<sup>45</sup> This pyramidalization is not found at the CCSD and restricted open shell Hartree-Fock (ROHF) levels of calculation.

As we have optimized the TCNE excited-state geometry only at the Hartree-Fock (HF) level, we have also computed the value of the 0-0 transition to the  $1B_{1u}$  state of ethene with HF optimized geometries, so to check the influence of geometry in the calculated spectrum. Using again CCSDR(3) excitation energies, we have got a value of 5.19 eV, 0.23 eV below our best estimate. In this context it is important to mention that the CC(3) energy at the HF geometry is only 0.01 eV below the CC(3) energy at the experimental geometry used by Roos and co-workers.<sup>12</sup> However, the corresponding vertical excitations are 8.08 eV (HF geometry) and 7.89 eV (experimental geometry). In contrast, the 0.04-eV

decrease encountered when comparing the results at the experimental and CCSD optimized geometries is completely due to the stabilization of the ground state.

### C. $A_{1g} \rightarrow B_{1u}$ transition of TCNE

The analysis in the previous section has proven the ability of the used basis set and method to properly describe the  $A_{1g} \rightarrow B_{1u} \pi\pi^*$  transition of ethylene. This is basically also the band appearing in the experimental spectrum of tetracyanoethylene, and then we can expect also that our treatment should deliver accurate results for the vertical excitation energies of TCNE. As previously discussed the difference between the experimental transition found in acetonitrile and the estimated vertical one in the same solvent is between 0.25 and 0.35 eV, around twice the expected error of the theoretical value.

An additional possible criticism to the above result may arise from the fact that we have used for the ground state the optimized DFT geometry instead of the experimental. Thus the vertical excitation energy at the experimental geometry derived from neutron-diffraction measurements<sup>6</sup> has also been computed. Using the  $5s4p1d$  basis, the *in vacuo* CCSDR(3) result is 5.24 eV, basically coincident with the value at DFT geometry of 5.23 eV. The same is encountered when comparing the calculated oscillator strengths in the CCLR formalism: 0.47 at the experimental geometry and 0.48 at the DFT optimized one. Furthermore, an identical behavior occurs at the CCSD optimized geometry, where an excitation energy of 5.26 eV with oscillator strength of 0.47 is found. On the other hand, and because of the shorter  $C \equiv N$  bond, the CCSDR(3) excitation energy at CASSCF geometry is 5.39 eV with  $f=0.49$ .

Given the extraordinarily large changes that were observed in the  $\pi \rightarrow \pi^*$  excitation energy of ethylene upon very small distortions of the ground-state geometry, we have also explored the ground-state hypersurface of TCNE using the small basis. As it can be expected, we have encountered that the elongation of the ethylenic bond of TCNE causes a substantial reduction of the excitation energy because of the stabilization of the excited state together with a destabilization of the ground state. Of course, such an elongation also favors the rotation around the  $C=C$  bond. Similarly, enlarging the cyanide bond a diminution of the excitation energy is achieved. The combined effect of all these distortions could in principle bring down the excited state so to approach the experimental value. Indeed, there are several geometries that present a rather small destabilization of the ground state but a significant decrease in the excitation energy. In particular, it is noticeable that the CC(3)/CCSDR(3) methods predicts that only 0.02 eV above the minimum of the DFT surface, the  $1B_{1u}$  state has stabilized almost 0.3 eV. This is achieved at a geometry defined by elongating 0.04 Å the ethylenic bond and 0.02 the cyanide one, with insignificant changes of the other geometrical parameters. Moreover, an additional internal rotation of less than 9° around the  $C=C$  bond, brings the excitation energy to 4.91 eV in the gas phase with only a destabilization of 0.03 eV of the ground state. The zero-point energy of the ground state calculated at the Hartree-Fock

level is  $11\,284.68\text{ cm}^{-1}$ , equivalent to 1.40 eV.

This clearly shows that in the vicinity of the lowest-energy structure the two considered potential-energies surfaces are not parallel at all, but instead they present very different slopes and consequently the corresponding minima are rather different and, indeed, the minimum of the  $\pi\pi^*$  excited state is a twisted  $D_{2d}$  structure at the ROHF level. Therefore there is no reason to expect that the most intense transition correspond to either the vertical or the 0-0 transition. Actually, using Hartree-Fock optimized geometries and zero-point energies and CCSDR(3) excitation energies, we have computed the *in vacuo* 0-0 transition to appear at 4.34 eV. The previous study on ethylene shows that the experimental value is probably higher, but on the other hand the effect of solvent will lower the energy of this 0-0 transition, especially if a better representation of the cavity were used. Therefore it does not seem unrealistic to suppose that the correct value is below 4.5 eV. The difference with respect to the experimental maximum would be then large enough to put in doubt whether such maximum is actually the 0-0 transition.

## IV. CONCLUSIONS

In this communication we have studied the vertical spectrum of tetracyanoethylene using coupled cluster theory. We have found that the lowest singlet-singlet transition, which corresponds to the excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) excitation, occurs at 5.16 eV in the gas phase and is lowered approximately 0.1 eV due to solvent effects in acetonitrile. This transition is basically homologous to the  $\pi\pi^*$  excitation in ethylene connecting the ground and the V excited states. The transition is assigned to the most intense band of the experimental spectrum of TCNE that appears in acetonitrile at 4.75 eV, a value around 0.3 eV below our theoretical estimate, which gives support to the idea that the mentioned transition is not vertical.

A parallel study on the ethene spectrum showed the quality of the basis sets and methods we used, by placing the V state 7.92 eV above the ground state and giving an energy for the 0-0 transition of 5.42 eV to be compared with the experimental value of 5.50 eV.

## ACKNOWLEDGMENTS

The authors thank Dr. Manuela Merchán for helpful discussions and suggestions. This work was supported by EU-TMR net "Molecular properties and Molecular Materials" (HPRN-CT-2000-00013). Financial support is also acknowledged from Spanish MCT (Plan Nacional  $I+D+I$ ) and European FEDER funds (Project No. BQU2001-2935-C02-01) and the Carlsberg Foundation.

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