Structural Dynamics of Bismuth Triiodide in Solution Triggered by Photoinduced Ligand-to-Metal Charge Transfer

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Supporting Information

ABSTRACT: Bismuth triiodide, BiI₃, is one of the simplest bismuth halides, which have recently attracted considerable attention because of their promising properties. Here, we investigate the structural dynamics of a photoinduced reaction of BiI₃ in solution phase using time-resolved X-ray liquidography (TRXL) and density functional theory (DFT) and time-dependent DFT (TDDFT) calculations. The photoreaction was initiated by excitation at 400 nm, which corresponds to the ligand-to-metal charge-transfer transition. The detailed structures and kinetic profiles of all relevant intermediate species from the TRXL data show that the trigonal planar structure of BiI₃, which is predicted to be the most stable structure of the lowest excited state by TDDFT calculation, was not observed, and the photoreaction proceeds via two parallel pathways within the time resolution of 100 ps: (i) isomer formation to produce iso-BiI_2—I, which relaxes back to the ground-state structure, and (ii) dissociation into BiI₂ and I⁻ radicals, which nongeminately recombine to generate ground-state BiI₃ and I₂.

Metal halides, a class of polyhalogenated compounds, have attracted much interest because of their remarkable photophysical and photochemical properties and their controllability with different ligands.¹–³ In particular, light-driven processes of metal halides in the liquid solution phase have been investigated intensely because of fundamental interest and their wide applicability for various optoelectronic materials.⁴−¹⁰ However, because of the presence of heavy atoms, photoexcited metal halides undergo complex relaxation pathways, both radiative and nonradiative, making it challenging to elucidate the detailed mechanisms of photoinduced processes. Among metal halides, bismuth-based compounds have come into the spotlight in many fields of chemistry and physics for their low toxicity and low cost compared with other metal halide compounds.¹⁰ For example, bismuth halides have recently been proposed as one of the most promising lead-free metal halide materials for solid-state perovskite photovoltaics.¹¹–¹⁴ In addition, they are good catalysts for various organic reactions, including Diels–Alder reactions and acylation reactions.¹⁵,¹⁶ Bismuth triiodide, BiI₃, is the simplest bismuth halide and can serve as an excellent model system to investigate the characteristics of bismuth halides. Initially, Molnar et al. pioneered the detailed molecular structure of BiI₃ using gas-phase electron diffraction combined with vibrational spectroscopy.¹⁷ While most of previous studies of BiI₃ have focused on the characterization of the structure and photophysical properties of solid-state BiI₃,¹⁸ Horvath et al. have demonstrated, in their studies on BiI₃(α−β−γ−δ)−, ultraviolet (UV) photoexcitation of BiI₃ in solution with the solvent of acetonitrile, subsequently leading to photoredox decomposition generating molecular iodine as a final product.¹⁹,²⁰ To the best of our knowledge, however, the mechanism of the UV-initiated photoreaction of BiI₃ in the liquid solution phase has never been investigated. In particular, the reaction intermediates involved in the photoreaction of BiI₃ and their detailed kinetics have not been determined yet. Although crystalline BiI₃ in the solid phase has been a hot topic because of their technological applications, it is necessary to elucidate the photochemical behavior of a constituent unit cell, that is, solvated molecular BiI₃ in solution, for a better understanding of the optoelectronic properties of the material.

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Previously, the major intermediates generated by photoexcitation of polyhalogenated compounds were identified by time-resolved spectroscopic and X-ray scattering experiments. In particular, isomeric species of polyhalogenated compounds have been identified as key intermediates involved in the relaxation of dissociative excited states. For example, Tarnovsky and co-workers have studied ultrafast photoisomerization of various polyhalide compounds in solution by using ultrafast time-resolved spectroscopy and quantum calculations. Recently, time-resolved X-ray solution scattering (TRXXS), also known as time-resolved X-ray liquidography (TRXL), has been widely used to directly capture the structures of transient intermediates. Using TRXL, Ahn et al. recently reported a global scheme for the reaction pathways of UV-excited CHI in cyclohexane and, especially, identified an isomeric reaction intermediate, iso-CHI-I. In addition, using TRXL, Marcellini and co-workers observed the solvent-dependent formation of two types of isomeric species of CHI,IBr.

In this work, we investigate the photoinduced structural dynamics of BiI4 in acetonitrile by TRXL. Upon UV excitation, BiI4 is expected to undergo photochemical reactions including dissociation, bond formation, and isomer formation. Three possible candidate intermediates based on the literature and our theoretical predictions by quantum calculation are presented in Figure 1. In the present study, we employ the excitation at 400 nm, which excites the lowest transition of BiI4 in acetonitrile solution. This transition has been assigned to the LMCT transition, which generally induces intramolecular photoredox reactions with the metal center reduced and ligands oxidized.

Experimental scattering curves measured at various time delays from a TRXL experiment are shown in Figure 2a, together with theoretical scattering curves that were fit to the experimental scattering curves using the best kinetic model, which will be discussed below.

It can be seen that the experimental and theoretical curves are in good agreement with each other, indicating the relevance of the kinetic model. In Figure 2b, difference radial intensities, $r^2\Delta R(r)$, obtained by sine-Fourier transform of the difference scattering curves in Figure 2a are shown together with theoretical $r^2\Delta R(r)$ curves that well reproduce the experimental ones. The scattering signal of a solution sample can be decomposed into (i) the solute-only term, (ii) the cage term, and (iii) the solvent-only term, as shown in Figures S1–S3 in the Supporting Information. Note that, as shown in Figure S1, the total scattering intensity of the solution sample is dominated by the solute-only term because of large atomic form factors of the heavy atoms in the solute molecule and the substantial structural changes of the solute molecule.

To find the best kinetic model that can describe the mechanism of photoreaction of BiI4, we examined four candidate reaction pathways: (i) formation of trigonal planar BiI4 with $D_{3h}$ symmetry, which is predicted as the most stable structure of the lowest singlet excited state $S_1$ according to our time-dependent density functional theory (TDDFT) calculations (which will be discussed below); (ii) formation of dissociation fragments (BiI2 + I); (iii) formation of an isomer, iso-BiI2−I, as observed in photoexcitations of various polyhalogenated compounds; and (iv) formation of a mixture of dissociation fragments (BiI2 + I) and iso-BiI2−I. As an example of examining these candidate pathways, we show in Figure 3 the results of the fitting analysis for the experimental scattering curve at 100 ps. The candidate pathway (i), that is, the formation of trigonal planar BiI4 with $D_{3h}$ symmetry, exhibits a marked discrepancy between the experimental curve and the theoretical curve, giving the highest $\chi^2$ value. The fit curve of the candidate pathway (ii) agrees well with the experimental curve up to $q = 6$ Å$^{-1}$ but shows deviation at high $q$ values of 6–9 Å$^{-1}$. By contrast, the fit curve of (iii) gives slightly better agreement at high $q$ values but deviates significantly in the low $q$ region around 1–2 Å$^{-1}$. The experimental curve is most satisfactorily reproduced with the candidate pathway (iv) that combines pathways (ii) and (iii), indicating that the LMCT transition induced by 400 nm excitation leads to both isomer formation and dissociation of BiI4. Accordingly, the theoretical scattering curves shown in Figure 2 were obtained with the kinetic model involving the candidate pathway (iv).

This finding can be more intuitively represented when the scattering intensities in $q$-space are sine-Fourier transformed into radial intensities in real space. As X-ray crystallography can determine the structure of a crystal in real space, the real space representation of the solution scattering signal directly visualizes the average structure of the solute molecules in solution, even though the solution scattering data are one-dimensional and therefore contain much less structural information than those from X-ray crystallography.
visualize the structural change of BiI3 with higher clarity, we focus on the solute-only difference radial intensities, $r^2 \Delta R_{\text{solute}}(r)$, at 100 ps. Details of how to extract the solute-only contribution are described in the Supporting Information. In Figure 4a–d, the theoretical $r^2 \Delta R_{\text{solute}}(r)$ curves for the four candidate pathways are compared with the experimental $r^2 \Delta R_{\text{solute}}(r)$ curve. In Figure 4e, various interatomic distances in the reactant and the candidate photoproducts are indicated by colored arrows, and these interatomic distances are indicated by vertical bars of corresponding colors at the bottom of Figure 4a–d.

For example, ground-state BiI3 has two types of atomic pair distances: the three equivalent Bi–I bond lengths of 2.82 Å and the three equivalent I···I distances of 4.26 Å. When some of these atomic pair distances are changed in the reaction, negative peaks will be observed at the original values of the interatomic distances in the ground-state BiI3, as indicated by downward bars in Figure 4a–d. Indeed, the experimental $r^2 \Delta R_{\text{solute}}(r)$ has (i) negative peaks at r values corresponding to the atomic pair distances in the ground-state BiI3 and (ii) broad positive features around 5–6 Å, which implies that one or more Bi–I distances in the ground-state BiI3 are changed and new atomic pairs with longer distances are formed in the reaction. For candidate pathway (i) shown in Figure 4a, there are considerable discrepancies between the theoretical and experimental $r^2 \Delta R_{\text{solute}}(r)$ as in the reciprocal space representation shown in Figure 3. In particular, theoretical $r^2 \Delta R_{\text{solute}}(r)$ for $D_{3h}$ trigonal planar BiI3 shows two derivative-like features at ~3 and ~5 Å. These features arise from the Bi–I and I···I distances of $D_{3h}$ trigonal planar BiI3, which are longer than those of ground-state BiI3, as represented by green upward bars in Figure 4a. For candidate pathway (ii) shown in Figure 4b, the theoretical curve decently reproduces the two negative peaks originating from the depletion of one Bi–I and two I···I distances of ground-state BiI3, but it does not describe at all the broad positive feature at distances longer than ~5 Å in the experimental $r^2 \Delta R_{\text{solute}}(r)$ because two Bi–I and one I···I distances of BiI2 are slightly shorter than those of ground-state BiI3. For candidate pathway (iii) shown in Figure 4c, the positive and negative features of the theoretical $r^2 \Delta R_{\text{solute}}(r)$ are located at the same positions as those of the experimental $r^2 \Delta R_{\text{solute}}(r)$ because of longer I···I and Bi–I distances of newly formed iso-BiI2 than those of depleted ground-state BiI3, but the intensities of those features in the theoretical and experimental $r^2 \Delta R_{\text{solute}}(r)$ do not match each other. In contrast, as shown in Figure 4d, candidate pathway (iv), which combines pathways (ii) and (iii), gives excellent agreement between the experimental and theoretical $r^2 \Delta R_{\text{solute}}(r)$, indicating the reaction mechanism involves the two parallel reaction pathways, that is, dissociation and isomer formation.

The reaction mechanism of photoinduced reaction of BiI3 in acetonitrile and the time-dependent concentrations of all the reactant and photoproduct species determined from the TRXL data are shown in panels (a) and (b) of Figure 5, respectively. According to the TRXL results, 52.6 ± 0.6% of ground-state BiIIII3 (where the oxidation number of Bi is indicated) is initially excited to the LMCT state, I·BiIIII3, resulting in the reduction of the central BiIIII atom to BiI and the oxidation of

Figure 2. TRXL signals of BiI3 in acetonitrile measured with excitation at 400 nm. (a) Experimental (black) and theoretical (red) difference scattering curves, $q\Delta S(q)$. (b) Difference radial intensities, $r^2 \Delta R(r)$, obtained by sine-Fourier transformation of $q\Delta S(q)$ in panel a.

Figure 3. Fits of the difference scattering curve at 100 ps using four candidate pathways: (i) formation of trigonal planar BiI3 with $D_{3h}$ symmetry, (ii) dissociation fragments (BiI2·+ I), (iii) iso-BiI2→I, and (iv) a mixture of iso-BiI2→I and dissociation fragments (BiI2·+ I). Experimental (black) and theoretical (red) difference scattering curves, $q\Delta S(q)$, are shown with the residuals (blue) obtained by subtracting the theoretical $q\Delta S(q)$ from the experimental $q\Delta S(q)$. The $\chi^2$ value and the molecular structures of photoproducts are also shown for each candidate pathway. Candidate (iv) gives the best fit.
the I ligand to the I radical. Subsequently, 68.3 ± 1.5% of the excited molecules rapidly relax back to the ground state while releasing a part of the photoexcitation energy as heat to surrounding solvent molecules. Among the remaining 31.7 ± 1.5% of excited molecules, 12.0 ± 0.6% isomerize to form iso-BiI2–I and 19.7 ± 1.0% dissociate to yield BiI2· and I · radicals. Because both of these reaction pathways occur faster than our temporal resolution (100 ps), the kinetic components corresponding to them are not identified from the TRXL data. The iso-BiI2–I isomer reisomerizes back to the ground state with a time constant of 3.90 ± 0.41 ns. The dissociation fragments, BiI2· and I ·, nongeminately recombine to form the ground state BiI3 and molecular iodine with bimolecular rates of 3.34 (±0.43) × 1010 M⁻¹ s⁻¹ and 1.90 (±0.48) × 1010 M⁻¹ s⁻¹, respectively. These mixed processes of the fast unimolecular relaxation and the two slow bimolecular recombination reactions can also be identified from right singular vectors (RSVs) obtained from singular value decomposition (SVD) of the TRXL data in a high-q region, where the solute term is dominant. As can be seen in Figure S5, the RSVs for both the experimental and theoretical scattering curves are well described by a sum of two exponential functions, of which one is attributed to the fast unimolecular relaxation and the other describes the slow bimolecular reactions.

To confirm the validity of the reaction mechanism involving the two parallel pathways, we performed the geometry optimization of the ground electronic states of BiI3 using density functional theory (DFT), and its results are illustrated in Tables S1 and S2. The ground-state BiI3 has a pyramidal structure with a Bi–I bond of 2.826 Å length and two Bi–I bonds of 2.824 Å length. Because the two types of Bi–I bond lengths are different by only 0.002 Å, the ground-state BiI3 can be regarded as belonging to the C₃v symmetry group, and we label it as S₀-C₃v. We also found the optimized structure of the isomer species, iso-BiI2–I, in S₀ state and labeled it as S₀-iso. S₀-iso is located at a shallow minimum with the energy of 1.73 eV relative to S₀-C₃v. From the calculated energies of (i) the transition state, S₀-TS, between S₀-iso and S₀-C₃v and (ii) the
dissociation fragments (BiI₂ + I⁻), the barrier from S₅ iso to S₅-
C₃ is estimated to be only 0.06 eV and the energy required for
dissociation into radicals should be at least 0.39 eV. Thus, after
the formation of S₅ iso, the relaxation back to the ground state
(S₅ C₃) should be favored over the dissociation into the
radical fragments, BiI₂ + I⁻. This result of DFT calculation on
the energetics of S₅ is consistent with the optimal kinetic
model, where iso-BiI₂ I relaxes back to the ground state
instead of being dissociated into radicals and the pathway of
isomer formation is parallel with the dissociation pathway.

The optimized structural parameters of the reactant and
photoproduction species determined from the TRXL experiment
and DFT calculations are presented in Figure 6. Overall, the
bond lengths obtained from the DFT calculations are
overestimated by 0.3–1.6% compared with the experimentally
determined values. Also, the dihedral angle of iso-BiI₂ I was
predicted to be −142.0° from the DFT calculation, in contrast
to −64.9° determined from the TRXL experiment, meaning
that the DFT-predicted geometry of iso-BiI₂ I is more planar
than the one determined by the TRXL experiment. We note
that the structure of iso-BiI₂ I strongly depends on the choice
of DFT functional and the solvation field, which was also the
case for iso-CHI₂ I, while the structure of BiI₃ is less sensitive
to those factors, as listed in Tables S1 and S2. The dependence
of optimized structure on DFT functional and the comparison
of DFT-optimized and TRXL-determined structures are
discussed in detail in the Supporting Information.

From the TRXL measurement, we found that photoexcited BiI₃
in acetonitrile undergoes two parallel reactions: (i) formation of iso-BiI₂ I and (ii) dissociation into BiI₂ and I⁻
radicals. The branching ratio between the isomer formation
and the dissociation is 38:62 with an uncertainty of 3. In
addition, the detailed structures of the photoproducts, iso-
BiI₂ I and BiI₂, were determined by virtue of structural
sensitivity of TRXL. In particular, it should be noted that Bi–I
bonds are shortened in both BiI₂ and iso-BiI₂ I compared
with that in the ground-state BiI₃. Such contraction of the Bi–I
bond induced by the photoreaction is consistent with recent studies of other trihalides, AX₃, where A = CH, B, or P and X =
I or Br. In addition, we note that the I–I bond (3.44 Å) of iso-
BiI₂ I is considerably long, even longer than Bi–I bonds
(2.68–2.82 Å), which are in principle expected to be longer
than I–I bonds, of the reactant and photoproduction of BiI₃,
including BiI₂, and iso-BiI₂ I. The long X–X bond is a
common structural feature of isomeric species of other
trihalides. Especially, the I–I bond of iso-BiI₂ I is significantly
longer than that of other trihalide isomers. The halogen–
halogen bond in isomeric species of various halocarbons has
the character of polar covalent bond and therefore can be
affected by the polar environment. According to a study on
CHBr₃, it was theoretically shown that the structure of iso-
CHBr₂ Br varies depending on the solvent polarity, especially
with the Br–Br bond length being proportional to the solvent
polarity. Additionally, the I–I bond of iso-BiI₂ I (3.44 Å) is
long in acetonitrile, which is a polar solvent, and especially
much longer than the I–I bond of an isomer, iso-CHI₂ I,
(2.92 Å) formed from the photoreaction of CHI₁ in nonpolar
cyclohexane, which was recently investigated using TRXL. In
addition, according to the study on CHBr₃, the lifetime of the
isomeric species changes depending on the solvent polarity,
from a few nanoseconds in polar solvents to microseconds
in nonpolar solvents. Such solvent dependence of lifetime of the
isomeric species can be attributed to the polar nature of the
transition state between iso-BiI₂ I and the ground state (S₀-
C₃) (see the Supporting Information and Table S2). Because
the transition state can be stabilized with solvation by polar
solvent molecules, the barrier for back isomerization to the
ground state becomes smaller. In fact, iso-BiI₂ I in (polar)
acetonitrile (3.90 ns) exhibits much shorter lifetime than iso-
CHI₂ I in (nonpolar) cyclohexane (330 ns).

The TRXL data show no evidence for the formation of
trigonal planar BiI₃ with D₃₃ symmetry, which is predicted
to be the most stable structure in the S₁ state of BiI₃. We propose
that, at the earliest stage of the photoreaction, the trigonal
planar BiI₃ with D₃₃ symmetry may serve as a primary reaction
intermediate that branches into the two reaction pathways, that
is, the formation of iso-BiI₂ I and the dissociation fragments.

In this work, we investigated the spatiotemporal kinetics of
photoinduced reaction of BiI₃ in solution. By analyzing the
time-dependent X-ray scattering signals, we identified
the kinetics and structures of major intermediate species. We also
performed DFT/TDDFT quantum calculations for BiI₃, which
support our experimental findings. Interestingly, trigonal planar
BiI₃ with D₃₃ symmetry is predicted as the optimum structure
of S₁ according to our calculation, but it was not observed from
the analysis of our TRXL data. This stable form of BiI₃ may
be the primary intermediate formed at the earliest stage of the
reaction. It should be feasible to directly observe the evolution
dynamics of this primary intermediate with ultrafast optical
spectroscopy or femtosecond X-ray scattering using an X-ray
free electron laser (XFEL). The present contribution may
initiate further studies of BiI₃ and related trihalide/metal halide
systems, which will enable us to extend our understanding of
the underlying reaction mechanism of those systems.

Figure 6. Comparison of structures of ground-state BiI₃, iso-BiI₂ I,
and BiI₂ determined from the experimental TRXL data and their
DFT-optimized structures. The values of the bond lengths and bond
angles determined from the global fit analysis of the TRXL data are
shown in black font, and those from DFT calculations are shown in
blue font in parentheses. For iso-BiI₂ I, the dihedral angle is also
indicated by a dashed circular arrow in the lower right panel.
Details of TRXL experiment, data processing, data analysis, density functional theory calculation, and molecular dynamics simulation; decomposition of solution scattering signal, \( q\Delta S(q, t) \) and \( \Delta R(r, t) \); experimental solute-only \( \rho^2 \Delta R(r, t) \); SVD analysis of experimental, theoretical, and mock data; polychromatic correction; DFT-optimized versus experimentally determined structures of BiI₃, BiI₅, and iso-BiI₂—I (PDF)

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**Notes**

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