Global Sampling of the Photochemical Reaction Paths of Bromoform by Ultrafast Deep-UV Through Near-IR Transient Absorption and ab initio Multiconfigurational Calculations

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Global sampling of the photochemical reaction paths of bromoform by ultrafast deep-UV through near-IR transient absorption and \textit{ab initio} multiconfigurational calculations

S. K. Pal,\textsuperscript{a,b} A. S. Mereshchenko,\textsuperscript{a} E. V. Butaeva, P. Z. El-Khoury,\textsuperscript{c} and A. N. Tarnovsky\textsuperscript{d}

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Ultrafast deep-ultraviolet through near infrared (210–950 nm) transient absorption spectroscopy complemented by \textit{ab initio} multiconfigurational calculations offers a global description of the photochemical reaction pathways of bromoform following 255-nm excitation in methylcyclohexane and acetonitrile solutions. Photoexcitation of CHBr\textsubscript{3} leads to the ground-state \textit{iso}-CHBr\textsubscript{3} product in a large quantum yield (\textasciitilde35\%), formed through two different mechanisms: concerted excited-state isomerization and cage-induced isomerization through the recombination of the nascent radical pair. These two processes take place on different time scales of tens of femtoseconds and several picoseconds, respectively. The novel ultrafast direct isomerization pathway proposed herein is consistent with the occurrence of a conical intersection between the first excited singlet state of CHBr\textsubscript{3} and the ground electronic state of \textit{iso}-CHBr\textsubscript{3}. Complete active space self-consistent field calculations characterize this singularity in the vicinity of a second order saddle point on the ground state which connects the two isomer forms. For cage-induced isomerization, both the formation of the nascent radical pair and its subsequent collapse into ground-state \textit{iso}-CHBr\textsubscript{3} are directly monitored through the deep-ultraviolet absorption signatures of the radical species. In both mechanisms, the optically active (i.e., those with largest Franck-Condon factors) C–Br–Br bending and Br–Br stretching modes of ground-state \textit{iso}-CHBr\textsubscript{3} have the largest projection on the reaction coordinate, enabling us to trace the structural changes accompanying vibrational relaxation of the non-equilibrated isomers through transient absorption dynamics. The \textit{iso}-CHBr\textsubscript{3} photoproduct is stable in methylcyclohexane, but undergoes either facile thermal isomerization to the parent CHBr\textsubscript{3} structure through a cyclic transition state stabilized by the polar acetonitrile medium (\textasciitilde300-ps lifetime), and hydrolysis in the presence of water. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4789268]

I. INTRODUCTION

The dynamics of photochemical reaction intermediates, non-equilibrated species featuring perturbed molecular and electronic structures, is an active area of investigation. Energy flow in such species, in part driven by the topology of the Franck-Condon (FC) region, cannot be predicted \textit{a priori}. Recent works stress that in many cases there are distinct parallels between the short-time reaction paths in the gas- and solution phases,\textsuperscript{1–4} despite different chemical outcomes in the different environments. This encourages comparing molecular dynamics in the two phases for a better understanding of the underlying processes in molecular systems and the nature of system-bath coupling. In this work, we investigate the photochemical reaction dynamics of bromoform, a polyhaloalkane molecule of significant interest to environmental photochemistry. Bromoform primarily originates from biogenic sources, such as phytoplankton and seaweeds in the ocean.\textsuperscript{4–8} Ultraviolet (UV) irradiation of polyhalomethanes in aqueous environments is associated with the release of a significant amount of strong acids, e.g., HBr from CHBr\textsubscript{3}.\textsuperscript{9,10} In addition, bromoform readily evaporates and is reputed to be the prevalent source of active bromine in the earth’s atmosphere.\textsuperscript{11,12}

The UV absorption spectrum of bromoform, which extends to around 310 nm, is dominated by the \( \tilde{X}^1A_1 \rightarrow \tilde{B}^1E \) transition to the second excited singlet state at \( \sim220 \) nm (5.63 eV).\textsuperscript{13} Low-lying singlet and triplet states are thought to mainly arise from single electron excitations from the Br lone pair \( \pi \) orbitals into the C–Br \( \sigma^* \) orbitals, \( n(\text{Br}) \rightarrow \sigma^*(\text{C–Br}) \). Resonant Raman spectra of CHBr\textsubscript{3} collected upon 266 and 239.5 nm excitation reveal a multidimensional evolution in the FC region, with an initial wavepacket motion along the Br–C–Br symmetric bend \( (v_6) \), the H–C–Br asymmetric bend \( (v_3) \), the Br–C–Br symmetric stretch \( (v_2) \), and the Br–C–Br asymmetric stretch \( (v_5) \).\textsuperscript{14} The UV photochemistry of gas-phase CHBr\textsubscript{3} has been the subject of extensive studies over the last two decades. An early 200-nm photolysis study of CHBr\textsubscript{3} suggested a primary loss of Br atoms and subsequent unimolecular decomposition of nascent hot CHBr\textsubscript{2} radicals to yield the detected CBr fragments.\textsuperscript{15} Following 193-nm excitation of CHBr\textsubscript{3}, a rapid loss of...
one Br atom from a repulsive excited electronic state was the only primary photolysis channel. However, 234- and 267-nm single-photon excitation of CHBr3 led both to atomic and molecular bromine elimination, with quantum yields of 0.74 and 0.26 and 0.84 and 0.16 for these two channels, respectively. Most of the bromine atoms were formed in the ground Br(3P1/2) rather than in the spin-orbit excited Br(3P3/2) state. The presence of dissociation pathway(s) in CHBr3 at short wavelengths other than breaking of a C–Br bond was consistent with the Br atom quantum yield measurements, yielding unity from 303 to 306 nm and only 0.76 at 266 nm. The North group revisited the photochemistry of CHBr3 and concluded a unity quantum yield for the Br-atom dissociation channel upon single-(248 nm)-photon excitation. Although CHBr fragments were observed, they were assigned to sequential photodissociation of a fraction of CHBr3 primary products. This controversy inspired further studies by Huang et al. who reported molecular elimination of Br2 in a 0.23 quantum yield upon 248-nm excitation of CHBr3. It was speculated that excited state CHBr3 species non-radiatively decay to highly excited vibrational states of the ground electronic state potential, where the concerted elongation of two C–Br bonds carries CHBr3 over the elimination barrier to form vibrationally excited Br2. The same group detected Br2 following 248-nm excitation of CF2Br2 and 1,1- and 1,2-C2H5Br2 nonethannethal, however, assigning these observations to ground-state asynchronous concerted elimination. More recently, Quandt, Reid, and co-workers invoked the (H)BrC–Br–Br (iso-CHBr3) isomer—a high-energy intermediate on the ground-state potential surface of CHBr3—to explain the observation of molecular bromine. A similar intermediate was previously proposed to rationalize the formation of molecular iodine in a high-energy (12 eV) photodissociation study of a structurally related halogenated alkane, namely, CH2I2. However, to date there have been no direct experimental or computational evidence for the importance of isomerization in the gas-phase photochemical decomposition.

In condensed phases, isomers implicated through the photodissociation of a carbon-halogen bond, followed by geminate recombination of the nascent radicals (cage-induced isomerization) have been well-characterized for several di- and polyhalogenated alkanes. Recently, the ultrafast (≤2 ps) formation of molecular iodine from iso-CF2I2 in nonpolar solvents suggested that these isomers may in some cases be precursors for molecular halogen elimination. For CHBr3 in cyclohexane, Phillips and co-workers observed the ISO-CHBr3 product at 0 and 10 ns delay times between the 282,4-nm Raman pump and 435.7-nm probe pulses. Using a similar nanosecond transient resonance Raman technique for CHBr3 in methanol, the CHBr2 radicals were identified using a 200-nm probe wavelength. A picosecond time-resolved resonance Raman (ps-TR3) investigation by the same group suggested that iso-CHBr3 is produced within the first several picoseconds after 267-nm photolysis of CHBr3 in acetonitrile solution containing 0.2% of water (ννννν). The iso-mer undergoes vibrational cooling within 50 ps, then decays with a 230-ps time constant with a concurrent buildup of CHBr2OH. This hydrolysis product was thought to be formed through an O–H insertion/HBr elimination reaction between iso-CHBr3 and water, thermodynamically accessible based on the MP2 calculations of the stationary points on the ground-state potential energy surface for the iso-CHBr3 + nH2O (n = 1, 2, 3) reaction. The HBr leaving group of the reaction dissociates into ions in aqueous environments, which explains the observed photochemical conversion of bromoform to bromide ions in aqueous solutions. The formation of iso-CHBr3 in neat bromoform and concentrated cyclohexane solutions was studied by Crim and co-workers using ultrafast transient absorption spectroscopy. In their work, a 390-nm transient absorption band emerges within the first 1 ps after 267-nm excitation of neat bromoform, decays with a 13-ps time constant, and serves as a precursor for another absorption band at 495 nm. The 390-nm band was assigned to iso-CHBr3, formed by the geminate recombination of the nascent radicals. The 495-nm band shifts to 430 nm in a 98%/2% cyclohexane/bromoform solution. This band was attributed to a charge-transfer complex (CTC) between bromoform and a Br-atom released by iso-CHBr3, based on an early work by Shoute and Neta who proposed that the 425-nm product band observed within 1 μs after pulse radiolysis of CHBr3 in cyclohexane arises from Br·CHBr3 CTC. Recently, Reid and co-workers trapped iso-CHBr3 following 220-nm irradiation of CHBr3 in Ar and Ne matrices. The absorption spectrum of iso-CHBr3 exhibits a 245-nm band, and a more intense 398-nm band (molecular extinction coefficient, ε = 18600 M–1 cm–1) with a ~560-nm shoulder. This is consistent with early observations of the absorption of color centers developed in frozen hydrocarbon solutions containing bromoform following their exposure to near-UV light.

In this work, broadband ultrafast transient absorption spectroscopy in conjunction with high level ab initio multiconfigurational and time-dependent density functional calculations reveal ultrafast population dynamics and structural changes in the UV photochemistry of bromoform, a prototypical polyhaloalkane molecule. The probing range is extended to 210 nm in this work, affording a global detection of all the photoproducts formed following UV excitation of CHBr3 in different media. The broadly tunable probe pulses employed herein are of utmost importance in a quest to study photodissociation reactions where the radical and/or ionic fragment species produced often absorb in the deep UV spectral region. Following excitation of bromoform in solution, direct experimental evidence is obtained for cage-induced recombination of the photogenerated radical pair which leads to the formation of the iso-CHBr3 product. We also observed the direct formation of iso-CHBr3 from the parent structure, namely, tetrahedral CHBr3. The ultrafast direct excited-state isomerization mechanism documented herein is the first reported mechanism of its kind for isomerization in di- and polyhalogenated alkanes. The observation is supported by complete active-space self-consistent field (CASSCF) calculations, revealing a readily accessible conical intersection which connects CHBr3 in its first excited singlet state to iso-CHBr3 on the ground electronic state. Vibrational energy flow along the reaction coordinate modes in the non-equilibrated isomer species, traced in acetonitrile and methylcyclohexane, helps.
us to envisage the complex energy landscape of the CHBr$_3$ system.

II. METHODS

A. Computational methods

Unconstrained geometry optimization was performed to locate the two isomer forms on the ground state potential energy surface. The geometry optimization, ground-state relaxed redundant coordinate scans, and ground-state intrinsic reaction coordinate (IRC) scans all were performed using the B3LYP, CAM-B3LYP, M06-2X, and MP2 methods. All calculations were performed in the gas phase, as well as in methycyclohexane, acetonitrile, and bromoform, simulated using the polarizable continuum model (PCM). The fully optimized density functional theory (DFT) iso-CHBr$_3$ ground-state minima were used to compute vertical excitation transition (VET) energies in all media considered in this work using time dependent density functional theory (TD DFT) and the polarizable continuum model (TD DFT/PCM). The VET energies of other possible photoproducts (CHBr$_2^-$, CHBr$_2^+$, and CH$_2$BrOH) were similarly computed to aid in assigning the measured transient absorption spectra. Using the aug-cc-pVXZ series (where X = D, T, Q) which constitutes a logical sequence of basis sets converging to the basis set limit, it was found that the geometrical parameters and spectroscopic quantities are almost converged with respect to a further increase in basis set description at the triple-$\zeta$ limit. Hence, all DFT/TDDFT calculations reported in the main text employ the aug-cc-pVTZ basis set, performed using GAUSSIAN 09. The multiconfigurational CASSCF and CASPT2 calculations were performed using MOLCAS 7.6. Using the B3LYP gradients from the ground-state IRC calculations of the path connecting CHBr$_3$ and iso-CHBr$_3$, single point CASSCF calculations (SA-CAS(16,12)/ANO-RCC-VTZP) of the ground- and first excited singlet state energies along the IRC path were performed. Single point CASPT2 calculations were also performed to include the effects of dynamic electron correlation. The solvent was again simulated by the PCM method, where cyclohexane parameters were used instead of their methycyclohexane analogues for technical reasons.

B. Ultrafast transient absorption

The experimental set-up used is based on a regeneratively amplified Ti:sapphire laser system (Hurricane, Spectra-Physics, 800 nm, 1 kHz). The fundamental output is 50:50 split into two beams with the first beam delivered to a “pump” optical parametric amplifier (TOPAS-C, Light Conversion Ltd.) to generate 255-nm pulses, which were then modulated at 0.5 kHz using a chopper synchronized to 1 kHz, and used for sample excitation. The second beam is further 40:10 split, the 10% portion further attenuated and sent to a delay line capable of up to 1150 ps delay, and then focused onto a 3-mm CaF$_2$ window to produce a white-light continuum spanning the 340–950 nm region. Alternatively, the 40% portion is sent to a “probe” TOPAS-C to produce the fourth harmonic of the signal (FHS) or fourth harmonic of the idler (FHI) outputs, which after sum-frequency mixing with the 10% portion of the amplified beam (pulses tunable from 210 to 265 nm and 267 to 300 nm for FHS and FHI, respectively) or directly (FHS, pulses tunable from 275 to 384 nm) were delayed and used as a deep-UV/UV probe. This or white-light continuum beams were split into a probe beam, focused onto the sample to a 160-µm diameter spot and overlapped at an angle of 8° with the pump beam focused to a 460-µm diameter spot, and a reference beam. The probe and reference beams were then dispersed through a monochromator/spectrograph, and recorded using a dual diode array or two matching photodiodes synchronized with the 1-kHz repetition rate of the laser system. Transient absorption ($\Delta A$) spectra were obtained by diode-array detection of the multiple (512) $\Delta A$ kinetic traces within the white-light continuum spectrum to which properly scaled single-wavelength $\Delta A$ kinetic traces were appended, acquired by scanning the “probe” TOPAS across the deep-UV/UV region coupled with photodiode detection. The CHBr$_3$ solutions were circulated through a 0.3-mm thick flowing jet. In several experiments in acetonitrile (anhydrous and mixtures with water), a Spectrosil UV quartz flow cell with a 0.2 mm path length was also used. To eliminate the contributions of rotational motion to $\Delta A$ signals, the polarization of the pump beam was set at the magic angle (54.7°) with respect to that of the probe beam using a Berek compensator. The pump energy was attenuated to 1.5 µJ to suppress two (pump)-photon absorption by the solvent. In doing so, the linearity of CHBr$_3$-related $\Delta A$ signals with excitation energy was also ensured. Deviations from the linearity were observed at energies larger than 3.5 µJ.

All $\Delta A$ signals were corrected for the group velocity dispersion of the probe light with the 25 fs accuracy, utilizing the position of the instrument response functions (IRF), namely, Gaussian-shaped $\Delta A$ signals observed in neat solvents as a result of the simultaneous absorption of a pump and a probe photon when the pump and probe pulses temporally overlap. The IRF width (fwhm) increases with an increase in probe photon energy from 139 fs in the visible range to 148 fs at 380 nm, 221 fs at 280 nm, and 387 fs at 214 nm in methycyclohexane. In acetonitrile, the IRF widths were smaller by a factor of 1.26 at wavelengths shorter than 380 nm.

The shape of the $\Delta A$ kinetic traces in the visible and deep-UV/UV spectral regions was found to be independent of CHBr$_3$ concentration up to 500 and 90 mM (limited by sample absorption), respectively. The $\Delta A$ spectra presented in this work correspond to the properly scaled and merged data for 30 mM CHBr$_3$ solutions from 210 to 265 nm and 85 mM CHBr$_3$ solutions in the remaining spectral range.

C. Materials and steady-state measurements

CHBr$_3$ (>99%) and spectroscopic-grade methycyclohexane were purchased from Sigma-Aldrich and used without further purification. We also used commercially available acetonitrile (Sigma-Aldrich, >99.5%), containing 0.2 vol. % of water (referred thereafter as “acetonitrile”), and mixed acetonitrile/H$_2$O solutions containing 2% and 5% of...
TABLE I. TD DFT/PCM vertical transition energies and corresponding oscillator strengths (in parentheses) calculated for the fully optimized iso-CHBr$_3$ structures using the aug-cc-pvTZ basis set in the gas-phase and two solvents considered in this work, simulated using the corresponding PCM parameters.

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<th>Acetonitrile</th>
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$^a$URPA/UB3LYP/6-311G(d,p).
$^b$URPA//B3LYP/6-311G(d,p).

dionized water. The UV absorption spectra measured using a Varian Cary 50 UV/vis spectrophotometer before and after time-resolved measurements showed minimal sample decomposition of less than a few percent. All experiments were performed at 21°C.

III. RESULTS

A. Computational results

The optimized structure of CHBr$_3$ consists of a distorted tetrahedron with C$_3$v symmetry (Table I of the supplementary material$^{75}$), and exhibits little dependence on the surrounding medium. The iso-CHBr$_3$ species has one bromine (Br3) migrated from its equilibrium position to form a bond with another bromine (Br2), i.e., (H)Br1C−Br2−Br3. Notable structural changes in comparison to CHBr$_3$ include smaller C−Br1 and C−Br2 bond lengths as well as significantly larger C−Br2−Br3 and dihedral H−C−Br1−Br2 angles (Table I of the supplementary material$^{75}$). The structure of iso-CHBr$_3$ depends on the nature of the solvating medium.

Increasing the solvent polarity leads to larger C−Br2−Br3 and H−C−Br1−Br2 angles, corresponding to a more linear and planar structure, and a significant (∼0.2 Å) increase in the Br2−Br3 bond length.

Intense electronic transitions of iso-CHBr$_3$ and other possible product species (CHBr$_2$·, CHBr$_2$+ and CHBr$_2$OH; see Table II of the supplementary material$^{75}$ for the corresponding optimized structures), computed using different density functionals, agree within 0.3 eV. Iso-CHBr$_3$ features several transitions carrying low oscillator strengths (f) in the red part of the spectrum, an intense transition in the 400-500 nm range, and less intense transitions at 250–260 nm and shorter wavelengths (Table I, and Table III of the supplementary material$^{75}$). Our calculations predict a significant redshift with increasing polarity for the intense transition of iso-CHBr$_3$ from 388 nm in the gas-phase to 423 nm in C$_6$H$_{11}$CH$_3$, and 478 nm in CH$_3$CN. CHBr$_2$· and CHBr$_2$+ are predicted to have intense 250-nm (f ∼ 0.09) and 270-nm (f ∼ 0.2) transitions, showing little solvatochromic shifts (Table II, and Table IV of the supplementary material$^{75}$). For CHBr$_2$OH in acetonitrile, a 225-nm transition (f ∼ 0.02) is predicted using
TABLE II. TD DFT vertical transition energies and corresponding oscillator strengths (in parenthesis) computed for possible photoproducts of CHBr$_3$ upon UV excitation (CHBr$_2^\cdot$, CHBr$_2^+$, and CHBr$_2$OH) using the aug-cc-pvTZ basis set in the three different media considered in this work.

<table>
<thead>
<tr>
<th>Photoproduct</th>
<th>Gas phase</th>
<th>Acetonitrile</th>
<th>Methylcyclohexane</th>
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<tbody>
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<td></td>
<td>CAM-B3LYP</td>
<td>263 (0.0000)</td>
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all three functionals, in addition to a slightly weaker 240-nm transition ($f \sim 0.015$) predicted using the B3LYP functional.

Relaxed redundant coordinate scans on the ground-state potential energy surface were performed along the C–Br–Br angle to locate a transition state for thermal isomerization (Table III), followed by full geometry optimization of the stationary points: CHBr$_3$, TS, and iso-CHBr$_3$ Table V of the supplementary material$^{75}$ summarizes the corresponding vibrational frequencies. The optimized first-order saddle point connects the two isomers, Fig. 1. In both C$_6$H$_{11}$CH$_3$ and CH$_3$CN, the motion along the IRC from the TS to the iso-CHBr$_3$ minimum is dominated by an increase in the C–Br–Br angle and a shortening of the Br–Br bond. Upon going from the gas phase to C$_6$H$_{11}$CH$_3$, all DFT methods used predict a slight ($\sim 10$ kJ mol$^{-1}$) decrease of the potential energy barrier for isomerization of iso-CHBr$_3$. This barrier is significantly lower in CH$_3$CN.

Relaxed scans along the C–Br bond in iso-CHBr$_3$ (towards molecular products) and single-point energy calculations at the radical pair asymptote were performed to explore possible decomposition channels of this isomer species, Fig. 2. It was found that the CHBr + Br$_2$ channel is connected to iso-CHBr$_3$ via a barrierless path and both decomposition channels are higher in energy than the channel populating the reactant well (CHBr$_3$). In acetonitrile, iso-CHBr$_3$ is located $\sim 17$ kJ mol$^{-1}$ lower than the isomerization TS, $\sim 79$ kJ mol$^{-1}$ more stable than the CHBr$_2$ + Br asymptote, and $\sim 192$ kJ mol$^{-1}$ lower in energy than the molecular bromine elimination channel, on average for B3LYP, CAM-B3LYP, and M06-2X density functional used. In methycyclohexane, the corresponding values are $\sim 38$, $\sim 52$, and $\sim 157$ kJ mol$^{-1}$. Above, single point energies of the radical pair products separated by 20 Å are given because the relaxed scan calculations seem to sample an ionic two-body dissociation channel.

Using molecular structures derived from B3LYP minimum energy path calculations as starting structures, a cross section of the ground and first excited singlet state was visualized using the CASSCF wavefunction (Fig. 3). The isomerization path on the S$_1$ state resembles its S$_0$ state counterpart, and both surfaces converge in the vicinity of the TS connecting CHBr$_3$ and iso-CHBr$_3$ in the gas phase as well as the solvents investigated, demonstrating the occurrence of a conical intersection (CI) between the two energy surfaces. The TS and CI are very close in terms of molecular structure. Note that this is not an optimized minimum-energy CI, but a manifestation of the intersection space near the ground state TS. As a result, the photophysical path from the CI to the iso-CHBr$_3$ minimum and the IRC path from the TS to the iso-CHBr$_3$ minimum likely intercept. To describe spectral changes accompanying the motion from the TS to the iso-CHBr$_3$ potential well, we calculated the VET energies of the isomer at several points along the IRC path. Because of the degeneracy of the two electronic states in this region of the potential, a multiconfigurational approach such as CASPT2/CASSCF is required to provide an adequate description of this system. The intense visible absorption VET of iso-CHBr$_3$ corresponds to an S$_0$ $\rightarrow$ S$_1$ excitation at the CASPT2 level of theory. The transition energy significant blueshifts by $\sim 1.5$ eV and the oscillator strength increases by three-to six times depending on the solvent upon going from the TS to the iso-CHBr$_3$ minimum, Fig. 4 and Table VI of the supplementary material.$^{75}$ The TD-B3LYP/aug-cc-pVTZ/PCM VET calculations, performed for illustrative purposes, were found to significantly deviate from

![FIG. 1. Relaxed redundant coordinate scans along the C–Br–Br angle in the isomer species suggest that iso-CHBr$_3$ is connected to the reactant (CHBr$_3$) through a transition state (TS).](Image)
FIG. 2. Relaxed redundant coordinate scans along the C−Br−Br and C−Br geometrical parameters in iso-CHBr₃ (towards the reactant and the molecular products) and single-point energy calculations at the radical pair asymptote performed to explore different possible decay channels of this isomer species in acetonitrile and methylcyclohexane.

their multiconfigurational analogues, Table VII of the supplementary material. The results of a two-dimensional relaxed redundant coordinate scan and corresponding VETs and oscillator strengths of the intense visible transition of iso-CHBr₃ along the C−Br−Br angle and Br−Br bond coordinates at two levels of theory are shown in Fig. 4 and Fig. 2, Tables VIII and IX of the supplementary material.

B. Experimental results

1. Steady-state UV absorption

The UV absorption spectrum of CHBr₃ in C₆H₁₁CH₃ consists of a broadband centered at ~225 nm, Fig. 5. Compared to the gas-phase spectrum of CHBr₃,⁷⁶, ⁷⁷ a moderate ~900 cm⁻¹ redshift of the solution spectrum is observed. Upon going from methylcyclohexane to acetonitrile the absorption spectrum blueshifts by about the same amount. In both solvents, the CHBr₃ absorption obeys the Lambert-Beer law up to the highest measured concentrations of 200 mM, (inset of Fig. 5). The measured maximum extinction coefficients, ε(221 nm) = 2050 M⁻¹ cm⁻¹ in CH₃CN and ε(225 nm) = 2452 M⁻¹ cm⁻¹ in C₆H₁₁CH₃ agree with previously reported values.⁷⁸, ⁷⁹

2. Solvent contribution to transient absorption spectra

Bell-like solvent signals due to two-(pump and probe-)photon absorption⁸ for high-energy probes as well as oscillatory solvent signals due to cross-phase modulation and impulsive stimulated Raman scattering⁸₀–⁸₄ for low-energy probes contaminate the short-time ΔA spectra measured for CHBr₃ solutions. This occurs from the zero time delay to time delays corresponding to the IRF half-width, e.g., the solvent contributes to the 100-fs ΔA CHBr₃ spectra at probe wavelengths shorter than 338 nm in methylcyclohexane and 260 nm in acetonitrile. As of a time delay of 0.3 ps, the ΔA signals predominantly arise from CHBr₃.

3. Bromoform in methylcyclohexane

The 300-fs ΔA spectrum exhibits the presence of two distinct ~260- and 360-nm bands and weaker band at 395 nm extending to 500 nm, Fig. 6. Note that the ΔA spectra
measured at 100 and 200 fs also manifests the 360- and 395-nm bands, though contaminated by the solvent response. An induction period up to 900 fs—where the entire $\Delta A$ spectrum reveals no appreciable spectral evolution—is followed by signal growth, initially taking place in the red and near-IR (650-780 nm) spectral regions. The $\Delta A$ signals in the 290-360 nm region start to decay at about 6 ps while the 255-nm absorption band grows and sharpens. The 360-780 nm absorption also develops at the same time delay, with a manifestation of an isosbestic point at 360 nm. The growth of the intense 420-nm band product absorption complete at 50 ps is accompanied by spectral narrowing kinetically manifested through a signal rise followed by a slower decay as the probe wavelength is tuned towards the band maximum. The 255-nm band and 212–240 nm transient absorption also sharpen between 20 and 50 ps. Between 100 and 1150 ps, the absorption in the 320–350 nm range somewhat decays whereas the 250- and 212–240 nm transient absorption also sharpen between 250 and 212 nm. The inset shows the sample absorbance measured at 280 nm in a set of cells with different pathlengths. The linear plot of the absorbance divided by the thickness of the cell used vs. the CHBr$_3$ concentration demonstrates that the sample obeys Lambert-Beer law in both solvents up to 200 mM.

FIG. 4. (Left) The B3LYP/aug-cc-pVTZ IRC scans connecting the isomerization TS and the iso-CHBr$_3$ minimum in methycyclohexane (a) and acetonitrile (b). Vertical arrows mark the selected points along the scans at which the VETs of iso-CHBr$_3$ were calculated. (CASPT2/CASSF/ANO-RCC-VTZP transition energies given in nm with oscillator strengths in parentheses.) The insets show the full IRC scans connecting the CHBr$_3$ and iso-CHBr$_3$ ground-state minima. Solvent was simulated using the PCM model with the acetonitrile or methycyclohexane parameters. (Right) B3LYP/aug-cc-pVTZ/PCM relaxed redundant coordinate two-dimensional mapping of the ground-state surface of iso-CHBr$_3$ in methycyclohexane along the C−Br−Br angle and Br−Br bond length. The red circles mark the angle and bond length coordinates at which the CASPT2/CASSF/ANO-RCC-VTZP VETs were computed with the PCM solvent description (the bold font values expressed in nm shown inside the red circles).

FIG. 5. (Left) Energetics of the gas-phase CHBr$_3$ system$^{17,20}$ The absorption spectrum$^{74,77}$ is shown adjacent to the assignment of the excited electronic states computed at the CCSD/aug-cc-pVDZ level of theory.$^{15}$ (Right) Steady-state absorption spectra of CHBr$_3$ in methycyclohexane and acetonitrile (maximum extinction coefficient $\varepsilon_{M} = 2452$ and 2050 M$^{-1}$ cm$^{-1}$, respectively) as well as in the gas-phase shown for comparison. The vertical bars correspond to the CCSD/aug-cc-pVDZ VET energies, where the bar height is proportional to the computed oscillator strength ($f$).$^{15}$ Note, that all $f$ values for the singlet-triplet excitation are multiplied by a factor of 5. The inset shows the sample absorbance measured at 280 nm in a set of cells with different pathlengths. The linear plot of the absorbance divided by the thickness of the cell used vs. the CHBr$_3$ concentration demonstrates that the sample obeys Lambert-Beer law in both solvents up to 200 mM.
11.3, 11.8, ps, and of zero amplitude at 780, 600, 550, and 415 nm, respectively. The minor $\Delta A$ evolution at long times is characterized by $\tau_4 = 500$ ps.

The best global fit analysis$^{64}$ of the 340–755 nm $\Delta A$ spectra ($\geq 150$ fs) yields a sum of five decay-associated spectra ($\epsilon_i$, where $i$ varies from A to E, which obey exponential time dependence with time constants $\tau_j$) and a permanent spectrum (F), Fig. 8. The $\tau_A = 720$ fs spectrum describes the short-time $\Delta A$ absorption, whereas the $\tau_B = 3.8$ ps and $\tau_C = 6.1$ ps spectra characterize the evolution to the blue and the red of the $\epsilon_D$ component, the 505-nm band revealed through global fitting. The decay of the 505-nm band ($\tau_D = 10.2$ ps) leads to the $\epsilon_E$ (420-nm band), which forms ($\tau_E = 710$ ps) the permanent $\epsilon_F$ spectrum.

4. Bromoform in acetonitrile

An intense 255-nm absorption band with a 370-nm shoulder that extends into the visible range is observed at 100 fs, Fig. 9. The 255-nm band sharpens between 1 and 10 ps, revealing a weak shoulder at 280 nm. From 376 to 400 nm, the $\Delta A$ signal rises slower, and not faster as expected if it were a consequence of the 255-nm band growth, suggesting that different product species are responsible for the 370- and 255-nm features. Visible transient absorption grows and narrows into a broad 505-nm band, which reaches a stable shape and exhibits maximum absorption at 50 ps, then decays to the noise level on a several hundred picoseconds time scale. This indicates that the species responsible for this band is completely equilibrated at 50 ps, and that the decay product(s) do not absorb in the visible range. A corresponding slow rise is detected in the 218- and 255-nm regions, suggesting that the absorbing species is the successor of the species responsible for the 505-nm band. The 255-nm band is narrower at 1 ns but otherwise similar to that observed at short times, and decays on a nanosecond time scale, similar to the 280-nm shoulder. However, the 218-nm transient absorption shows no evolution between 500 and 1000 ps. This behavior suggests the presence of several UV absorbing species.

Multiexponential fits to the CHBr$_3$ $\Delta A$ signals ($\geq 150$ fs) reveal five characteristic stages (Fig. 7): (i) an induction period pronounced in the UV range to $\sim 600$ fs, also present in the visible range as a minor decay which becomes slower as the probe wavelength is tuned towards the 505-nm band, e.g., $\tau_1 = 220$ fs at 780 nm, 450 fs at 650 nm, and 950 fs at 500 nm; (ii and iii) the growth and spectral narrowing of the 505-nm band with longer rise times as the wavelength approaches 505 nm ($\tau_2 = 1.4, 2.8, 4.2$, and $5.8$ ps in tuning from 780 to 700, 650, and 600 nm) and a slower rise/decay ($\tau_3 \sim 12$ ps) when probing inside/outside the 505-nm band. These components are also present in the UV region; (iv) the decay of the 505-nm band ($\tau_3 = 259 \pm 37$ ps) and the corresponding rise of the deep-UV absorption; (v) the 255-nm band decay ($\tau_5 = 3.5$ ns). The same $\tau_3$ is found for the 280-nm shoulder under the assumption that it decays single-exponentially to zero.

The best global fit of the 340–755 nm $\Delta A$ spectra for CHBr$_3$ in acetonitrile yields the same model as the one for methylcyclohexane solutions, with similar interpretations of the decay-associated spectra except for the $\tau_D$-component, which represents narrowing of $\epsilon_D$ without spectral shifting, Fig. 8.

5. Bromoform in acetonitrile upon addition of water

For CHBr$_3$ (20 mM) in acetonitrile (0.2% H$_2$O), and acetonitrile with 2% and 5% amounts of water, the $\Delta A$ kinetic traces at 218-, 250-, and 500 nm are not affected by the presence of water up to a $\sim 10$ ps time delay, Fig. 10. However, the decay of the 505-nm product band is considerably accelerated with $\tau_4 = 259 \pm 37$ ps, 95 $\pm 15$ ps, and 56 $\pm 3$ ps for 0.2%, 2%, and 5% of H$_2$O, whereas $\tau_4$ is measured to be 310 $\pm 20$ ps in anhydrous acetonitrile. The 218-nm $\Delta A$ signal rises faster when more water is present, with roughly the same time constants (234, 111, and 52 ps) as the decay of the 505-nm product band. For the 2% and 5% of H$_2$O solutions, the rise is followed by a decay proceeding faster when more water is present (time constants, 152 and 71 ps), followed by a slower decay. In the same solutions, the 250-nm $\Delta A$ kinetic traces show a signal rise followed by a slower decay, both rendered faster upon addition of more water. The rise time constants match the decay time constants of the 505-nm band, and the slow decay time constants change from 190 $\pm 60$ ps to 100 $\pm 16$ ps for 2% and 5% of H$_2$O, i.e., very similar to those at 218 nm. Within the experimental accuracy, a 3.5-ns
6. Bromine in bromoform

To characterize the absorption band of a CTC between Br atom and CHBr₃, we selectively excited solutions of Br₂ (10 mM) in bromoform at 420 nm. The short-time ΔA signal is dominated by a 390-nm absorption band, Fig. 11. This band undergoes almost no change up to a time delay of 2 ps. As time progresses further, the 390-band gradually decays with the formation of a very broad transient absorption band spanning the entire visible region at 50 ps, which continues to decay.

decay time constant at 218- and 250-nm is independent of water concentration.
FIG. 8. Decay-associated spectra ($\epsilon_i$) of the global fit analysis for CHBr$_3$ in methylcyclohexane (left) and acetonitrile (right) under the assumption of consecutive exponential decay. The analysis of the 340–765 nm range of measured $\Delta A$ spectra yields five components (A, B, C, D, E) and a permanent spectrum (F). The resulting time constants are given besides the corresponding $\epsilon_i$ spectra.

IV. DISCUSSION

A. Electronic absorption spectrum and transitions

Taking into account the close similarity of the UV absorption spectra of CHBr$_3$ in the gas-phase and solutions, and the absorption blueshift with increasing the solvent polarity from methylcyclohexane to acetonitrile (Fig. 5), the solution spectra can be similarly assigned to $n$(Br) $\rightarrow$ $\sigma^*$($-$C–Br) transitions. According to ab initio coupled cluster calculations of gas-phase CHBr$_3$, its two low-energy singlet-singlet transitions are located at 243 and 220 nm (Fig. 5). The $\tilde{X}$ $^1$A$_1$ $\rightarrow$ $\tilde{B}$ $^1$E transition (220 nm) is, by far, the most intense transition in the UV spectrum of bromoform ($f = 2.2 \times 10^{-2}$). The lowest energy transition $\tilde{X}$ $^1$A$_1$ $\rightarrow$ $\tilde{A}$ $^1$A$_2$ state (243 nm) is formally dipole forbidden ($f = 0$), although this transition may borrow intensity from the close-lying $\tilde{X}$ $^1$A$_1$ $\rightarrow$ $\tilde{B}$ $^1$E transition. There are four triplet states in the UV range. The third triplet state, $\tilde{c}$ $^3$A$_1$ at 239 nm, has about 10-times larger oscillator strength ($f = 3.1 \times 10^{-3}$) than other three states ($\tilde{a}$ $^3$E, $\tilde{b}$ $^3$E, and $\tilde{a}$ $^3$A$_2$), so that the $\tilde{X}$ $^1$A$_1$ $\rightarrow$ $\tilde{c}$ $^3$A$_1$ transition may also contribute to the long-wavelength part of the spectrum. The lowest-energy triplet state ($\tilde{a}$ $^3$A$_2$) is dissociative towards CHBr$_2$ + Br. Considering the similarity between the UV absorption spectra of CHBr$_3$ in the gas-phase and solutions under study, 255-nm excitation promotes bromoform.

FIG. 9. 255-nm $\Delta A$ spectra of CHBr$_3$ in acetonitrile. Panels (a), (b), and (c) show the $\Delta A$ spectra at short, intermediate, and long-time time delays, which are expressed in picoseconds and given in panel legends. (Top insets) The B3LYP VETs of the iso-CHBr$_3$, CHBr$_2$, and CHBr$_2$OH product species carrying oscillator strengths larger than 0.05.

FIG. 10. The $\Delta A$ kinetic traces (symbols) for CHBr$_3$ (20 mM) in acetonitrile with 0.2% of water, and acetonitrile with 2% and 5% of water measured in a 0.2-mm thick flow cell at 500 nm, 218 nm, and 250-nm following 255-nm excitation with an incident energy of 0.85 $\mu$J pulse$^{-1}$.

FIG. 11. The inset displays transient absorption spectra of Br$_2$ (10 mM) in CHBr$_3$ measured in a 2-mm spinning cell after 420-nm excitation with an energy of 4.8 $\mu$J pulse$^{-1}$. The main window shows the 1-ps $\Delta A$ spectrum from the inset (line plus symbols) superimposed on the transient absorption measured 1 ps after 267-nm excitation of a 90%/10% (v/v) mixture of CHBr$_3$ in cyclohexane (line) previously reported by Crim and co-workers.
into a superposition of the $A_1A_2$ and $B_1E$ singlet states with some contribution of the $c^{3}A_1$ triplet state.

B. Energetics of the system and comparison to previous computational results

Despite some similarities between our ground-state calculations and previous ground-state calculations by Reid and co-workers (single-point CCSD(T)/aug-cc-PVTZ energies at the MP2 stationary points), the difference in the solvent media (gas-phase vs. solution) warrant a brief discussion. Gas-phase iso-CHBr$_3$ is found bound relative to the CHBr$_2^-+\text{Br}^-$ asymptote by 63 kJ mol$^{-1}$ and the CHBr$_2^-+\text{Br}^-$ asymptote by 159 kJ mol$^{-1}$. The TS of CHBr$_3 \rightarrow$ iso-CHBr$_3$ isomerization is found at 47 kJ mol$^{-1}$ above ground-state iso-CHBr$_3$ and 251 kJ mol$^{-1}$ above ground-state CHBr$_3$. This is quantitatively consistent with our DFT calculations in methylcyclohexane (Table III), although in acetonitrile we predict an increased energy gap between iso-CHBr$_3$ and the CHBr$_2^-+\text{Br}^-$ and CHBr$_3+\text{Br}_2$ asymptotes, consistent with the polar nature of iso-CHBr$_3$. Furthermore, in acetonitrile the TS of CHBr$_3 \rightarrow$ iso-CHBr$_3$ isomerization lies at about 17 kJ mol$^{-1}$ above ground-state iso-CHBr$_3$, i.e., substantially closer. This result is consistent with the more polar nature of the thermal isomerization TS compared to iso-CHBr$_3$ and stronger stabilization of the former by polar acetonitrile—a concept also documented by our group in the thermal isomerization of a similar system (CH$_2$Br$_2 \rightarrow$ iso-CH$_2$Br$_2$).

C. Nature of visible product absorption

The equilibrated visible $\Delta A$ band in methylcyclohexane and acetonitrile solutions of CHBr$_3$ can be assigned to the ground-state iso-CHBr$_3$ photoprodust. TD-DFT/PCM VET energies in a given solvent (thereafter, we will refer to the TD-B3LYP results) support the assignment of the 424-nm band observed in C$_6$H$_{11}$CH$_3$ as well as 505-nm band observed in CH$_3$CN to iso-bromoform. For non-polar solvents such as methylcyclohexane, a comparison with the matrix isolation results on CHBr$_3$ is helpful to confirm our photoprocess assignment. The absorption bands of matrix-isolated iso-CHBr$_3$, though influenced in width and position by the low-temperature matrix environment, are similar to the ones we observed in methylcyclohexane. Furthermore, the position of the 424-nm band of iso-CHBr$_3$ in methylcyclohexane is consistent with the nanosecond transient resonance Raman study that identified this product species utilizing 455 nm probe pulses. The ps-TR$^3$ study identified the iso-bromoform product following 267-nm excitation of CHBr$_3$ in acetonitrile/water mixtures. The previously isomer lifetimes reported are very close to the decay time constants of the 505-nm product band in our experiments.

Other product species, such as CHBr$_2^-$ radicals and CT complexes between Br$^-$ fragments and solvent molecules can be excluded as responsible for the visible $\Delta A$ bands observed. CHBr$_2^-$ does not absorb significantly at wavelengths longer than 262 nm, Figs. 6 and 9, Table II. The absorption bands of the CT complexes of Br with acetonitrile and methylcyclohexane are located in the UV range peaking at 270 nm and 365–370 nm, respectively. Moreover, one-(255-nm)-photon excitation of CHBr$_3$ induces the visible $\Delta A$ signal observed according to the measured energy dependence, thus ruling out species like CHBr$_3^+$, the formation of which is typically implicated through multiphoton excitation. Finally, the steady-state absorption spectra of CHBr$_3$ obeyed the Lambert-Beer law up to a 200 mM concentration in the both solvents studied, showing no aggregation of CHBr$_3$. In methylcyclohexane the shape of the 10- and 500-ps $\Delta A$ spectra (Fig. 3 of the supplementary material), and the time profile of the 420-nm $\Delta A$ kinetic traces are independent of CHBr$_3$ concentration in the 2–500 mM range, ruling out that the $\Delta A$ spectra in the 1-ns time window studied may be due products of bimolecular reactions between the photolysis fragments and CHBr$_3$ molecules, e.g., Br·CHBr$_3$ CT complexes. The shape the 425-nm band due to iso-bromoform in the 500-ps $\Delta A$ spectrum (Fig. 6) is identical to that observed in the pulse radiolysis study of CHBr$_3$ in cyclohexane and assigned to the Br·CHBr$_3$ CT complexes, leading to the re-assignment of the latter band to iso-CHBr$_3$.

D. Solvatochromic shifts of the isomer visible absorption

The vibrational fundamentals in the 100–200 cm$^{-1}$ region observed in transient resonance Raman spectra following UV excitation of di- and polyhalomethanes CH$_2$I$_2$, CH$_3$I, CH$_3$Br$_2$, CHBr$_3$, and CBr$_4$ suggest the formation of isomer photoprodusts featuring C–I–I and/or C–Br–Br moieties. The fact that these fundamentals are pronounced for 350–470 nm Raman probes suggests that the intense absorption bands of the isomers observed in this spectral region are associated with the C–X–X chromophore (X = I or Br). On the basis of DFT structure and VET energy calculations of the above isolated compounds, it was proposed that the shortening of the X–X bond length of the C–X–X chromophore correlates with the high-energy shift of the electronic transition energy, and that the C–X bond length is less important. Our relatively high level calculations demonstrate that the above premise is valid and accounts for the solvatochromic shifts observed for iso-bromoform. Indeed, for iso-CHBr$_3$, an increase in the Br–Br bond length (2.698, 2.763, 2.834, and 2.949 Å in the gas-phase, methylcyclohexane, bromoform, and acetonitrile, respectively, Table I of the supplementary material) results in a red-shifted of the VET energy (388, 423, 449, and 477 nm in the same media, Table I). The C–Br–Br angle in iso-CHBr$_3$ also affects the VET energies; however, the effect of the Br–Br bond length is dominant at the isomer ground-state minimum. Moreover, even where the same medium is considered, there is a strong correlation between the position of the intense visible transition and the Br–Br bond length of the isomer. This is demonstrated using single-point CASPT2/CASSCF calculations of the VET energies of iso-CHBr$_3$ along the ground-state IRC path. From the TS to the iso-CHBr$_3$ minimum, the Br–Br bond length decreases by ~0.48 Å, whereas the position of the intense visible transition blueshifts by ~1.5 eV, Fig. 4 and Table VI of the supplementary material.
E. Reactions of iso-CHBr3 in acetonitrile-water mixture and methanol

We found that the iso-CHBr3 lifetime (τ4) is shorter when more water is present in acetonitrile/water solutions, in close agreement with the ps-TR3 findings. According to Phillips and co-workers, this is a manifestation of an O−H insertion/HBr elimination reaction of iso-CHBr3 with water,

\[
\text{CHBr}_2-\text{Br}+n\text{H}_2\text{O} = \text{CHBr}_2\text{OH}+\text{HBr}+(n-1)\text{H}_2\text{O},
\]

where \( k_i \) is the decay rate constant in the absence of water, and \( k_q \) is the second-order rate constant for the reaction (Fig. 4 of the supplementary material). The fit yields \( k_i = (276 \pm 32 \text{ ps})^{-1} \), which agrees with the iso-CHBr3 lifetime in acetonitrile with traces of water (283 ps) and anhydrous acetonitrile (310 ps). The \( k_q \) value is calculated to be \((5.46 \pm 0.54) \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \), four times less than the diffusion-controlled limit in acetonitrile \((1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})\) (Ref. 87), suggesting that the reaction (1) is controlled by a potential energy barrier. This conclusion is consistent with the previously reported MP2 calculations of the relative energy profile for the reaction (1).9,10

F. Assignment of UV absorption

Based on the UV photochemistry of bromoform in the gas phase, we expect that in solution a fraction of electronically excited CHBr3 molecules dissociates to form a CHBr2 + Br radical pair. Halogen atom fragments form CT complexes with solvent molecules on a sub-1 ps time scale, such as Br·C6H11CH3 absorbing at 365–370 nm and Br·CH3CN absorbing at 272 nm. Our TD-DFT/PCM VET energy calculations show that CHBr2 should exhibit an intense electronic transition at about 260 nm. In methylvyclohexane, the 255-nm band due to CHBr2 and the 360-nm band due to Br·C6H11CH3 CTC were observed at short times after excitation of CHBr3, whereas at intermediate and long times the 255-nm band has a contribution from iso-CHBr3 absorption. In acetonitrile, 255-nm CHBr2 band at short time delays is also present at longer times when iso-CHBr3 has decayed. The 280-nm shoulder which can be assigned to the Br·CH3CN CTC provides further support for the radical-pair photodissociation mechanism.

The hydrolysis product, CHBr2OH, also contributes to the deep-UV/UV absorption at intermediate and long times in acetonitrile. CHBr2OH exhibits an electronic transition at ~245 nm, with \( f \) values comparable to that of the 253-nm transition of CHBr2, Table II. According to Eq. (1), the decay of iso-CHBr3 should lead to the concurrent rise of CHBr2OH, as observed for acetonitrile/H2O solutions through the \( \Delta \alpha \) rise times at 218 and 250 nm which match the decay time constants of iso-CHBr3. In acetonitrile solutions containing 2% and 5% of water, the rise of the \( \Delta \alpha \) signal is followed by a decay, suggesting further hydrolysis of CHBr2OH consistent with Phillips and co-workers, with the remaining 218-nm \( \Delta \alpha \) signal (Fig. 10) attributed to high-energy electronic transitions of CHBr2. The decay of iso-CHBr3 in acetonitrile/0.2% H2O thus leads to the absorption contribution from CHBr2OH to the deep-UV absorption of CHBr3. The leaving group of reaction (1), HBr, has a small dissociation constant in acetonitrile (pK = 5.51) and, as a result, mostly exists in its molecular form, absorbing outside the probing region.

Finally, the 1000-ps \( \Delta \alpha \) spectrum in C6H11CH3 is nearly superimposable in the deep-UV region from 210 to 235 nm with that in CH3CN, where Br− ions have an intense absorption band \((\varepsilon = 10220 \text{ M}^{-1} \text{ cm}^{-1} \text{ at } 218 \text{ nm})\) (Figs. 6 and 9). As the C−Br bond homolysis in CHBr3 takes place in gaseous phase, or is expected in the presence of non-polar solvents, the above observation suggests that Br− anions, and therefore, the CHBr2+ counter-cations, are not formed in any appreciable amount following 255-nm excitation of CHBr3 in acetonitrile.

G. Excitation of Br2 in CHBr3 solutions in comparison to excitation of neat CHBr3

Excitation at 420 nm promotes Br2 into the bound \( B \) and repulsive \( 1\pi_u \) excited electronic states. In the gas phase, the \( 1\pi_u \) state dissociates into bromine atoms with unit efficiency. In solution, this state is thought to be coupled to the moderately bound \( A\pi \) states—the deepest, nested excited states of Br2. Following prompt predissociation of the \( B \) state and cage recombination, the same \( A\pi \) states are populated. In liquid water, an upper limit for the predissociation is 270 fs and the recombinated population in the \( A\pi \) states peaks at 1 ps. For Br2 in CCl4, a quantum yield for trapping in the \( A\pi \) states is about 60%, whereas a ~20% (Refs. 95 and 96) fraction of the Br atom fragments escapes the solvent cage. These “free” Br atoms rapidly, on a time scale of several hundreds of femtoseconds, form CT complexes with solvent molecules detectable through the intense CT absorption bands, and undergo diffusion-controlled recombination on a microsecond time scale.

Predissociation and complexation likely take place within the first 0.5 ps following 420-nm excitation of Br2 in CHBr3. Therefore, the 390-nm \( \Delta \alpha \) band observed is predominantly due to Br·CHBr3 CT complexes (Fig. 11). The decay of this band after 2 ps is then due to recombination. It is slightly slower than reported for Br2 in water, but overall consistent with recombination time scales reported for molecular halogens, e.g., thoroughly studied I2 in alkanes and chlorinated alkanes. The Br2 \( A\pi \) states absorb at 250–300 nm, well outside the probed spectral region. The extinction coefficient of Br·CHBr3 CTC is expected to be about 20 times bigger than \( \varepsilon = 160 \text{ M}^{-1} \text{ cm}^{-1} \) in the visible band maximum of Br2. About the same \( \varepsilon \) is expected for the recombinated hot Br2 species dispersed along the ground-state potential. Compared to the absorption of the Br·CHBr3 CT complexes at the short time (0.5 ps), both the hot ground-state absorption and Br2 bleach are likely to be minor.

The 0.5-ps \( \Delta \alpha \) spectrum observed following 420-nm excitation of Br2 in CHBr3 is identical to the 1-ps \( \Delta \alpha \) spectrum reported by Crim and co-workers in neat CHBr3.
Fig. 11. Therefore, we propose to reassign the previously reported 390-nm band\(^59\) to a CT complex between a Br-atom fragment and neighboring CHBr\(_3\) molecules. This is consistent with the lack of vibrational relaxation in the 390-nm band\(^59\) because translational thermalization of Br- is fast\(^59\) so that the nascent complexes carry little excess of vibrational energy. Our TD-B3LYP VET energy calculations (Table III of the supplementary material\(^75\)) suggest that the successor 495-nm band observed\(^59\) may be attributed to \(\text{iso-CHBr}_3\). It is not trivial to comment on the nature of \(\text{iso-CHBr}_3\) vs. the Br·CHBr\(_3\) CTC, and thus the relative stability of the two species on ultrafast time scales. One would expect, however, that the electrostatic attraction between Br- and CHBr\(_3\) in the complex is less energetically favorable than chemical bonding in \(\text{iso-CHBr}_3\) which possesses a significant covalent character.\(^61\) The Br- loss from the Br·CHBr\(_3\) CTC is then expected with its subsequent bonding to a nearby CHBr\(_2\)-gemininate fragment to form \(\text{iso-CHBr}_3\). The decay of the 390-nm band and the rise of the 495-nm band occurring on similar picosecond time scale\(^59\) agree with this mechanism. We document a similar behavior in the photo-induced dynamics of the Br2/CHBr\(_3\) system where bond (re)formation between two nascent Br-atom fragments is favored over the formation of the Br·CHBr\(_2\) CTC complex. The sharpening and blueshift of the visible product band from 490 to 430 nm with a decreasing polarity of the CHBr\(_3\)/C\(_6\)H\(_{14}\) mixtures observed by Crim and co-workers\(^59\) parallels the solvatochromic changes observed for \(\text{iso-CHBr}_3\) from acetonitrile to methycyclohexane (absorption band sharpening and blueshift from 505 to 425 nm). Finally, our steady-state and transient absorption spectra of CHBr\(_3\) do not provide any evidence for the proposed pre-aggregation of bromoform.\(^59\)

H. Product quantum yields

We estimated the peak visible extinction coefficients of equilibrated \(\text{iso-CHBr}_3\), \(\varepsilon_S\) (493 nm) = 8360 M\(^{-1}\) cm\(^{-1}\) in CH\(_3\)CN and \(\varepsilon_S\) (425 nm) = 11000 M\(^{-1}\) cm\(^{-1}\) in C\(_6\)H\(_{14}\)/CH\(_3\) and from the known absorption spectrum of this isomer in a ∼1:500 Ne matrix (\(\varepsilon_M\) ≈ 18600 M\(^{-1}\) cm\(^{-1}\))\(^61\) on the basis of the conservation rule of the transition dipole strength.\(^100\) The quantum yields for the formation of \(\text{iso-CHBr}_3\) (\(\phi_{\text{iso-CHBr}_3}\)) were determined using the amplitudes of the visible \(\Delta\Delta\) absorption bands (at 50 ps in CH\(_3\)CN and 100 ps in C\(_6\)H\(_{14}\)/CH\(_3\)) as a measure of the isomer concentration. The formation of the benzophenonetetraline triplet state in unit quantum yield\(^101\) and subsequent 525-nm triplet-triplet absorption band in acetonitrile solution (\(\tau_T\) = 6250 M\(^{-1}\) cm\(^{-1}\)) (Refs. 101 and 102) is chosen as a reference. We found \(\phi_{\text{iso-CHBr}_3}\) = 39% ± 4% in C\(_6\)H\(_{14}\)/CH\(_3\), and upon a factor of exp\(^50/259\) correction for the isomer decay, \(\phi_{\text{iso-CHBr}_3}\) = 31% ± 7% in CH\(_3\)CN.

In acetonitrile at 1 ns, CHBr\(_2\)-, Br·CH\(_3\)CN CTC, and CHBr\(_2\)OH as well as the photoinduced depletion of ground-state CHBr\(_3\) contribute to the UV part of the 1-ns \(\Delta\Delta\) spectrum. Having subtraced the \(\tau_\Delta\) = 259 ps component associated with the \(\text{iso-CHBr}_3\) decay and the formation of CHBr\(_2\)OH and CHBr\(_3\), and separated the residual \(\Delta\Delta\) signal into absorption of Br·CH\(_3\)CN CTC and CHBr\(_2\)-, the quantum yield of the Br- fragment (\(\phi_B\)) at 1 ns is estimated to be 61% ± 11%. Further, assuming that CHBr\(_2\)- and Br·CH\(_3\)CN CTC (\(\varepsilon = 1470\) M\(^{-1}\) cm\(^{-1}\))\(^137\) are present in equimolar amounts with the correction for a 61% depletion of ground-state CHBr\(_3\), the previously unknown \(\varepsilon\) at the 253-nm band maximum of CHBr\(_2\) is estimated to be ∼3030 M\(^{-1}\) cm\(^{-1}\). The nascent radical pair cannot separate from the rigid matrix cage and collapse into either CHBr\(_2\) or \(\text{iso-CHBr}_3\). Therefore, a viable suggestion is that the amplitude difference of the 1-ns UV \(\Delta\Delta\) band in methycyclohexane and the \(\text{iso-CHBr}_3\) UV band in the matrix (Fig. 6) is due to CHBr\(_2\). This gives a ∼60% quantum yield of this species in methycyclohexane at 1 ns. This also implies that photoexcited CHBr\(_3\) molecules that do not collapse into \(\text{iso-CHBr}_3\) predominantly end up as solvent-separated radicals under our experimental conditions. This further suggests that the recovery of ground-state CHBr\(_3\), either via internal conversion of photoexcited CHBr\(_3\) or through the recombination of the radical pair, is minor. The decay of Br·solvent CT complexes observed within about 20 ps is, therefore, due to the radical geminate combination into \(\text{iso-CHBr}_3\).

We analyzed the \(\Delta\Delta\) data to determine whether Br\(_2\) formation occurs in our single-photon excitation experiments because of the previous reports of molecular halogen elimination from gas-phase CHBr\(_3\)\(^17,21\) and \(\text{iso-CF}_2\)\(_3\) photoproduction of \(\text{CF}_2\)\(_3\) in n-hexane.\(^54,56\) Br\(_2\) is stable and non-reactive with both solvents, and “inverse” carbene insertion recombination is slow,\(^103\) so the molecular elimination product is expected to survive much longer than 1 ns. Recombination of Br-atom fragments to form Br\(_2\) is unimportant at 1 ns as it takes hundreds of nanoseconds under the experimental conditions used in this work (a ∼1%-5% fraction of sub-100 mM CHBr\(_3\) excited, ∼10\(^{10}\) M\(^{-1}\) s\(^{-1}\) diffusion rate constants of Br\(_\bullet\)). An upper limit of the quantum yield of Br\(_2\) consistent with our data may be estimated as 10% in acetonitrile at 1 ns when absorption of the isomer product has decayed using the 394-nm band of Br\(_2\) (\(\varepsilon = 160\) M\(^{-1}\) cm\(^{-1}\)). The details of the above quantum yield calculations are given in Figs. 5 and 7 of the supplementary material.\(^75\)

I. Photochemical dynamics and isomerization mechanism

In our experiments, a 255-nm photon promotes CHBr\(_3\) into a mixture of the \(\tilde{A}^1\tilde{A}_2\), \(\tilde{c}^3\tilde{A}_1\), and \(\tilde{B}^1\tilde{E}\) excited states. A fraction of the excited bromoform undergoes rapid dissociation where the molecule exits the Franck-Condon region within the first 100 fs to form the CHBr\(_2\)- radical in CH\(_3\)CN and Br·C\(_6\)H\(_{12}\)CH\(_3\) CT complex detected. The 100-fs 395-nm \(\Delta\Delta\) band in C\(_6\)H\(_{14}\)/CH\(_3\), and possibly, the 100-fs 370-nm \(\Delta\Delta\) feature in CH\(_3\)CN, is assigned on the basis of the transient and spectral evolution of this band, to ground-state \(\text{iso-CHBr}_3\). This formation is much faster than cage-induced isomerization. In this process, primary fragments resulting from photochemical bond breaking collide with the surrounding solvation shell and recoil to the coupling region between the parent and isomer states, where hopping to the isomer potential surface takes place.\(^104,105\) Typical fragment collision times are on the order of 100–200 fs, depending on the solvating medium.\(^104,106–108\) If the excited molecule dissociates

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on a ~50 fs time scale, fragment recombination via a single collision with the surrounding solvent cage should occur in about 300 fs. Therefore, we propose that a fraction of the excited CHBr$_3$ undergoes direct isomerization leading to the ground-state iso-CHBr$_3$ observed (100 fs). These species are responsible for the observed short-time transient absorption and its induction period described through the A- and B components in the decay-associated spectra (Fig. 8). The isomer absorption is constant up to a time delay of ~1 ps in methylcyclohexane (somewhat shorter in acetonitrile). This suggests that the relaxation of ground-state iso-CHBr$_3$ on this time scale involves neither a change in energy of the optically active modes—which modulate the intensity in the measured vibronic spectrum—nor a structural change. At 3 ps, the 360-nm band due to Br-C$_6$H$_4$CH$_3$ CT complexes starts to decay. The decay accompanied by isomer absorption growth predominantly in the red region of the spectrum, which continues to about 20 ps. This constitutes direct evidence for isomerization via cage-induced radical geminate combination. While the incoming Br atom approaches the CHBr$_3$ fragment to form ground-state iso-CHBr$_3$, the early release of exoergicity emerges initially as vibrational excitation of the reaction coordinate modes. A spectral shift of an electronic transition to lower frequencies is a typical signature of an increased vibrational excitation in a molecular system. The C- and D-components (Fig. 8) describing the vibrationally relaxing iso-CHBr$_3$ exhibit a broad maximum between 650 and 700 nm and peak at the same 510-nm wavelength, respectively, and thus are similar in both solvents (apart from the different radical contribution in the UV). The vibrationally relaxed isomers (E-component) exhibit a transient absorption maximum at a much longer wavelength (505 nm), and are attained at a slower rate ($\tau_D = 24.6$ ps) in acetonitrile when compared to methylcyclohexane (425-nm, $\tau_D = 10.2$ ps).

Iso-CHBr$_3$ is stable in methylcyclohexane up to the longest measured time delay of 1.2 ns, consistent with the observation of this species at 10 ns after excitation of bromoform in cyclohexane in the previous nanosecond transient resonance Raman work. Our DFT calculations attribute this to a relatively large barrier for thermal isomerization back into the parent molecule (average for three density functionals used, ~38 kJ mol$^{-1}$), implying that the thermal stability of iso-CHBr$_3$ extends to the microsecond time domain. Previous studies also showed that isomers of di- and polyhalomethanes may survive to microseconds in non-polar and weakly polar solvents. In acetonitrile, iso-CHBr$_3$ decays well within 1 ns via hydrolysis and thermal isomerization. Iso-CHBr$_3$ reacts quickly with water present in acetonitrile solutions by an O–H insertion/Hi elimination reaction, giving rise to an unstable hydrolysis product, namely, CHBr$_2$OH. However, even in CH$_3$CN with traces of water, the iso-CHBr$_3$ lifetime is ~300 ps. Our calculations attribute such a fast decay to thermal isomerization in which the cyclic, polar transition state of C$_1$ symmetry is stabilized by acetonitrile solvation to an about 17 kJ mol$^{-1}$ energy above iso-CHBr$_3$. The radical decomposition of iso-CHBr$_3$ requires larger activation energy by a factor of four, and is thus less likely to occur. The slow 3.5-ns decay of the UV absorption can be assigned either to secondary hydrolysis of CHBr$_2$OH and/or radical recombination. This decay is not observed in methylcyclohexane. Possible reasons for the aforementioned are the lack of hydrolysis and/or larger viscosity of C$_6$H$_4$CH$_3$ compared with CH$_3$CN (0.67 vs. 0.36 cP, respectively, 25 °C[109]). With recombination rates being close to or diffusion-limited, corresponding time constants increase with increasing solvent viscosity, placing radical recombination outside the time range probed in these experiments. The photochemical reaction mechanisms proposed on the basis of the collective above-mentioned observations are summarized in Fig. 12.

### J. Structural change and energy flow

Ultrafast radiationless relaxation of excited electronic states, in the present work leading to the formation of ground-state iso-CHBr$_3$ on a 100-fs time scale, is a well-known manifestation of surface crossing. Our CASSCF calculations locate a conical intersection between the CHBr$_3$ lowest singlet excited $\tilde{A}$ $^1A_2$ and iso-CHBr$_3$ ground states. Internal conversion between close-lying electronic states is extremely fast, so either excitation of CHBr$_3$ into the first singlet excited $\tilde{A}$ $^1A_2$ state and/or the second singlet excited $\tilde{E}$ state followed by internal conversion to the $\tilde{A}$ $^1A_2$ state are possible reaction channels, which lead to direct formation of iso-CHBr$_3$. Major structural changes upon going from the parent molecule to iso-CHBr$_3$ consist of CHBr$_3$ losing its tetrahedral structure to become more planar as well as one of the Br atoms migrating from the carbon atom to one of the two adjacent bromines. The later motion can be viewed as a superposition of Br–C–Br bending with Br–C–Br symmetric and asymmetric stretching vibrations. Interestingly, the same modes are Raman-active upon of 266- and 239.5-nm excitation, indicating that the initial motion on low-lying electronic excited states is along the aforementioned coordinates. The same vibrational modes also have the largest projection on the computed downhill excited-state reaction path leading to the CI. Thus, the CI which connects the CHBr$_3$ $\tilde{A}$ $^1A_2$ and iso-CHBr$_3$ ground states is energetically and dynamically accessible to mediate the concerted excited state isomerization. The structure of the isomerization path from the CI, or more precisely from the TS, to the ground-state iso-CHBr$_3$ minimum is determined by the C–Br–Br bending and Br–Br stretching modes. Consequently, relaxation along the reaction path initially deposts the excess vibrational energy into the Br–C–Br bending and Br–C–Br stretching modes of excited-state CHBr$_3$ and, after the CI, into the C–Br–Br bending and Br–Br stretching modes of ground-state iso-CHBr$_3$. An inspection of the reaction path modes shows their coupling to CBr1 and CH stretching modes, suggesting a possibility of intramolecular vibrational energy redistribution. The $\tilde{A}$ $^1A_2$ potential energy surface is steep outside the Franck-Condon region (Fig. 3). A wavepacket initially localized in the Franck-Condon region rapidly propagates on the $\tilde{A}$ $^1A_2$ surface. The wavepacket further accelerates upon passing through the steeper part of the surface in the vicinity of the CI, and spreads significantly upon reaching the isomer ground-state potential well. In agreement with this interpretation, the nascent 100-fs iso-CHBr$_3$ molecules exhibit broad absorption to the blue (strong) and to the red
The relaxed isomers. Mapping the visible transition energy of iso-CHBr$_3$ along the C–Br–Br bending and Br–Br bond stretching coordinates suggests that this absorption is characteristic of a C–Br–Br angular distribution in the $80^\circ$–$130^\circ$ range and a Br–Br bond length spread in the 2.5–3.0 Å range in the nascent isomers (Fig. 4). This is consistent with a rapid delocalization of the imparting wavepacket over a significant part of the ground-state well. In methylvyclohexane and acetonitrile, the wavepacket delocalization as well as onset of vibrationally energy flow out from the initially excited C–Br–Br bending and Br–Br stretching modes (characterized by the induction time) are similar. This is a remarkable observation which demonstrates that despite the vast difference in solute-solvent interactions and their time scales in these two solvents, the initial nuclear dynamics is unaltered.

The second mechanism responsible for the isomer formation is cage-induced isomerization, taking place on a 20-ps time scale. Similar to the picture drawn by ab initio molecular mechanisms simulations of the closely related CH$_3$I$_2$ system, the C–Br–Br angle and the Br–Br bond length are most logical reaction coordinates for the motion towards the equilibrium isomer structure for cage-induced isomerization in the CHBr$_3$/iso-CHBr$_3$ system. An approach by a Br-atom fragment of the Br moiety of the CHBr$_2$ fragment due to velocity reversal caused by collisions with the solvent cage prepares a far-from-equilibrium iso-CHBr$_3$ structure with an elongated Br–Br bond and a broad distribution of C–Br–Br angles, as a result of the large orientational cone of acceptance of bromine. As a result, the vibrational energy released in cage-induced isomerization channels into the C–Br–Br bending and Br–Br stretching modes along the reaction coordinate. The same vibrational modes are relevant for ground-state isomerization. The observation that the vibrationally hot isomers formed via cage-induced isomerization absorb to the red of the optimized C–Br–Br angle and Br–Br bond length positions are reached later than in acetonitrile. Since a significant similarity exists in the preceding relaxation of the isomers in both solvents, this observation is consistent with a shorter Br–Br bond of the optimized structure of iso-CHBr$_3$ in C$_6$H$_{11}$CH$_3$ than CH$_3$CN (Table I of the supplementary material).

Finally, a three to six times solvent-dependent increase of the oscillator strength of the intense visible transition of the relaxing ground-state iso-CHBr$_3$ species (Fig. 4) is not expected based on the conservation rule of the transition dipole moment. This observation evidences that the geometry and excess as a function of time and relaxing towards the equilibrium geometry, monitored through the high-energy shift of the electronic transition.

The flow of vibrational energy out of the C–Br–Br bending and Br–Br stretching modes revealed through the decay-associated spectra of component C ($\tau_c$) takes about the same time in CH$_3$CN and C$_6$H$_{11}$CH$_3$. This is because the isomers occupy the high-density manifold of vibrational states (10 cm$^{-1}$/cm$^{-1}$) where the relaxation is essentially intramolecular and not influenced by the bath. Such behavior has been observed in similar molecules in the liquid phase at excess energies corresponding to CH stretch fundamental excitation. The similar D-spectra in both solvents manifest a similar degree of vibrational excitation in the C–Br–Br bending and Br–Br stretching modes. The isomer population is now colder and hence closer to the ground-state bottom, where the density of vibrational states decreases. At this point, vibrational relaxation slows down and becomes more sensitive to the solvent properties. In acetonitrile, spectral narrowing from D to E ($\tau_D = 24.6$ ps) indicates further vibrational relaxation; however, the band shift does not occur. This suggests that the equilibrium C–Br–Br angle and Br–Br bond length are largely reached within $\tau_c = 4.9$ ps and that further relaxation involves other vibrational modes. In methylvyclohexane, the 500-nm D component further shifts to the 425-nm E component ($\tau_D = 10.2$ ps), indicating that in this solvent the equilibrium C–Br–Br angle and Br–Br bond length positions are reached later than in acetonitrile. Since a significant similarity exists in the preceding relaxation of the isomers in both solvents, this observation is consistent with a shorter Br–Br bond of the optimized structure of iso-CHBr$_3$ in C$_6$H$_{11}$CH$_3$ than CH$_3$CN (Table I of the supplementary material).

FIG. 12. Proposed photochemical reaction pathways following UV excitation of bromoform. The lifetimes and absorption maxima are shown in blue and red colors for acetonitrile and methylvyclohexane, respectively.
V. CONCLUSIONS

We have presented a global description of the photochemical reaction path of CHBr3 upon 255-nm excitation. In both methylocyclohexane and acetonitrile, photoexcitation of CHBr3 leads to the iso-CHBr3 product in a large quantum yield (∼35%) via two isomerization mechanisms occurring on distinctly different time scales. The sub-100 fs direct excited-state isomerization is mediated by a conical intersection between the lowest excited singlet state of CHBr3 and the ground state of iso-CHBr3 with the formation of the isomer structures spreading over a significant part of the ground-state potential. The direct isomerization reaction path is dominated by Br−C−Br bending and Br−C−Br stretching modes in the CHBr3 region of the potential and the C−Br−Br bending and Br−Br stretching modes on the iso-CHBr3 side. For the cage-induced isomerization mechanism, the solvent arrests the separation of the nascent Br− + CH2Br2− radical pair, which collapses to ground-state iso-CHBr3 on a time scale of several picoseconds, leading to the unrelaxed isomers with elongated Br−Br bonds. In both solvents, the initial shortening of the Br−Br bond and relaxation along the C−Br−Br angle of this species are overdamped, taking place on similar time scales. After 10 ps, vibrational relaxation involves other modes in acetonitrile, whereas the change of the Br−Br bond length continues to longer times in methylocyclohexane where the equilibrium Br−Br bond is shorter. Vibrational relaxation is complete at about 50 ps in both solvents. In acetonitrile, iso-CHBr3 undergoes either facile thermal isomerization to the parent CHBr3 molecule through the cyclic transition state stabilized by the polar solvent (a lifetime of 310 ps in anhydrous CH3CN) and, in the presence of water, hydrolysis with the formation of CHBr2OH. In methylocyclohexane, iso-CHBr3 is stable on much longer time scales.

The combined experimental and ab initio multiconfigurational investigation identifies a previously undocumented ultrafast excited-state isomerization pathway of bromoform through a conical intersection that connects the two isomer forms. This conical intersection is accessible in all environments studied (gas phase, CH3CN, and C6H11CH3), with obvious implications for the UV photochemistry of isolated bromoform. A caging medium provides an effective way for the nascent Br−CHBr2 moiety while the Br atom is migrating from carbon to the adjacent bromine of CHBr2−, may also be cast as the “roaming reaction mechanism.”116,117 Whether this direct isomerization mechanism is widespread for polyhalogenated alkanes, or constitutes a unique feature of the CHBr3 system, remains to be investigated.

Spectrally broadband probe pulses, encompassing the deep-UV/UV region, were utilized in this work. This ensures the detection of all absorbing species as well as their relaxation at different stages of the photochemical reaction. This has provided a tool for a “global” description of the photochemical reaction pathways and, therefore, carries an important advantage over ultrafast techniques where probing is either limited to a narrow spectral window or spectral window or thus selective probing of transient reaction intermediates is not possible. The role of radicals in the photochemistry of polyhalomethanes is often speculated because of experimental difficulties to detect these short-lived, UV-absorbing species.37 The cage-induced isomerization of polyhalomethanes has been frequently invoked in literature32-34,37-52 but in fact this study is the first of its kind, where the formation of the nascent radical pair and its collapse on a several picosecond time scale into ground-state iso-CHBr3 (in methylocyclohexane) are directly monitored. Overall, this work has revealed that combining state-of-the-art approaches in ultrafast transient absorption spectroscopy and ab initio multiconfigurational calculations makes it possible to trace ultrafast structural dynamics of small molecular systems in solution.

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