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**Author(s):** Tuononen, Heikki; Suontamo, Reijo; Valkonen, Jussi; Laitinen, Risto

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**Electronic Structures and Spectroscopic Properties of  $6\pi$ -Electron Ring Molecules  
and Ions  $E_2N_2$  and  $E_4^{2+}$  ( $E = S, Se, Te$ )**

Heikki M. Tuononen,<sup>†</sup> Reijo Suontamo,<sup>\*,†</sup> Jussi Valkonen,<sup>†</sup> and Risto S. Laitinen<sup>\*,‡</sup>

Departments of Chemistry, University of Jyväskylä, P.O Box 35, FIN-40014 Jyväskylä,  
Finland and University of Oulu, P.O Box 3000, FIN-90014 Oulu, Finland.

E-mail: [suontamo@cc.jyu.fi](mailto:suontamo@cc.jyu.fi)

Tel.: (35814) 260-2605

Fax.: (35814) 260-2501

E-mail: [risto.laitinen@oulu.fi](mailto:risto.laitinen@oulu.fi)

Tel: (3588) 553-1611

Fax: (3588) 553-1608

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<sup>†</sup> University of Jyväskylä

<sup>‡</sup> University of Oulu

**Abstract**

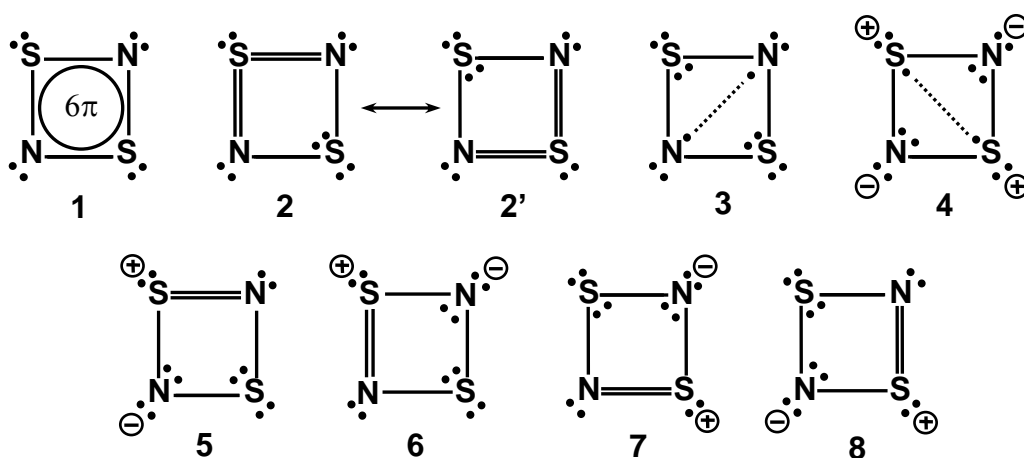
The electronic structures and molecular properties of square-planar  $6\pi$ -electron ring molecules and ions  $E_2N_2$  and  $E_4^{2+}$  ( $E = S, Se, Te$ ) were studied using various *ab initio* methods and density functionals. All species were found to contain singlet diradical character in their electronic structures. Detailed analysis of the CAS wave function of  $S_2N_2$  in terms of different valence bond structures gives largest weight for a Lewis-type singlet diradical VB structure in which the two unpaired electrons reside on nitrogen atoms, though the relative importance of the different VB structures is highly dependent on the level of theory. The diradical character in both  $E_2N_2$  and  $E_4^{2+}$  was found to increase in the series  $S < Se < Te$ . The diradical nature of the chemical species is manifested in the prediction of molecular properties, in which the coupled cluster and multiconfigurational approaches, as well as the BPW91 functional show consistent performance.  $^{77}Se$  NMR chemical shifts of chalcogen cations  $S_xSe_{4-x}^{2+}$  ( $x = 0-3$ ) were calculated with CAS, BPW91 and B3PW91 methods using the GIAO formalism. The hybrid functional B3PW91 shows inferior performance, but both CAS and BPW91 unquestionably confirm the experimental assignment and are able to predict the NMR chemical shifts of these computationally difficult cases with excellent accuracy.

## Introduction

Over the last 30 years, a limited number of tetraatomic square-planar  $6\pi$ -electron ring molecules and ions containing atoms of groups 15 and 16 have been experimentally characterized. Most widely known examples are disulfur dinitride  $S_2N_2$ ,<sup>1,2</sup> pnictogen dianions  $Sb_4^{2-}$ <sup>3</sup> and  $Bi_4^{2-}$ ,<sup>4</sup> and chalcogen dications such as  $S_4^{2+}$ ,  $Se_4^{2+}$ , and  $Te_4^{2+}$ .<sup>5</sup> The latest experimental additions are the crystal structures of  $As_4^{2-}$ <sup>6</sup> and  $P_4^{2-}$ .<sup>7</sup> These molecules and ions are chemically interesting for variety of reasons, but their extraordinary bonding arrangement renders them important also from a purely theoretical viewpoint. The electronic structures of these seemingly simple chemical systems have turned out to be rather complex and have therefore been in the focus of many theoretical discussions.

The electronic structure and bonding has most often been discussed in the context of  $S_2N_2$  due to its role in the synthesis of the superconducting polymeric sulfur nitride  $(SN)_x$ .<sup>1,2</sup> Based on the localized CNDO/2 orbitals, Adkins and Turner first pictured bonding in  $S_2N_2$  with four localized  $\sigma$ -bonds and six delocalized  $\pi$ -electrons **1** thus implying some similarity with aromatic structures.<sup>8</sup> A similar conclusion was also drawn by Jafri *et al.* using canonical RHF orbitals.<sup>9</sup> Findlay *et al.*<sup>10</sup> later refined the scheme by using localized RHF orbitals to analyze bonding in  $S_2N_2$ . They concluded that the structure is best described as a resonance between the two symmetry-broken Lewis structures **2** and **2'**. By contrast, Skrezenek and Harcourt have showed that the primary Lewis-type valence bond structure for  $S_2N_2$  resembles the spin-paired diradical structure **3** with a long N $\cdots$ N bond across the ring, and that the singlet diradical structure **4** and the

four zwitterionic Lewis structures **5** – **8** make smaller contributions to the ground state resonance scheme.<sup>11,12,13</sup> Similar conclusion was also drawn by Fujimoto *et al.* via INDO calculations.<sup>15</sup> This view was however later questioned by Gerratt *et al.*<sup>16</sup> who used spin-coupled VB theory calculations to show that the structure is a diradical in nature but addressed the diradical character solely to the sulfur atoms, as described in the structure **4**. The most recent contribution to the discussion of bonding in  $S_2N_2$  comes from Thorsteinsson and Cooper who utilized the newly developed CASVB method to analyze the different bonding models.<sup>17</sup> They found the diradical structure **4** to be lowest in energy, but the alternatives **2-2'** and **3** were too close to allow any definite conclusions to be made.



Although  $S_2N_2$  has been the focus of many in-depth theoretical studies, the electronic structures of other valence isoelectronic square planar  $6\pi$ -electron rings have been discussed in lesser detail. In the majority of theoretical studies their electronic structures have been described without making any reference to the suggested singlet diradical character of  $S_2N_2$ .<sup>18-20</sup> In many cases ions such as  $P_4^{2-}$  and  $S_4^{2+}$  have simply been considered as aromatic and the delocalized models similar to the structure **1** have

been used to describe their bonding.<sup>7,18,21</sup> Their possible diradical nature has been stressed only by few authors. Skrezenek and Harcourt<sup>12,22</sup> have considered  $S_4^{2+}$  to be a singlet diradical in an analogous manner to  $S_2N_2$  and Lopez *et al.*<sup>23</sup> have stated that the hypothetical square-planar molecule  $P_2O_2$  should be highly diradical in nature and addressed the diradical character to phosphorus atoms.

Despite the fact that no general agreement of the electronic structures of tetraatomic square-planar  $6\pi$ -electron rings has yet been reached, several theoretical studies discussing their chemical properties have been published.<sup>24-27</sup> Since the prediction of chemical properties of molecules requires a well-based description of their electronic structures, the validity of such predictions can be questioned. If a molecule has a considerable diradical character, it must also be properly taken into account in theoretical calculations. Typical quantum chemical methods such as RHF and MP2 are incapable of treating static electron correlation and produce meaningless results in cases where these effects are important. In this respect it is rather interesting that only one multiconfigurational *ab initio* study of the structures and molecular properties of square-planar  $6\pi$ -electron rings has been presented.<sup>28</sup> Clearly both their electronic structures and molecular properties merit reinvestigation using high level *ab initio* theory.

In this work we report a rigorous *ab initio* treatment of the electronic structures and molecular properties of  $E_2N_2$  molecules and  $E_4^{2+}$  cations ( $E = S, Se, Te$ ). They were chosen due to the wealth of experimental information available. The possible radical nature of the molecules is discussed by using both symmetry-broken Hartree-Fock formalism and true multiconfigurational *ab initio* methods. The main purpose of the

study is to clarify the numerous uncertainties associated with their electronic structures and give a uniform description of their bonding. We also discuss the harmonic vibrational frequencies and  $^{77}\text{Se}$  NMR chemical shifts at various levels of theory.

## Computational Details

All calculations were carried out for  $\text{E}_2\text{N}_2$  molecules and  $\text{E}_4^{2+}$  cations ( $\text{E} = \text{S}, \text{Se}$  or  $\text{Te}$ ). Throughout the calculations, molecules and ions were orientated in the  $xy$ -plane in such a way that their principal rotation axis ( $C_2$  or  $C_4$ ) coincided with the  $z$ -axis. Nitrogen atoms of  $\text{E}_2\text{N}_2$  were located on the  $x$ -axis and chalcogen atoms on the  $y$ -axis. Full point group symmetries ( $D_{2h}$  or  $D_{4h}$ ) were used whenever possible. Dunning's correlation consistent basis set of triple-zeta quality, cc-pVTZ, were used for all atoms except tellurium for which a quasi-relativistic large core effective core potential was used together with a corresponding triple-zeta valence basis set, SDB-cc-pVTZ. All basis sets were used as they are referenced in the EMSL basis set library.<sup>29</sup>

Geometries were fully optimized in their singlet ground states using several different theoretical methods: RHF, MP2,<sup>30</sup> CCSD,<sup>31</sup> CCSD(T),<sup>32</sup> CAS,<sup>33</sup> and CASPT2.<sup>34</sup> Two density functionals, BPW91<sup>35,36</sup> and B3PW91,<sup>36,37</sup> were also used in the optimizations. In CAS calculations, the active space consisted of full valence space and included all possible configurations that arise from the distribution of 22 valence electrons in 11 highest occupied and 5 lowest virtual orbitals *i.e.* [22,16]-CAS. The active space was considerably reduced in CASPT2 calculations due to larger computational cost

of the method. Only MOs that were involved in the most important configurations of [22,16]-CAS wave functions were retained in the active space. Thus, the active space in CASPT2 calculations included only the lowest unoccupied and two highest occupied orbitals *i.e.* [4,3]-CAS.

Harmonic vibrational frequencies were calculated for all optimized geometries. For methods for which analytical second derivatives were not implemented, frequencies were calculated using finite differences of energy. Due to the lack of ECP support in the program code, vibrational frequencies for tellurium compounds were not calculated at the [22,16]-CAS level of theory. The  $^{77}\text{Se}$  nuclear magnetic shielding tensors were calculated for cyclic chalcogen cations  $\text{S}_x\text{Se}_{4-x}^{2+}$  ( $x = 0-3$ ) using the GIAO ansatz<sup>38</sup> and BPW91 or B3PW91 density functionals, as well as the [22,16]-CAS method. All structures were fully optimized at the corresponding level of theory prior to the NMR calculations. Dimethylselenide  $\text{Me}_2\text{Se}$  was used as a reference for  $^{77}\text{Se}$  NMR chemical shift.

All calculations were carried out using Gaussian 98,<sup>39</sup> Dalton 1.2.1,<sup>40</sup> and Molpro 2002.6<sup>41</sup> sets of programs. gOpenMol<sup>42,43</sup> was used in the visualization of the molecular orbitals.

## Results and Discussion

**Geometries.** Table 1 shows the optimized metric parameters of  $\text{E}_2\text{N}_2$  and  $\text{E}_4^{2+}$  calculated at different levels of theory along with the corresponding experimental values. The experimental data for  $\text{S}_2\text{N}_2$  is taken from Mikluski *et al.*<sup>1,2</sup> The Se–N bond length is an



average value of the Se–N bond lengths in a complex  $[\text{Pd}_2(\mu\text{-Se}_2\text{N}_2)\text{Cl}_6]^{2-}$ <sup>44</sup> in which the bridging  $\text{Se}_2\text{N}_2$  ligand shows  $D_{2h}$  symmetry.

The experimental bond lengths for  $\text{S}_4^{2+}$  and  $\text{Te}_4^{2+}$  are also average values calculated from the structural parameters of corresponding cations in different salts in which they show a slightly deformed  $D_{4h}$  symmetry.<sup>18</sup> In the case of  $\text{Se}_4^{2+}$ , the experimental bond length is taken from  $\text{Se}_4[\text{Bi}_4\text{Cl}_{14}]$ , since it is the only known example of an  $\text{E}_4^{2+}$  cation with an exact square-planar  $D_{4h}$  symmetry in the solid state.<sup>45</sup>

Considering the general performance associated with the different theoretical methods, the values in Table 1 show no distinct anomalies. Therefore, no visible indication of the extraordinary electronic nature of these molecules is evident from the calculated geometrical parameters alone. In the case of  $\text{E}_2\text{N}_2$  molecules, RHF clearly predicts too short bonds, whereas MP2 overestimates them by nearly the same amount. Overestimation of the bond lengths is also evident for BPW91, which predicts geometrical parameters comparable to MP2. Both coupled cluster methods give significantly better agreement with the experimental values. Multiconfigurational CAS method predicts slightly too long bond lengths but the inclusion of dynamic electron correlation via perturbation theory, CASPT2, gives a nearly perfect match with both experimental values. Equally good performance is also noted for the hybrid functional B3PW91 which predicts good geometrical parameters only at a fraction of the computational cost of CCSD(T) or CASPT2.

For the  $\text{E}_4^{2+}$  cations, RHF seems to predict bond lengths closest to the experimental values. All other methods give bond lengths slightly longer than the experimental ones.

This extremely good performance of RHF is however purely accidental. The systematic inconsistency between the experimental and high level theoretical bond parameters probably comes from the fact that no theoretical calculations take into account the effects caused by anion-cation interactions and crystallographic packing. These interactions to the molecular geometry should be minimal for the crystal of  $\text{Se}_4^{2+}$  in which the cation has a ideal  $D_{4h}$  symmetry. The best match between experimental data and post RHF calculations is indeed obtained in the case of  $\text{Se}_4^{2+}$ .

**Molecular Orbital Analysis of Bonding in  $\text{E}_2\text{N}_2$  and  $\text{E}_4^{2+}$ .** The RHF/cc-pVTZ valence molecular orbitals of optimized  $\text{S}_2\text{N}_2$  and  $\text{S}_4^{2+}$  are shown in Figure 1. An in-depth description of MOs is done only for  $\text{S}_2\text{N}_2$  and  $\text{S}_4^{2+}$  since the valence MO diagrams for the corresponding selenium and tellurium compounds are essentially similar to those of the sulfur compounds.

In the MO picture, the valence orbitals of  $\text{S}_2\text{N}_2$  ( $D_{2h}$ ) can be classified as follows. The  $\sigma$ -bonding framework in the molecule contains the MOs  $5a_g$ ,  $3b_{3u}$ ,  $4b_{2u}$  and  $2b_{1g}$ . Orbitals  $6a_g$ ,  $7a_g$ ,  $4b_{3u}$  and  $5b_{2u}$  are also  $\sigma$  MOs and although some of them show bonding character inside the ring they can all be regarded as primarily nonbonding combinations of s,  $p_x$  and  $p_y$  orbitals of both nitrogen and sulfur. The four  $p_z$  orbitals of sulfur and nitrogen make one bonding  $\pi$  MO  $2b_{1u}$ , two nonbonding MOs  $b_{2g}$  and  $2b_{3g}$ , and one antibonding MO  $3b_{1u}$ . The two nonbonding orbitals are the highest occupied MOs with nearly equal energies and the antibonding MO  $3b_{1u}$  is the lowest unoccupied orbital. There are four bonding  $\sigma$  MOs in total, which qualitatively make four  $\sigma$ -bonds. In

addition, the bonding  $2b_{1u}$  orbital forms one four-center two-electron  $\pi$ -bond. The total bond order for each individual bond is therefore 1.25 which is slightly less than what could be concluded from the experimental bond length 1.654 Å alone.<sup>1,2,46</sup>

The MO description of  $S_4^{2+}$  follows closely that of  $S_2N_2$ . Due to additional symmetry in the cation ( $D_{4h}$ ) there are now several degenerate sets of orbitals. The  $\sigma$ -bonding framework is formed by MOs  $4a_{1g}$ ,  $9e_u$ ,  $10e_u$  and  $2b_{2g}$ . The MOs  $4b_{1g}$ ,  $5a_{1g}$ ,  $11e_u$  and  $12e_u$  are nonbonding  $\sigma$  orbitals and MOs  $2a_{2u}$ ,  $3e_g$ ,  $4e_g$  and  $2b_{2u}$  are the  $\pi$  bonding, nonbonding and antibonding combinations of  $p_z$  orbitals, respectively. Again the theoretical bond order is 1.25 which matches well with the average of experimental S–S bond lengths in  $S_4^{2+}$  cations, 2.00 Å.<sup>14,46</sup>

In the MO picture the electronic structures of both  $E_2N_2$  and  $E_4^{2+}$  look very similar and show similarities with the delocalized model **1**.

**The Singlet Diradical Nature of  $E_2N_2$  and  $E_4^{2+}$ .** In an SCF calculation, the variational procedure ensures that all converged solutions are stationary points in the energy hypersurface. This however does not guarantee that the solutions correspond to either local or global energy minima. To ensure that a solution is a true minimum, the second derivatives of the energy with respect to MO coefficients should also be calculated *i.e.* the stability of the SCF solution should be checked. Although the stability test is seldom done in practice, it is a useful and cost-efficient method to ensure that the chosen approach is flexible enough to give even a qualitatively correct description of the system.

To gain more insight in the electronic structures of  $E_2N_2$  and  $E_4^{2+}$ , the stabilities of RHF, BPW91 and B3PW91 SCF solutions in the optimized geometries were tested by relaxing various symmetry constraints. All RHF solutions were found to contain a negative eigenvalue(s) in the stability matrix, thereby indicating that they do not represent true minima.<sup>48</sup> For all  $E_2N_2$  molecules the negative eigenvalue exists in  $B_{3u}$  symmetry and the  $b_{2g} \rightarrow b_{1u}$  excitation dominates in the corresponding eigenvector. Two negative eigenvalues are observed for  $E_4^{2+}$  cations. Both values exist in the  $E_u$  symmetry subproblem and the two  $e_g \rightarrow b_{2u}$  excitations dominate the corresponding eigenvectors. For  $E_2N_2$  the excitation corresponds to the HOMO-1  $\rightarrow$  LUMO transition and for  $E_4^{2+}$  to two different HOMO  $\rightarrow$  LUMO transitions. This implies that the UHF type wave functions generated by mixing various RHF MOs would yield symmetry-broken solutions that have a lower energy for all molecules.

Contrary to the RHF SCF case, no internal instabilities were detected for BPW91 or B3PW91 solutions. However, for both density functionals the smallest eigenvalue(s) in the stability matrixes exists in the  $B_{3u}$  and  $E_u$  symmetries and show magnitudes less than 0.1 a.u.. The enhanced stability of the DFT solutions comes mainly from the fact that in the DFT formalism of electronic structure theory, electron correlation is included in the description, and the electron density, not the wave function, plays the key role. Although the wave function itself might be multideterminantal in character, the total electron density can still be adequately expressed as a single Slater determinant. This is most evident in the case of ozone for which nearly all traditional RHF based *ab initio* methods predict erroneous properties even though reasonable results can be obtained with all available density functionals.<sup>50</sup>

All RHF SCF solutions were further optimized in the symmetry-broken UHF framework. A subsequent stability analysis proved that the resulting symmetry-broken wave functions represent true minima. Since a singlet UHF solution can be found at lower energy for each  $E_2N_2$  and  $E_4^{2+}$ , all molecules are singlet diradicals in nature and the corresponding RHF solutions do not correctly describe their ground states.<sup>51</sup> A detailed inspection of properties of the symmetry-broken UHF wave functions gives a first-order approximation of the origin of the diradical character.

The negative eigenvalue in the stability matrix of all  $E_2N_2$  molecules corresponds to HOMO-1  $\rightarrow$  LUMO transition which implies that they are the MOs most altered in the broken symmetry approach. Their mixing produces four one-electron orbitals whose spatial forms are depicted for  $S_2N_2$  in Figure 2. Orbitals  $\pi_\alpha$  and  $\pi_\beta$  correspond to the RHF MO  $b_{2g}$  and orbitals  $\pi_\alpha^*$  and  $\pi_\beta^*$  to the MO  $3b_{1u}$ . As evident from Figure 2, the symmetry-broken UHF wave function has a  $C_{2v}$  symmetry and includes spin polarization with one electron localized in each nitrogen atom. Since the symmetry-broken UHF wave function is a single Slater determinant, it cannot contain a solution where the spins of electrons in orbitals  $\pi_\alpha$  and  $\pi_\beta$  are reversed. Therefore the use of broken-symmetry formalism leads to nonzero total atomic spin densities for nitrogen atoms. Although this is somewhat unphysical in nature, the symmetry-broken wave function addresses the diradical character in  $E_2N_2$  molecules to nitrogen rather than to sulfur atoms. In fact, if the diradical character were addressable to sulfur atoms, the negative eigenvalue in the stability matrix would then correspond to HOMO  $\rightarrow$  LUMO transition. This is clearly not the case, since all eigenvalues in the  $B_{2u}$  symmetry remain positive throughout the stability analysis.

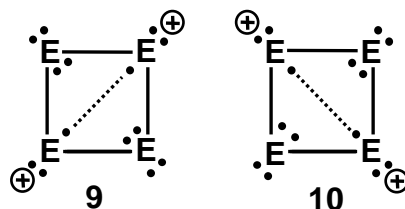
In the case of  $E_4^{2+}$  cations the situation is somewhat more complex. Since the highest occupied orbitals are the two degenerate MOs of  $e_g$  symmetry, there are now two eigenvectors associated with the negative eigenvalues corresponding to the two possible HOMO  $\rightarrow$  LUMO transitions. This means that the symmetry-broken UHF solution can be made by mixing either one of the HOMOs with the LUMO. Hence, the symmetry of the wave function can be broken with respect to two different  $C_2$  axes in the cation. Although both solutions are equal in energy, a single Slater-type wave function can only represent one of them. The resulting symmetry-broken solution therefore resembles that of  $E_2N_2$  with unpaired electrons residing on two chalcogen atoms in the opposite corners of the square planar ring.

**Multiconfigurational Treatment of  $E_2N_2$  and  $E_4^{2+}$ .** The use of a symmetry-broken UHF wave function provides only a qualitatively correct picture of the radical character in  $E_2N_2$  and  $E_4^{2+}$ . A proper *ab initio* treatment of static electron correlation involves the use of a multiconfigurational description. The results from the stability analysis indicate that at least two configurations,  $\Phi_1 = \dots(b_{3u})^2(b_{2g})^2(b_{3g})^2$  and  $\Phi_2 = \dots(b_{3u})^2(b_{2g})^0(b_{3g})^2(b_{1u})^2$  are needed in order to describe adequately the electronic structures of the  $E_2N_2$  molecules. In the case of  $E_4^{2+}$  cations, three configurations are needed due to additional symmetry,  $\Theta_1 = \dots(e_u)^2(e_g)^2(e_g)^2$ ,  $\Theta_2 = \dots(e_u)^2(e_g)^2(e_g)^0(b_{2u})^2$  and  $\Theta_3 = \dots(e_u)^2(e_g)^0(e_g)^2(b_{2u})^2$ .<sup>53</sup>

In order to quantify the radical character of  $E_2N_2$  and  $E_4^{2+}$ , the geometries of all molecules were re-optimized with the [22,16]-CAS method. The most important CI-vector coefficients of the CAS wave functions are presented in Table 2. A useful index

for the diradical character of a molecule can be derived from the multiconfigurational SCF method as the ratio of the squares of the CI coefficients for the ground state ( $C_1$ ) and the doubly excited state ( $C_2$ ).<sup>56</sup> For a “perfect diradical”, one would have both configurations equally populated, so  $C_1 = C_2 = 1/\sqrt{2}$  and the diradical character can then conveniently be defined as  $\frac{C_2^2}{(1/\sqrt{2})^2} \times 100\% = 2C_2^2 \times 100\%$ . In the case of present molecules, the weakest diradical  $S_2N_2$  has 6 % of diradical character and the strongest  $Te_2N_2$  has nearly 10 % of diradical character.<sup>57</sup> For comparison, the corresponding value calculated from the [18,12]-CAS/cc-pVTZ wave function of ozone is 26 %. Since the electronic structure of  $E_4^{2+}$  cations involves three important configurations, the same quantifying index can not be applied readily. However, the radical character in these cations increases in the same series,  $S < Se < Te$ .

The [22,16]-CAS wave function of  $S_2N_2$  can be analyzed in terms of Lewis-type valence bond structures **3** and **4** which gives a more accessible description of bonding in  $E_2N_2$ . A simplified analysis using idealized  $p_z$  orbitals shows that the structure **3** has a 34% weight in the CAS wave function whereas the weight for the structure **4** is only 14%. The structure **4** has a smaller weight since the configuration  $\Phi_3 = \dots(b_{3u})^2(b_{2g})^2(b_{3g})^0(b_{1u})^2$ , which corresponds to the excitation of two electrons from HOMO to LUMO, makes only a minor contribution to the CAS wave function. In the case of  $E_4^{2+}$  cations, the two symmetry related diradical structures **9** and **10** have equal weights in the CAS wave function.



The results from the analysis of MO wave functions support the earlier conclusions of Skrezenek and Harcourt,<sup>11,22</sup> Harcourt *et al.*<sup>14</sup> and Fujimoto *et al.*<sup>15</sup> that the best single Lewis-type VB structure for  $E_2N_2$  molecules is the structure **3**. The relative importance of the different VB structures seems however to be highly dependent on the level of theory as seen by the diverging opinions in chemical literature.<sup>9-17,22</sup> Since different but equally valid theoretical approaches come to dissimilar conclusions, it is perhaps best not to give unjustified significance to any particular model.<sup>58</sup> After all, none of the proposed bonding models is by itself sufficient for a complete description of the system. This is especially true for different molecular geometries for which the relative weights of the three models **2-2'**, **3** and **4** can vary greatly. Common to all theoretical analyses is that they demonstrate that the simple view of cyclic electron delocalization as described by structure **1** is clearly an oversimplification of bonding in  $E_2N_2$  and  $E_4^{2+}$  and suffices only to disguise the extraordinary features of these systems.

**Spectroscopic Properties.** A proper treatment of static electron correlation is especially critical when predicting first- and second-order molecular properties. A well-known example is the prediction of harmonic vibrational frequencies for ozone. As the nuclear



motion changes the relative weights of the ionic and diradical structures, the calculation of the vibrational frequencies is especially sensitive to the quality of the wave function.<sup>50</sup> Multiconfigurational methods are reported to give good results only if adequate configuration spaces are used, and it has been stated that the inclusion of large number of diverse configurations in the reference function is far more important than the accurate description of dynamic correlation with MRCI.<sup>59</sup> By virtue of the infinite-order feature of the coupled cluster and quadratic configuration interaction methods, they have also the ability to handle moderate amounts of static electron correlation, and have therefore been successfully used in the prediction of vibrational frequencies of computationally difficult cases.<sup>60</sup>

The calculated harmonic vibrational frequencies for  $E_2N_2$  and  $E_4^{2+}$  are listed in Table 3. For some normal modes, the calculated RHF and MP2 frequencies of  $S_2N_2$  show differences of several hundred wave numbers and are generally far off the corresponding experimental values. Although experimental data is not available for  $Se_2N_2$  or  $Te_2N_2$ , both RHF and MP2 show similar performance when different theoretical methods are compared. Due to the inherent radical nature of the molecules, single determinant RHF and MP2 methods are clearly incapable of describing consistently all normal modes of  $E_2N_2$ . Although the [22,16]-CAS gives a more balanced description, calculated frequencies are still slightly underestimated due to the neglect of dynamic electron correlation effects. This is corrected by CASPT2, whose good performance shows that the smaller active space is adequate to describe the static part of the electron correlation, and that the perturbation method is sufficient for the dynamic part. Coupled cluster methods are also less sensitive to the quality of the RHF wave function and model the

diradical nature quite effectively. Both CCSD and CCSD(T) give an uniform description of all normal modes and predict frequencies that are in better agreement with the experimental values. Both applied density functionals also perform well.

For  $E_4^{2+}$  cations, the failure of RHF and MP2 is not as severe as in the case of  $E_2N_2$  since reasonable estimates of vibrational frequencies are obtained with all theoretical methods. This is most likely due to cancellation of errors which arises from the higher molecular symmetry. Nuclear motion in  $E_4^{2+}$  changes primarily the relative weights of configurations  $\Theta_2$  and  $\Theta_3$ , whereas the weight of the RHF configuration  $\Theta_1$  stays virtually unchanged. This partially cancels the effect of diradical structures and the RHF wave function becomes an equally good approximation for the different nuclear geometries. Since the E–E bond lengths in  $E_4^{2+}$  cations were generally predicted longer than the corresponding experimental values, nearly all calculated frequencies are slightly underestimated. A correct ordering of the normal modes is predicted with every method. The B3PW91, coupled cluster and CASPT2 show the best performance.

Although the vibrational frequencies of the  $E_4^{2+}$  cations are well reproduced even at RHF and MP2 levels of theory, several authors have drawn attention to the apparent difficulties in the calculation of  $^{77}\text{Se}$  NMR chemical shifts for  $\text{Se}_4^{2+}$ .<sup>24,63</sup> Recently reported GIAO RHF/6-41+G\*//MP2/6-41G\* and MP2/6-41+G\*//MP2/6-41G\*  $^{77}\text{Se}$  NMR chemical shifts for  $\text{Se}_4^{2+}$  are 3821 and 154 ppm, respectively.<sup>24</sup> Comparison with the experimental value of 1936 ppm<sup>64</sup> shows that both methods completely fail to describe the system, since deviations from experiment are roughly  $\pm 2000$  ppm. Clearly the  $D_{4h}$  symmetry of the cation does not allow any error compensation, when the derivatives of

the energy are calculated with respect to nuclear spin and external magnetic field, and multiconfigurational methods would be needed if better performance is sought with *ab initio* methods. By contrast to the unsatisfactory performance of RHF and MP2, Schreckenbach *et al.*<sup>63</sup> have reported a GIAO DFT study in which they obtained a chemical shift of 1834 ppm using the BP86 functional. This value compares much better with the experimental chemical shift.

In addition to  $\text{Se}_4^{2+}$ , several other selenium containing heterochalcogen cationic rings with the composition  $\text{S}_x\text{Se}_{4-x}^{2+}$  ( $x = 1-3$ ) have been reported by Collins *et al.*<sup>65</sup> These species have been identified using  $^{77}\text{Se}$  NMR spectroscopy. The spectrum exhibits several resonances very close to the  $\text{Se}_4^{2+}$  chemical shift. Two resonances at 1939 and 2032 ppm were observed in a ratio 1:2 with a satellite doublet around each of them. These resonances were consequently assigned to the  $\text{SSe}_3^{2+}$  cation. The assignment of the three other resonances at 1890, 1954 and 2023 ppm was however done more tentatively. Upon increasing the S:Se ratio of the reaction mixture, the resonance peak at 1954 ppm was found to increase in intensity and was therefore assigned to the most sulfur-rich cation  $\text{S}_3\text{Se}^{2+}$ . The two peaks at 1890 and 2023 ppm were assigned to *trans*- and *cis*- $\text{S}_2\text{Se}_2^{2+}$  cations, respectively, based on their relative intensities and NMR data for related  $\text{Te}_2\text{Se}_2^{2+}$  species.<sup>65</sup> Although all assignments are mutually consistent with the different selenium environments in these cations, no experimental or theoretical proof has yet been presented that would confirm the interpretation of the  $^{77}\text{Se}$  NMR spectrum.

To test the validity of the tentative NMR spectral assignment and to compare the performance of various theoretical methods in prediction of chemical shifts for cationic chalcogen rings, we have now calculated the chemical shifts of  $\text{Se}_4^{2+}$  and heterochalcogen

cationic rings  $S_xSe_{4-x}^{2+}$  with GIAO-CAS and GIAO-DFT methods using BPW91 and B3PW91 functionals.<sup>66</sup> The calculated chemical shifts are listed in Table 4 along with the experimentally assigned values. Since the static electron correlation is described in the [22,16]-CAS wave function, it clearly outperforms both RHF and MP2 and predicts  $^{77}\text{Se}$  chemical shifts of only 50 ppm in error for both  $\text{Se}_4^{2+}$  and  $\text{SSe}_3^{2+}$ . The pure density functional BPW91 yields an even closer agreement with an error of less than 20 ppm. The calculated BPW91 chemical shift for  $\text{Se}_4^{2+}$ , 1941 ppm, is evidently the best reported match to date. The hybrid functional B3PW91 performs worst in the current case and greatly overestimates chemical shifts of all cations. It also predicts, however, a correct order for the chemical shifts. The good performance of CAS and BPW91 with the two  $\text{Se}_4^{2+}$  and  $\text{SSe}_3^{2+}$  cations that show unambiguous assignments strongly suggests that the calculated chemical shifts for the three other cations can also be considered reliable. The calculated chemical shifts for  $\text{S}_3\text{Se}^{2+}$ , *cis*- $\text{S}_2\text{Se}_2^{2+}$  and *trans*- $\text{S}_2\text{Se}_2^{2+}$  cations support the experimental assignment.

A significantly better agreement between the experimental and B3PW91 chemical shifts can be obtained if one uses the experimental chemical shift of  $\text{Se}_4^{2+}$  as a reference (see Table 4). This suggests that a nearly constant error is made when chemical shifts are calculated using the hybrid functional instead of the pure GGA one. The error presumably comes from the use of constant fraction of the RHF exact exchange in the B3PW91 functional, which in the current case leads to unphysical delocalized exchange-correlation hole functions.<sup>68</sup> More local treatment of the exchange is a much better approximation of the true situation and the pure GGA functional therefore performs

better. The better performance of pure DFT functionals over hybrid functionals has also been reported in the theoretical calculation of  $^{17}\text{O}$  chemical shifts of ozone.<sup>69</sup>

The agreement between experimental and CAS chemical shifts can also be improved by using  $\text{Se}_4^{2+}$  as a reference chemical shift. The main source of error in this case is most likely the lack of dynamic electron correlation in the CAS formalism.

As the values in Table 4 show, either pure density functionals or multiconfigurational *ab initio* methods are needed in order to calculate the  $^{77}\text{Se}$  chemical shifts of tetraatomic chalcogen rings with sufficient accuracy. In this respect, the recently reported good performance of RHF in the prediction of the  $^{31}\text{P}$  NMR chemical shift of square-planar  $\text{P}_4^{2-}$  anion seems controversial.<sup>7</sup> However, calculations at the [22,16]-CAS level show that for this system the CI coefficient of the RHF wave function is 0.972, which is considerably larger than that in the case of  $\text{Se}_4^{2+}$  (0.890). Therefore, even RHF is able to give a qualitatively correct description of the electronic structure of  $\text{P}_4^{2-}$  and predict the NMR chemical shift with good quantitative accuracy. The weight of the RHF wave function in a multiconfigurational description of other cyclic tetrapnictogen dianions has yet not been determined.

## Conclusions

The electronic structures of square-planar  $6\pi$ -electron rings  $\text{E}_2\text{N}_2$  and  $\text{E}_4^{2+}$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ) were studied using various *ab initio* methods and density functionals. Internal instabilities in the RHF wave functions showed that all molecules have significant singlet diradical

character in their electronic structure. The singlet diradical nature was further confirmed by using both symmetry-broken Hartree-Fock formalism and multiconfigurational CAS method. In addition to the RHF configuration, the CAS wave functions contain significant contributions from HOMO-1  $\rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO doubly excited configurations. Analysis of the S<sub>2</sub>N<sub>2</sub> CAS wave function in terms of different valence bond structures gives largest weight for the singlet diradical Lewis-type VB structure in which the unpaired electrons reside on nitrogen atoms. The relative importance of the different VB structures seems, however, to be highly dependent on the level of theory. The diradical character in E<sub>2</sub>N<sub>2</sub> and E<sub>4</sub><sup>2+</sup> was found to increase in the series S < Se < Te.

The intrinsic diradical nature of E<sub>2</sub>N<sub>2</sub> and E<sub>4</sub><sup>2+</sup> was shown to impose requirements on the theoretical methods used in the calculation of their molecular properties. Single determinant methods are able to predict molecular properties of E<sub>2</sub>N<sub>2</sub> and E<sub>4</sub><sup>2+</sup> only at coupled cluster levels of theory. Multiconfigurational CAS and CASPT2 are theoretically the most rigorous *ab initio* methods available for the treatment of static electron correlation, and they perform very well in the current case. The hybrid density functional B3PW91 outperforms the pure BPW91 functional in prediction of both molecular geometry and vibrational frequencies and produces equally good results as the best performing *ab initio* methods. The extremely good performance of B3PW91 is however contrasted by its failure in the calculation of <sup>77</sup>Se NMR chemical shifts of S<sub>x</sub>Se<sub>4-x</sub><sup>2+</sup> (x = 0-3) cationic rings. The pure density functional BPW91 and CAS perform substantially better and are able to predict the NMR chemical shifts of these computationally very challenging systems with superior accuracy. BPW91 and CAS methods not only show

the best reported performance to date, but also unquestionably confirm the tentative assignment of the experimental NMR spectrum of  $S_xSe_{4-x}^{2+}$  cations.

Although all tetraatomic square-planar  $6\pi$ -electron rings are valence isoelectronic, comparison between the  $P_4^{2-}$  and  $Se_4^{2+}$  CAS wave functions showed that their diradical character can vary greatly. Hence, care should be taken when using theoretical methods to predict molecular properties of any species in this group. For chemical systems such as  $P_4^{2-}$ , even RHF and MP2 are sufficient, but the need of multiconfigurational *ab initio* treatment should be checked in every case. The varying performance of the two different density functionals illustrates that caution should also be exercised when using DFT to study the molecular properties of diradical systems. The detailed investigation of electronic structure becomes especially critical when no experimental data is available for comparison.

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**Supporting Information Available.** A table of total energies is available on the Internet only. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**Table 1.** Optimized Geometries of E<sub>2</sub>N<sub>2</sub> and E<sub>4</sub><sup>2+</sup> (E = S, Se, Te) Calculated with Various Methods Using cc-pVTZ Basis Set

<b>molecule</b>		<b>BPW91</b>	<b>B3PW91</b>	<b>RHF</b>	<b>MP2</b>	<b>CCSD</b>	<b>CCSD(T)</b>	<b>CAS</b>	<b>CASPT2</b>	<b>exptl.</b>
S <sub>2</sub> N <sub>2</sub>	<i>r</i> (SN)	1.675	1.648	1.608	1.677	1.647	1.664	1.679	1.656	1.658 <sup>a</sup>
	∠ SNS	88.7	89.1	90.1	88.2	89.3	89.0	88.9	88.7	90.4 <sup>a</sup>
	∠ NSN	91.3	90.9	89.9	91.8	90.7	91.0	91.1	91.3	89.6 <sup>a</sup>
Se <sub>2</sub> N <sub>2</sub>	<i>r</i> (SeN)	1.828	1.797	1.749	1.841	1.794	1.816	1.832	1.796	1.802 <sup>b</sup>
	∠ SeNSe	90.0	90.5	91.8	88.9	90.7	90.3	90.1	89.7	–
	∠ NSeN	90.0	89.5	88.8	91.1	89.3	89.7	89.9	90.3	–
Te <sub>2</sub> N <sub>2</sub>	<i>r</i> (TeN)	2.007	1.979	1.927	2.035	1.973	1.997	2.017	1.981	–
	∠ TeNTe	91.4	92.0	93.6	89.9	92.3	91.7	91.4	91.1	–
	∠ NTeN	88.6	88.0	86.4	90.1	87.7	88.3	88.6	88.9	–
S <sub>4</sub> <sup>2+</sup>	<i>r</i> (SS)	2.061	2.033	1.992	2.054	2.032	2.051	2.074	2.045	2.00 <sup>c</sup>
Se <sub>4</sub> <sup>2+</sup>	<i>r</i> (SeSe)	2.341	2.310	2.267	2.340	2.315	2.336	2.361	2.312	2.296 <sup>d</sup>
Te <sub>4</sub> <sup>2+</sup>	<i>r</i> (TeTe)	2.708	2.687	2.657	2.707	2.691	2.710	2.748	2.707	2.68 <sup>c</sup>

<sup>a</sup> Refs. 1 and 2. <sup>b</sup> Ref. 44. <sup>c</sup> Ref. 18. <sup>d</sup> Ref. 45.



**Table 2.** CAS CI-vector Coefficients ( $C_i$ ) for  $E_2N_2$  and  $E_4^{2+}$  ( $E = S, Se, Te$ )

<b>molecule</b>	<b><math>C_1</math></b>	<b><math>C_2</math></b>	<b><math>C_3</math></b>
$S_2N_2$	0.925	-0.178	-0.064
$Se_2N_2$	0.908	-0.202	-0.061
$Te_2N_2$	0.898	-0.216	-0.069
$S_4^{2+}$	0.907	-0.142	-0.142
$Se_4^{2+}$	0.890	-0.154	-0.154
$Te_4^{2+}$	0.887	-0.161	-0.161

**Table 3.** Harmonic Vibrational Frequencies for  $E_2N_2$  and  $E_4^{2+}$  Calculated at Different Levels of Theory Using cc-pVTZ Basis Set

molecule	method	$\nu_1(A_g)$	$\nu_2(A_g)$	$\nu_3(B_{1g})$	$\nu_4(B_{1u})$	$\nu_5(B_{2u})$	$\nu_6(B_{3u})$
$S_2N_2$	BPW91	881	605	891	456	645	744
	B3PW91	953	652	945	483	684	815
	RHF	1124	752	1072	545	659	963
	MP2	829	615	874	467	774	788
	CCSD	974	670	962	479	668	834
	CCSD(T)	913	637	917	467	654	785
	CAS	891	620	865	462	604	758
	CASPT2	924	648	914	476	687	790
	exptl. <sup>a</sup>	–	–	–	474	663	795
$Se_2N_2$	BPW91	761	347	726	335	561	605
	B3PW91	825	378	782	353	602	664
	RHF	980	443	894	399	602	787
	MP2	675	350	690	351	675	679
	CCSD	844	393	794	360	596	683
	CCSD(T)	785	369	751	344	578	635
	CAS	764	352	730	334	535	609
	CASPT2	816	393	762	360	590	652
$Te_2N_2$	BPW91	682	256	657	273	551	557
	B3PW91	727	276	702	284	585	600
	RHF	856	315	801	315	598	703
	MP2	569	253	603	295	626	590
	CCSD	739	286	713	289	583	613
	CCSD(T)	687	269	670	277	562	569
	CASPT2	717	289	675	293	520	577

**Table 3.** Continued

<b>molecule</b>	<b>method</b>	<b>v<sub>1</sub>(A<sub>g</sub>)</b>	<b>v<sub>2</sub>(B<sub>1g</sub>)</b>	<b>v<sub>3</sub>(B<sub>2g</sub>)</b>	<b>v<sub>4,5</sub>(E<sub>u</sub>)</b>	<b>v<sub>6</sub>(B<sub>2u</sub>)</b>
S <sub>4</sub> <sup>2+</sup>	BPW91	538	329	582	483	226
	B3PW91	577	356	622	515	237
	RHF	662	435	702	551	260
	MP2	532	326	581	579	232
	CCSD	585	369	627	518	236
	CCSD(T)	551	346	594	496	226
	CAS	524	348	569	472	223
	CASPT2	547	332	597	520	225
	exptl. <sup>b</sup>	587	383	603-590	542	–
Se <sub>4</sub> <sup>2+</sup>	BPW91	300	160	319	277	108
	B3PW91	320	173	340	293	114
	RHF	360	214	381	305	120
	MP2	294	154	315	338	113
	CCSD	323	179	342	292	111
	CCSD(T)	305	167	324	281	107
	CAS	286	168	306	265	105
	CASPT2	294	157	319	286	103
	exptl. <sup>b</sup>	323	184	327-324	302	–
Te <sub>4</sub> <sup>2+</sup>	BPW91	207	96	218	195	64
	B3PW91	217	102	229	203	65
	RHF	237	124	251	209	69
	MP2	207	91	220	225	67
	CCSD	220	106	231	204	66
	CCSD(T)	209	99	221	197	64
	CASPT2	207	92	221	203	62
	exptl. <sup>b</sup>	213	106	~214	187	–

<sup>a</sup> Ref. 61. <sup>b</sup> Ref. 62.

**Table 4.**  $^{77}\text{Se}$  NMR Chemical Shifts Calculated at Different Levels of Theory Using cc-pVTZ Basis Set <sup>a</sup>

<b>molecule</b>	<b>BPW91</b>	<b>B3PW91</b>	<b>[22,16]-CAS</b>	<b>exptl.<sup>b</sup></b>
$\text{Se}_4^{2+}$	1941 [1936]	2120 [1936]	1893 [1936]	1936
$\text{SSe}_3^{2+}$ ( <b>SeSeSe</b> )	1924 [1919]	2087 [1903]	1892 [1935]	1939
$\text{SSe}_3^{2+}$ ( <b>SeSeSe</b> )	2049 [2044]	2229 [2045]	1965 [2008]	2032
<i>cis</i> - $\text{S}_2\text{Se}_2^{2+}$	2042 [2037]	2198 [2014]	1967 [2010]	2023
<i>trans</i> - $\text{S}_2\text{Se}_2^{2+}$	1873 [1868]	2013 [1829]	1858 [1901]	1890
$\text{S}_3\text{Se}^{2+}$	2001 [1996]	2135 [1951]	1941 [1984]	1954

<sup>a</sup> The chemical shifts are reported relative to  $\text{Me}_2\text{Se}$ . Values in square brackets are obtained using the experimental chemical shift of  $\text{Se}_4^{2+}$  as a reference. <sup>b</sup> Ref. 64.

**Figure Captions**

**Figure 1.** RHF/cc-pVTZ valence molecular orbitals of (a)  $S_2N_2$  and (b)  $S_4^{2+}$ .

**Figure 2.** Highest symmetry-broken UHF/cc-pVTZ orbitals of  $S_2N_2$ .

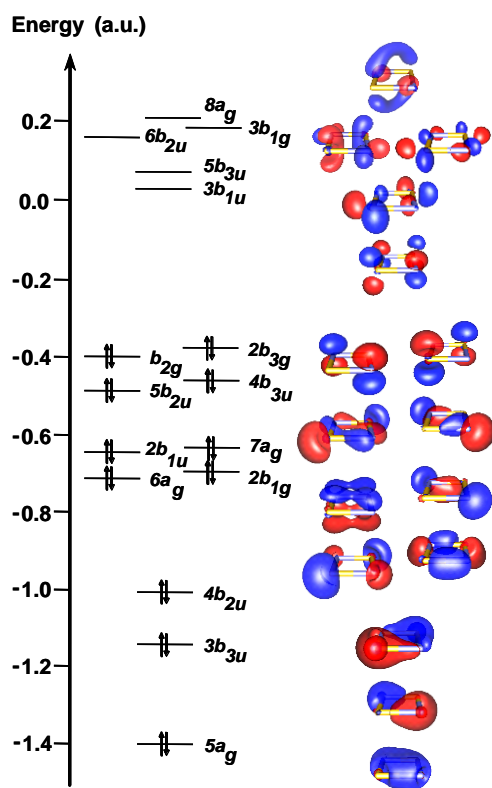


Figure 1(a).

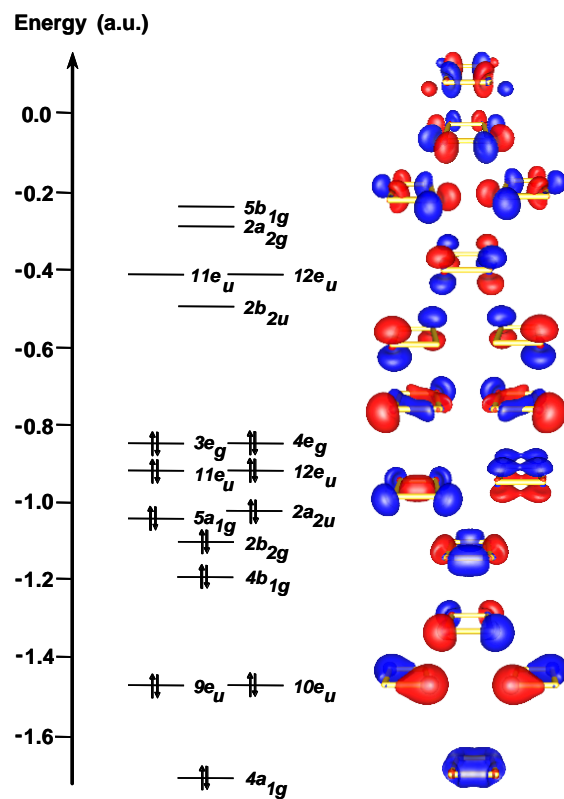


Figure 1(b).

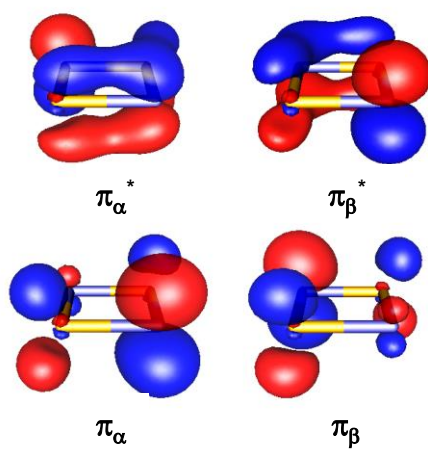


Figure 2.