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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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Ultrafast deep-ultraviolet through near infrared (210–950 nm) transient absorption spectroscopy complemented by *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_3 leads to the ground-state *iso*- CHBr_3 product in a large quantum yield ($\sim 35\%$), 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_3 and the ground electronic state of *iso*- CHBr_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 *iso*- CHBr_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 *iso*- CHBr_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 *iso*- CHBr_3 photoproduct is stable in methylcyclohexane, but undergoes either facile thermal isomerization to the parent CHBr_3 structure through a cyclic transition state stabilized by the polar acetonitrile medium (~ 300 -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 *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,^{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.^{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_3 .^{9,10} In addition, bromoform readily evaporates and is reputed to be the prevalent source of active bromine in the earth's atmosphere.^{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 ~ 220 nm (5.63 eV).¹³ Low-lying singlet and triplet states are thought to mainly arise from single electron excitations from the Br lone pair *n* orbitals into the C–Br σ^* orbitals, $n(\text{Br}) \rightarrow \sigma^*(\text{C}–\text{Br})$. Resonant Raman spectra of CHBr_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 (ν_6), the H–C–Br asymmetric bend (ν_3), the Br–C–Br symmetric stretch (ν_2), and the Br–C–Br asymmetric stretch (ν_5).¹⁴ The UV photochemistry of gas-phase CHBr_3 has been the subject of extensive studies over the last two decades. An early 200-nm photolysis study of CHBr_3 suggested a primary loss of Br atoms and subsequent unimolecular decomposition of nascent hot $\text{CHBr}_2\cdot$ radicals to yield the detected CBr fragments.¹⁵ Following 193-nm excitation of CHBr_3 , a rapid loss of

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one Br atom from a repulsive excited electronic state was the only primary photolysis channel.¹⁶ However, 234- and 267-nm single-photon excitation of CHBr_3 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.¹⁷ Most of the bromine atoms were formed in the ground $\text{Br}(^2\text{P}_{3/2})$ rather than in the spin-orbit excited $\text{Br}(^2\text{P}_{1/2})$ state.^{17,18} The presence of dissociation pathway(s) in CHBr_3 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.¹⁹ The North group revisited the photochemistry of CHBr_3 and concluded a unity quantum yield for the Br-atom dissociation channel upon single-(248 nm)-photon excitation.²⁰ Although CHBr fragments were observed, they were assigned to sequential photodissociation of a fraction of $\text{CHBr}_2\cdot$ primary products. This controversy inspired further studies by Huang *et al.* who reported molecular elimination of Br_2 in a 0.23 quantum yield upon 248-nm excitation of CHBr_3 .²¹ It was speculated that excited state CHBr_3 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 CHBr_3 over the elimination barrier to form vibrationally excited Br_2 .²¹ The same group detected Br_2 following 248-nm excitation of CF_2Br_2 ²² and 1,1- and 1,2- $\text{C}_2\text{H}_4\text{Br}_2$,²³ nonetheless, assigning these observations to ground-state asynchronous concerted elimination. More recently, Quandt, Reid, and co-workers^{24,25} invoked the $(\text{H})\text{BrC—Br—Br}$ (*iso*- CHBr_3) isomer—a high-energy intermediate on the ground-state potential surface of CHBr_3 —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, CH_2I_2 .^{26–28} 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)^{29,30} have been well-characterized for several di- and polyhalogenated alkanes.^{31–53} Recently, the ultrafast (≤ 2 ps) formation of molecular iodine from *iso*- CF_2I_2 in non-polar solvents^{54–56} indeed suggested that these isomers may in some cases be precursors for molecular halogen elimination. For CHBr_3 in cyclohexane, Phillips and co-workers observed the *iso*- CHBr_3 product at 0 and 10 ns delay times between the 282.4-nm Raman pump and 435.7-nm probe pulses.⁴³ Using a similar nanosecond transient resonance Raman technique for CHBr_3 in methanol, the $\text{CHBr}_2\cdot$ radicals were identified using a 200-nm probe wavelength.⁵⁷ A picosecond time-resolved resonance Raman (ps-TR³) investigation by the same group suggested that *iso*- CHBr_3 is produced within the first several picoseconds after 267-nm photolysis of CHBr_3 in acetonitrile solution containing 0.2% of water (v/v).^{9,10} The isomer undergoes vibrational cooling within 50 ps, then decays with a 230-ps time constant with a concurrent buildup of CHBr_2OH . This hydrolysis product was thought to be formed

through an O—H insertion/HBr elimination reaction between *iso*- CHBr_3 and water, thermodynamically accessible based on the MP2 calculations of the stationary points on the ground-state potential energy surface for the *iso*- $\text{CHBr}_3 + n\text{H}_2\text{O}$ ($n = 1, 2, 3$) reaction. The HBr leaving group of the reaction dissociates into ions in aqueous environments,^{9,10} which explains the observed photochemical conversion of bromoform to bromide ions in aqueous solutions.⁵⁸ The formation of *iso*- CHBr_3 in neat bromoform and concentrated cyclohexane solutions was studied by Crim and co-workers using ultrafast transient absorption spectroscopy.⁵⁹ 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*- CHBr_3 , 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 $\cdot$ atom released by *iso*- CHBr_3 ,⁵⁹ 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 CHBr_3 in cyclohexane arises from Br $\cdot$ - CHBr_3 CTC.⁶⁰ Recently, Reid and co-workers trapped *iso*- CHBr_3 following 220-nm irradiation of CHBr_3 in Ar and Ne matrices.^{61,62} The absorption spectrum of *iso*- CHBr_3 exhibits a 245-nm band, and a more intense 398-nm band (molecular extinction coefficient, $\epsilon = 18600 \text{ M}^{-1} \text{ cm}^{-1}$) with a ~ 560 -nm shoulder.⁶¹ 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.^{63,64}

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 CHBr_3 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*- CHBr_3 product. We also observed the direct formation of *iso*- CHBr_3 from the parent structure, namely, tetrahedral CHBr_3 . 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 CHBr_3 in its first excited singlet state to *iso*- CHBr_3 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 methylcyclohexane, 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 ($\text{CHBr}_2\cdot$, CHBr_2^+ , and CHBr_2OH) 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,⁶⁵ 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 ζ contraction. Hence, all DFT/TDDFT calculations reported in the main text employ the aug-cc-pVTZ basis set, performed using GAUSSIAN 09.⁶⁶ The multiconfigurational CASSCF^{67–69} and CASPT2⁷⁰ calculations were performed using MOLCAS 7.6.⁷¹ 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 methylcyclohexane 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).^{36,37,54,72} 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 (ΔA) spectra were obtained by diode-array detection of the multiple (512) ΔA kinetic traces within the white-light continuum spectrum to which properly scaled single-wavelength ΔA 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 ΔA 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 ΔA signals with excitation energy was also ensured. Deviations from the linearity were observed at energies larger than 3.5 μJ .

All ΔA 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 ΔA 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.^{73,74} 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 methylcyclohexane. In acetonitrile, the IRF widths were smaller by a factor of 1.26 at wavelengths shorter than 380 nm.

The shape of the ΔA 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 ΔA 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 methylcyclohexane 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_2O 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*-CHBr₃ 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.

<i>iso</i> -CHBr ₃	Gas phase		Methylcyclohexane	Acetonitrile
	This work	Literature		
B3LYP	652 (0.0001)		664 (0.0002)	699 (0.0001)
	601 (0.0005)	Ref. 43 ^a	620 (0.0005)	670 (0.0001)
	388 (0.3426)	427 (0.0005)	423 (0.4762)	477 (0.4071)
	308 (0.0148)	407 (0.031)	317 (0.0207)	341 (0.0163)
	290 (0.0348)	395 (0.6)	295 (0.0016)	321 (0.0039)
	284 (0.0070)	251 (0.0003)	285 (0.0505)	271 (0.0593)
	274 (0.0066)	239 (0.11)	270 (0.0056)	263 (0.0047)
	257 (0.1354)		258 (0.1357)	257 (0.1519)
	238 (0.0769)		244 (0.0894)	252 (0.0841)
	219 (0.0074)		216 (0.0113)	207 (0.0566)
	520 (0.0002)		525 (0.0002)	590 (0.0002)
	481 (0.0012)	Ref. 61 ^b	492 (0.0015)	547 (0.0000)
CAM-B3LYP	375 (0.4326)	570 (0.0002)	413 (0.5553)	512 (0.1625)
	278 (0.0073)	530 (0.0006)	290 (0.0092)	359 (0.0000)
	267 (0.0138)	393 (0.42)	277 (0.0127)	336 (0.0001)
	264 (0.0403)	289 (0.0065)	259 (0.0479)	267 (0.2649)
	223 (0.0412)	277 (0.0006)	229 (0.0708)	222 (0.0176)
	216 (0.0138)		216 (0.0113)	222 (0.0168)
	211 (0.0106)		207 (0.0059)	217 (0.5720)
	204 (0.0817)		206 (0.1507)	205 (0.1102)
	503 (0.0002)		506 (0.0002)	527 (0.0004)
	464 (0.0010)		472 (0.0014)	513 (0.0235)
	367 (0.4189)		400 (0.5480)	473 (0.3482)
	273 (0.0046)		285 (0.0096)	335 (0.0080)
M06-2X	270 (0.0366)		273 (0.0158)	321 (0.0197)
	261 (0.0211)		262 (0.0407)	249 (0.1166)
	218 (0.0341)		223 (0.0703)	236 (0.1235)
	214 (0.0131)		212 (0.0138)	216 (0.0062)
	213 (0.0193)		210 (0.0225)	210 (0.1165)
	202 (0.0249)		202 (0.1038)	202 (0.1034)

^aURPA/UB3LYP/6-311G(*d,p*).

^bURPA//B3LYP/6-311G(*d,p*).

deionized 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 CHBr₃ consists of a distorted tetrahedron with C_{3v} symmetry (Table I of the supplementary material⁷⁵), and exhibits little dependence on the surrounding medium. The *iso*-CHBr₃ 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 CHBr₃ 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 material⁷⁵). The structure of *iso*-CHBr₃ 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*-CHBr₃ and other possible product species (CHBr₂[•], CHBr₂⁺, and CHBr₂OH; see Table II of the supplementary material⁷⁵ for the corresponding optimized structures), computed using different density functionals, agree within 0.3 eV. *Iso*-CHBr₃ 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 material⁷⁵). Our calculations predict a significant red-shift with increasing polarity for the intense transition of *iso*-CHBr₃ from 388 nm in the gas-phase to 423 nm in C₆H₁₁CH₃, and 478 nm in CH₃CN. CHBr₂[•] and CHBr₂⁺ are predicted to have intense 250-nm (*f* $\sim$ 0.09) and 270-nm (*f* $\sim$ 0.2) transitions, showing little solvatochromic shifts (Table II, and Table IV of the supplementary material⁷⁵). For CHBr₂OH in acetonitrile, a 225-nm transition (*f* $\sim$ 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 ($\text{CHBr}_2\cdot$, CHBr_2^+ , and CHBr_2OH) using the aug-cc-pvTZ basis set in the three different media considered in this work.

		Gas phase	Acetonitrile	Methylcyclohexane
$\text{CHBr}_2\cdot$	B3LYP	422 (0.0003)	419 (0.0002)	422 (0.0003)
		283 (0.0000)	279 (0.0000)	282 (0.0000)
		271 (0.0000)	269 (0.0000)	270 (0.0000)
		267 (0.0002)	265 (0.0005)	266 (0.0004)
		262 (0.0616)	260 (0.0802)	262 (0.0843)
		261 (0.0025)	259 (0.0048)	260 (0.0037)
		236 (0.0064)	233 (0.0081)	235 (0.0082)
		222 (0.0001)	220 (0.0003)	221 (0.0003)
		219 (0.0000)	217 (0.0000)	218 (0.0000)
		215 (0.0149)	215 (0.0224)	217 (0.0231)
		376 (0.0002)	375 (0.0001)	376 (0.0001)
	CAM-B3LYP	263 (0.0000)	260 (0.0000)	262 (0.0000)
		253 (0.0000)	252 (0.0000)	252 (0.0000)
		251 (0.0002)	249 (0.0003)	250 (0.0003)
		248 (0.0699)	246 (0.0888)	245 (0.0936)
		242 (0.0029)	240 (0.0058)	241 (0.0044)
		223 (0.0045)	221 (0.0057)	222 (0.0057)
		211 (0.0000)	209 (0.0001)	210 (0.0001)
		204 (0.0000)	203 (0.0000)	204 (0.0252)
		203 (0.0188)	203 (0.0244)	203 (0.0000)
		405 (0.0002)	404 (0.0001)	405 (0.0001)
	M06-2X	269 (0.0000)	268 (0.0000)	268 (0.0000)
		266 (0.0000)	262 (0.0000)	264 (0.0000)
		255 (0.0002)	252 (0.0004)	254 (0.0004)
		250 (0.0014)	247 (0.0034)	249 (0.0023)
		245 (0.0648)	243 (0.0874)	245 (0.0925)
		217 (0.0045)	216 (0.0060)	216 (0.0060)
		213 (0.0173)	212 (0.0226)	214 (0.0236)
		209 (0.0167)	208 (0.0175)	209 (0.0193)
		206 (0.0012)	205 (0.0000)	206 (0.0000)
		399 (0.0000)	390 (0.0000)	395 (0.0000)
CHBr_2^+	B3LYP	375 (0.0001)	368 (0.0001)	372 (0.0001)
		269 (0.1795)	273 (0.2270)	275 (0.2329)
		190 (0.0220)	191 (0.0275)	191 (0.0292)
		187 (0.0665)	188 (0.0823)	188 (0.0817)
		376 (0.0000)	368 (0.0000)	373 (0.0000)
	CAM-B3LYP	355 (0.0001)	349 (0.0001)	353 (0.0001)
		264 (0.2038)	268 (0.2524)	270 (0.2587)
		183 (0.0275)	184 (0.0335)	184 (0.0355)
		178 (0.0376)	179 (0.0463)	179 (0.0459)
	M06-2X	384 (0.0000)	375 (0.0000)	380 (0.0000)
		365 (0.0001)	358 (0.0001)	362 (0.0002)
		263 (0.1999)	267 (0.2482)	269 (0.2546)
		182 (0.0264)	183 (0.0329)	183 (0.0348)
		179 (0.0378)	179 (0.0464)	180 (0.0462)
		241 (0.0168)	245 (0.0167)	
CHBr_2OH	B3LYP	231 (0.0014)	234 (0.0075)	
		227 (0.0117)	226 (0.0223)	
		211 (0.0064)	210 (0.0081)	
		199 (0.0005)	197 (0.0038)	
		223 (0.0130)	225 (0.0167)	
	CAM-B3LYP	214 (0.0004)	214 (0.0026)	
		211 (0.0064)	210 (0.0093)	
		199 (0.0039)	198 (0.0050)	
		180 (0.0194)	179 (0.0372)	
	M06-2X	224 (0.0137)	226 (0.0172)	
		214 (0.0006)	215 (0.0015)	
		211 (0.0044)	211 (0.0103)	
		200 (0.0025)	199 (0.0033)	
		178 (0.0151)	175 (0.0560)	

TABLE III. Energies of the transition state (TS) and the *iso*-CHBr₃ species relative to the energy of the CHBr₃ parent structure calculated at the B3LYP, CAM-B3LYP, M06-2X, and MP2 levels all using the aug-cc-pvTZ basis set.

Species	Method	Relative energy (kJ mol ⁻¹)			
		Isolated	Methylcyclohexane	Methanol	Acetonitrile
TS	B3LYP	222.3	204.7	167.6	167.2
	CAM-B3LYP	258.5	237.1	187.7	187.0
	M06-2X	265.0	243.7	195.2	195.7
	MP2	283.4	267.9	216.5	222.0
<i>iso</i> -CHBr ₃	B3LYP	174.6	162.0	143.0	142.7
	CAM-B3LYP	213.7	203.2	172.2	171.7
	M06-2X	219.0	209.8	184.3	184.4
	MP2	205.4	201.6	197.3	205.2

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: CHBr₃, TS, and *iso*-CHBr₃. Table V of the supplementary material⁷⁵ summarizes the corresponding vibrational frequencies. IRC B3LYP/aug-cc-pvTZ calculations rigorously confirm that the optimized first-order saddle point connects the two isomers, Fig. 1. In both C₆H₁₁CH₃ and CH₃CN, the motion along the IRC from the TS to the *iso*-CHBr₃ 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 C₆H₁₁CH₃, all DFT methods used predict a slight (~ 10 kJ mol⁻¹) decrease of the potential energy barrier for isomerization of *iso*-CHBr₃. This barrier is significantly lower in CH₃CN.

Relaxed scans along the C–Br bond in *iso*-CHBr₃ (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. 1. Relaxed redundant coordinate scans along the C–Br–Br angle in the isomer species suggest that *iso*-CHBr₃ is connected to the reactant (CHBr₃) through a transition state (TS).

Fig. 2. It was found that the CHBr + Br₂ channel is connected to *iso*-CHBr₃ via a barrierless path and both decomposition channels are higher in energy than the channel populating the reactant well (CHBr₃). In acetonitrile, *iso*-CHBr₃ is located ~ 17 kJ mol⁻¹ lower than the isomerization TS, ~ 79 kJ mol⁻¹ more stable than the CHBr₂ + Br asymptote, and ~ 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 methylcyclohexane, the corresponding values are ~ 38 , ~ 52 , and ~ 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 S₁ state resembles its S₀ state counterpart, and both surfaces converge in the vicinity of the TS connecting CHBr₃ and *iso*-CHBr₃ 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 photochemical path from the CI to the *iso*-CHBr₃ minimum and the IRC path from the TS to the *iso*-CHBr₃ minimum likely intercept. To describe spectral changes accompanying the motion from the TS to the *iso*-CHBr₃ 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 CASPT2//CASSCF is required to provide an adequate description of this system. The intense visible absorption VET of *iso*-CHBr₃ corresponds to an S₀ → S₃ excitation at the CASPT2 level of theory. The transition energy significant blueshifts by ~ 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*-CHBr₃ 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. 2. Relaxed redundant coordinate scans along the C–Br–Br and C–Br geometrical parameters in iso-CHBr_3 (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.⁷⁵ The results of a two-dimensional relaxed redundant coordinate scan and corresponding VETs and oscillator strengths of the intense visible transition of iso-

CHBr_3 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.⁷⁵

B. Experimental results

1. Steady-state UV absorption

The UV absorption spectrum of CHBr_3 in $\text{C}_6\text{H}_{11}\text{CH}_3$ consists of a broadband centered at ~ 225 nm, Fig. 5. Compared to the gas-phase spectrum of CHBr_3 ,^{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 CHBr_3 absorption obeys the Lambert-Beer law up to the highest measured concentrations of 200 mM, (inset of Fig. 5). The measured maximum extinction coefficients, $\epsilon(221 \text{ nm}) = 2050 \text{ M}^{-1} \text{ cm}^{-1}$ in CH_3CN and $\epsilon(225 \text{ nm}) = 2452 \text{ M}^{-1} \text{ cm}^{-1}$ in $\text{C}_6\text{H}_{11}\text{CH}_3$ 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 absorption⁷⁴ for high-energy probes as well as oscillatory solvent signals due to cross-phase modulation and impulsive stimulated Raman scattering^{80–84} for low-energy probes contaminate the short-time ΔA spectra measured for CHBr_3 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 CHBr_3 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 CHBr_3 .

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

FIG. 3. Intrinsic reaction coordinate calculations of the ground-state isomerization path connecting CHBr_3 and iso-CHBr_3 at the B3LYP/aug-cc-pvTZ level of theory (solid line), and the results of single point CASSCF (16,12)/ANO-RCC-VTZP calculations on the ground and lowest-lying excited singlet states (S_0 and S_1 , solid and open symbols) along the B3LYP path are shown.

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).

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 ΔA 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 ΔA 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 420-nm product bands only exhibit minor growth.

Multieponential fitting of the ΔA kinetic traces at selected wavelengths illustrates the course of the transient absorption dynamics, Fig. 7. The ΔA signals (≥ 200 fs) can be described by a sum of four exponential functions (time constants, τ_{1-4}) and a permanent background. Wavelength-dependent decay/rise τ_1 of several hundred femtoseconds and minor amplitudes describes the induction period. In the visible range, the wavelength-dependent τ_2 (rise) and τ_3 (decay) major components depict the growth and narrowing of the 420-nm band: $\tau_2 = 3.4, 5.5, 8.7$, and 13 ps and $\tau_3 = 6.3$,

FIG. 5. (Left) Energetics of the gas-phase CHBr_3 system.^{17,20} The absorption spectrum^{76,77} is shown adjacent to the assignment of the excited electronic states computed at the CCSD/aug-cc-pVDZ level of theory.¹³ (Right) Steady-state absorption spectra of CHBr_3 in methycyclohexane and acetonitrile (maximum extinction coefficient $\epsilon_M = 2452$ and $2050 \text{ M}^{-1} \text{ cm}^{-1}$, 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).¹³ 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.

FIG. 6. 255-nm ΔA spectra of CHBr_3 in methylcyclohexane. Panels a, b, and c correspond to short, intermediate, and long time delays, which are expressed in picoseconds and given in legends. Note, the 100-fs ΔA spectrum for $\lambda > 330$ nm was obtained by subtracting appropriately scaled solvent contribution. Panel c shows the product absorption spectrum ($\square$) previously assigned to a $\text{Br} \cdot \text{CHBr}_3$ complex⁶⁰ and the product absorption spectrum produced following irradiation of CHBr_3 in a ~ 5 K Ne matrix⁶¹ assigned to *iso*- CHBr_3 product ($\blacktriangle$). Top insets: the B3LYP/PCM VETs of the *iso*- CHBr_3 and $\text{CHBr}_2 \cdot$ species carrying oscillator strengths larger than 0.05.

11.3, 11.8, ps, and of zero amplitude at 780, 600, 550, and 415 nm, respectively. The minor ΔA evolution at long times is characterized by $\tau_4 = 500$ ps.

The best global fit analysis⁸⁴ of the 340–755 nm ΔA spectra (≥ 150 fs) yields a sum of five decay-associated spectra (ε_i , where i varies from A to E, which obey exponential time dependence with time constants τ_i) and a permanent spectrum (F), Fig. 8. The $\tau_A = 720$ fs spectrum describes the short-time ΔA 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 ε_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 ε_E (420-nm band), which forms ($\tau_E = 710$ ps) the permanent ε_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 ΔA 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.

Multieponential fits to the CHBr_3 ΔA signals (≥ 150 fs) reveal five characteristic stages (Fig. 7): (i) an induction period pronounced in the UV range to ~ 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 ($\tau_4 = 259 \pm 37$ ps) and the corresponding rise of the deep-UV absorption; (v) the 255-nm band decay ($\tau_5 = 3.5$ ns). The same τ_5 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 ΔA 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 τ_D -component, which represents narrowing of ε_D without spectral shifting, Fig. 8.

5. Bromoform in acetonitrile upon addition of water

For CHBr_3 (20 mM) in acetonitrile (0.2% H_2O), and acetonitrile with 2% and 5% amounts of water, the ΔA kinetic traces at 218-, 250-, and 500 nm are not affected by the presence of water up to a ~ 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 ± 15 ps, and 56 ± 3 ps for 0.2%, 2%, and 5% of H_2O , whereas τ_4 is measured to be 310 ± 20 ps in anhydrous acetonitrile. The 218-nm ΔA 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_2O 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 ΔA 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 ± 60 ps to 100 ± 16 ps for 2% and 5% of H_2O , i.e., very similar to those at 218 nm. Within the experimental accuracy, a 3.5-ns

FIG. 7. Early- and intermediate-time ΔA kinetic traces (symbols) for CHBr_3 in methylcyclohexane (left panels) and acetonitrile (right panels). The inset shows kinetic traces up to 1150 ps, the longest investigated time delay. The solid red lines are multiexponential fits to the data points. The ΔA signals measured upon excitation of neat solvent under the same experimental conditions are shown as blue lines.

decay time constant at 218- and 250-nm is independent of water concentration.

6. Bromine in bromoform

To characterize the absorption band of a CTC between Br atom and CHBr_3 , we selectively excited solutions of Br_2

(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.

FIG. 8. Decay-associated spectra (ε_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 ΔA spectra yields five components (A, B, C, D, E) and a permanent spectrum (F). The resulting time constants are given besides the corresponding ε_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 po-

FIG. 9. 255-nm ΔA spectra of CHBr_3 in acetonitrile. Panels (a), (b), and (c) show the ΔA 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_2OH product species carrying oscillator strengths larger than 0.05.

FIG. 10. The ΔA 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 $0.85 \mu\text{J pulse}^{-1}$.

larity from methylcyclohexane to acetonitrile (Fig. 5), the solution spectra can be similarly assigned to $n(\text{Br}) \rightarrow \sigma^*(\text{C}-\text{Br})$ transitions.^{78,79} 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).¹³ The $\tilde{X}^1A_1 \rightarrow \tilde{B}^1E$ 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 $\tilde{X}^1A_1 \rightarrow \tilde{A}^1A_2$ state (243 nm) is formally dipole forbidden ($f = 0$), although this transition may borrow intensity from the close-lying $\tilde{X}^1A_1 \rightarrow \tilde{B}^1E$ transition.¹³ There are four triplet states in the UV range. The third triplet state, $\tilde{c}^3A_1$ at 239 nm, has about 10-times larger oscillator strength ($f = 3.1 \times 10^{-3}$) than other three states ($\tilde{a}^3E$, $\tilde{b}^3E$, and $\tilde{a}^3A_2$), so that the $\tilde{X}^1A_1 \rightarrow \tilde{c}^3A_1$ transition may also contribute to the long-wavelength part of the spectrum. The lowest-energy triplet state ($\tilde{a}^3A_2$) is dissociative towards $\text{CHBr}_2\cdot + \text{Br}\cdot$.¹³ 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. 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 $4.8 \mu\text{J pulse}^{-1}$. The main window shows the 1-ps ΔA 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.⁵⁹

into a superposition of the $\tilde{A}^1A_2$ and $\tilde{B}^1E$ singlet states with some contribution of the $\tilde{c}^3A_1$ 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),⁶¹ the difference in the solvent media (gas-phase vs. solution) warrant a brief discussion. Gas-phase *iso*-CHBr₃ is found bound relative to the CHBr₂· + Br· asymptote by 63 kJ mol⁻¹ and the CHBr + Br₂ asymptote by 159 kJ mol⁻¹.⁶¹ The TS of CHBr₃ → *iso*-CHBr₃ isomerization is found at 47 kJ mol⁻¹ above ground-state *iso*-CHBr₃ and 251 kJ mol⁻¹ above ground-state CHBr₃. This is quantitatively consistent with our DFT calculations in methylcyclohexane (Table III), although in acetonitrile we predict an increased energy gap between *iso*-CHBr₃ and the CHBr₂· + Br· and CHBr + Br₂ asymptotes, consistent with the polar nature of *iso*-CHBr₃. Furthermore, in acetonitrile the TS of CHBr₃ → *iso*-CHBr₃ isomerization lies at about 17 kJ mol⁻¹ above ground-state *iso*-CHBr₃, i.e., substantially closer. This result is consistent with the more polar nature of the thermal isomerization TS compared to *iso*-CHBr₃ and stronger stabilization of the former by polar acetonitrile—a concept also documented by our group in the thermal isomerization of a similar system (CH₂Br₂ → *iso*-CH₂Br₂).⁸⁵

C. Nature of visible product absorption

The equilibrated visible ΔA band in methylcyclohexane and acetonitrile solutions of CHBr₃ can be assigned to the ground-state *iso*-CHBr₃ photoproduct. 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 C₆H₁₁CH₃ as well as 505-nm band observed in CH₃CN to *iso*-bromoform. For non-polar solvents such as methylcyclohexane, a comparison with the matrix isolation results on CHBr₃⁶¹ is helpful to confirm our photoproduct assignment. The absorption bands of matrix-isolated *iso*-CHBr₃, 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*-CHBr₃ in methylcyclohexane is consistent with the nanosecond transient resonance Raman study that identified this product species utilizing 435.7 nm probe pulses.⁴³ The ps-TR³ study identified the *iso*-bromoform product following 267-nm excitation of CHBr₃ in acetonitrile/water mixtures.^{9,10} The previously isomer lifetimes reported^{9,10} are very close to the decay time constants of the 505-nm product band in our experiments.

Other product species, such as CHBr₂· radicals and CT complexes between Br· fragments and solvent molecules can be excluded as responsible for the visible ΔA bands observed. CHBr₂· 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 methylcyclo-

hexane are located in the UV range peaking at 270 nm³⁷ and 365–370 nm,⁸⁶ respectively. Moreover, one-(255-nm)-photon excitation of CHBr₃ induces the visible ΔA signal observed according to the measured energy dependence, thus ruling out species like CHBr₃⁺, the formation of which is typically implicated through multiphoton excitation. Finally, the steady-state absorption spectra of CHBr₃ obeyed the Lambert-Beer law up to a 200 mM concentration in the both solvents studied, showing no aggregation of CHBr₃. In methylcyclohexane the shape of the 10- and 500-ps ΔA spectra (Fig. 3 of the supplementary material⁷⁵), and the time profile of the 420-nm ΔA kinetic traces are independent of CHBr₃ concentration in the 2–500 mM range, ruling out that the ΔA spectra in the 1-ns time window studied may be due products of bimolecular reactions between the photolysis fragments and CHBr₃ molecules, e.g., Br·CHBr₃ CT complexes. The shape the 425-nm band due to *iso*-bromoform in the 500-ps ΔA spectrum (Fig. 6) is identical to that observed in the pulse radiolysis study⁶¹ of CHBr₃ in cyclohexane and assigned to the Br·CHBr₃ CT complexes, leading to the re-assignment of the latter band to *iso*-CHBr₃.

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 CH₂I₂, CHI₃, CH₂Br₂, CHBr₃, and CBr₄ suggest the formation of isomer photoproducts featuring C–I–I and/or C–Br–Br moieties.⁴³ 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 or 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.⁴³

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*-CHBr₃, 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 material⁷⁵) 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*-CHBr₃ 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*-CHBr₃ along the ground-state IRC path. From the TS to the *iso*-CHBr₃ 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.⁷⁵

E. Reactions of *iso*-CHBr₃ in acetonitrile-water mixture and methanol

We found that the *iso*-CHBr₃ lifetime (τ_4) is shorter when more water is present in acetonitrile/water solutions, in close agreement with the ps-TR³ findings.^{9,10} According to Phillips and co-workers,^{9,10} this is a manifestation of an O–H insertion/HBr elimination reaction of *iso*-CHBr₃ with water,

The *iso*-bromoform decay time constants in the presence of water can be fitted to Stern-Volmer equation:

$$1/\tau_4 = k_i + k_q[\text{H}_2\text{O}], \quad (2)$$

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 material⁷⁵). 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 ps¹⁰) 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,^{15–21} 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,^{37,88,89} such as Br·C₆H₁₁CH₃ absorbing at 365–370 nm⁸⁶ and Br·CH₃CN absorbing at 272 nm.³⁷ Our TD-DFT/PCM VET energy calculations show that CHBr₂· should exhibit an intense electronic transition at about 260 nm. In methylcyclohexane, 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 ΔA 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 ΔA signals is followed by a decay, suggesting further hydrolysis of CHBr₂OH con-

sistent with Phillips and co-workers,^{9,10} with the remaining 218-nm ΔA 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 CHBr₂·. The leaving group of reaction (1), HBr, has a small dissociation constant in acetonitrile ($\text{p}K = 5.51^{90}$) and, as a result, mostly exists in its molecular form, absorbing outside the probing region.

Finally, the 1000-ps ΔA 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 ($\epsilon = 10220 \text{ M}^{-1} \text{ cm}^{-1}$ at 218 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 π_u excited electronic states.⁹¹ In the gas phase, the ¹ π_u state dissociates into bromine atoms with unit efficiency.⁹² In solution, this state is thought to be coupled to the moderately bound *A/A'* states—the deepest, nested excited states of Br₂.⁹¹ Following prompt predissociation of the *B* state and cage recombination, the same *A/A'* states are populated.^{91–94} In liquid water, an upper limit for the predissociation is 270 fs and the recombined population in the *A/A'* states peaks at 1 ps.⁹⁴ For Br₂ in CCl₄, a quantum yield for trapping in the *A/A'* states is about 60%,⁹⁵ 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-controlled⁹⁶ 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 ΔA 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,⁹⁴ but overall consistent with recombination time scales reported for molecular halogens, e.g., thoroughly studied I₂ in alkanes and chlorinated alkanes.^{97–99} The Br₂ *A/A'* states absorb at 250-nm,⁹¹ well outside the probed spectral region. The extinction coefficient of Br·CHBr₃ CTC is expected to be about 20 times bigger than $\epsilon = 160 \text{ M}^{-1} \text{ cm}^{-1}$ in the visible band maximum of Br₂.³⁷ About the same ϵ is expected for the recombined 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 ΔA spectrum observed following 420-nm excitation of Br₂ in CHBr₃ is identical to the 1-ps ΔA spectrum reported by Crim and co-workers⁵⁹ in neat CHBr₃,

Fig. 11. Therefore, we propose to reassign the previously reported 390-nm band⁵⁹ to a CT complex between a Br· atom fragment and neighboring CHBr₃ molecules. This is consistent with the lack of vibrational relaxation in the 390-nm band⁵⁹ because translational thermalization of Br· is fast⁵⁹ so that the nascent complexes carry little excess of vibrational energy. Our TD-B3LYP VET energy calculations (Table III of the supplementary material⁷⁵) suggest that the successor 495-nm band observed⁵⁹ may be attributed to *iso*-CHBr₃. It is not trivial to comment on the nature of *iso*-CHBr₃ vs. the Br·CHBr₃ 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 CHBr₃ in the complex is less energetically favorable than chemical bonding in *iso*-CHBr₃ which possesses a significant covalent character.⁶¹ The Br· loss from the Br·CHBr₃ CTC is then expected with its subsequent bonding to a nearby CHBr₂· geminate fragment to form *iso*-CHBr₃. The decay of the 390-nm band and the rise of the 495-nm band occurring on similar picosecond time scale⁵⁹ agree with this mechanism. We document a similar behavior in the photo-induced dynamics of the Br₂/CHBr₃ system where bond (re)formation between two nascent Br-atom fragments is favored over the formation of the Br·CHBr₃ CT complex. The sharpening and blueshift of the visible product band from 490 to 430 nm with a decreasing polarity of the CHBr₃/C₆H₁₄ mixtures observed by Crim and co-workers⁵⁹ parallels the solvatochromic changes observed for *iso*-CHBr₃ from acetonitrile to methylcyclohexane (absorption band sharpening and blueshift from 505 to 425 nm). Finally, our steady-state and transient absorption spectra of CHBr₃ 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 *iso*-CHBr₃, ϵ_S (493 nm) = 8360 M⁻¹ cm⁻¹ in CH₃CN and ϵ_S (425 nm) = 11000 M⁻¹ cm⁻¹ in C₆H₁₁CH₃, from the known absorption spectrum of this isomer in a ~1:500 Ne matrix ($\epsilon_M \approx 18600$ 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 *iso*-CHBr₃ ($\phi_{iso-CHBr_3}$) were determined using the amplitudes of the visible ΔA absorption bands (at 50 ps in CH₃CN and 100 ps in C₆H₁₁CH₃) as a measure of the isomer concentration. The formation of the benzophenone triplet state in unit quantum yield¹⁰¹ and subsequent 525-nm triplet-triplet absorption band in acetonitrile solution ($\epsilon_T = 6250$ M⁻¹ cm⁻¹ (Refs. 101 and 102)) is chosen as a reference. We found $\phi_{iso-CHBr_3} = 39\% \pm 4\%$ in C₆H₁₁CH₃, and upon a factor of $\exp^{50/259}$ correction for the isomer decay, $\phi_{iso-CHBr_3} = 31\% \pm 7\%$ in CH₃CN.

In acetonitrile at 1 ns, CHBr₂·, Br·CH₃CN CTC, and CHBr₂OH as well as the photoinduced depletion of ground-state CHBr₃ contribute to the UV part of the 1-ns ΔA spectrum. Having subtracted the $\tau_4 = 259$ ps component associated with the *iso*-CHBr₃ decay and the formation of CHBr₂OH and CHBr₃, and separated the residual ΔA signal into absorption of Br·CH₃CN CTC and CHBr₂·, the quantum yield of the Br· fragment ($\phi_{Br\cdot}$) at 1 ns is esti-

mated to be $61\% \pm 11\%$. Further, assuming that CHBr₂· and Br·CH₃CN CTC ($\epsilon = 1470$ M⁻¹ cm⁻¹³⁷) are present in equimolar amounts with the correction for a 61% depletion of ground-state CHBr₃, the previously unknown ϵ at the 253-nm band maximum of CHBr₂· is estimated to be ~ 3030 M⁻¹ cm⁻¹. The nascent radical pair cannot separate from the rigid matrix cage and collapse into either CHBr₃ or *iso*-CHBr₃. Therefore, a viable suggestion is that the amplitude difference of the 1-ns UV ΔA band in methylcyclohexane and the *iso*-CHBr₃ UV band in the matrix (Fig. 6) is due to CHBr₂·. This gives a $\sim 60\%$ quantum yield of this species in methylcyclohexane at 1 ns. This also implies that photoexcited CHBr₃ molecules that do not collapse into *iso*-CHBr₃ predominantly end up as solvent-separated radicals under our experimental conditions. This further suggests that the recovery of ground-state CHBr₃, either via internal conversion of photoexcited CHBr₃ 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 *iso*-CHBr₃.

We analyzed the ΔA data to determine whether Br₂ formation occurs in our single-photon excitation experiments because of the previous reports of molecular halogen elimination from gas-phase CHBr₃^{17,21} and *iso*-CF₂I₂ photoproduct of CF₂I₂ in *n*-hexane.^{54,56} Br₂ 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 Br₂ is unimportant at 1 ns as it takes hundreds of nanoseconds under the experimental conditions used in this work (a $\sim 1\%$ – 5% fraction of sub-100 mM CHBr₃ excited, $\sim 10^{10}$ M⁻¹ s⁻¹ diffusion rate constants of Br⁹⁵). An upper limit of the quantum yield of Br₂ 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 Br₂ ($\epsilon = 160$ 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 CHBr₃ into a mixture of the $\tilde{A}^1A_2$, $\tilde{c}^3A_1$, and $\tilde{B}^1E$ 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 CHBr₂· radical in CH₃CN and Br·C₆H₁₁CH₃ CT complex detected. The 100-fs 395-nm ΔA band in C₆H₁₁CH₃, and possibly, the 100-fs 370-nm ΔA feature in CH₃CN, is assigned on the basis of the temporal and spectral evolution of this band, to ground-state *iso*-CHBr₃. 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

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 $\text{Br} \cdot \text{C}_6\text{H}_{11}\text{CH}_3$ 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 $\text{Br} \cdot$ atom approaches the $\text{CHBr}_2 \cdot$ 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.⁴³ 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.^{34,36} 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,^{9,10} giving rise to an unstable hydrolysis product, namely, CHBr_2OH . However, even in CH_3CN 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_2OH and/or radical recombina-

tion. This decay is not observed in methylcyclohexane. Possible reasons for the aforementioned are the lack of hydrolysis and/or larger viscosity of $\text{C}_6\text{H}_{11}\text{CH}_3$ compared with CH_3CN (0.67 vs. 0.36 cP, respectively, 25 °C¹⁰⁹). 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.¹¹⁰ 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,^{111,112} so either excitation of CHBr_3 into the first singlet excited $\tilde{A}^1A_2$ state and/or the second singlet excited ^1E 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 266- and 239.5-nm excitation,¹⁴ 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 deposits 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

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 methylcyclohexane, respectively.

(weaker) of the relaxed isomers. Mapping the visible transition energy of *iso*-CHBr₃ 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°–130° 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 methylcyclohexane 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 mechanics simulations of the closely related CH₂I₂ system,³⁵ 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 CHBr₃/*iso*-CHBr₃ system. An approach by a Br-atom fragment of the Br moiety of the CHBr₂· fragment due to velocity reversal caused by collisions with the solvent cage prepares a far-from-equilibrium *iso*-CHBr₃ 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 relaxed *iso*-CHBr₃ suggests that the relaxation dynamics is overdamped.¹¹³ Within this picture, the isomer species remain at the side of the ground-state potential corresponding to elongated Br—Br bond distances, losing vibrational energy

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 (τ_c) takes about the same time in CH₃CN and C₆H₁₁CH₃. 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.¹¹⁴ 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.^{114,115} 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 methylcyclohexane, 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*-CHBr₃ in C₆H₁₁CH₃ than CH₃CN (Table I of the supplementary material⁷⁵).

Finally, a three to six times solvent-dependent increase of the oscillator strength of the intense visible transition of the relaxing ground-state *iso*-CHBr₃ species (Fig. 4) is not expected based on the conservation rule of the transition dipole moment.¹⁰⁰ This observation evidences that the geometry and

electronic structure changes in *iso*-CHBr₃ are strongly coupled, which may be a general feature of polyatomic reaction intermediates and products formed in far from equilibrium geometries. Therefore, the time-dependent spectral shifts observed are not mere manifestations of vibrationally hot *iso*-CHBr₃ absorption to the red of vibrationally relaxed *iso*-CHBr₃, but arise from the complex character of the electronic structure of the ground-state isomer species.

V. CONCLUSIONS

We have presented a global description of the photochemical reaction path of CHBr₃ upon 255-nm excitation. In both methylcyclohexane 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· + CHBr₂· 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 methylcyclohexane 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 methylcyclohexane, *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 isomer products to rapidly dissipate their excess internal energy. The absence of a stabilizing medium around highly energetic *iso*-CHBr₃ would lead to further reaction channels in this product species such as, e.g., breaking apart with the formation of carbene and molecular bromine. Direct excited-state isomerization of CHBr₃, as it involves the reorientation of the 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 polyhalomethane molecules 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 literature^{32–34,37–52} 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 methylcyclohexane) 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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