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Blue absorption and red emission of Bi$^{2+}$ in solids: strongly spin-orbit coupled 6p levels in low symmetry fields.

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Abstract

Wave function embedded cluster ab initio calculations on a (BiO$_8$)$_{14}^{14-}$ cluster under the effects of a high symmetry $O_h$ confinement potential are used to study the energies of the $^2P_{1/2}$, $^2P_{3/2}(1)$, and $^2P_{3/2}(2)$ spin-orbit coupling levels of the 6s$^2$6p configuration of Bi$^{2+}$ in $O_h$, $D_{4h}$, $D_{2h}$, $D_4$, $D_{2d}$, $D_2$, $S_4$, $C_{4v}$, $C_4$, $C_{3v}$, $C_{2v}$, $C_2$, $C_s$, and $C_1$ fields, together with the $^2P_{1/2} \rightarrow ^2P_{3/2}(1)$ and $^2P_{1/2} \rightarrow ^2P_{3/2}(2)$ absorption oscillator strengths and $^2P_{3/2}(1)$ radiative lifetime. These levels are responsible for the blue absorptions and the red-orange emissions produced when Bi$^{2+}$ is doped in borates, phosphates, sulphates, and other hosts. It is found that the splitting of $^2P_{3/2}$ is mainly due to the tetragonal $D_{4h}$ and orthorhombic $D_{2h}$ components of the actual field. It is enhanced by Bi going towards two or four ligands. The intensities of the $^2P_{1/2} \rightarrow ^2P_{3/2}(1)$ and $^2P_{1/2} \rightarrow ^2P_{3/2}(2)$ absorptions are mostly induced by the Bi displacements and by tetragonal scalenoidal $D_{2d}$ fields. The most favorable fields for a large splitting of the $^2P_{3/2}$ level that could drive a red shift of the $^2P_{3/2}(1) \rightarrow ^2P_{1/2}$ emission are the $C_{2v}$ and $C_s$ fields resulting from the combination of $D_{2h}$ orthorhombic fields and Bi approaching two or four ligands on the main orthorhombic planes.

Keywords: Ab initio, bismuth, Bi$^{2+}$, spin-orbit coupling, low symmetry fields, red emission, blue absorption
I. INTRODUCTION

The $\text{Bi}^{2+}$ ion has recently motivated a new line of approach in the search of new red phosphors for energy efficient solid-state lighting devices.\textsuperscript{1–7} This line finds its grounds on the earlier work of Blasse et al.,\textsuperscript{8} who considered the rarely reported divalent bismuth species as responsible for the red-orange luminescence of bismuth activated $\text{SrB}_4\text{O}_7$. By extension, $\text{Bi}^{2+}$ was assumed to cause the red luminescence of bismuth activated alkaline earth sulfates already reported in 1886 by Lecoq de Boisbaudran\textsuperscript{9} and of bismuth activated phosphates reported in 1949 by Kröger et al.\textsuperscript{10} (cf. Ref. 11).

What makes this ion attractive for blue-LED based white light illuminating devices is the fact that it has a red-orange emission band at around 17000 cm\textsuperscript{-1} that can be excited with blue light at around 21000 cm\textsuperscript{-1} in borates, sulfates, and phosphates,\textsuperscript{1,3,8} and both the excitation and the emission are in principle susceptible to being tailored by selection of the hosts. These electronic transitions have been interpreted as $6p \rightarrow 6p$ parity forbidden transitions between local states associated with the spin-orbit $^2P_{1/2}$ and $^2P_{3/2}$ levels of the $6s^26p$ configuration of $\text{Bi}^{2+}$.\textsuperscript{1,3,8} The low symmetry fields acting on the $\text{Bi}^{2+}$ ion in the solid hosts are responsible for:

1. the splitting of $^2P_{3/2}$ into two $^2P_{3/2}(1)$ and $^2P_{3/2}(2)$ levels, which enables a $^2P_{1/2} \rightarrow ^2P_{3/2}(2)$ excitation and a $^2P_{3/2}(1) \rightarrow ^2P_{1/2}$ emission, and
2. the breaking of the electric dipole selection rule, which makes both transitions allowed and gives a finite value to the $^2P_{3/2}(1)$ radiative lifetime (12.6 $\mu$s in $\text{SrB}_4\text{O}_7$;Bi$^{2+}$ [Refs. 2,7,8,12]).

Wave-function-based embedded-cluster \textit{ab initio} calculations on $\text{Bi}^{2+}$-doped $\text{SrB}_4\text{O}_7$ have been shown to be reliable enough so as to help interpreting its electronic structure\textsuperscript{7} and its vibrational structure.\textsuperscript{13} Although such calculations are far from routine and they are time consuming, they can in principle be performed in other $\text{Bi}^{2+}$-doped hosts in a one-by-one basis. Nevertheless, as in the case of Ce$^{3+}$-doped garnets,\textsuperscript{14,15} we can expect the relevant level energies and wave functions of $\text{Bi}^{2+}$ in solids with oxygen coordination to be dominated, up to first-order, by the bonding interactions between Bi and its first oxygen coordination shell, subject to the basic confinement embedding effects of the host, whereas other specific host embedding effects are important at higher orders of approximation and they will refine the results. Then, an \textit{ab initio} calculation of a cluster of $\text{Bi}^{2+}$ and its oxygen coordination shell under the effects of a high symmetry confinement potential should provide the basics of the $^2P_{1/2}$, $^2P_{3/2}(1)$, and $^2P_{3/2}(2)$ levels.
On the basis of such idea, we report in this paper a basic ab initio study of the energies of the $^2P_{1/2}$, $^2P_{3/2}(1)$, and $^2P_{3/2}(2)$ levels of the $6s^26p$ configuration of Bi$^{2+}$ in low symmetry fields created by oxygen coordinations, of the two absorption oscillator strengths, and of the radiative lifetime of the emitting, first excited state. We explored fields of $O_h$, $D_{4h}$, $D_{2h}$, $D_4$, $D_{2d}$, $D_2$, $S_4$, $C_{4v}$, $C_4$, $C_{3v}$, $C_{2v}$, $C_2$, $C_1$, and $C_{1v}$ symmetries. The results are expected to be helpful in the search for new hosts for Bi$^{2+}$ with tailored blue absorptions and red emissions.

II. METHOD

The ab initio calculations in this paper are designed to study the splitting of the $^2P_{1/2}$ and $^2P_{3/2}$ atomic levels of the $6s^26p$ configuration of Bi$^{2+}$ in a number of low symmetry fields that could be found in solids where Bi$^{2+}$ occupied a site with a first coordination shell of oxygens. These energy levels are responsible for the blue absorptions and the red emissions of the Bi$^{2+}$-doped solids and, accordingly, we not only calculated their energies but also the corresponding absorption oscillator strengths and emitting state radiative lifetimes.

Here we study low symmetry fields originated by arbitrary atomic displacements within a (BiO$_8$)$_{14^-}$ cluster. Although 9-fold oxygen coordination has been found for Bi$^{2+}$ in some solids, the 8-fold coordinated cluster allows us to start from a high symmetry ($O_h$) that serves as a reference for all level splittings. Besides, the $6p \rightarrow 6p$ transitions are forbidden in this highly symmetric reference, so that it is also useful to see the origin of the absorption intensities and of the limited lifetime of the emitting state. We expect the symmetry and strength of the effective field generated by the oxygen ligands, rather than their number, to be the main factor dominating these transitions.

We embedded the (BiO$_8$)$_{14^-}$ cluster in a $O_h$ host potential that was kept constant in all the calculations. In this way, the embedding potential contributes electrostatic and quantum (exchange and Pauli repulsion) interactions with the host, which are important to confine the electrons in the local region around Bi$^{2+}$, and it provides a high symmetry environment, so that all the low symmetry effects are ascribable to the interactions between Bi and its first oxygen coordination shell.

The quantum mechanical calculation have been performed with the MOLCAS suite of programs. In brief, these are AIMP embedded cluster SA-CASSCF/MS-CASPT2/RASSI-SO DKH calculations. They include Bi-O bonding effects, static and dynamic electron correlation ef-
ffects, scalar and spin-orbit coupling relativistic effects, and cubic host embedding effects. The details are the following: For each nuclear configuration of the \((\text{BiO}_8)^{14-}\) embedded cluster, we performed, in a first step, scalar relativistic calculations with the many-electron second-order Douglas-Kroll-Hess (DKH) Hamiltonian.\(^{17,18}\) These were state-average complete-active-space self-consistent-field (SA-CASSCF) calculations with the active space that results from distributing 3 electrons in 3 active molecular orbitals with main character Bi 6s, 6p, which provided occupied and empty molecular orbitals to feed subsequent multi-state second-order perturbation theory calculations (MS-CASPT2),\(^{22-25}\) where the dynamic correlation of 77 electrons have been taken into account (the 5d, 6s, 6p electrons of Bi and 2s, 2p electrons of the O atoms). We used the standard IPEA value (0.25 au).\(^{26}\) In a second step, we included spin-orbit coupling effects by adding the AMFI approximation of the DKH spin-orbit coupling operator\(^{27}\) to the scalar relativistic Hamiltonian. In this step, we used the spin-free-state-shifting operator as a means to combine spin-orbit couplings calculated with statically correlated wave functions and spin-orbit free energies calculated with dynamic correlation\(^{28}\) and, accordingly, we performed restricted-active-space state-interaction spin-orbit calculations (RASSI-SO)\(^{29,30}\) with the transformed CASSCF wave functions (first-order wave functions of the MS-CASPT2 method) and the MS-CASPT2 energies. All the calculations are all-electron, with atomic natural orbital (ANO) relativistic basis sets for bismuth and oxygen,\(^{31}\) with respective contractions \(\{25s22p16d12f4g\}/\{11s10p9d6f4g\}\) and \(\{14s9p4d\}/\{4s3p2d\}\).

In all these calculations, the Hamiltonian of the \((\text{BiO}_8)^{14-}\) cluster was supplemented with a cubic embedding Hamiltonian that was previously used in a study of the 4f and 5d levels of Ce\(^{3+}\) in \(D_2\) 8-fold oxygen coordination.\(^{14}\) It is the \textit{ab initio} model potential embedding Hamiltonian (AIMP)\(^{32}\) of a SrO host in its high pressure CsCl lattice structure\(^{33}\) (\(Pm\bar{3}m\), no. 221), which provides a perfect 8-fold cubic oxide coordination of the cationic site. The embedding potential of this 8-fold coordinated cubic oxide was computed with a lattice constant \(\alpha = 2.87\ \text{Å}\), in Hartree-Fock self-consistent embedded-ions calculations (SCEI),\(^{34}\) in which the input embedding AIMP used for the Sr\(^{2+}\) and O\(^{2-}\) ions of SrO are consistent with the output AIMP obtained out of the HF orbitals of the embedded Sr\(^{2+}\) and O\(^{2-}\) ions.

The effective fields of different symmetries have been generated by means of coordinated displacements of the oxygen and the bismuth atoms of the BiO\(_8\) moiety. The chosen basic distortions of the BiO\(_8\) reference cube are defined in Table I and shown in Figs. 1 and 2. Note that the energies are invariant under sign change of the distortions \(S_3\) to \(S_8\).
Combinations of the basic distortions lead to lower symmetries. The specific combinations of basic distortions chosen in this work and the symmetry fields they produce are listed in Table II. Their graphical representations are included in Figs. 3 to 7. The minimum Bi-O and O-O distances reached with the explored distortions represented in these figures are also shown in Table II in order to give an idea of the size of the distortions.

The electronic states under consideration are usually labeled \(2P_{1/2}, 2P_{3/2}(1),\) and \(2P_{3/2}(2)\), in reference to their main free-ion characters. At the spin-orbit coupling level considered here, all of them are Kramers doublets. The previous notation is convenient and we will use it in the discussion (Sec. III). In the \(O_h\) group they are labeled \(1E_{1/2}, u\) and \(1G_{3/2}, u\), the last one with additional double degeneracy. In \(D_{4h}\) they are \(1E_{1/2}, u\), \(2E_{1/2}, u\), and \(1E_{3/2}, u\); in \(D_{2h}\), \(1E_{1/2}, 2E_{1/2},\) and \(1E_{3/2}\), and in all other groups studied here they are \(1E_{1/2}, 2E_{1/2},\) and \(3E_{1/2}\).

The electronic absorption oscillator strengths have been calculated as:

\[
f_{abs}(a \rightarrow b) = \frac{2}{3} \Delta E_{ab} \mu_{ab}^2,
\]

where \(a\) stands for the ground level \(2P_{1/2}\) and \(b\) for the final level, either \(2P_{3/2}(1)\) or \(2P_{3/2}(2)\). \(\Delta E_{ab}\) is the electronic transition energy, in hartree (1 hartree = 219474.625 cm\(^{-1}\)) and \(\mu_{ab}^2\) is defined in terms of the electric dipole transition moments (in au) between one of the two degenerate states \(\gamma_a\) of the ground level and the two degenerate states \(\gamma_b\) of the final, excited level:

\[
\mu_{ab}^2 = \sum_{\gamma_b=1}^2 |\langle a \gamma_a | \hat{\mu} | b \gamma_b \rangle|^2.
\]

The lifetime for spontaneous emission from the first excited level \(2P_{3/2}(1)\), \(\tau_{rad}\), is \(\tau_{rad} = 1/A_{ab}\), where \(b\) stands for \(2P_{3/2}(1)\) and \(a\) for the ground level \(2P_{1/2}\), which is the only one below the emitter. The Einstein coefficient for spontaneous emission is calculated as:

\[
A_{ab} = \frac{2 \omega_{ab}^3 \mu_{ab}^2}{3 \epsilon_0 hv^3} = \frac{16 \pi^3 \mu_{ab}^2}{3 \epsilon_0 h \lambda_{ab}^3},
\]

where \(\omega_{ab}\) is the emission angular frequency, \(\omega_{ab} = 2\pi c / \lambda_{ab}\), \(\lambda_{ab}\) is the emission wavelength, \(h\) is Planck’s constant, \(c\) the velocity of light, and \(\epsilon_0\) the permittivity of vacuum. No local field corrections have been included.\(^{37}\) If \(\Delta E_{ab}\) is expressed in cm\(^{-1}\) and \(\mu_{ab}\) in au, the expression for \(A_{ab}\) in s\(^{-1}\) becomes: \(A_{ab} = 2.02608 \times 10^{-6} \Delta E_{ab}^3 \mu_{ab}^2\) (Ref. 35).
The results of the energies of the excited states $^2P_{3/2}(1)$ and $^2P_{3/2}(2)$ relative to the ground state $^2P_{1/2}$, the corresponding first and second absorption electric dipole oscillator strengths, $f_{\text{abs}}(^2P_{1/2} \rightarrow ^2P_{3/2}(1))$ and $f_{\text{abs}}(^2P_{1/2} \rightarrow ^2P_{3/2}(2))$, and the emitting state $^2P_{3/2}(1)$ radiative lifetime $\tau_{\text{rad}}$, are shown in Figs. 3 to 7 for fields of different symmetries.

Fig. 3 shows that the energies of the excited degenerate $^2P_{3/2}$ levels in $O_h$ symmetry are only very slightly dependent on the strength of the field. The tetragonal $D_{4h}$ and orthorhombic $D_{2h}$ fields can provide large splittings of $^2P_{3/2}(1)$ and $^2P_{3/2}(2)$, even though they do not give any intensity to the absorptions and the emission. These splittings corresponds to a $G_{3/2} \otimes e_g$ Jahn-Teller coupling between a $G_{3/2,u}$ doubly degenerate spin-orbit coupling level (apart from Kramers degeneracy) and a doubly degenerate $e$ vibration. This vibronic coupling is isomorphic with the well known $E \otimes e_g$ Jahn-Teller coupling problem\(^{38}\) between an $E$ doubly degenerate level and the doubly degenerate $e_g$ vibration. The fact that the splittings observed in the two $D_{4h}$ and $D_{2h}$ fields are very similar indicates that the Jahn-Teller coupling experienced by Bi\(^{2+}\) matches the linear JT coupling limit very well, leading to an almost perfect Mexican hat type of $G_{3/2} \otimes (e_g \theta + e_g \varepsilon)$ energy surfaces,\(^{38}\) without significant energy barriers connecting the three equivalent $D_{4h}$ minima. This is even more clear in Fig. 11 of the Supplementary Material, where cross sections of these surfaces along the $e_g \theta$ and $e_g \varepsilon$ vibrational coordinates are shown.

In Fig. 3 we also observe that the tetragonal trapezoidal $D_4$ and the tetragonal scalenoidal $D_{2d}$ fields created by the $e_u \theta$ and $e_u \varepsilon$ deformations $S_4$ and $S_5$, do not produce significant $^2P_{3/2}$ splittings. Note that these vibrations are not Jahn-Teller active for the $G_{3/2,u}$ states (cf. Fig. 12 of Supplemental Material). The $D_{2d}$ field gives relevant intensity to the transitions, but the $D_4$ field does only give a negligible amount, even when it is as intense as in garnets. [The $S_4(e_u \theta)$ and $S_5(e_u \varepsilon)$ distortions defined here coincide with the $S_5(e_u \theta)$ and $S_6(e_u \varepsilon)$ distortions of the (CeO\(_8\))\(^{13-}\) cluster in $D_2$ sites of garnets used in Refs. 14 and 15, where the value of the $e_u \theta$ distortion was found to lie between 0.95 and 1.09 Å in 21 different garnets and the value of the $e_u \varepsilon$ distortion between -0.2 and 0.1 Å.]

Effects of fields resulting from combinations of two $S_2$-$S_5$ deformations are shown in Fig. 4. A combination of $S_2$ and $S_3$ gives basically the same results as the individual $S_2$ or $S_3$, in correspondence with the topology of the Mexican hat energy surface, and it is not shown in the
Figure. The $D_2$ field resulting from combining $S_4$ and $S_5$ gives a very small splitting of $^2P_{3/2}$, as expected from the individual distortions, together with intensities that correspond to $S_5$ alone. The combinations of $S_2$-$S_3$ with $S_4$-$S_5$ lead to $C_4$, $S_4$, $D_2$, and $C_{2v}$ fields. Regardless of their symmetry, all of them give important splittings, which are originated by the contributions of the two former $e_g$ individual distortions, $S_2$ or $S_3$. Only the $D_2$, $S_4$, and $C_{2v}$ fields with contributions from $S_5$ give relevant intensities; the intensities in $D_2$ and $C_4$ fields from combining $S_2$-$S_3$ with $S_4$ are negligible. It is clear that it is not the symmetry of the field, but the contributions behind it, what are responsible for the splitting of $^2P_{3/2}$ and for the intensities of the $^2P_{1/2} \rightarrow ^2P_{3/2}(1)$ and $^2P_{1/2} \rightarrow ^2P_{3/2}(2)$ transitions.

The previous fields basically sample different angular distributions of the coordination shell of $\text{Bi}^{2+}$, with small variations of Bi-O distances. In Fig. 5 we show the effects of $C_{4v}$, $C_{3v}$, $C_{2v}$, $C_3$, and $C_1$ fields due to selective changes of Bi-O distances. They also contain some ligand angular distribution effects, though. It is interesting to see that the $^2P_{3/2}$ splitting and emitting state lifetime show similar behaviors in all these fields, no matter if $\text{Bi}^{2+}$ approaches one, two, or four oxygen atoms. This suggests that the components of the basic splitting enabling fields are similar in all cases. The relative values of the first and second absorption oscillator strengths are more sensitive to the symmetry of field during the approach of $\text{Bi}^{2+}$ to the ligands: the second absorption is more intense in $C_{3v}$, $C_{2v}$, and $C_1$ fields, the first one in $C_{4v}$, and they are similar in $C_3$. In summary, the movement of $\text{Bi}^{2+}$ towards the ligands creates relevant splittings and rises the oscillator strengths; it is less efficient than the $D_{4h}$ and $D_{2h}$ tetragonal distortions at splitting the $^2P_{3/2}$ level, and as efficient as the $D_{2d}$ tetragonal deformations at giving intensity to the $^2P_{1/2} \leftrightarrow ^2P_{3/2}$ transitions.

Combined effects of ligand angular distributions and selective Bi-O distance changes are shown in Figs. 6 to 9. In Fig. 6 we see that the combination of the $D_{4h}$ tetragonal distortion with a Bi displacement along the $C_4$ axis, leading to a $C_{4v}(z)$ field, give a complicated behavior, which is not shown in any other combination. It is the result of a balance of positive and negative contributions of the same type: The effect of $S_8$ (positive and negative) on the level splitting is the same than the effect of compressed $D_{4h}$ distortions produced by negative $S_2$ values. It is, however, opposite to the effect of elongated $D_{4h}$ distortions produced by positive $S_2$ values. As a result, whereas elongated and compressed $D_{4h}$ fields split $^2P_{3/2}$ equally, only the compressed $D_{4h}$ field is effective if Bi is displaced along the $C_4$ axis. For other displacements of Bi, the effectiveness of elongated and compressed $D_{4h}$ fields are similar.
Fig. 7 shows that the splittings of $^{2}P_{3/2}$ produced by $D_{2h}$ orthorhombic fields are added to the splittings due to Bi displacements towards the ligands when these take place without leaving the main orthorhombic planes and lead to $C_{2v}$ and $C_{s}$ fields. This is not the case when Bi abandons the orthorhombic main planes to give a $C_{1}$ field. Figs. 8 and 9 indicate that the combinations of tetragonal trapezoidal $D_{4}$ and tetragonal scalenoidal $D_{2d}$ fields do not enhance the splittings due to Bi approaching the ligands.

The overall results show that a large splitting of the $^{2}P_{3/2}$ level that could drive a red shift of the $^{2}P_{3/2}(1) \rightarrow ^{2}P_{1/2}$ emission is not associated with the symmetry of the actual field. The low symmetry of the field is not particularly relevant for the splitting: many $C_{1}$ fields do not lead to an important splitting and $C_{s}$ fields can give either small or large splittings. The same happens with higher symmetry fields, like $C_{2v}$, $C_{4}$, $C_{4v}$, or $D_{2}$. Some high symmetry fields give relevant splittings, like $S_{4}$, $D_{2h}$, and $D_{4h}$, and some do not, like $D_{4}$ and $D_{2d}$. The important factor is the composition of the actual field. All fields with tetragonal $D_{4h}$ and orthorhombic $D_{2h}$ contributions give important $^{2}P_{3/2}$ splittings. They are enhanced by selective approaches of Bi to the ligands. These Bi displacements and tetragonal scalenoidal $D_{2d}$ fields give intensities to the first and second absorptions.

The results also indicate that the low symmetry fields that break the parity rule and make the present $6p \rightarrow 6p$ transitions allowed, give an upper limit to the oscillator strengths in the order of $10^{-4}$-10$^{-3}$. Similarly, radiative lifetimes of $^{2}P_{3/2}(1)$ seem to be bound by a lower limit of around 10-100 $\mu$s.

The $C_{2v}$ and $C_{s}$ fields resulting from the combination of $D_{2h}$ orthorhombic fields and Bi displacements towards the ligands on the main orthorhombic planes produce the largest $^{2}P_{3/2}$ splittings (cf. Fig. 7). They do not have oscillator strengths and emitting state lifetimes specially different from other fields.

A recent ab initio study of SrB$_{4}$O$_{7}$:Bi$^{2+}$ using the SrB$_{4}$O$_{7}$ embedding potential, which contains not only the first-neighbor field effects considered here but also the host effects, gave a $^{2}P_{3/2}$ splitting as large as 7200 cm$^{-1}$ (3460 cm$^{-1}$ experiment$^{2,7,12}$), first and second absorption oscillator strengths of $4 \times 10^{-4}$ and $1 \times 10^{-3}$, and a $^{2}P_{3/2}(1)$ radiative lifetime of 17 $\mu$s without field corrections (experiment is 12.6 $\mu$s$^{2,7,8,12}$). In this material Bi$^{2+}$ occupies a $C_{s}$ Sr site with 9-fold oxygen coordination$^{39}$ (Fig. 10). This result seems to fit well with the $C_{s}$ field resulting from the $D_{2h}$ orthorhombic field created by a $S_{3}(e_{g}e)$ distortion plus an approach of Bi towards two or four ligands. Emission lifetimes in the range of 6-17 $\mu$s have been reported
for Bi\(^{2+}\) in CaSO\(_4\), SrSO\(_4\), and BaSO\(_4\) (Refs. 2, 40), and in Sr\(_2\)P\(_4\)O\(_7\) and Ba\(_2\)P\(_4\)O\(_7\) (Refs. 3, 41). In Ba\(_2\)P\(_4\)O\(_7\), the oscillator strength of the \(^2P\(_{1/2}\) \rightarrow ^2P\(_{3/2}(1)\) absorption has been estimated to be as large as 0.03.\(^{41}\)

IV. CONCLUSIONS

SA-CASSCF/MS-CASPT2/RASSI-SO DKH wave function \textit{ab initio} calculations on a (BiO\(_8\))\(^{14−}\) cluster under the effects of an \(O_h\) confinement embedding potential have provided the energies of the \(^2P\(_{1/2}\), ^2P\(_{3/2}(1)\), and \(^2P\(_{3/2}(2)\) spin-orbit coupling levels of the \(6s^26p\) configuration of Bi\(^{2+}\) in \(O_h, D_{4h}, D_{2h}, D_4, D_{2d}, D_2, S_4, C_{4v}, C_4, C_{3v}, C_{2v}, C_2, C_s,\) and \(C_1\) fields created by oxygen coordination, together with the \(^2P\(_{1/2}\) \rightarrow ^2P\(_{3/2}(1)\) and \(^2P\(_{1/2}\) \rightarrow ^2P\(_{3/2}(2)\) absorption oscillator strengths and \(^2P\(_{3/2}(1)\) radiative lifetime.

The results indicate that it is not the symmetry of the actual field, but its tetragonal \(D_{4h}\) and orthorhombic \(D_{2h}\) components, what are responsible for the splitting of \(^2P\(_{3/2}\). \)Bi going towards two or four oxygen ligands enhances the splitting. The intensities of the first and second absorptions are mostly induced by these Bi displacements and by tetragonal scalenoidal \(D_{2d}\) fields.

The most favorable fields for a large splitting of the \(^2P\(_{3/2}\) level that could drive a red shift of the \(^2P\(_{3/2}(1)\) \rightarrow ^2P\(_{1/2}\) emission in oxygen coordination are the \(C_{2v}\) and \(C_s\) fields resulting from the combination of \(D_{2h}\) orthorhombic fields and Bi approaching two or four ligands on the main orthorhombic planes.

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TABLE I: Definitions of the basic distortions of a cubic BiO$_8$ moiety chosen in this work. The oxygen labels and the cartesian axes are defined in Fig. 1. $\hat{R}_{D_{2h}}$ and $\hat{R}_{D_2}$ are the $D_{2h}$ and $D_2$ symmetrization operators: the normalized additions of the respective group symmetry operations. $\delta x_1$, $\delta y_1$, and $\delta z_1$, are the cartesian displacement of O$_1$ from its position in the reference cube: $\delta x_1 = x_1 - x_{1,\text{ref}}$, etc. The $O_h$ irreducible representations of the coordinates and the point symmetry groups of the BiO$_8$ moiety after the atomic displacements of the individual coordinates are given. The reference cube has $d(\text{Bi-O})=2.55$ Å.

\[
\hat{R}_{D_{2h}} = \frac{1}{\sqrt{8}} \left( \hat{I} + \hat{C}_{2y} + \hat{C}_{2z} + \hat{i} + \hat{C}_{x} + \hat{\sigma}_{xy} + \hat{\sigma}_{xz} + \hat{\sigma}_{yz} \right) \\
\hat{R}_{D_2} = \frac{1}{2} \left( \hat{I} + \hat{C}_{2xy} + \hat{C}_{2x} + \hat{C}_{2z} \right)
\]

<table>
<thead>
<tr>
<th>Coord</th>
<th>Definition</th>
<th>$O_h$ irrep</th>
<th>Point group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>$\frac{1}{\sqrt{3}} \hat{R}<em>{D</em>{2h}} (\delta x_1 + \delta y_1 + \delta z_1)$</td>
<td>$a_1g$</td>
<td>$O_h$</td>
</tr>
<tr>
<td>$S_2$</td>
<td>$\frac{1}{\sqrt{6}} \hat{R}<em>{D</em>{2h}} (-\delta x_1 - \delta y_1 + 2\delta z_1)$</td>
<td>$e_g \theta$</td>
<td>$D_{4h}$</td>
</tr>
<tr>
<td>$S_3$</td>
<td>$\frac{1}{\sqrt{2}} \hat{R}<em>{D</em>{2h}} (\delta x_1 - \delta y_1)$</td>
<td>$e_g \epsilon$</td>
<td>$D_{2h}$</td>
</tr>
<tr>
<td>$S_4$</td>
<td>$\frac{1}{2} \hat{R}_{D_2} (\delta x_1 - \delta y_1 + \delta x_2 + \delta y_2)$</td>
<td>$e_u \theta$</td>
<td>$D_4$</td>
</tr>
<tr>
<td>$S_5$</td>
<td>$\frac{1}{2} \hat{R}_{D_2} (\delta x_1 - \delta y_1 - \delta x_2 - \delta y_2)$</td>
<td>$e_u \epsilon$</td>
<td>$D_{2d}$</td>
</tr>
<tr>
<td>$S_6$</td>
<td>$\delta x_{\text{Bi}}$</td>
<td>$t_{1u}x$</td>
<td>$C_{4v}$</td>
</tr>
<tr>
<td>$S_7$</td>
<td>$\delta y_{\text{Bi}}$</td>
<td>$t_{1u}y$</td>
<td>$C_{4v}$</td>
</tr>
<tr>
<td>$S_8$</td>
<td>$\delta z_{\text{Bi}}$</td>
<td>$t_{1u}z$</td>
<td>$C_{4v}$</td>
</tr>
</tbody>
</table>
TABLE II: Combined distortions explored in this work that lead to low symmetry fields. Minimum Bi-O and O-O distances reached in the explored distortions, in Å.

<table>
<thead>
<tr>
<th>Symmetry Distortion</th>
<th>g distortions</th>
<th>\text{min } \textit{d} (Bi-O)</th>
<th>\text{min } \textit{d} (O-O)</th>
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<tr>
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<td>( S_1 )</td>
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<td>( S_2 )</td>
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<td>( S_3 )</td>
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<td>2.74</td>
</tr>
<tr>
<td>( D_4 )</td>
<td>( S_4 )</td>
<td>2.55</td>
<td>2.94</td>
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<td>2.69</td>
</tr>
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<td>2.71</td>
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<td>( S_2 = S_4 )</td>
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</tr>
<tr>
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<td>2.71</td>
</tr>
<tr>
<td>( C_{2v(z)} )</td>
<td>( S_3 = S_5 )</td>
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<td>2.94</td>
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<tr>
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<td>( S_5 = S_6 = S_7 = S_8 )</td>
<td>2.21</td>
<td>2.84</td>
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</table>
Figure captions

FIG. 1: Atomic labels and cartesian axes of the BiO$_8$ moiety used in this work. Red arrows indicate the $S_1$ distortion defined in Table I.

FIG. 2: $S_2$ to $S_8$ basic distortions of the BiO$_8$ moiety chosen in this work as defined in Table I. $S_1$ is represented in Fig. 1.

FIG. 3: Bottom: Energies of the first excited state $^2P_{3/2}(1)$ (red lines) and second excited state $^2P_{3/2}(2)$ (blue lines) relative to the ground state $^2P_{1/2}$, $\Delta E$, in $O_h$, $D_{4h}$, $D_{2h}$, $D_4$, and $D_{2d}$ fields. Middle: First and second absorption electric dipole oscillator strengths, $f_{\text{abs}}(^2P_{1/2} \rightarrow ^2 P_{3/2}(1))$ (full red lines) and $f_{\text{abs}}(^2P_{1/2} \rightarrow ^2 P_{3/2}(2))$ (full blue lines); emitting state $^2P_{3/2}(1)$ radiative lifetime $\tau_{\text{rad}}$ (dashed red lines). Top: Distortions of the BiO$_8$ moiety leading to the fields.

FIG. 4: Energies of the first and second excited states relative to the ground state, $\Delta E$; first and second absorption electric dipole oscillator strengths, $f_{\text{abs}}$; and emitting state radiative lifetime, $\tau_{\text{rad}}$, in $D_{2(xy)}$, $C_4$, $S_4$, $D_{2(x)}$, and $C_{2v(z)}$ fields. See Fig. 3 caption for the meanings of the lines.

FIG. 5: Energies of the first and second excited states relative to the ground state, $\Delta E$; first and second absorption electric dipole oscillator strengths, $f_{\text{abs}}$; and emitting state radiative lifetime, $\tau_{\text{rad}}$, in $C_{4v(z)}$, $C_{2v(yz)}$, $C_{3v(xy)}$, $C_{s(yz)}$, and $C_1$ fields. See Fig. 3 caption for the meanings of the lines.

FIG. 6: Energies of the first and second excited states relative to the ground state, $\Delta E$; first and second absorption electric dipole oscillator strengths, $f_{\text{abs}}$; and emitting state radiative lifetime, $\tau_{\text{rad}}$, in $C_{4v(z)}$, $C_{4(z)}$, $C_{s(yz)}$, and $C_1$ fields. See Fig. 3 caption for the meanings of the lines.
FIG. 7: Energies of the first and second excited states relative to the ground state, $\Delta E$; first and second absorption electric dipole oscillator strengths, $f_{\text{abs}}$; and emitting state radiative lifetime, $\tau_{\text{rad}}$, in $C_{2v}(z)$, $C_{2v}(y)$, $C_{s(yz)}$, and $C_{1}$ fields. See Fig. 3 caption for the meanings of the lines.

FIG. 8: Energies of the first and second excited states relative to the ground state, $\Delta E$; first and second absorption electric dipole oscillator strengths, $f_{\text{abs}}$; and emitting state radiative lifetime, $\tau_{\text{rad}}$, in $C_{4}(z)$, $C_{2}(y)$, and $C_{1}$ fields. See Fig. 3 caption for the meanings of the lines.

FIG. 9: Energies of the first and second excited states relative to the ground state, $\Delta E$; first and second absorption electric dipole oscillator strengths, $f_{\text{abs}}$; and emitting state radiative lifetime, $\tau_{\text{rad}}$, in $C_{2v}(z)$, $C_{s(yz)}$, and $C_{1}$ fields. See Fig. 3 caption for the meanings of the lines.

FIG. 10: Oxygen coordination of Bi$^{2+}$ in a $C_{s}$ Sr site of SrB$_{4}$O$_{7}$:Bi$^{2+}$. The Sr-O distances in the undoped host are: Sr-O$_{a}$ 2.73 Å, Sr-O$_{b}$ 2.47 Å, Sr-O$_{c}$ 2.68 Å, Sr-O$_{d}$ 2.79 Å, and Sr-O$_{e}$ 2.90 Å [Ref. 39].
Figure 1. Seijo and Barandiarán
Figure 2. Seijo and Barandiarán
Figure 3. Seijo and Barandiarán
Figure 4. Seijo and Barandiarán
Figure 5. Seijo and Barandiarán
Figure 6. Seijo and Barandiarán
Figure 7. Seijo and Barandiarán
Figure 8. Seijo and Barandiarán
Figure 9. Seijo and Barandiarán
Figure 10. Seijo and Barandiarán