

# Analysis of the Effect of Spin–Orbit Coupling on the Electronic Structure and Excitation Spectrum of the $\text{Bi}_2^{2-}$ Anion in $(\text{K-crypt})_2\text{Bi}_2$ on the Basis of Relativistic Electronic Structure Calculations

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Received: November 22, 2004

The  $\text{Bi}_2^{2-}$  anions that have been characterized in  $(\text{K-crypt})_2\text{Bi}_2$  are isoelectronic with  $\text{O}_2$  but are diamagnetic and EPR-silent, unlike  $\text{O}_2$ . The UV–vis spectrum measured for  $(\text{K-crypt})_2\text{Bi}_2$  shows two broad absorption peaks located at 2.05 and 2.85 eV, but no absorption at lower energies down to 0.62 eV. To account for these observations, the electronic structures of the isoelectronic diatomic dianions  $\text{Q}_2^{2-}$  ( $\text{Q} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$ ) were compared on the basis of relativistic density functional theory calculations, and the electronic excitations of  $\text{Bi}_2^{2-}$  were analyzed on the basis of relativistic configuration interaction calculations. The extent of spin–orbit coupling, brought about by the relativistic effect, increases steadily in the order  $\text{N} < \text{P} < \text{As} < \text{Sb} < \text{Bi}$  such that the “closed-shell” state is more stable than the “open-shell” state for  $\text{Bi}_2^{2-}$ , while the opposite is the case for  $\text{N}_2^{2-}$ ,  $\text{P}_2^{2-}$ ,  $\text{As}_2^{2-}$ , and  $\text{Sb}_2^{2-}$ . The nature of the electronic excitations of  $\text{Bi}_2^{2-}$  was assigned and discussed from the viewpoint of molecular orbitals in the absence of spin–orbit coupling.

## 1. Introduction

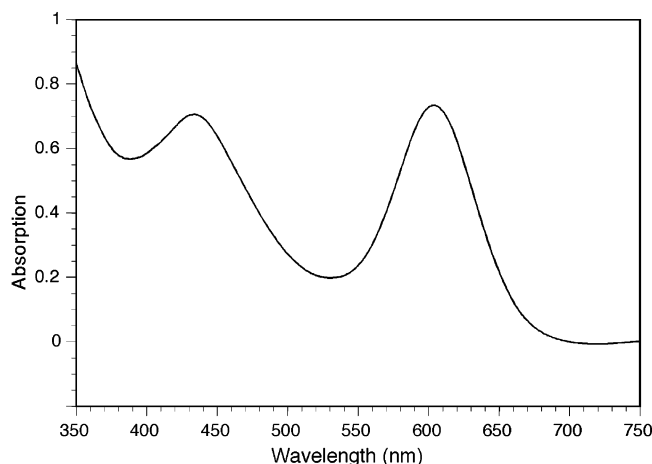
Molecular orbital (MO) pictures provide a useful framework of thinking about the electronic structures of a variety of molecules. Nevertheless, they often become inadequate for molecules made up of heavy elements. For example, the paramagnetism of  $\text{O}_2$  is readily explained in terms of its triplet ground state, since there are only two electrons to fill its doubly degenerate HOMO (i.e., the pi-antibonding orbitals,  $\pi^*$ ). By analogy, a dianion  $\text{Bi}_2^{2-}$  that is isoelectronic with  $\text{O}_2$  would have been expected to possess a similar electronic structure and exhibit paramagnetism. First principles electronic structure calculations using relativistic effective-core potentials confirmed this expectation.<sup>1</sup> However, the  $\text{Bi}_2^{2-}$  anions characterized in  $(\text{K-crypt})_2\text{Bi}_2$  show diamagnetic properties (here crypt refers to 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane).  $(\text{K-crypt})_2\text{Bi}_2$  exhibits negative and temperature-independent magnetic susceptibility in the range 10–300 K and is EPR-silent at room and liquid nitrogen temperatures.<sup>1,2</sup> Therefore,

unlike paramagnetic  $\text{O}_2$ , the  $\text{Bi}_2^{2-}$  anions of  $(\text{K-crypt})_2\text{Bi}_2$  behave as if their ground state is “singlet” with no unpaired electrons. It is well known that relativistic effects in heavy atoms lead to a very strong spin–orbit coupling and can exert a profound influence on the chemical bonding of compounds involving such elements.<sup>3–21</sup> Indeed, it has been pointed out that paramagnetic effects can be largely suppressed when spin–orbit coupling becomes large compared to thermal energy.<sup>4</sup> The ground state of neutral diatomic molecule  $\text{Bi}_2$  has been examined by electronic structure calculations including spin–orbit coupling within Hartree–Fock<sup>14–16</sup> and DFT schemes.<sup>17–21</sup> In describing the valence electronic structure of a diatomic species such as  $\text{Bi}_2^{2-}$ , it is necessary to consider spin–orbit coupling explicitly for valence electrons. Furthermore, the UV–vis spectrum determined for  $(\text{K-crypt})_2\text{Bi}_2$  in ethylenediamine solution at room temperature shows two broad absorption peaks located at 2.05 and 2.85 eV, but no absorption peaks at lower energies down to 0.62 eV (see below). The electronic excitations responsible for this observation are not well understood.

In the present work we examine how the increase in spin–orbit coupling affects the valence electronic structures of the isoelectronic diatomic dianions  $\text{Q}_2^{2-}$  ( $\text{Q} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$ ) on

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**Figure 1.** UV-vis spectrum of (K-crypt)<sub>2</sub>Bi<sub>2</sub> in ethylenediamine at room temperature. The peaks are located at 435 nm (2.85 eV) and 605 nm (2.05 eV).

the basis of relativistic density functional theory (DFT) calculations, analyze the electronic excitations of Bi<sub>2</sub><sup>2-</sup> on the basis of relativistic configuration interaction (CI) calculations and interpret the UV-vis spectrum determined for (K-crypt)<sub>2</sub>Bi<sub>2</sub> in ethylenediamine solution. Our work is organized as follows. Section 2 briefly summarizes the synthesis and physical properties of (K-crypt)<sub>2</sub>Bi<sub>2</sub>, and section 3 our relativistic DFT and CI calculations for an isolated Bi<sub>2</sub><sup>2-</sup> anion. The nature of the ground state of Bi<sub>2</sub><sup>2-</sup> is discussed in section 4 on the basis of the relativistic DFT calculations. In section 5 we discuss on the basis of the relativistic DFT calculations the nature of the one-electron orbitals of Bi<sub>2</sub><sup>2-</sup> as well as the electronic excitations expected for Bi<sub>2</sub><sup>2-</sup>. In section 6 we describe results of our relativistic CI calculations for Bi<sub>2</sub><sup>2-</sup>, assign the electronic excitation spectrum of (K-crypt)<sub>2</sub>Bi<sub>2</sub>, and discuss briefly why the present relativistic DFT calculations are inadequate for describing electronic excitations. Our main conclusions are summarized in section 7.

## 2. Experimental Section

(K-crypt)<sub>2</sub>Bi<sub>2</sub> was synthesized from the precursor K<sub>3</sub>Bi<sub>2</sub> as described before.<sup>1,2</sup> Its UV-vis spectrum (Figure 1) in ethylenediamine was taken at room temperature on a Perkin-Elmer UV/VIS/NIR spectrometer Lambda 19 in the range 250–2000 nm (i.e., 4.96–0.62 eV). It shows two peaks at 435 and 605 nm (Figure 1) and no absorption peaks at lower energies down to 0.62 eV. At energies below 0.62 eV, the spectrum is very complex due to the presence of solvent molecules, ethylenediamine, and large organic molecules such as 2,2,2-crypt. This makes it impossible to draw any meaningful conclusion about the electronic excitations of the Bi<sub>2</sub><sup>2-</sup> anion below 0.62 eV.

The magnetization of 11 mg of (K-crypt)<sub>2</sub>Bi<sub>2</sub> was measured at a field of 3T over the range 10–300 K on a Quantum Design MPMS SQUID magnetometer. The results show negative and temperature independent magnetic susceptibility varying in the range of (–1.3 to –2.7) × 10<sup>–4</sup> emu/mol. The measurements were carried out in a special holder designed for air-sensitive compounds where the sample is confined between two quartz rods that are tightly fitted in a sealed quartz tube. EPR measurements of ethylenediamine solutions of the compound were carried out on a Varian EC-1365E spectrometer at both room and liquid-nitrogen temperatures and showed that the compound is EPR silent. All operations were carried out in a nitrogen-filled glovebox with moisture level below 1 ppm.

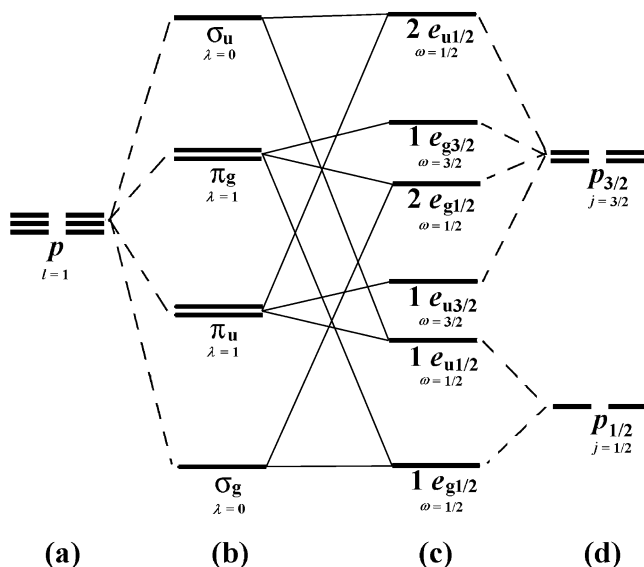
## 3. Relativistic Electronic Structure Computations

**3.1. DFT Calculations.** The Beijing density function program<sup>22,23</sup> was used for our four-component fully relativistic DFT calculations for Q<sub>2</sub><sup>2-</sup> (Q = N, P, As, Sb, Bi). The 2s/2p orbitals of N, the 3s/3p orbitals of P, the 4s/4p/3d orbitals of As, the 5s/5p/4d orbitals of Sb, and the 6s/6p/5d orbitals of Bi are considered as valence shells, while other orbitals are frozen in the core. The Becke88<sup>24</sup> and Perdew86<sup>25</sup> functionals were selected as the exchange-correlation functionals. For the calculations of the orbital energies of Q<sub>2</sub><sup>2-</sup>, the Q–Q bond lengths of Q<sub>2</sub><sup>2-</sup> were optimized by minimizing their total electronic energies. For the calculations of the excitation energies of Bi<sub>2</sub><sup>2-</sup>, the Bi–Bi bond length was set to the experimental value (i.e., 2.8377 Å) found for (K-crypt)<sub>2</sub>Bi<sub>2</sub>. The Kramers unrestricted scheme was used to treat the open-shell systems.<sup>23</sup>

**3.2. CI Calculations.** To analyze the UV-vis spectrum of (K-crypt)<sub>2</sub>Bi<sub>2</sub> in more detail, a series of relativistic CI calculations were carried out for Bi<sub>2</sub><sup>2-</sup>. For this purpose, a relativistic effective core potential of Wildman et al.<sup>26</sup> was employed to describe the inner-shell electrons of the bismuth atom, and the 5d, 6s, and 6p electrons were treated as valence electrons. We employed the (6s6p6d1f)/[4s4p4d1f] atomic orbital basis set for Bi,<sup>26</sup> which was augmented by one more f function with an optimized exponent of 0.12.

In our relativistic CI calculations two different computational methods were adopted. In the first approach, a self-consistent field (SCF) calculation was combined with a large scale CI to obtain highly correlated  $\Lambda$ -S wave functions in the absence of spin-orbit coupling. As a next step a spin-orbit matrix for a relatively small number of  $\Lambda$ -S states ( $\leq 100$ ) was diagonalized to obtain energies and wave functions for the final  $\Omega$  states. Thus, this approach is characterized as  $\Lambda$ -S contracted spin-orbit CI (LSC-SO-CI) calculations. In the second approach, we treated the electrostatic and spin-orbit interactions simultaneously without first obtaining correlated  $\Lambda$ -S functions, so that all selected configurations of various space and spin symmetries form the basis for the multireference spin-orbit CI (MR-SO-CI) calculations. The MR-SO-CI method is computationally much more demanding than the LSC-SO-CI method. More details for both methods were described elsewhere.<sup>27,28</sup>

The standard multireference single- and double-excitation CI approach<sup>29</sup> was used to obtain the  $\Lambda$ -S electronic energies, wave functions and transition moments. The calculations were carried out employing the Table Direct-CI<sup>30,31</sup> version of the MRD-CI package including configuration selection and perturbative corrections. The MO's that are predominantly occupied by the 5d<sup>10</sup> electrons were frozen at the CI stage of the calculations. A selection threshold of  $T = 0.3 \times 10^{-6} E_h$  was used in the LSC-SO-CI and MR-SO-CI methods. In the LSC-SO-CI scheme, eight to twelve lowest roots were calculated for each of all possible singlet and triplet irreducible representations, and typical sizes of the selected CI spaces were 1.8–3.2 × 10<sup>5</sup> in each case. Quintet states are less important for the low-energy Bi<sub>2</sub><sup>2-</sup> spectrum, and only two to four roots were obtained for them, with CI spaces varying from 80 000 to 120 000 selected configurations, depending on symmetry. The importance of higher excitations in the LSC-SO-CI treatment were assessed by applying the generalized multireference analogue of the Davidson correction<sup>32,33</sup> to the extrapolated  $T = 0$  energies of each root. There is a good overall agreement between the data computed in the LSC-SO-CI and MR-SO-CI approaches (see section 6). However, in the MR-SO-CI method, all configurations that have strong coupling with the states of



**Figure 2.** One-electron energy levels of a homonuclear diatomic dication  $Q_2^{2-}$  ( $Q = N, P, As, Sb, Bi$ ) derived primarily from the valence p orbitals of Q: (a) The p orbitals of two Q atoms without considering spin–orbit coupling, (b) the molecular orbitals of  $Q_2^{2-}$  formed from the p orbitals without considering spin–orbit coupling, (c) the relativistic dimer levels of  $Q_2^{2-}$  formed from the p orbitals under spin–orbit coupling, and (d) the p orbitals of two Q atoms under spin–orbit coupling. The one-electron energy levels of  $Q_2^{2-}$  derived mainly from the valence s orbitals of Q, which lie below the p-block levels described above, are not shown, and the slight mixing between the s- and p-block levels is neglected for simplicity.

interest can be directly included in the secular matrix to be diagonalized. The latter is particularly important for systems containing very heavy atoms such as Bi. This suggests that the MR–SO–CI approach would be more accurate in the present case.

#### 4. Nature of the Electronic Ground State

**4.1. Atomic and Dimer Orbitals.** When spin–orbit coupling is neglected, all the p orbitals of each atom are degenerate (Figure 2a). (For simplicity of our discussion, we describe only the valence p orbitals of each atom Q.) Once a diatomic molecule is formed, the spherical symmetry of the individual atoms is lowered to cylindrical symmetry, and thus only the angular momentum pointed along the inter-nuclear axis is meaningful. The orbital angular momentum of a diatomic molecule along the inter-nuclear axis is designated by  $\lambda$ , analogous to the  $l$  quantum number for an electron of an atom:  $\lambda = 0$  for  $\sigma$ -type orbitals, and  $\lambda = 1$  for  $\pi$ -type orbitals (Figure 2b).

The coupling of the spin angular momentum  $s$  and the angular momentum  $\lambda$  leads to a net angular momentum, which is analogous to the  $j$  angular momentum for an electron of an atom. The resulting angular momentum is denoted by  $\omega$ . For example,  $\omega = |\lambda \pm 1/2|$  for a spin-1/2 electron. As a consequence, under spin–orbit coupling, the  $\sigma$  ( $\lambda = 0$ ) level becomes the  $\omega = 1/2$  level, whereas the  $\pi$  ( $\lambda = 1$ ) level splits into the  $\omega = 1/2$  and  $\omega = 3/2$  levels. Because the  $z$ -component of  $\omega$  (i.e.,  $m_\omega$ ) is given by  $m_\omega = \pm\omega$  by the cylindrical symmetry, each relativistic dimer orbital is 2-fold degenerate and hence will be denoted by the symbol e. The relativistic dimer levels resulting from the p orbitals under spin–orbit coupling are depicted in Figure 2c. The occurrence of these levels is easily accounted for by introducing spin–orbit coupling first into the p orbitals of an

**TABLE 1: Results of Relativistic DFT Calculations for  $Q_2^{2-}$  ( $Q = N, P, As, Sb, Bi$ )<sup>a</sup>**

	$N_2^{2-}$	$P_2^{2-}$	$As_2^{2-}$	$Sb_2^{2-}$	$Bi_2^{2-}$	
$\epsilon(p_{3/2}) - \epsilon(p_{1/2})^a$	0.019	0.055	0.282	0.632	1.969	
$\epsilon(1e_{g3/2}) - \epsilon(2e_{g1/2})^{a,b}$	0.01	0.03	0.14	0.25	0.57	
$(E_{OS} - E_{CS})^{a,c}$	-0.88	-0.46	-0.30	-0.11	+0.26	
Q–Q lengths <sup>d</sup>	OS	1.3664	2.1528	2.4044	2.7951	3.0101
	CS	1.3658	1.1584	2.4121	2.8109	3.0199

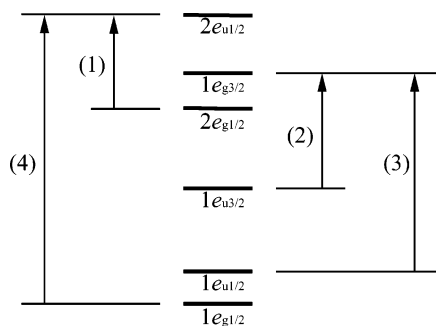
<sup>a</sup> The energies are given in eV units. <sup>b</sup> The energies were calculated by using the CS states with the optimized bond lengths. <sup>c</sup> The energies were calculated by using the optimized bond lengths. <sup>d</sup> The optimized bond lengths are given in Å units.

atom to split them into  $p_{1/2}$  ( $j = 1/2, m_j = \pm 1/2$ ) and  $p_{3/2}$  ( $j = 3/2, m_j = \pm 1/2, \pm 3/2$ ) (Figure 2d). Then the  $p_{1/2}$  orbitals of the two individual atoms interact to form the  $e_{g1/2}$  and  $e_{u1/2}$  orbitals. Likewise, the  $p_{3/2}$  orbitals interact to form the  $e_{g1/2}$ ,  $e_{u1/2}$ ,  $e_{g3/2}$ , and  $e_{u3/2}$  orbitals (Figure 2d to 2c). The correlations between the MO levels of Figure 2b and the relativistic dimer levels of Figure 2c, indicated by the solid lines, are discussed in section 5.2.

**4.2. Ground State.** For  $Q_2^{2-}$  ( $Q = N, P, As, Sb, Bi$ ), there remain two electrons for the  $2e_{g1/2}$ ,  $1e_{g3/2}$  and  $2e_{u1/2}$  levels after completely filling all the levels up to  $1e_{u3/2}$ . The energy gap between  $2e_{g1/2}$  and  $1e_{g3/2}$  is small when spin–orbit coupling is weak, and increases as spin–orbit coupling becomes stronger. Thus, there are two low-energy electron configurations to consider,  $(2e_{g1/2})^2(1e_{g3/2})^0$  and  $(2e_{g1/2})^1(1e_{g3/2})^1$ . (Unless mentioned otherwise, it will be assumed that all levels below  $2e_{g1/2}$  are each doubly filled.) The terms “singlet” and “triplet” states are valid concepts in MO pictures where spin–orbit coupling is neglected. However, these states can interact and mix when spin–orbit coupling is turned on. Thus, it is more appropriate to describe the  $(2e_{g1/2})^2(1e_{g3/2})^0$  configuration as a “closed-shell” (CS) state, and  $(2e_{g1/2})^1(1e_{g3/2})^1$  as an “open-shell” (OS) state.

The computational results for  $Q_2^{2-}$ , summarized in Table 1, indicate that the energy gap between the  $2e_{g1/2}$  and  $1e_{g3/2}$  levels is large for strong spin–orbit coupling, and the CS state becomes more stable than the OS state.<sup>34</sup> The energy difference between the  $p_{3/2}$  and  $p_{1/2}$  levels of Q increases in the order  $N < P < As < Sb < Bi$ , and so does the energy difference between the  $2e_{g1/2}$  and  $1e_{g3/2}$  levels of  $Q_2^{2-}$ . The state energy difference,  $\Delta E = E_{OS} - E_{CS}$ , is largest for  $N_2^{2-}$  and decreases steadily in the order  $N > P > As > Sb > Bi$ . The OS state is more stable than the CS state for  $N_2^{2-}$ ,  $P_2^{2-}$ ,  $As_2^{2-}$  and  $Sb_2^{2-}$ , but the opposite is the case for  $Bi_2^{2-}$ . The latter explains why the  $Bi_2^{2-}$  anions of (K-crypt)<sub>2</sub>Bi<sub>2</sub> behave as if they have no unpaired electrons in contrast to the case of the isoelectronic O<sub>2</sub>.<sup>1,2</sup>

It is noted that the optimized bond length of the CS state  $Bi_2^{2-}$ , 3.0101 Å, is longer than the experimental value, 2.8377 Å. The exchange and correlation functionals used here tend to slightly overestimate bond lengths.<sup>20</sup> Furthermore, our calculations were carried out for an isolated  $Bi_2^{2-}$  anion, whereas the  $Bi_2^{2-}$  anions in the crystal structure of (K-crypt)<sub>2</sub>Bi<sub>2</sub> are coordinated with the counterbalancing cations  $K^+$ . The polarization of the valence electron density distribution of  $Bi_2^{2-}$  by the surrounding  $K^+$  cations will effectively reduce the electrostatic repulsion between the two Bi atoms and hence shorten the Bi–Bi bond length. In addition, we note that the effective core potential used has a large core. The omission of the outer core might also have contributed to the long Bi–Bi bond length optimized from the present DFT calculations.<sup>35</sup>



**Figure 3.** Four low-energy electronic excitations of  $\text{Bi}_2^{2-}$ .

**TABLE 2: Compositions of the Ground and Four Excited Configurations of  $\text{Bi}_2^{2-}$  and the Associated Excitation Energies Obtained by Relativistic DFT Calculations**

state	composition	excitation energy (eV) <sup>a</sup>
$(2e_{g1/2})^2(1e_{g3/2})^0$	$0_g^+$	
$(2e_{g1/2})^1(2e_{u1/2})^1$	$0_u^+, 0_u^-, 1_u$	0.90
$(1e_{u3/2})^1(1e_{g3/2})^1$	$0_u^+, 0_u^-, 3_u$	1.17
$(1e_{u1/2})^1(1e_{g3/2})^1$	$1_u, 2_u$	2.21
$(1e_{g1/2})^1(2e_{u1/2})^1$	$0_u^+, 0_u^-, 1_u$	3.11

<sup>a</sup> Calculated for  $\text{Bi}_2^{2-}$  with the Bi–Bi distance 2.8377 Å found in (K-crypt) $\text{Bi}_2$ .

## 5. Excitation Spectrum of $\text{Bi}_2^{2-}$ from the Viewpoint of One-Electron Orbitals

**5.1. DFT Calculations of the Excitation Energies.** In the CS state of  $\text{Bi}_2^{2-}$  represented by the orbitals of Figure 2c, the  $1e_{g1/2}$ ,  $1e_{u1/2}$ ,  $1e_{u3/2}$ , and  $2e_{g1/2}$  levels, are doubly filled while the  $1e_{g3/2}$  and  $2e_{u1/2}$  levels are empty. Electronic excitations are allowed between occupied u- and unoccupied g-levels, and between occupied g- and unoccupied u-levels. Figure 3 depicts four low-energy one-electron excitations: (1)  $2e_{g1/2} \rightarrow 2e_{u1/2}$ , (2)  $1e_{u3/2} \rightarrow 1e_{g3/2}$ , (3)  $1e_{u1/2} \rightarrow 1e_{g3/2}$ , and (4)  $1e_{g1/2} \rightarrow 2e_{u1/2}$ . We calculated the energies of these excitations for  $\text{Bi}_2^{2-}$  with Bi–Bi distance of 2.8377 Å on the basis of relativistic DFT using Slater’s transition state technique (Table 2).<sup>36–38</sup> This method excludes the possibility of transitions between empty levels (e.g.,  $1e_{g3/2} \rightarrow 2e_{u1/2}$ ) from contributing to the excitation energy spectrum because both levels are unoccupied in the ground state.

Relativistic DFT calculations are based on the single-determinant method, so that each excitation energy determined by these calculations represents an “average” value that involves several states from the viewpoint of the CI method. Therefore, it is necessary to examine the compositions of the ground and four excited states. The ground-state configuration  $(2e_{g1/2})^2(1e_{g3/2})^0$  has the  $0_g^+$  symmetry under the classification of relativistic states under cylindrical symmetry. According to the  $\omega$ – $\omega$  coupling scheme, the coupling of  $\omega_1$  and  $\omega_2$  states yields  $\Omega = |\omega_1 - \omega_2|$  and  $\omega_1 + \omega_2$  states. Thus, the coupling of  $\omega_1 = 1/2$  and  $\omega_2 = 1/2$  states generates  $\Omega = 0^+$ ,  $0^-$ , and 1 states.<sup>39</sup> Therefore, the excited configurations  $(2e_{g1/2})^1(2e_{u1/2})^1$  and  $(1e_{g1/2})^1(2e_{u1/2})^1$  generate  $0_u^+$ ,  $0_u^-$ , and  $1_u$  states. Similarly, the coupling of  $\omega_1 = 1/2$  and  $\omega_2 = 3/2$  states leads to  $\Omega = 1$  and 2 states, so the excited configuration  $(1e_{u1/2})^1(1e_{g3/2})^1$  generates  $1_u$  and  $2_u$  states. The coupling of  $\omega_1 = 3/2$  and  $\omega_2 = 3/2$  states leads to  $\Omega = 0^+$ ,  $0^-$ , and 3, so the excited configuration  $(1e_{u3/2})^1(1e_{g3/2})^1$  generates  $0_u^+$ ,  $0_u^-$ , and  $3_u$  states.

According to the selection rules for electronic transitions between relativistic states under cylindrical symmetry, the  $0_g^+ \rightarrow 0_u^+$  and  $0_g^+ \rightarrow 1_u$  excitations are allowed, whereas the  $0_g^+ \rightarrow 0_u^-$ ,  $0_g^+ \rightarrow 2_u$ , and  $0_g^+ \rightarrow 3_u$  excitations are forbidden. Therefore, all four excitations of Figure 3, i.e.,  $2e_{g1/2} \rightarrow 2e_{u1/2}$ ,

$1e_{u3/2} \rightarrow 1e_{g3/2}$ ,  $1e_{u1/2} \rightarrow 1e_{g3/2}$ , and  $1e_{g1/2} \rightarrow 2e_{u1/2}$ , are allowed. Thus it is tempting to suggest that the two absorption peaks at 2.05 and 2.85 eV (Figure 1) in the UV–vis spectrum of (K-crypt) $\text{Bi}_2$  are associated with the excitations  $1e_{u1/2} \rightarrow 1e_{g3/2}$  (2.21 eV) and  $1e_{g1/2} \rightarrow 2e_{u1/2}$  (3.11 eV), respectively, and that the remaining two predicted excitations, i.e.,  $2e_{g1/2} \rightarrow 2e_{u1/2}$  (0.90 eV) and  $1e_{u3/2} \rightarrow 1e_{g3/2}$  (1.17 eV) are not observed experimentally because their transition probabilities are very small. However, this reasoning is incorrect, as discussed in the following.

**5.2. Relativistic Orbitals in Terms of Nonrelativistic Orbitals.** In relativistic theory an atomic orbital is represented by four components, two large components and two small components. For simplicity, we will consider only the two large components of an atomic orbital. Then, the atomic  $p_{1/2}$  and  $p_{3/2}$  orbitals (for positive  $m_s$  values) of Bi are written as<sup>3</sup>

$$p_{1/2}(m_s = 1/2): \phi_a \propto \begin{bmatrix} -\sqrt{1/3}p_z \\ -\sqrt{1/3}(p_x + ip_y) \end{bmatrix} \quad (1a)$$

$$p_{3/2}(m_s = 3/2): \phi_b \propto \begin{bmatrix} \sqrt{1/2}(p_x + ip_y) \\ 0 \end{bmatrix} \quad (1b)$$

$$p_{3/2}(m_s = 1/2): \phi_c \propto \begin{bmatrix} \sqrt{2/3}p_z \\ -\sqrt{1/6}(p_x + ip_y) \end{bmatrix} \quad (1c)$$

where the  $p_x$ ,  $p_y$ , and  $p_z$  are the p orbitals of Bi in the absence of spin–orbit coupling, and the z-axis taken along the Bi–Bi axis.

To understand the nature of the dimer orbitals under spin–orbit coupling (Figure 2c), we first consider “equal-weight” linear combinations of the relativistic atomic orbitals  $\phi_a$ ,  $\phi_b$ , and  $\phi_c$  listed in eq 1. The two different Bi atoms of a  $\text{Bi}_2^{2-}$  anion may be distinguished by the site indices 1 and 2. Then,

$$\phi_a(1) + \phi_a(2) = \begin{bmatrix} -\sqrt{1/3}\sigma_z^* \\ -\sqrt{1/3}(\pi_x + i\pi_y) \end{bmatrix} \quad (2a)$$

$$\phi_a(1) - \phi_a(2) = \begin{bmatrix} -\sqrt{1/3}\sigma_z \\ -\sqrt{1/3}(\pi_x^* + i\pi_y^*) \end{bmatrix} \quad (2b)$$

$$\phi_b(1) + \phi_b(2) = \begin{bmatrix} \sqrt{1/2}(\pi_x + i\pi_y) \\ 0 \end{bmatrix} \quad (2c)$$

$$\phi_b(1) - \phi_b(2) = \begin{bmatrix} \sqrt{1/2}(\pi_x^* + i\pi_y^*) \\ 0 \end{bmatrix} \quad (2d)$$

$$\phi_c(1) + \phi_c(2) = \begin{bmatrix} \sqrt{2/3}\sigma_z^* \\ -\sqrt{1/6}(\pi_x + i\pi_y) \end{bmatrix} \quad (2e)$$

$$\phi_c(1) - \phi_c(2) = \begin{bmatrix} \sqrt{2/3}\sigma_z \\ -\sqrt{1/6}(\pi_x^* + i\pi_y^*) \end{bmatrix} \quad (2f)$$

where  $\sigma$  represents the sigma-bonding orbital  $\sigma_g$ , and  $\sigma^*$  the sigma-antibonding orbital  $\sigma_u$ , in the absence of spin–orbit coupling. Likewise,  $\pi$  represents the pi-bonding orbital  $\pi_u$ , and  $\pi^*$  the pi-antibonding orbital  $\pi_g$ , in the absence of spin–orbit coupling. The six dimer orbitals of a  $\text{Bi}_2^{2-}$  anion under spin–orbit coupling (Figure 2c) can be decomposed in terms of the orbitals listed in eq 2. Results of this analysis are summarized in Table 3. On the basis of eq 2 and Table 3, it is straightforward to establish the correlations between the MO levels of Figure



**TABLE 3: Major and Minor Components of the Six Levels  $1e_{g1/2}$ ,  $1e_{u1/2}$ ,  $1e_{u3/2}$ ,  $2e_{g1/2}$ ,  $1e_{g3/2}$ , and  $2e_{u1/2}$  of  $Bi_2^{2-}$  Obtained from Relativistic DFT Calculations**

	major component	minor component
$1e_{g1/2}$	$\phi_a(1) - \phi_a(2)$	$\phi_c(1) - \phi_c(2)$
$1e_{u1/2}$	$\phi_a(1) + \phi_a(2)$	$\phi_c(1) + \phi_c(2)$
$1e_{u3/2}$	$\phi_b(1) + \phi_b(2)$	
$2e_{g1/2}$	$\phi_c(1) - \phi_c(2)$	$\phi_a(1) - \phi_a(2)$
$1e_{g3/2}$	$\phi_b(1) - \phi_b(2)$	
$2e_{u1/2}$	$\phi_c(1) + \phi_c(2)$	$\phi_a(1) + \phi_a(2)$

2b and the relativistic dimer levels of Figure 2c as indicated by the solid lines.

The relativistic  $1e_{g1/2}$  and  $2e_{g1/2}$  levels consist mainly of the  $[\phi_a(1) - \phi_a(2)]$  and  $[\phi_c(1) - \phi_c(2)]$  orbitals, which are made up of the  $\sigma$  and  $\pi^*$  MO character (eqs 2b and 2f). Likewise, the relativistic  $1e_{u1/2}$  and  $2e_{u1/2}$  levels consist mainly of the  $[\phi_a(1) + \phi_a(2)]$  and  $[\phi_c(1) + \phi_c(2)]$  orbitals, which are made up of the  $\sigma^*$  and  $\pi$  MO character (eqs 2a and 2e). In other words, the spin–orbit coupling induces the mixing of the sigma-bonding and the pi-antibonding MO character, and that of the sigma-antibonding and the pi-bonding MO character. It is of interest to see how this orbital mixing comes about. Under spin–orbit coupling, the  $\sigma$  and  $\sigma^*$  ( $\lambda = 0$ ) levels become  $\omega = 1/2$  levels, whereas the  $\pi$  and  $\pi^*$  ( $\lambda = 1$ ) levels split into  $\omega = 1/2$  and  $\omega = 3/2$  levels. The levels of an identical  $\omega$  value can interact and hence mix together, but the resulting dimer orbitals must be either gerade or ungerade in symmetry. Thus, the gerade  $\omega = 1/2$  levels combine  $\sigma$  and  $\pi^*$  orbitals (eqs 2b and 2f), while the ungerade  $\omega = 1/2$  levels combine  $\sigma^*$  and  $\pi$  orbitals (eqs 2a and 2e). The  $\sigma$  and  $\sigma^*$  orbitals with  $\omega = 1/2$  do not mix due to their difference in symmetry. For the same reason, the  $\pi$  and  $\pi^*$  orbitals with  $\omega = 3/2$  do not mix (eqs 2c and 2d). When the spin–orbit coupling is strong, the quantum number  $\lambda$  is not a good quantum number any more, so that the MO terms such as the sigma and pi bonding/antibonding levels become meaningless.

**5.3. Consideration of Transition Dipole Moments.** The probability  $P$  of the electronic excitation from a filled orbital  $\phi_i$  to an empty orbital  $\phi_f$  is given by  $P \propto |\langle \phi_i | \bar{M} | \phi_f \rangle|^2$ , where  $\bar{M} = e\bar{r}$ . In this section, we evaluate the transition dipole moment  $\langle \phi_i | \bar{M} | \phi_f \rangle$  for the four transitions  $2e_{g1/2} \rightarrow 2e_{u1/2}$ ,  $1e_{u3/2} \rightarrow 1e_{g3/2}$ ,  $1e_{u1/2} \rightarrow 1e_{g3/2}$ , and  $1e_{g1/2} \rightarrow 2e_{u1/2}$ . To simplify our discussion, we note from Table 3 that the major components of the six dimer orbitals are given by

$$\begin{aligned}
 1e_{g1/2} &\leftarrow \phi_a(1) - \phi_a(2) \\
 1e_{u1/2} &\leftarrow \phi_a(1) + \phi_a(2) \\
 1e_{u3/2} &\leftarrow \phi_b(1) + \phi_b(2) \\
 2e_{g1/2} &\leftarrow \phi_c(1) - \phi_c(2) \\
 1e_{g3/2} &\leftarrow \phi_b(1) - \phi_b(2) \\
 2e_{u1/2} &\leftarrow \phi_c(1) + \phi_c(2)
 \end{aligned} \quad (3)$$

Using only these major components, the transition dipole

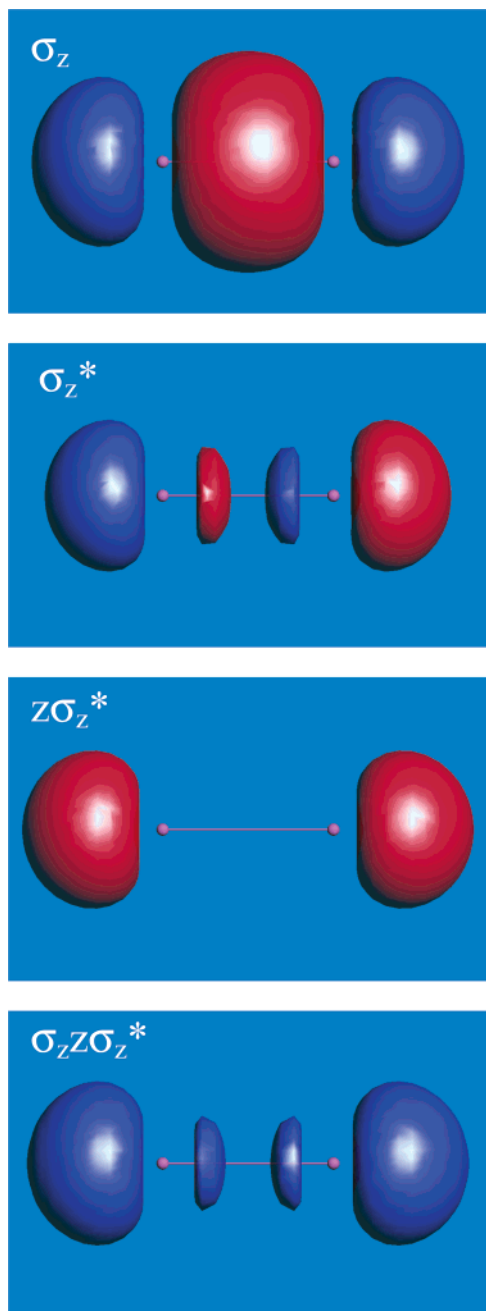
moments associated with the four electronic excitations are written as

$$\begin{aligned}
 \langle 2e_{g1/2} | \bar{M} | 2e_{u1/2} \rangle &\propto (2/3) \langle \sigma_z | \bar{r} | \sigma_z^* \rangle + (1/3) \langle \pi_x^* | \bar{r} | \pi_x \rangle \\
 \langle 1e_{u3/2} | \bar{M} | 1e_{g3/2} \rangle &\propto \langle \pi_x | \bar{r} | \pi_x^* \rangle = \langle \pi_x^* | \bar{r} | \pi_x \rangle \\
 \langle 1e_{u1/2} | \bar{M} | 1e_{g3/2} \rangle &\propto \sqrt{1/6}(1+i) \langle \sigma_z^* | \bar{r} | \pi_x^* \rangle \\
 \langle 1e_{g1/2} | \bar{M} | 2e_{u1/2} \rangle &\propto (\sqrt{2}/3)(-\langle \sigma_z | \bar{r} | \sigma_z^* \rangle + \langle \pi_x^* | \bar{r} | \pi_x \rangle) \quad (4)
 \end{aligned}$$

where the equivalence between  $\langle \pi_x^* | \bar{r} | \pi_x \rangle$  and  $\langle \pi_x | \bar{r} | \pi_x^* \rangle$  was taken into consideration, and so was that between  $\langle \sigma_z^* | \bar{r} | \pi_x^* \rangle$  and  $\langle \sigma_z^* | \bar{r} | \pi_x \rangle$ . By symmetry, the nonzero term of  $\langle \sigma_z | \bar{r} | \sigma_z^* \rangle$  is given by  $\langle \sigma_z | z | \sigma_z^* \rangle$ , that of  $\langle \pi_x^* | \bar{r} | \pi_x \rangle$  by  $\langle \pi_x^* | x | \pi_x \rangle$ , and that of  $\langle \sigma_z^* | \bar{r} | \pi_x^* \rangle$  by  $\langle \sigma_z^* | x | \pi_x^* \rangle$ . Therefore, eq 4 is simplified as

$$\begin{aligned}
 \langle 2e_{g1/2} | \bar{M} | 2e_{u1/2} \rangle &\propto (2/3) \langle \sigma_z | z | \sigma_z^* \rangle + (1/3) \langle \pi_x^* | z | \pi_x \rangle \\
 \langle 1e_{u3/2} | \bar{M} | 1e_{g3/2} \rangle &\propto \langle \pi_x^* | x | \pi_x \rangle \\
 \langle 1e_{u1/2} | \bar{M} | 1e_{g3/2} \rangle &\propto \sqrt{1/6}(1+i) \langle \sigma_z^* | x | \pi_x^* \rangle \\
 \langle 1e_{g1/2} | \bar{M} | 2e_{u1/2} \rangle &\propto (\sqrt{2}/3)(-\langle \sigma_z | z | \sigma_z^* \rangle + \langle \pi_x^* | z | \pi_x \rangle) \quad (5)
 \end{aligned}$$

It is important to consider whether the values of transition dipole moments such as  $\langle \sigma_z | z | \sigma_z^* \rangle$ ,  $\langle \pi_x^* | x | \pi_x \rangle$ , and  $\langle \sigma_z^* | x | \pi_x^* \rangle$  are large or small on symmetry considerations. Note that the term  $\langle \sigma_z | z | \sigma_z^* \rangle$  is equivalent to  $\langle \sigma_z | z | \sigma_z^* \rangle$ , i.e., the overlap integral between  $\sigma_z$  and  $\sigma_z^*$ . Likewise,  $\langle \pi_x^* | x | \pi_x \rangle$  is equivalent to  $\langle \pi_x^* | x | \pi_x \rangle$ , and  $\langle \sigma_z^* | x | \pi_x^* \rangle$  to  $\langle \sigma_z^* | x | \pi_x^* \rangle$ . To visualize our symmetry considerations, we calculate the MO's of  $Bi_2^{2-}$  using the extended Hückel tight binding method and generate boundary surface plots of the MO's and their product functions.<sup>40</sup> Figure 4 presents the boundary surface density plots of the MO's  $\sigma_z$  and  $\sigma_z^*$  as well as the product functions  $\sigma_z \sigma_z^*$  and  $\sigma_z z \sigma_z^*$ . It is clear that  $\sigma_z$  and  $\sigma_z^*$  have the same symmetry and the regions of their large values match. Consequently, the function  $\sigma_z z \sigma_z^*$  has large values so that its integrated value (i.e.,  $\langle \sigma_z | z | \sigma_z^* \rangle$ ) is expected to be large. The boundary surface plots of  $\pi_x^*$ ,  $\pi_x$ ,  $z\pi_x$ , and  $\pi_x^* z \pi_x$  are shown in Figure 5.  $\pi_x^*$  and  $z\pi_x$  have the same symmetry and the regions of their large values match, so that the  $\langle \pi_x^* | z | \pi_x \rangle$  value is expected to be large. Indeed, organic conjugated molecules are known to exhibit strong absorptions due to the  $\pi \rightarrow \pi^*$  transitions. Figure 6 shows the boundary surface density plots of  $\sigma_z^*$ ,  $\pi_x^*$ ,  $x\pi_x^*$  and  $\sigma_z^* x \pi_x^*$ .  $\sigma_z^*$  and  $x\pi_x^*$  do not have the same symmetry and the regions of their large values do not match. Therefore, the  $\langle \sigma_z^* | x | \pi_x^* \rangle$  value is not expected to be large. In agreement with this qualitative discussion, our calculations using only the Bi 6p orbitals show that the ratio  $\langle \sigma_z | z | \sigma_z^* \rangle$  to  $\langle \pi_x^* | z | \pi_x \rangle$  to  $\langle \sigma_z^* | x | \pi_x^* \rangle$  is 1.00:0.94:0.22. Consequently,  $\langle 1e_{u3/2} | \bar{M} | 1e_{g3/2} \rangle$  is large due to the large  $\langle \pi_x^* | z | \pi_x \rangle$  term, while  $\langle 1e_{u1/2} | \bar{M} | 1e_{g3/2} \rangle$  is small due to the small  $\langle \sigma_z^* | x | \pi_x^* \rangle$  term.  $\langle 1e_{g1/2} | \bar{M} | 2e_{u1/2} \rangle$  is small because the  $\langle \sigma_z | z | \sigma_z^* \rangle$  and  $\langle \pi_x^* | z | \pi_x \rangle$  terms cancel each other, but  $\langle 2e_{g1/2} | \bar{M} | 2e_{u1/2} \rangle$  is large because the  $\langle \sigma_z | z | \sigma_z^* \rangle$  and  $\langle \pi_x^* | z | \pi_x \rangle$  terms reinforce each other. The above discussion suggests that the two lower-energy excitations  $2e_{g1/2} \rightarrow 2e_{u1/2}$  and  $1e_{u3/2} \rightarrow 1e_{g3/2}$  should lead to strong absorptions, but the two higher-energy excitations  $1e_{u1/2} \rightarrow 1e_{g3/2}$  and  $1e_{g1/2} \rightarrow 2e_{u1/2}$  to weak absorptions. According to the symmetry analysis of the transition dipole moments given above, the UV–vis absorption peaks centered at 2.05 and 2.85

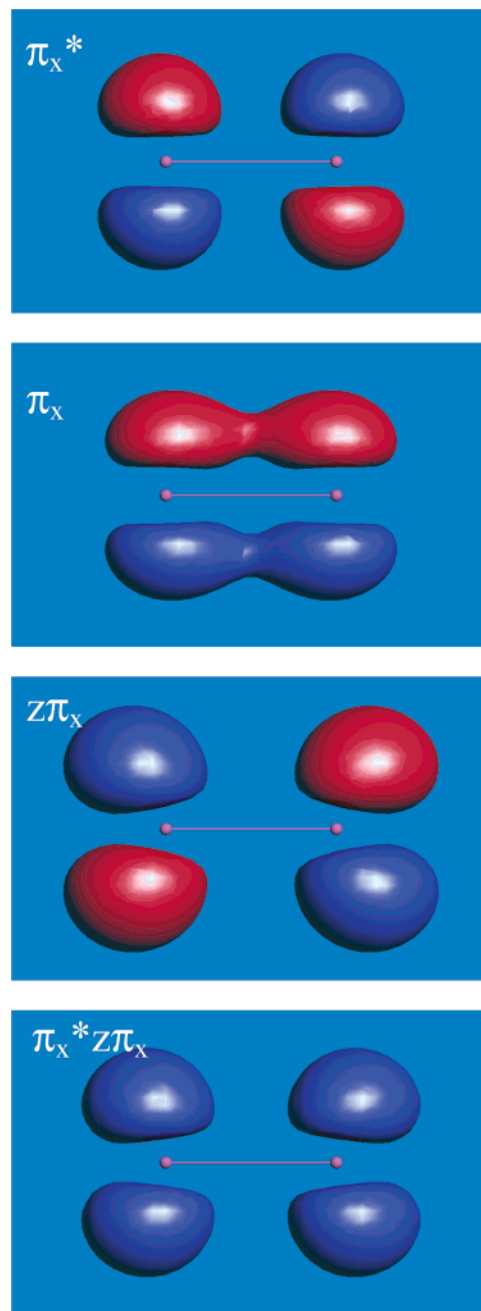


**Figure 4.** Boundary surface density plots of  $\sigma_z$ ,  $\sigma_z^*$ ,  $z\sigma_z^*$ , and  $\sigma_z z\sigma_z^*$  of  $\text{Bi}_2^{2-}$  calculated for the discussion of  $\langle \sigma_z | z | \sigma_z^* \rangle$ . The densities used for the plots are  $0.025/(\text{au})^{-3/2}$ ,  $0.05/(\text{au})^{-3/2}$ ,  $0.12/(\text{au})^{-1/2}$ , and  $0.003/(\text{au})^{-2}$  for  $\sigma_z$ ,  $\sigma_z^*$ ,  $z\sigma_z^*$ , and  $\sigma_z z\sigma_z^*$ , respectively. The positive and negative values are presented by red and blue colors, respectively. The  $z$ -axis is taken along the Bi-Bi axis.

eV cannot be assigned to the excitations  $1e_{u1/2} \rightarrow 1e_{g3/2}$  (2.21 eV) and  $1e_{g1/2} \rightarrow 2e_{u1/2}$  (3.11 eV), respectively.

## 6. Description of the Excitation Spectrum of $\text{Bi}_2^{2-}$ by CI

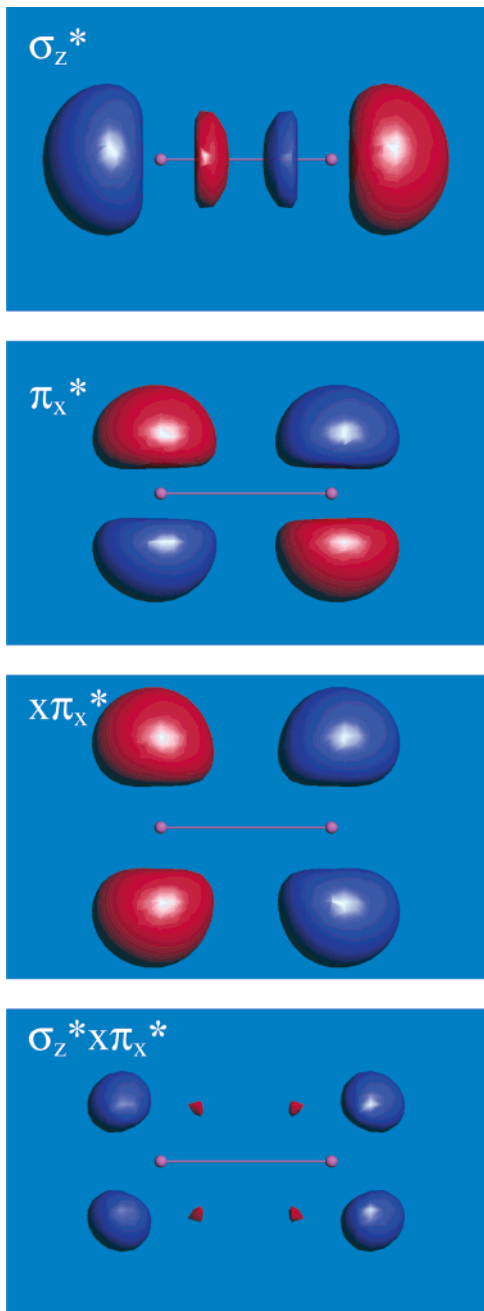
**6.1. Relative Energies of the Ground and Low-Lying Excited States.** Table 4 summarizes the relative energies of the low-lying g- and u-states of  $\text{Bi}_2^{2-}$  calculated by the two CI methods at Bi-Bi = 2.910 Å (the approximate equilibrium distance of the ground state) as well as the largest  $\Lambda$ -S contributions to these states. The ground state  $X0_g^+$  of  $\text{Bi}_2^{2-}$  has the  $0_g^+$  symmetry and is mainly composed of the  $^3\Sigma_g^-$  and  $^1\Sigma_g^+$  contributions, both dominated by the  $(\dots\sigma_g^2\pi_u^4\pi_g^2)$  configuration, i.e., the “closed-shell” state described in section 4.2.



**Figure 5.** Boundary surface density plots of  $\pi_x^*$ ,  $\pi_x$ ,  $z\pi_x$ , and  $\pi_x^* z\pi_x$  of  $\text{Bi}_2^{2-}$  calculated for the discussion of  $\langle \pi_x^* | z | \pi_x \rangle$ . The densities used for the plots are  $0.05/(\text{au})^{-3/2}$ ,  $0.05/(\text{au})^{-3/2}$ ,  $0.06/(\text{au})^{-1/2}$ , and  $0.003/(\text{au})^{-2}$  for  $\pi_x^*$ ,  $\pi_x$ ,  $z\pi_x$ , and  $\pi_x^* z\pi_x$ , respectively.

As expected, the contribution of  $^1\Sigma_g^+$  to the ground state is significantly high ( $\sim 29\%$ ) due to a strong spin-orbit interaction in  $\text{Bi}_2^{2-}$ . Accurate determination of the ground-state spectroscopic constants gives  $R_e = 2.954$  Å and  $\omega_e = 123$   $\text{cm}^{-1}$ . This equilibrium Bi-Bi distance,  $R_e$ , is shorter than 3.010 Å obtained from the present DFT calculations but is still too long compared with the experimental value of 2.8377 Å (see ref 35 for further discussion).

The second lowest-lying g-state, i.e.,  $1_g(I)$ , corresponds to the “open-shell” state described in section 4.2. The third low-lying g-state  $2_g$  arises mainly from the  $^1\Delta_g$  contribution with some  $^3\Pi_g$  component. The next g-states lie notably higher in energy and are not discussed here because electronic transitions from the  $X0_g^+$  ground state to them are forbidden. The four lowest-lying u-states are made up of the  $^3\Pi_u(\dots\sigma_g^2\pi_u^4\pi_g\sigma_u)$



**Figure 6.** Boundary surface density plots of  $\sigma_z^*$ ,  $\pi_x^*$ ,  $x\pi_x^*$ , and  $\sigma_z^* x \pi_x^*$  of  $\text{Bi}_2^{2-}$  calculated for the discussion of  $\langle \sigma_z^* | x | \pi_x^* \rangle$ . The densities used for the plots are  $0.05/(\text{au})^{-3/2}$ ,  $0.05/(\text{au})^{-3/2}$ ,  $0.06/(\text{au})^{-1/2}$ , and  $0.003/(\text{au})^{-2}$  for  $\sigma_z^*$ ,  $\pi_x^*$ ,  $x\pi_x^*$ , and  $\sigma_z^* x \pi_x^*$ , respectively.

configuration. The  $1_u(\text{I})$  state is almost a 50/50 mixture of  $^3\Pi_u^-$  ( $\dots\sigma_g^2\pi_u^4\pi_g\sigma_u$ ) and  $^1\Pi_u$  ( $\dots\sigma_g^2\pi_u^4\pi_g\sigma_u$ ), which again shows a strong influence of the spin–orbit interaction. The  $1_u(\text{II})$  state is an orthogonal complement to  $1_u(\text{I})$ . Table 4 shows that the u-states lying higher than  $1_u(\text{II})$  with excitation energies in the 1.0–1.6 eV range are composed of various combinations of  $^1,^3\Sigma_u^-$ ,  $^1,^3\Sigma_u^+$ , and  $^1,^3\Delta_u$ . All of these states are described mainly by two configurations  $\sigma_g^2\pi_u^3\pi_g^3$  and  $\sigma_g^2\pi_u^4\pi_g\pi_u^*$ , and thus correspond to the  $\pi_u \rightarrow \pi_g$  and  $\pi_g \rightarrow \pi_u^*$  excitations from the ground state. Here the  $\pi_u^*$  orbital refers to the lowest-lying virtual orbital of the  $\pi_u$  symmetry, which is made up of the diffuse Bi p-orbitals and hence has a Rydberg character. For excitations in the electric dipole approximation, the  $0_u^-$ ,  $2_u$ , and

**TABLE 4: Excitation Energies (in eV) Calculated for the 3 Lowest g-States and 13 Lowest u-States of  $\text{Bi}_2^{2-}$  Employing the LSC–SO–CI and MR–SO–CI Methods<sup>a</sup>**

state	LSC–SO–CI	MR–SO–CI	main $\Lambda$ -S contribution
$X0_g^+$	0	0	$^3\Sigma_g^-, ^1\Sigma_g^+$
$1_g(\text{I})$	0.37	0.35	$^3\Sigma_g^-$
$2_g(\text{I})$	0.56	0.59	$^1\Delta_g, ^3\Pi_g$
$0_u^-(\text{I})$	0.023	0.14	$^3\Pi_u$
$1_u(\text{I})$	0.054	0.15	$^3\Pi_u, ^1\Pi_u$
$0_u^+(\text{I})$	0.065	0.14	$^3\Pi_u$
$2_u(\text{I})$	0.75	0.84	$^3\Pi_u$
$1_u(\text{II})$	0.82	0.89	$^1\Pi_u, ^3\Pi_u$
$0_u^-(\text{II})$	1.02	1.01	$1,2 ^1\Sigma_u^-, 1 ^3\Sigma_u^+$
$3_u(\text{I})$	1.06	1.06	$1,2 ^3\Delta_u$
$0_u^-(\text{III})$	1.45	1.42	$2 ^3\Sigma_u^+, 1,2 ^1\Sigma_u^-$
$1_u(\text{III})$	1.49	1.46	$1,2 ^3\Delta_u$
$0_u^+(\text{II})$	1.48	1.47	$1 ^3\Sigma_u^+, 1 ^1\Sigma_u^+$
$1_u(\text{IV})$	1.56	1.60	$1 ^3\Sigma_u^-, 2 ^3\Sigma_u^+$
$2_u(\text{II})$	1.62	1.60	$1 ^1\Delta_u, 1,2 ^3\Delta_u$
$1_u(\text{V})$	1.78	1.84	$2 ^3\Pi_u, 1 ^3\Sigma_u^+, 2 ^5\Pi_u$

<sup>a</sup> The vertical excitation energies are calculated at the Bi–Bi distance of 2.910 Å.

**TABLE 5: Low-Lying u-States, to Which Excitations from the  $X0_g^+$  Ground State Are Dipole-Allowed, Their Leading Configurations, Excitation Energies  $\Delta E$ , Transition Dipole Moments  $\mu$  (LSC–SO–CI), and Oscillator Strengths  $f^a$**

state	leading configuration	$\Delta E/\text{eV}$	$\mu/\text{ea}_0$	$f$
$X0_g^+$	$\sigma_g^2\pi_u^4\pi_g^2$	0		
$0_u^+(\text{I})$	$\pi_g \rightarrow \sigma_u$	0.14	1.916	0.013
$1_u(\text{I})$	$\pi_g \rightarrow \sigma_u$	0.15	1.649	0.010
$1_u(\text{II})$	$\pi_g \rightarrow \sigma_u$	0.89	0.228	0.001
$1_u(\text{III})$	$\pi_g \rightarrow \pi_u^*$	1.46	0.216	0.002
$0_u^+(\text{II})$	$\pi_g \rightarrow \pi_u^*$	1.47	1.655	0.100
$1_u(\text{IV})$	$\pi_g \rightarrow \pi_u^*$	1.60	0.252	0.002
$1_u(\text{V})$	$\pi_u \rightarrow \pi_g$	1.84	0.286	0.004
$1_u(\text{VI})$	$\pi_u \rightarrow \pi_g$	1.88	0.235	0.003
$0_u^+(\text{III})$	$\pi_u \rightarrow \pi_g$	2.09	0.986	0.050
$1_u(\text{VIII})$	$\sigma_g \rightarrow \sigma_u$	2.21	0.577	0.018
$0_u^+(\text{IV})$	$\pi_u \rightarrow \sigma_g^*$	2.24	0.663	0.024
$1_u(\text{IX})$	$\pi_u \rightarrow \sigma_g^*, \pi_u^2 \rightarrow \pi_g\sigma_u$	2.25	0.138	0.001
$1_u(\text{X})$	$\pi_u \rightarrow \pi_g, \pi_g \rightarrow \pi_u^*$	2.30	0.126	0.001
$0_u^+(\text{V})$	$\sigma_g \rightarrow \sigma_u$	2.39	1.922	0.216
$1_u(\text{XI})$	$\pi_g \rightarrow \pi_u^*, \pi_u \rightarrow \pi_g$	2.44	0.216	0.003
$1_u(\text{XII})$	$\pi_g^2 \rightarrow \pi_u^*, \sigma_g^*, \pi_g \rightarrow \sigma_u^*$	2.54	0.292	0.005
$0_u^+(\text{VI})$	$\pi_g \rightarrow \pi_u^*$	2.57	0.626	0.025
$1_u(\text{XIII})$	$\pi_u \rightarrow \pi_g^*$	2.60	0.231	0.003
$0_u^+(\text{VII})$	$\pi_g \rightarrow \sigma_u$	2.66	0.418	0.011
$1_u(\text{XVII})$	$\pi_u \rightarrow \sigma_g^*, \pi_u^2 \rightarrow \pi_g^*\sigma_u$	2.86	0.133	0.001
$0_u^+(\text{IX})$	$\pi_u \rightarrow \pi_g^*$	2.87	0.615	0.027
$1_u^+(\text{XIII})$	$\pi_u \rightarrow \pi_g^*$	2.87	0.329	0.008

<sup>a</sup> Vertical excitation energies are calculated at the Bi–Bi distance of 2.910 Å. Only states with  $f \geq 0.001$  are presented.

$3_u$  states are not important. The  $0_u^+$  and  $1_u$  states of this group will be discussed in more detail below.

**6.2. Assignment of the Excitation Spectrum.** The  $0_u^+$  and  $1_u$  states up to excitation energies of 2.9 eV are summarized in Table 5 with the associated transition dipole moments ( $\mu$ ) and the oscillator strengths ( $f$ ). The degeneracy of the  $1_u$  states was taken into account, with  $\mu$  values defined as  $\mu = \sqrt{\mu_x^2 + \mu_y^2}$ . The oscillator strength is related to the transition dipole moment as  $f \propto \Delta E \mu^2$ , where  $\Delta E$  is the excitation energy associated with the transition dipole moment. Table 5 also summarizes the orbital character of the leading excitations (from the viewpoint

of one-electron orbitals in the absence of spin-orbit coupling). The excitation energies for the states up to  $1_u(V)$  were calculated by the MR-SO-CI method, and those for the higher-lying states by the LSC-SO-CI method.

As already discussed in the previous section, the three lowest u-states of Table 5,  $0_u^+(I)$  and  $1_u(I,II)$ , are mainly determined by the  $1,^3\Pi_u(\dots\sigma_g^2\pi_u^4\pi_g\sigma_u)$  contributions and thus correspond to the  $\pi_g \rightarrow \sigma_u$  excitation (i.e., the  $\pi^* \rightarrow \sigma^*$  excitation in the notation of section 5.3). The present relativistic CI calculations show that the three transitions associated with  $X0_g^+ \rightarrow 0_u^+(I)$ ,  $1_u(I,II)$  have very small excitation energies, and the transition dipole moments for two of the three are not small. The  $X0_g^+ \rightarrow 0_u^+(I)$  transition is a parallel one, so it is obvious that this transition cannot be caused by the  $\pi^* \rightarrow \sigma^*$  excitation. In this case, an essentially multireference character of the electronic states of  $Bi_2^{2-}$  plays a decisive role, which originates from high density of states corresponding to different electronic configurations and very strong spin-orbit interaction among them. The latter induces a notable mixing of the  $1,^3\Sigma_u^-(\dots\sigma_g\pi_u^4\pi_g^2\sigma_u)$  and  $^3\Sigma_u^-(\dots\sigma_g^2\pi_u^3\pi_g^3)$  character into the  $0_u^+(I)$  state, which leads to altogether 9.4% of its wave function. The corresponding excitations with respect to the ground state are  $\sigma_g \rightarrow \sigma_u$  (i.e.,  $\sigma \rightarrow \sigma^*$ ) and  $\pi_u \rightarrow \pi_g$  (i.e.,  $\pi \rightarrow \pi^*$ ), which are strong as shown in section 5.3.

A situation with the perpendicular  $X0_g^+ \rightarrow 1_u(I)$  transition is quite different. It is caused by the  $\pi^* \rightarrow \sigma^*$  excitation, which according to the analysis of section 5.3 must be weak. However, the present CI calculations show that the  $\sigma^*$  orbital acquires a lot of Rydberg character, which was not taken into account in the DFT treatment. This explains why the perpendicular transition moment is relatively large as well, although somewhat smaller than the parallel one (see Table 5 and note the  $\sqrt{2}$  factor accounting for the degeneracy of the  $1_u(I)$  state). The small frequency factors (i.e., the small excitation energies  $\Delta E$ ) of these transitions, however, lead to weak oscillator strengths. Therefore, these transitions cannot account for the experimental UV-vis spectrum of (K-crypt) $_2Bi_2$ .

The next group of u-states,  $0_u^+(II)$  and  $1_u(III,IV)$ , lies in the 1.47–1.60 eV energy range and arises from the  $\pi_g \rightarrow \pi_u^*$  excitation. The transition from  $X0_g^+$  to one of these states,  $0_u^+(II)$ , is characterized by a large transition dipole moment ( $\mu = 1.655 e a_0$ ) and  $f \approx 0.10$ . This type of excitation was not considered in section 5, because the Rydberg-type  $\pi_u^*$  orbital was not considered in the DFT calculations. In the UV-vis spectrum of (K-crypt) $_2Bi_2$ , a small and very broad hump is observed at  $\sim 1.55$  eV (i.e.,  $\sim 800$  nm). Additional calculations at internuclear separations around the  $X0_g^+$  equilibrium distance show that the  $0_u^+(II)$  state has a minimum at a shorter distance ( $\sim 2.805$  Å), which should lead to a broad absorption due to transitions to various vibrational levels of the upper state. Thus, one might speculate if the observed experimental feature at  $\sim 1.55$  eV is related to the  $X0_g^+ \rightarrow 0_u^+(II)$  transition. However, this assignment is unreasonable, as discussed below.

The next-highest states,  $1_u(V,VI)$  and  $0_u^+(III)$ , as well as  $1_u(X)$  lying slightly higher, originate from the  $\pi_u \rightarrow \pi_g$  excitation. In terms of the  $j-j$  coupling discussed in section 5.3, the  $X0_g^+ \rightarrow 0_u^+(III)$  excitation corresponds to the  $1e_{u3/2} \rightarrow 1e_{g3/2}$  transition, which was predicted to have a large transition dipole moment. The calculated  $\mu$  value for this transition is indeed fairly large,  $0.986 e a_0$ , and it is positioned at 2.09 eV. Thus, one might consider that the  $X0_g^+ \rightarrow 0_u^+(III)$  excitation leads to the absorption at  $\sim 2.05$  eV (Figure 1). In addition, one might suggest that the  $X0_g^+ \rightarrow 1_u(VIII)$ ,  $0_u^+(IV)$  transitions can also contribute to this absorption (halfwidth  $\sim 0.25$  eV), while the

$X0_g^+ \rightarrow 1_u(V,VI)$  transitions are partly responsible for the long wavelength tail of this peak. However, this picture has two weak points. First, the  $X0_g^+ \rightarrow 0_u^+(III)$  transition is too weak ( $f = 0.050$ ) compared with the  $X0_g^+ \rightarrow 0_u^+(II)$  excitation to explain the strong absorption around 2.05 eV. Second, there is one more strong transition,  $X0_g^+ \rightarrow 0_u^+(V)$ , which is calculated to lie at 2.39 eV, i.e., almost exactly at the midpoint between the two experimental peaks at 2.05 and 2.85 eV.

The theoretical and experimental spectra of  $Bi_2^{2-}$  are best matched by supposing that the calculated excitation energies of the low-lying  $0_u^+$  states (mainly responsible for the absorption in the observed spectral range) are underestimated by 0.4–0.6 eV. Under this assumption, the  $X0_g^+ \rightarrow 0_u^+(II)$  transition (with excitation energy of 1.47 eV) is responsible for the strong band at  $\sim 2.05$  eV, and the  $X0_g^+ \rightarrow 0_u^+(V)$  transition (with excitation energy of 2.39 eV) for the strong peak at  $\sim 2.85$  eV. The  $X0_g^+ \rightarrow 0_u^+(V)$  transition has a large transition dipole moment ( $1.922 e a_0$ ) and a large oscillator strength ( $f = 0.216$ ), because its leading configuration  $\sigma \rightarrow \sigma^*$  leads to a large transition dipole moment as discussed in section 5.3. Then, the  $X0_g^+ \rightarrow 0_u^+(III)$ ,  $1_u(VIII)$ ,  $0_u^+(IV)$  excitations should give rise to the nonvanishing absorption in the region between the two absorption peaks. The increase in the absorption intensity at energies higher than 3.3 eV (Figure 1) is probably caused by a large number of relatively weak contributions resulting from a very high density of electronic states in this energy range (for simplicity, this is not shown in Table 5).

There are several possible causes for the above-mentioned underestimation of the excitation energies for the low-lying  $0_u^+$  states. For example, the energy of the ground state  $X0_g^+$  is underestimated, as often found for the MRD-CI methods. In addition, the positions of the calculated maxima in the absorption spectrum can be influenced by the shifting of the potential energy curves of the excited states with respect to that of the ground state, and also by the dependence of the transition dipole moment on the internuclear distance. It should also be recalled that the  $Bi_2^{2-}$  dianion of (K-crypt) $_2Bi_2$  present in ethylenediamine solution is not identical to an isolated free  $Bi_2^{2-}$  dianion in vacuum.

The relativistic DFT calculations are far less adequate than are the relativistic CI calculations for the analysis of the UV-vis spectrum of  $Bi_2^{2-}$ . For example, the  $X0_g^+ \rightarrow 0_u^+(II)$  excitation, which is responsible for the strong absorption at  $\sim 2.05$  eV and whose leading configuration is  $\pi_g \rightarrow \pi_u^*$ , is not described because the relativistic DFT calculations do not take into consideration Rydberg-type orbitals such as  $\pi_u^*$ . A strong admixture of Rydberg character to the  $\sigma_u$  (i.e.,  $\sigma^*$ ) orbital also causes an increase in the  $X0_g^+ \rightarrow 1_u(I)$  transition moment in comparison with the DFT analysis. For the low-energy parallel transition,  $X0_g^+ \rightarrow 0_u^+(I)$ , an essentially multireference character of the upper state leads to a fairly strong transition moment. The primary reason for the shortcoming of the DFT method in this case is that it is based on a single-determinant wave function, so electronic excitations are described as transitions between occupied and unoccupied one-electron orbitals. In principle, DFT calculations can provide more accurate estimates of excitation energies when multideterminant wave functions are used to describe electronic excitations.<sup>41–43</sup>

## 7. Concluding Remarks

Our relativistic DFT calculations for the isoelectronic diatomic dianions  $Q_2^{2-}$  ( $Q = N, P, As, Sb, Bi$ ) show that the closed-shell state  $(2e_{g1/2})^2(1e_{g3/2})^0$  is more stable than the open-shell state  $(2e_{g1/2})^1(1e_{g3/2})^1$  for  $Bi_2^{2-}$ , while the opposite is the case



for  $\text{N}_2^{2-}$ ,  $\text{P}_2^{2-}$ ,  $\text{As}_2^{2-}$ , and  $\text{Sb}_2^{2-}$ . This explains why, unlike paramagnetic  $\text{O}_2$ , the  $\text{Bi}_2^{2-}$  anions of  $(\text{K-crypt})_2\text{Bi}_2$  are diamagnetic and EPR-silent. Our relativistic CI calculations suggest that the  $\text{XO}_g^+ \rightarrow 0_u^+(\text{II})$  transition is responsible for the strong peak around 2.05 eV, and the  $\text{XO}_g^+ \rightarrow 0_u^+(\text{V})$  transition for the strong peak at  $\sim 2.85$  eV. The nonvanishing absorption in the region between the two peaks is probably caused by the  $\text{XO}_g^+ \rightarrow 0_u^+(\text{III})$ ,  $1_u(\text{VIII})$ , and  $0_u^+(\text{IV})$  transitions and an increase in the absorption intensity at energies higher than 3.3 eV by a large number of relatively weak contributions from a very high density of electronic states in this energy range.

**Acknowledgment.** This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Grant DE-FG02-86ER45259 and by the National Science Foundation under grant CHE-0098004.

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- (35) In principle one could take more electrons (e.g., 5s and 5p electrons) out of the core to prove this point computationally. Such calculations were not carried out because an important goal of our work is to describe the excited states and absorption of  $\text{Bi}_2^{2-}$ , which makes it unreasonable to consider more valence electrons. Furthermore, even if there is a small systematic overestimation of the Bi–Bi bond length, it should be more or less the same for all states so that the overestimation of the Bi–Bi bond length is not really important for electronic transitions.
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- (39) Here the superscripts + and – for an  $\Omega = 0$  state mean that the wave function is respectively symmetric and antisymmetric with respect to the mirror plane of symmetry that goes through the molecular axis. This symmetry element does not exist for the  $\Omega \neq 0$  states.
- (40) Our calculations for  $\text{Bi}_2^{2-}$  were carried out by employing the SAMOA (Structure and Molecular Orbital Analyzer) program package (Dai, D.; Ren, J.; Liang, W.; Whangbo, M.-H., <http://chvawm.chem.ncsu.edu/>, 2002). Our calculations used the Bi–Bi bond length of 3 Å and the double- $\zeta$  Slater type orbitals for the Bi 6p orbitals (Clementi, E.; Roetti, C., *Atomic Data Nuclear Data Tables* **1974**, *14*, 177). To be consistent with our discussion based solely on the Bi 6p orbitals, the Bi 6s orbitals were omitted from our calculations. However, the inclusion of these orbitals does not change our conclusion.
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