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ABSTRACT

We employ few-cycle pulses to strong-field-ionize di-iodomethane (CH_2I_2) and femtosecond extreme ultraviolet (XUV) transient absorption spectroscopy to investigate the subsequent ultrafast dissociative ionization and vibrational wave packet dynamics. Probing in the spectral region of the I $4d$ core-level transitions, the time-resolved XUV differential absorption spectra reveal the population of several electronic states of CH_2I_2^+ by strong-field ionization. Global analysis reveals three distinct time scales for the observed dynamics: 20 ± 2 fs, 49 ± 6 fs, and 157 ± 9 fs, ascribed to relaxation of the CH_2I_2^+ parent ion from the Franck-Condon region, dissociation of high-lying excited states of CH_2I_2^+ to I^+ (3P_2), CH_2I , and I_2^+ ($^2\Pi_{3/2,g}$), and dissociation of CH_2I_2^+ to I ($^2P_{3/2}$) and CH_2I^+ , respectively. Oscillatory features in the time-resolved XUV differential absorption spectra point to the generation of vibrational wave packets in both the residual CH_2I_2 and the CH_2I_2^+ parent ion. Analysis of the oscillation frequencies and phases reveals, in the case of neutral CH_2I_2 , C–I symmetric stretching induced by bond softening and I–C–I bending driven by a combination of bond softening and R-selective depletion. In the case of CH_2I_2^+ , both the fundamental and first overtone frequencies of the I–C–I bending mode are observed, indicating large-amplitude I–C–I bending motion, in good agreement with results obtained from *ab initio* simulations of the XUV transition energy along the I–C–I bend coordinate. These results show that femtosecond XUV absorption spectroscopy is well-suited for studying ultrafast photodissociation and vibrational wave packet dynamics.

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I. INTRODUCTION

Intense laser-matter interaction¹ forms the basis for initiating and probing ultrafast quantum dynamics in molecules via phenomena such as high-order harmonic generation,^{2–4} above-threshold

ionization,^{5–7} nonsequential double ionization,^{8,9} and laser-induced electron diffraction.^{10,11} These processes have enabled the tomographic imaging of molecular orbitals^{12,13} as well as the observation of nonadiabatic multielectron dynamics,^{7,14} coherent electronic wave packet dynamics,^{15–17} and transient molecular structures,^{2,18,19}

all captured on subcycle time scales. On longer time scales, coherent vibrational dynamics,^{20,21} strong-field-induced photoisomerization,^{22,23} and Coulomb explosion^{20,24} have been observed as well, most commonly by either photofragment kinetic energy release or ion-ion coincidence measurements. The possibility of employing intense laser fields to manipulate the outcome of chemical reactions via the dynamic Stark effect^{25,26} and laser-induced conical intersections^{27,28} has also motivated the exploration of intense laser-molecule interaction. When effected by few-cycle laser pulses, strong-field ionization also provides access to radical cationic species, whose ultrafast chemical dynamics can be investigated with minimal interference from field-dressed states. Vibrational coherences produced by strong-field ionization also permit the identification of ion electronic states²⁹ and precision measurements of vibrational frequencies.³⁰

An emerging technique for interrogating the ultrafast dynamics that accompany intense laser-molecule interaction is extreme ultraviolet (XUV) transient absorption spectroscopy.^{31–33} The element specificity and the distinct XUV transition energies of the various photoproducts, in addition to the exquisite time resolution—down to the subfemtosecond regime^{34,35}—offered by time-resolved XUV absorption spectroscopy, make it well suited for the study of ultrafast molecular dynamics. Moreover, recent advances in the simulation of XUV absorption spectra facilitate quantitative comparisons between experiment and theory.^{36–38} Aside from photodissociation dynamics, initiated either by weak-field, perturbative photoexcitation^{39–42} or by strong-field dissociative ionization,^{43–46} coherent vibrational⁴⁷ and electronic⁴⁸ wave packet dynamics have also been observed by XUV transient absorption spectroscopy.

Our recent study of iodomethane (CH_3I) by femtosecond XUV absorption spectroscopy resolved dissociative ionization dynamics⁴⁹ and elucidated the various contributing mechanisms that give rise to intense laser-induced vibrational wave packet motion in both the neutral and parent ion species.⁵⁰ In this work, we extend these studies to a more complicated molecule, di-iodomethane (CH_2I_2). These organoiodine compounds play an important role in atmospheric photochemistry⁵¹ and the radiochemistry of iodine.⁵² Compared to CH_3I , CH_2I_2 has more states that are associated with the hole in the equatorial lone pairs of the iodine atoms—in CH_3I^+ , these are the spin-orbit-split $\tilde{X}^+$ ($^2E_{3/2}$) and $\tilde{X}^+$ ($^2E_{1/2}$) states, whereas CH_2I_2^+ yields the $\tilde{X}^+$ (2B_2), $\tilde{A}^+$ (2A_2), $\tilde{B}^+$ (2B_1), and $\tilde{C}^+$ (2A_1) states⁵³—hence potentially supporting more dissociation pathways. Moreover, the presence of a low-frequency I–C–I bending mode in CH_2I_2 , in addition to the C–I symmetric stretching mode, offers the possibility of observing multimode vibrational wave packet dynamics. Finally, beyond dissociation to give atomic I, the possibility of I_2^+ formation is expected to enrich the ultrafast chemical dynamics of CH_2I_2^+ , analogous to the extensively studied process of I_2 elimination from highly excited states of CH_2I_2 .^{54–56} In the present study, we find that strong-field ionization of CH_2I_2 populates a multitude of ion states, hence giving rise to multiple dissociation channels. Multimode coherent vibrational motion is observed in neutral CH_2I_2 , driven by a combination of bond softening and R-selective depletion, and a large-amplitude I–C–I bending mode wave packet, corroborated by *ab initio* calculations, is observed in the case of CH_2I_2^+ .

II. METHODS

A. Experimental methods

A detailed description of the experimental apparatus for femtosecond XUV absorption spectroscopy can be found in Ref. 50. Briefly, the 3-mJ, 25-fs output of an amplified femtosecond Ti:sapphire laser system is spectrally broadened in a helium-filled hollow-core fiber before temporally recompressed by chirped mirrors to yield few-cycle laser pulses of 5.6-fs duration. The XUV probe pulse is produced via high-order harmonic generation, effected by focusing 0.8-mJ of the few-cycle laser pulse into a 2.4-mm path length argon gas cell. The strong-field ionization pump pulse is produced by focusing 0.2-mJ of the few-cycle laser pulse to a peak intensity of 1.9×10^{14} W/cm². The pump and probe pulses are spatially and temporally overlapped in a 3-mm-long quasistatic gas cell filled with 8 mbar of CH_2I_2 vapor (Sigma Aldrich, 99%). The XUV beam that is transmitted through the sample gas cell is spectrally dispersed on a flat-field XUV grating and detected by an X-ray CCD camera. The spectral resolution in the photon energy range of interest is 47 meV. A variable time delay between the pump and probe pulses is introduced by means of a computer-controlled piezodriven delay stage positioned in the path of the pump beam. During data acquisition, the delay stage alternates between time delay t and -500 fs, giving the XUV spectra $S(E, t)$ and $S(E, -500 \text{ fs})$, respectively. The differential absorption signal is then given by $\Delta A(E, t) = -\log[S(E, t)/S(E, -500 \text{ fs})]$. Referencing the XUV spectrum collected at each time delay to the spectrum collected at -500 fs suppresses the effect of long-term drift of the XUV intensity and minimizes the effect of any residual scattered pump beam that is incident on the CCD camera.⁵⁷

B. Computational methods

Density functional theory (DFT) was employed to compute the energies and vibrational frequencies of CH_2I_2^+ , and time-dependent DFT (TD-DFT) was employed to calculate the iodine 4*d* core level transition energies of CH_2I_2^+ as the function of the I–C–I bond angle. Partial geometry optimizations involve scanning through a series of fixed I–C–I bond angles, while relaxing the other coordinates. TD-DFT and calculations of the potential energy curves employed the M062x functional⁵⁸ and the def2-TZVP basis set.^{59,60} All calculations were performed by using the Gaussian09 software package.⁶¹ The reported *ab initio* vibrational frequencies have been scaled by 0.945.⁶²

III. RESULTS AND DISCUSSION

A. Static XUV photoabsorption spectrum

The static XUV absorption spectrum of CH_2I_2 reveals two prominent bands at 50.3 and 52.1 eV (Fig. 1), which can be assigned to transitions from the spin-orbit-split iodine 4*d* core levels to the $\sigma_{\text{C-I}}^*$ orbital that is localized along the C–I bonds (Table I). The observed peak positions are slightly shifted to those observed for CH_3I (50.6 and 52.3 eV), which suggests that the presence of an additional C–I chromophore does not have any significant effect on the $\text{I } 4d \rightarrow \sigma_{\text{C-I}}^*$ transition energies. Additional peaks located at 54.4 and 56.1 eV can be assigned to transitions from the spin-orbit-split $\text{I } 4d$

FIG. 1. Static XUV photoabsorption spectrum of CH_2I_2 .

core level to a Rydberg state of $\text{I } 6p$ character, analogous to those observed for CH_3I .^{50,66}

B. Population of multiple electronic states of CH_2I_2^+

The time-resolved differential XUV absorption (ΔA) spectra of strong-field-ionized CH_2I_2 is shown in Fig. 2(a), and the differential

TABLE I. Observed XUV absorption peaks for CH_2I_2^+ , I , I^+ , and CH_2I_2 , their assignments to the $\text{I } 4d$ core-level transitions, and the transition energies obtained from the literature. Data for CH_2I_2 are obtained from the static photoabsorption spectrum, data for CH_2I_2^+ are obtained from the 10-fs ΔA spectrum, and data for I , I^+ , and I_2^+ are obtained from the 1-ps ΔA spectrum.

Species	Peak position (eV)	Peak position, lit. (eV)	Transition
CH_2I_2^+	46.1	46.13 ^a	$4a_1^{-1} \rightarrow 4d_{5/2}^{-1}$
	46.4	46.48 ^a	$2b_1^{-1} \rightarrow 4d_{5/2}^{-1}$
	46.9	46.93 ^a	$1a_2^{-1} \rightarrow 4d_{5/2}^{-1}$
	47.2	47.23 ^a	$3b_2^{-1} \rightarrow 4d_{5/2}^{-1}$
	47.9	47.86 ^a	$4a_1^{-1} \rightarrow 4d_{3/2}^{-1}$
	48.2	48.21 ^a	$2b_1^{-1} \rightarrow 4d_{3/2}^{-1}$
	48.7	48.66 ^a	$1a_2^{-1} \rightarrow 4d_{3/2}^{-1}$
	49.0	48.96 ^a	$3b_2^{-1} \rightarrow 4d_{3/2}^{-1}$
	51.3 ^b	...	$3b_2^{-1} \rightarrow 4d_{5/2}^{-1} 3b_2^{-1} \sigma_{C-I}^*$
	53.0 ^b	...	$3b_2^{-1} \rightarrow 4d_{3/2}^{-1} 3b_2^{-1} \sigma_{C-I}^*$
$\text{I } (^2P_{3/2})$	46.0	45.94 ^c	$^2P_{3/2} \rightarrow ^2D_{5/2}$
$\text{I}^+ (^3P_2)$	47.3	47.32 ^c	$^3P_2 \rightarrow ^3D_3$
	49.0	48.95 ^c	$^3P_2 \rightarrow ^3P_2$
	49.2	49.17 ^c	$^3P_2 \rightarrow ^3D_1$
$\text{I}_2^+ (^2\Pi_{3/2,g})$	47.9	47.85 ^d	
CH_2I_2	50.6	...	$^1A_1 \rightarrow 4d_{5/2}^{-1} \sigma_{C-I}^*$
	52.3	...	$^1A_1 \rightarrow 4d_{3/2}^{-1} \sigma_{C-I}^*$

^aCalculated based on literature values for the valence (Ref. 53) and $\text{I } 4d$ core level (Ref. 63) binding energies of CH_2I_2 .

^bThis transition is expected to overlap with the $\text{I } 4d \rightarrow \sigma_{C-I}^*$ XUV transition energies of the valence hole excited states.

^cReference 64.

^dCalculated based on literature values for the valence (Ref. 65) and $\text{I } 4d$ core level (Ref. 63) binding energies of I_2 .

FIG. 2. (a) Time-resolved differential XUV absorption spectrum of strong-field-ionized CH_2I_2 . (b) Differential XUV absorption spectra collected at 10-fs and 1-ps time delay are shown in red and blue lines, respectively. The 10-fs absorption spectrum is fit to a sum of Gaussian functions to identify the absorption peaks of the various CH_2I_2^+ ion states in the Franck-Condon region.

absorption spectra recorded at time delays of 10 fs and 1 ps are shown in Fig. 2(b). The negative differential absorption peaks at 50.6 and 52.2 eV arise from the depletion of the neutral CH_2I_2 species by strong-field ionization. The positive absorption features in the 10-fs ΔA spectrum can be assigned to $\text{I } 4d$ core level absorption resonances of the CH_2I_2^+ parent ion. The presence of multiple peaks and the large width of the main peak centered at 47.1 eV suggest that more than one ion state is initially produced by strong-field ionization. Indeed, the ΔA spectrum can be fit to multiple sets of peaks, whereby each set comprises a pair of transitions from the spin-orbit-split $\text{I } 4d$ core level to a given valence state. The peak positions obtained from the fit are summarized in Table I. The $\text{I } 4d_{5/2}^{-1} - 4d_{3/2}^{-1}$ splitting, set as a global fit parameter, is found to be 1.78 ± 0.01 eV, in relatively good agreement with the literature value of 1.738 eV.⁶³

According to valence photoelectron spectroscopy, the four lowest-energy electronic states of the CH_2I_2^+ ion result from the removal of electrons from orbitals with binding energies of 9.46 eV ($3b_2^{-1}$), 9.76 eV ($1a_2^{-1}$), 10.21 eV ($2b_1^{-1}$), and 10.56 eV ($4a_1^{-1}$).⁵³ (Here, the orbital that is symmetric with respect to reflection about the CI_2 plane is taken to be the b_2 orbital.) These states originate from the symmetric and antisymmetric combinations of the equatorial lone pairs on the I atoms. The $\text{I } 4d$ core level transition energies of these states can be estimated from the differences between the binding energies of the spin-orbit-split $\text{I } 4d_{5/2}^{-1}$ (56.69 eV) and $4d_{3/2}^{-1}$ (58.42 eV) core levels⁶³ of CH_2I_2 and the binding energies of the valence states⁵³ and are summarized in Table I. The agreement between the observed and calculated transition energies suggests that the electronically excited $\tilde{A}^+$, $\tilde{B}^+$, and $\tilde{C}^+$ states of CH_2I_2^+ , in

addition to the $\tilde{X}^+$ ground state, are produced by the strong-field ionization of CH_2I_2 .

Given the highly nonlinear dependence of strong-field ionization rates on the orbital binding energies, the population of the electronically excited ion states, with binding energies that are 0.30–1.10 eV greater than the 9.46-eV binding energy of the $3b_2$ HOMO, might seem surprising. However, this observation is consistent with results obtained from previous high-order harmonic interferometry^{15,17} and angle-dependent ionization⁶⁷ measurements, which elucidate the participation of multiple molecular orbitals in intense laser-induced dynamics. In the case of CH_2I_2 , we note that previous experiments employing 30-fs laser pulses have linked the appearance of multiple I–C–I bending frequencies to the population of CH_2I_2^+ electronically excited states by strong-field ionization.⁶⁸

C. Ultrafast dissociative ionization dynamics

The ΔA spectrum collected at a later time delay of 1 ps is marked by the appearance of new peaks that can be attributed to photodissociation products. Global analysis of the ΔA time traces in the spectral range of 45.5–49.5 eV, where photoproduct absorption dominates, is performed by fitting them to the function

$$\Delta A(E, t) = y_0(E) + \text{IRF}(t) * \left\{ \theta(t) \times \left[\Delta A_0(E) + \sum_{i=1}^3 \Delta A_i(E) e^{-t/\tau_i} \right] \right\}, \quad (1)$$

where E is the probe photon energy, t is the time delay, $y_0(E)$ is the overall offset at E , $\text{IRF}(t)$ is the instrument response function, $\theta(t)$ is the step function, $\Delta A_0(E)$ is the offset after time-zero, reflecting the ΔA spectrum in the limit of large time delays, and $\Delta A_i(E)$ is the decay associated difference spectrum that is associated with the time constant τ_i . Following our previous work, we model $\text{IRF}(t)$ by using a Gaussian function with a full-width-at-half-maximum (FWHM) of 10 fs.⁵⁰ The global fit yields time constants $\tau_1 = 20 \pm 2$ fs, $\tau_2 = 49 \pm 6$ fs, and $\tau_3 = 157 \pm 9$ fs. The corresponding decay associated difference spectra, $\Delta A_1(E)$, $\Delta A_2(E)$, and $\Delta A_3(E)$, are shown in Fig. 3(a). In the limit of nonoverlapping absorption resonances, $\Delta A_i(E) < 0$ indicates the formation of a species that absorbs at photon energy E , whereas $\Delta A_i(E) > 0$ suggests the decay of a species that absorbs at photon energy E . When the absorption resonances of two or more species overlap at photon energy E , the sign of $\Delta A_i(E)$ depends on the relative abundance of the species and their relative absorption cross sections.

Examination of the individual decay associated difference spectra $\Delta A_i(E)$ provides insight into the origin of the observed time constants. We begin by considering the dynamics characterized by the time constant $\tau_3 = 157 \pm 9$ fs. $\Delta A_3(E)$ suggests that photoproducts with absorption maxima at 46.0 eV and 47.4 eV are produced on this time scale. The narrow absorption at 46.0 eV of $\Delta A_3(E)$ is readily assigned to the $^2P_{3/2} \rightarrow ^2D_{5/2}$ transition of ground-state atomic I [Table I and Fig. 3(b)], in good agreement with the transition energy of 45.94 eV reported in the literature.⁶⁴ This assignment suggests that the broad feature that is peaked at 47.4 eV originates from CH_2I^+ [Fig. 3(c)], the byproduct of dissociation from CH_2I_2^+ , whose significantly larger width as compared to the narrow XUV

FIG. 3. (a) Decay associated difference spectra $\Delta A_i(E)$ obtained from global fit and experimentally measured and globally fitted XUV differential absorption time traces at probe photon energies of (b) 46.0 eV ($I^2P_{3/2}$), (c) 47.4 eV (CH_2I^+), (d) 47.8 eV ($I_2^+ \ ^2\Pi_{3/2,g}$), and (e) 49.0 eV ($I^+ \ ^3P_2$). The species whose absorption dominates the various probe photon energies are given in parentheses.

transition of atomic I could be attributed to a high degree of vibrational excitation that exists in CH_2I^+ . The formation of vibrationally excited CH_2I^+ is unsurprising, considering that its planar geometry is significantly different from the nonplanar geometry of CH_2I_2^+ ; the photodissociation of the analog ion CH_2Br_2^+ has been shown to yield highly vibrationally excited CH_2Br^+ as well.⁶⁹ While the dissociation of CH_2I_2^+ should give rise to positive features in $\Delta A_3(E)$, it is possible that these features, unobserved in the present work, are masked by the negative features that are associated with the CH_2I^+ photoproduct (see below).

$\Delta A_2(E)$ exhibits a broad, positive absorption band peaked at 47.2 eV, which decays with a time constant of 49 ± 6 fs while simultaneously giving rise to photoproducts whose absorption is peaked

at 47.9 eV and 48.4 eV. One possible assignment for the peak at 47.9 eV is the $^2\Pi_{3/2,g} \rightarrow 4d_{5/2}^{-1}$ transition of I_2^+ [Table I and Fig. 3(d)], in good agreement with the transition energy of 47.85 eV estimated from the valence and $4d$ core-level binding energies of I_2 .^{63,65} Note that I_2^+ elimination from strong-field-ionized CH_2I_2 has previously been observed by mass spectrometry.^{71,72} We tentatively assign the feature at 48.4 eV to the CH_2I radical that is produced simultaneously with I^+ . Indeed, the XUV absorption signature of I^+ (3P_2) appears prominently in the ΔA spectra collected at 1-ps time delay [Table I and Fig. 2(b)]; the peaks observed at 49.0 eV [Fig. 3(e)] and 49.2 eV can be assigned to the $^3P_2 \rightarrow ^3P_2$ and $^3P_2 \rightarrow ^3D_1$ transitions of I^+ , with reported peak positions of 48.95 eV and 49.17 eV, respectively.⁶¹ Furthermore, we note that the XUV absorption of the CH_2I radical is located between the XUV transitions of atomic I and CH_2I_2 , in good agreement with previous findings for the CH_2Br radical.⁷⁰ The common time scales for formation of I^+ and I_2^+ is surprising, even if they originate from the same electronic state of the $CH_2I_2^+$ parent ion (see below), and warrants further investigation.

$\Delta A_1(E)$ is dominated by a broad negative feature peaked at 47.2 eV that mirrors the positive feature observed in $\Delta A_2(E)$. We assign the time constant $\tau_1 = 20 \pm 2$ fs to vibrational relaxation of a particular ion state of $CH_2I_2^+$ from the Franck-Condon region, yielding a broad absorption peaked at 47.2 eV. From our analysis of $\Delta A_2(E)$, we infer that this ion state subsequently dissociates to give both I^+ and I_2^+ on the 49-fs time scale. Previous photoionization efficiency measurements of CH_2I_2 yield appearance energies of 12.77 eV and 12.76 eV for I^+ (3P_2) and I_2^+ ($^2\Pi_{3/2,g}$), respectively.⁷³ The almost identical appearance energies suggest that the I^+ (3P_2) and I_2^+ ($^2\Pi_{3/2,g}$) species observed in the present work arise from the dissociation of a common ion state, most likely the highly excited $\tilde{D}^+$ (2B_2) state. This ion state is produced by removing an electron from the $2b_2$ orbital, which has a binding energy of 12.75 eV.⁵³ The estimated transient absorption bands of the $\tilde{D}^+$ (2B_2) state in the Franck-Condon region—43.94 eV and 45.67 eV for the $2b_2^{-1} \rightarrow I4d_{5/2}^{-1}$ and $2b_2^{-1} \rightarrow I4d_{3/2}^{-1}$ transitions, respectively—reside beyond the XUV probe spectral range of the present work and are therefore unobserved. However, vibrational relaxation on the 20-fs time scale shifts the $2b_2^{-1} \rightarrow I4d_{3/2}^{-1}$ transition into the probe spectral range, leading to a broad absorption signature peaked at 47.2 eV; the spin-orbit-split $2b_2^{-1} \rightarrow I4d_{5/2}^{-1}$ transition remains unobserved because its calculated transition energy of 45.4 eV lies beyond the probe energy range of the present experiment.

To identify the origin of the atomic I ($^2P_{3/2}$) photoproduct, we note that the measured time constant for the formation of atomic I ($^2P_{3/2}$) from $CH_2I_2^+$ is 157 ± 9 fs, similar to the C–I dissociation time constant of 121 ± 3 fs observed for the $2-C_3H_7I^+$ ⁷⁴ but shorter than that observed for CH_3I^+ (0.76 ± 0.16 ps).⁴⁹ The difference in the dissociation times of CH_3I^+ and $2-C_3H_7I^+$ can be attributed to the C–I dissociation energies being much larger for the former (2.105 eV) than the latter (0.128 eV). In the case of $CH_2I_2^+$, the rapid C–I dissociation time and the I ($^2P_{3/2}$) appearance energy⁶⁹ of 10.55 eV suggests that dissociation most likely occurs via the $\tilde{C}^+$ (2A_1) state. The lower-lying electronic states, with vertical binding energies >0.3 -eV lower than the appearance energy of atomic I, are unlikely to support such an ultrafast C–I bond dissociation.

D. Vibrational wave packet dynamics of CH_2I_2

Aside from the dissociation dynamics of CH_2I_2 , inspection of the signal in the bleaching region of the time-resolved ΔA spectrum [Fig. 2(a)] reveals pronounced amplitude and energy modulations as a function of pump-probe time delay. The oscillation frequencies can be obtained from the 2D plot of the FFT amplitude as a function of probe photon energy and oscillation frequency [Fig. 4(a)]. The plot reveals peaks at 112 and 490 cm^{-1} . These frequencies can be assigned to the I–C–I bend and C–I symmetric stretch modes, previously observed at 121 and 486 cm^{-1} ,⁷⁵ respectively. Our *ab initio* calculations yield 114 and 485 cm^{-1} for the I–C–I bend and C–I symmetric stretch modes, respectively (Table II). Given that the FFT amplitude profile of a species exhibiting vibrational wave packet dynamics follows the first derivative of its absorption spectrum,⁷⁶ the appearance of four lobes in the 2D FFT plot for each frequency component is consistent with the simultaneous modulation of the $I 4d_{5/2} \rightarrow \sigma_{C-I}^*$ and $I 4d_{3/2} \rightarrow \sigma_{C-I}^*$ transition energies by wave packet motion.

Beyond the 2D FFT plot, the oscillatory features are also observed in the first-moment time trace [Fig. 4(b)],

$$\langle E^{(1)}(t) \rangle = \frac{\int_{E_i}^{E_f} dE E \Delta A(E, t)}{\int_{E_i}^{E_f} dE \Delta A(E, t)}, \quad (2)$$

where $\Delta A(E, t)$ is the differential absorption signal at probe photon energy E and time delay t , and E_i and E_f define the range over which the first-moment is computed; here, E_i and E_f correspond to 50.0 and 50.7 eV, respectively. $\langle E^{(1)}(t) \rangle$ can be fit to a

FIG. 4. (a) Plot of FFT amplitude as a function of probe photon energy and oscillation frequency. (b) First-moment time trace computed about the CH_2I_2 depletion region between 50.0 and 50.7 eV. The dashed line is the data, and the solid line is the fit.

TABLE II. Summary of calculated vibrational frequencies of neutral CH_2I_2 and CH_2I_2^+ ions.

Mode	CH_2I_2 (cm^{-1})	CH_2I_2^+ (cm^{-1})	Assignment
ν_1	3003	2981	CH_2 symm. stretch
ν_2	1351	1332	CH_2 bending
ν_3	485	565	CI symm. stretch
ν_4	114	125	CI_2 bending
ν_5	1031	949	CH_2 twisting
ν_6	3086	3088	CH_2 asymm. stretch
ν_7	707	755	CH_2 rock
ν_8	1103	1034	CH_2 wagging
ν_9	580	497	CI asymm. stretch

sum of two oscillatory functions with frequencies $111 \pm 1 \text{ cm}^{-1}$ and $488 \pm 1 \text{ cm}^{-1}$ and cosinusoidal phases $-(0.22 \pm 0.03)\pi$ rad and $-(0.49 \pm 0.02)\pi$ rad, respectively. Based on the repulsive nature of the iodine $4d$ -core-excited potential along the I–C–I symmetric stretch and bending modes, we infer that a phase of $-\pi/2$ rad suggests wave packet motion initiated by bond softening⁷⁷ [Fig. 5(a)], whereas wave packet motion launched from the outer (inner) turning point by R-selective depletion^{78,79} leads to a phase of 0 (π) rad [Fig. 5(b)]. Hence, the phase observed for the I–C–I symmetric stretch unambiguously shows that its wave packet motion is driven by bond softening [Fig. 5(c)]. This observation can be rationalized based on the similar C–I bond lengths (2.123 Å for CH_2I_2 and 2.120 Å for CH_2I_2^+) and symmetric stretch frequencies (485 cm^{-1} for CH_2I_2 and 565 cm^{-1} for CH_2I_2^+) obtained from *ab initio* calculations. As previously found for the case of CH_3I , these conditions suppress R-selective depletion and favor bond softening.⁵⁰

On the other hand, the cosinusoidal phase of the I–C–I bend deviates beyond the experimental error from the phases expected for either bond softening ($-\pi/2$ rad) or R-selective depletion (0 or π rad). One plausible explanation is the simultaneous launching of the bending mode wave packet by bond softening and

R-selective depletion, such that the observed oscillatory signal can be expressed as

$$\cos(\omega t + \phi) = \cos \phi \cos \omega t - \sin \phi \cos(\omega t - \pi/2), \quad (3)$$

where ω is the oscillation frequency, t is the time delay, and ϕ is the observed cosinusoidal phase. The first and second terms on the right-hand side of Eq. (3) encode R-selective depletion and bond softening, respectively; based on the equilibrium I–C–I angles of CH_2I_2^+ (94.4°) and CH_2I_2 (115.1°), we only consider the launching of a wave packet by R-selective depletion from the outer turning point (see below). For $\phi = -(0.22 \pm 0.03)\pi$ rad, we obtain $\cos \phi = 0.77$ and $-\sin \phi = 0.64$. These coefficients suggest that R-selective depletion slightly dominates over bond softening in initiating the I–C–I bending mode wave packet.

E. Large-amplitude vibrational wave packet motion of CH_2I_2^+

The differential XUV absorption spectrum collected as a function of time delay exhibits pronounced modulations in the vicinity of the CH_2I_2^+ absorption resonances. The 2D FFT plot computed in that spectral region reveals a strong oscillation at 113 cm^{-1} and a relatively weaker signal at 224 cm^{-1} [Fig. 4(a)]. The 113-cm^{-1} component is assigned to the I–C–I bending mode of the CH_2I_2^+ $\tilde{X}^+$ state. Previous studies of strong-field-ionized CH_2I_2 by time-resolved mass spectrometry observed similar I–C–I bending mode wave packet motion with an oscillation frequency of 111 cm^{-1} ^{71,80} although two other reported I–C–I bending mode frequencies (96 cm^{-1} and 130 cm^{-1}), assigned to wave packet propagation on electronically excited ionic states,⁶⁸ are not observed in the present work. Since the FFT amplitude profile of a species exhibiting wave packet motion follows the first derivative of its absorption spectrum, the observed minimum at 47.7 eV suggests that the XUV absorption maximum of the $\tilde{X}^+$ (2B_2) state is located at 47.7 eV, considerably shifted from its absorption maximum of 47.2 eV in the 10-fs ΔA spectrum. This spectral shift is indicative of ultrafast structural rearrangement of the CH_2I_2^+ ion from the Franck-Condon region to its equilibrium geometry.^{49,74}

FIG. 5. Schematic illustrations of the generation of vibrational wave packets in neutral CH_2I_2 by (a) bond softening and (b) R-selective depletion. (c) The subsequent time-dependent position of the vibrational wave packet ($\langle Q(t) \rangle$), the accompanying time-evolution of the XUV transition energy ($\langle E_{wp}(t) \rangle$), and the first-moment time trace ($\langle E^{(1)}(t) \rangle$) are shown in the top, middle, and bottom panels, respectively. The solid and dashed lines correspond to trajectories induced by bond softening and R-selective depletion, respectively.

Inspection of the calculated vibrational frequencies of the CH_2I_2^+ parent ion does not reveal any normal mode that can be assigned to the observed oscillation frequency of 224 cm^{-1} (Table II). Here, we consider the various possibilities for the origin of this oscillation. First, this frequency could be associated with a vibrational mode for one of the electronically excited states of CH_2I_2^+ . However, previous *ab initio* calculations yield I–C–I bending frequencies of 118 cm^{-1} , 123 cm^{-1} , and 128 cm^{-1} for the CH_2I_2^+ $\tilde{A}^+$, $\tilde{B}^+$, and $\tilde{C}^+$ excited states, respectively.⁶⁸ As such, we exclude the possibility that the 224-cm^{-1} frequency originates from the electronically excited states of CH_2I_2^+ . Second, the vibrational frequency could be associated with the I_2^+ ($^2\Pi_{3/2,g}$) photoproduct that is observed in the XUV differential absorption spectrum collected at 1-ps time delay. However, the vibrational frequency of I_2^+ ($^2\Pi_{3/2,g}$) is 240 cm^{-1} ,⁶⁵ significantly different from the observed frequency of 224 cm^{-1} . Moreover, its FFT amplitude profile does not reveal a minimum at 47.9 eV, where the XUV absorption maximum of I_2^+ ($^2\Pi_{3/2,g}$) resides. As such, we rule out the possibility that the observed frequency is due to I_2^+ ($^2\Pi_{3/2,g}$). Finally, we consider the possibility that the 224-cm^{-1} oscillation arises from the overtone of the I–C–I bending mode. In such cases, the FFT amplitude profile of the overtone follows the second derivative of the XUV absorption.⁷⁶ Hence, the dip that is observed at 47.7 eV in the FFT amplitude profile of the 113-cm^{-1} component should appear as a maximum in the FFT amplitude profile of the 224-cm^{-1} component. Indeed, the central peak of the 224-cm^{-1} FFT amplitude profile is at 47.7 eV, coinciding with the position of the dip that appears in the FFT amplitude profile of the 113-cm^{-1} oscillation. Hence, we assign the 224-cm^{-1} vibrational frequency to the overtone of the I–C–I bend of ground-state CH_2I_2^+ . Interestingly, even though previous studies of CH_2I_2^+ produced by strong-field ionization did not observe such an overtone,^{71,80} it appears prominently in CH_2BrI^+ and CH_2ClI^+ similarly prepared via strong-field ionization.⁸¹

The observation of the overtone frequency in the vibrational wave packet analysis suggests that CH_2I_2^+ produced via strong-field ionization exhibits large-amplitude I–C–I bending motion. To further quantify the wave packet motion, we employ singular-value decomposition to remove the population dynamics from the XUV differential absorption spectrum collected as a function of time delay. The resultant plot reveals a modulation of the XUV transition energy between 47.3 and 48.6 eV (Fig. 6). The oscillation can be fit

FIG. 6. Time-resolved differential XUV absorption spectra in the region of the CH_2I_2^+ absorption after removal of the population dynamics, revealing a pronounced modulation in the XUV transition energy due to wave packet motion. The solid line is a fit to two cosinusoidal functions.

FIG. 7. (a) Computed 4d core-level transition energy as a function of I–C–I angle in CH_2I_2^+ . (b) Potential energy curve of ground-state CH_2I_2^+ as a function of the I–C–I angle.

to a combination of two cosinusoidal functions, with frequencies $111 \pm 1\text{ cm}^{-1}$ and $222 \pm 2\text{ cm}^{-1}$ and amplitudes $0.64 \pm 0.02\text{ eV}$ and $0.18 \pm 0.02\text{ eV}$, respectively. To rationalize the large observed modulation of the XUV transition energy, we employ TD-DFT to compute the I 4d core-level transition energy of CH_2I_2^+ as a function of the I–C–I angle [Fig. 7(a)] as well as DFT to obtain the potential energy curve of ground-state CH_2I_2^+ along the I–C–I bend coordinate [Fig. 7(b)]. Since the molecular geometry is effectively frozen during strong-field ionization by a few-cycle laser pulse, the different equilibrium I–C–I bond angles of CH_2I_2 (115.1°) and CH_2I_2^+ (94.4°) supports the launching of I–C–I bending wave packets from the outer turning point of the CH_2I_2^+ potential via the displacive mechanism.⁸² The inner turning point, isoenergetic to the outer turning point, is located at an I–C–I angle of 80.7° . The calculated XUV transition energies at the inner and outer turning points are 48.9 and 47.3 eV, respectively. The difference of 1.6 eV is in relatively good agreement with the experimentally observed peak-to-peak modulation of 1.3 eV.

IV. CONCLUSIONS AND OUTLOOK

We have employed femtosecond XUV absorption spectroscopy to investigate the ultrafast dynamics that accompany the interaction of intense laser fields with CH_2I_2 . Strong-field ionization of CH_2I_2 yields, at 10-fs time delay, an XUV absorption spectrum with contributions from the $\tilde{A}^+$ (2A_2), $\tilde{B}^+$ (2B_1), and $\tilde{C}^+$ (2A_1) electronically excited states of CH_2I_2^+ , in addition to the $\tilde{X}^+$ (2B_2) ground state. Global analysis of the temporal evolution of the XUV absorption spectrum reveals multiple ultrafast dissociative ionization channels, which yield I ($^2P_{3/2}$) with a time constant of $157 \pm 9\text{ fs}$ and both I^+ (3P_2) and I_2^+ ($^2\Pi_{3/2,g}$) with a formation time of $49 \pm 6\text{ fs}$. In

addition, ultrafast structural rearrangement on a time scale of 20 ± 2 fs is also observed. The atomic I^+ and I_2^+ photoproducts most likely originate from the highly excited $\tilde{D}^+$ (2B_2) state, whereas atomic I is probably produced via the $\tilde{C}^+$ (2A_1) state. Pronounced modulations in the differential XUV absorption spectrum as a function of time delay encodes vibrational wave packet of neutral CH_2I_2 and the CH_2I_2^+ parent ion. In the case of neutral CH_2I_2 , wave packet motion along the symmetric C–I stretching mode is launched by bond softening, whereas both bond softening and R-selective depletion contribute to the vibrational coherence of the I–C–I bending mode. The vibrational wave packet of CH_2I_2^+ is associated with the displacively excited I–C–I bending mode, whose large-amplitude motion is reflected in the >1 -eV modulation of the XUV transition energy and the appearance of the overtone frequency in the modulation.

Future experiments that extend the probe spectral range to lower photon energies (<45 eV), coupled with pump fluence dependence measurements, can be used to elucidate the XUV absorption signatures of ion excited states that lie above the $\tilde{C}^+$ state, hence identifying the possible population of high-energy ion excited states by strong-field ionization and permitting access to their subsequent ultrafast dissociation dynamics. Furthermore, the angular dependence of ionization rates for the different orbitals can potentially be obtained from studies of oriented CH_2I_2 , in which the relative peak areas of the different ion excited states in the XUV transient absorption spectrum are analyzed as a function of the relative polarization between the ionizing pump and the XUV probe beams. Finally, theoretical simulations of the potential energy surfaces of the various ion states can be used to clarify the origin of the various photoproducts of dissociative ionization. The elimination of I_2^+ is particularly intriguing because it does not exhibit any vibrational coherence despite its formation on an ultrashort time scale.

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REFERENCES

- ¹T. Brabec and F. Krausz, *Rev. Mod. Phys.* **72**, 545–591 (2000).
- ²H. J. Wörner, J. B. Bertrand, D. V. Kartashov, P. B. Corkum, and D. M. Villeneuve, *Nature* **466**, 604–607 (2010).
- ³T. Popmintchev, M.-C. Chen, P. Arpin, M. M. Murnane, and H. C. Kapteyn, *Nat. Photonics* **4**, 822–832 (2010).
- ⁴N. L. Wagner, A. Wüest, I. P. Christov, T. Popmintchev, X. Zhou, M. M. Murnane, and H. C. Kapteyn, *Proc. Natl. Acad. Sci. U. S. A.* **103**, 13279–13285 (2006).
- ⁵R. Forbes, A. E. Boguslavskiy, I. Wilkinson, J. G. Underwood, and A. Stolow, *J. Chem. Phys.* **147**, 054305 (2017).
- ⁶A. Ferré, A. E. Boguslavskiy, M. Dagan, V. Blanchet, B. D. Bruner, F. Burgy, A. Camper, D. Descamps, B. Fabre, N. Fedorov, J. Gaudin, G. Geoffroy, J. Mikosch, S. Patchkovskii, S. Petit, T. Ruchon, H. Soifer, D. Staedter, I. Wilkinson, A. Stolow, N. Dudovich, and Y. Mairesse, *Nat. Commun.* **6**, 5952 (2015).
- ⁷A. E. Boguslavskiy, J. Mikosch, A. Gijsbertsen, M. Spanner, S. Patchkovskii, N. Gador, M. J. J. Vrakking, and A. Stolow, *Science* **335**, 1336–1340 (2012).
- ⁸C. Cornaggia and P. Hering, *Phys. Rev. A* **62**, 023403 (2000).
- ⁹B. Walker, B. Sheehy, L. F. DiMauro, P. Agostini, K. J. Schafer, and K. C. Kulander, *Phys. Rev. Lett.* **73**, 1227–1230 (1994).
- ¹⁰T. Zuo, A. D. Bandrauk, and P. B. Corkum, *Chem. Phys. Lett.* **259**, 313–320 (1996).
- ¹¹M. Meckel, D. Comtois, D. Zeidler, A. Staudte, D. Pavičić, H. C. Bandulet, H. Pépin, J. C. Kieffer, R. Dörner, D. M. Villeneuve, and P. B. Corkum, *Science* **320**, 1478–1482 (2008).
- ¹²J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum, and D. M. Villeneuve, *Nature* **432**, 867–871 (2004).
- ¹³C. Vozzi, M. Negro, F. Calegari, G. Sansone, M. Nisoli, S. De Silvestri, and S. Stagira, *Nat. Phys.* **7**, 822–826 (2011).
- ¹⁴M. Lezius, V. Blanchet, D. M. Rayner, D. M. Villeneuve, A. Stolow, and M. Y. Ivanov, *Phys. Rev. Lett.* **86**, 51–54 (2001).
- ¹⁵O. Smirnova, Y. Mairesse, S. Patchkovskii, N. Dudovich, D. Villeneuve, P. Corkum, and M. Y. Ivanov, *Nature* **460**, 972–977 (2009).
- ¹⁶S. Haessler, J. Caillat, W. Boutou, C. Giovanetti-Teixeira, T. Ruchon, T. Auguste, Z. Diveki, P. Breger, A. Maquet, B. Carré, R. Taïeb, and P. Salières, *Nat. Phys.* **6**, 200–206 (2010).
- ¹⁷P. M. Kraus, B. Mignolet, D. Baykusheva, A. Rupeny, L. Horný, E. F. Penka, G. Grassi, O. I. Tolstikhin, J. Schneider, F. Jensen, L. B. Madsen, A. D. Bandrauk, F. Remacle, and H. J. Wörner, *Science* **350**, 790–795 (2015).
- ¹⁸C. I. Blaga, J. Xu, A. D. DiChiara, E. Sistrunk, K. Zhang, P. Agostini, T. A. Miller, L. F. DiMauro, and C. D. Lin, *Nature* **483**, 194–197 (2012).
- ¹⁹S. Baker, J. S. Robinson, C. A. Haworth, H. Teng, R. A. Smith, C. C. Chirilă, M. Lein, J. W. G. Tisch, and J. P. Marangos, *Science* **312**, 424–427 (2006).
- ²⁰Y. Malakar, W. L. Pearson, M. Zohrabi, B. Kaderiya, K. Raju P., F. Ziaee, S. Xue, A. T. Le, I. Ben-Itzhak, D. Rolles, and A. Rudenko, *Phys. Chem. Chem. Phys.* **21**, 14090–14102 (2019).
- ²¹L. Fang and G. N. Gibson, *Phys. Rev. Lett.* **100**, 103003 (2008).
- ²²H. Xu, C. Marceau, K. Nakai, T. Okino, S.-L. Chin, and K. Yamanouchi, *J. Chem. Phys.* **133**, 071103 (2010).
- ²³N. Ekanayake, T. Severt, M. Nairat, N. P. Weingartz, B. M. Farris, B. Kaderiya, P. Feizollah, B. Jochim, F. Ziaee, K. Borne, K. Raju P., K. D. Carnes, D. Rolles, A. Rudenko, B. G. Levine, J. E. Jackson, I. Ben-Itzhak, and M. Dantus, *Nat. Commun.* **9**, 5186 (2018).
- ²⁴R. Itakura, P. Liu, Y. Furukawa, T. Okino, K. Yamanouchi, and H. Nakano, *J. Chem. Phys.* **127**, 104306 (2007).
- ²⁵D. Townsend, B. J. Sussman, and A. Stolow, *J. Phys. Chem. A* **115**, 357–373 (2011).
- ²⁶B. J. Sussman, D. Townsend, M. Y. Ivanov, and A. Stolow, *Science* **314**(5797), 278–281 (2006).
- ²⁷M. E. Corrales, J. González-Vázquez, G. Balerdi, I. R. Solá, R. de Nalda, and L. Bañares, *Nat. Chem.* **6**, 785 (2014).
- ²⁸I. R. Solá, J. González-Vázquez, R. de Nalda, and L. Bañares, *Phys. Chem. Chem. Phys.* **17**, 13183–13200 (2015).
- ²⁹L. Fang and G. N. Gibson, *Phys. Rev. A* **75**, 063410 (2007).
- ³⁰T. Ando, A. Iwasaki, and K. Yamanouchi, *Phys. Rev. Lett.* **120**, 263002 (2018).
- ³¹A. Bhattacharjee and S. R. Leone, *Acc. Chem. Res.* **51**, 3203–3211 (2018).
- ³²Z.-H. Loh and S. R. Leone, *J. Phys. Chem. Lett.* **4**, 292–302 (2013).
- ³³R. Geneaux, H. J. B. Marroux, A. Guggenmos, D. M. Neumark, and S. R. Leone, *Philos. Trans. R. Soc., A* **377**, 20170463 (2019).
- ³⁴K. Ramasesha, S. R. Leone, and D. M. Neumark, *Annu. Rev. Phys. Chem.* **67**, 41–63 (2016).
- ³⁵E. Goulielmakis, Z.-H. Loh, A. Wirth, R. Santra, N. Rohringer, V. S. Yakovlev, S. Zherebtsov, T. Pfeifer, A. M. Azzeer, M. F. Kling, S. R. Leone, and F. Krausz, *Nature* **466**, 739–743 (2010).
- ³⁶A. D. Dutoi and S. R. Leone, *Chem. Phys.* **482**, 249–264 (2017).
- ³⁷S. P. Neville, V. Averbukh, M. Ruberti, R. Yun, S. Patchkovskii, M. Chergui, A. Stolow, and M. S. Schuurman, *J. Chem. Phys.* **145**, 144307 (2016).
- ³⁸Y. Kobayashi, T. Zeng, D. M. Neumark, and S. R. Leone, *Struct. Dyn.* **6**, 014101 (2019).

- ³⁹A. R. Attar, A. Bhattacharjee, and S. R. Leone, *J. Phys. Chem. Lett.* **6**, 5072–5077 (2015).
- ⁴⁰K. Schnorr, A. Bhattacharjee, K. J. Oosterbaan, M. G. Delcey, Z. Yang, T. Xue, A. R. Attar, A. S. Chatterley, M. Head-Gordon, S. R. Leone, and O. Gessner, *J. Phys. Chem. Lett.* **10**, 1382–1387 (2019).
- ⁴¹A. R. Attar, A. Bhattacharjee, C. D. Pemmaraju, K. Schnorr, K. D. Closser, D. Prendergast, and S. R. Leone, *Science* **356**, 54–59 (2017).
- ⁴²Y. Kobayashi, K. F. Chang, T. Zeng, D. M. Neumark, and S. R. Leone, *Science* **365**, 79–83 (2019).
- ⁴³F. Lackner, A. S. Chatterley, C. D. Pemmaraju, K. D. Closser, D. Prendergast, D. M. Neumark, S. R. Leone, and O. Gessner, *J. Chem. Phys.* **145**, 234313 (2016).
- ⁴⁴M.-F. Lin, D. M. Neumark, O. Gessner, and S. R. Leone, *J. Chem. Phys.* **140**, 064311 (2014).
- ⁴⁵Z.-H. Loh and S. R. Leone, *J. Chem. Phys.* **128**, 204302 (2008).
- ⁴⁶A. S. Chatterley, F. Lackner, C. D. Pemmaraju, D. M. Neumark, S. R. Leone, and O. Gessner, *J. Phys. Chem. A* **120**, 9509–9518 (2016).
- ⁴⁷E. R. Hosler and S. R. Leone, *Phys. Rev. A* **88**, 023420 (2013).
- ⁴⁸H. Timmers, X. Zhu, Z. Li, Y. Kobayashi, M. Sabbar, M. Hollstein, M. Reduzzi, T. J. Martínez, D. M. Neumark, and S. R. Leone, *Nat. Commun.* **10**, 3133 (2019).
- ⁴⁹Z. Wei, J. Li, S. T. See, and Z.-H. Loh, *J. Phys. Chem. Lett.* **8**, 6067–6072 (2017).
- ⁵⁰Z. Wei, J. Li, L. Wang, S.-T. See, M. H. Jhon, Y. Zhang, F. Shi, M. Yang, and Z.-H. Loh, *Nat. Commun.* **8**, 735 (2017).
- ⁵¹A. Saiz-Lopez, J. M. C. Plane, A. R. Baker, L. J. Carpenter, R. von Glasow, J. C. Gómez Martín, G. McFiggans, and R. W. Saunders, *Chem. Rev.* **112**, 1773–1804 (2012).
- ⁵²K.-H. Neeb, *The Radiochemistry of Nuclear Power Plants with Light Water Reactors* (De Gruyter, Berlin, Boston, 2011), pp. 591–658.
- ⁵³A. W. Potts, H. J. Lempka, D. G. Streets, W. C. Price, W. C. Price, and D. W. Turner, *Philos. Trans. R. Soc. London* **268**, 59–76 (1970).
- ⁵⁴Q. G. Zhang, U. Marvet, and M. Dantus, *Faraday Discuss.* **108**, 63–80 (1997).
- ⁵⁵S.-Y. Chen, P.-Y. Tsai, H.-C. Lin, C.-C. Wu, K.-C. Lin, B. J. Sun, and A. H. H. Chang, *J. Chem. Phys.* **134**, 034315 (2011).
- ⁵⁶U. Marvet, Q. G. Zhang, E. J. Brown, and M. Dantus, *J. Chem. Phys.* **109**, 4415–4427 (1998).
- ⁵⁷Z.-H. Loh, M. Khalil, R. E. Correa, and S. R. Leone, *Rev. Sci. Instrum.* **79**, 073101 (2008).
- ⁵⁸Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* **120**, 215–241 (2008).
- ⁵⁹J. D. Chai and M. Head-Gordon, *J. Chem. Phys.* **128**, 084106 (2008).
- ⁶⁰F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- ⁶¹M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji *et al.*, GAUSSIAN 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.
- ⁶²I. M. Alecu, J. Zheng, Y. Zhao, and D. G. Truhlar, *J. Chem. Theory Comput.* **6**, 2872–2887 (2010).
- ⁶³J. N. Cutler, G. M. Bancroft, and K. H. Tan, *J. Chem. Phys.* **97**, 7932–7943 (1992).
- ⁶⁴G. O'Sullivan, C. McGuinness, J. T. Costello, E. T. Kennedy, and B. Weinmann, *Phys. Rev. A* **53**, 3211–3226 (1996).
- ⁶⁵M. C. R. Cockett, J. G. Goode, K. P. Lawley, and R. J. Donovan, *J. Chem. Phys.* **102**, 5226–5234 (1995).
- ⁶⁶T. N. Olney, G. Cooper, and C. E. Brion, *Chem. Phys.* **232**, 211–237 (1998).
- ⁶⁷S. G. Walt, N. Bhargava Ram, A. von Conta, O. I. Tolstikhin, L. B. Madsen, F. Jensen, and H. J. Wörner, *J. Phys. Chem. A* **119**, 11772–11782 (2015).
- ⁶⁸D. Geißler, T. Rozgonyi, J. González-Vázquez, L. González, S. Nichols, and T. Weinacht, *Phys. Rev. A* **82**, 011402 (2010).
- ⁶⁹J. H. Huang, D. D. Xu, W. H. Fink, and W. M. Jackson, *J. Chem. Phys.* **115**, 6012–6017 (2001).
- ⁷⁰A. R. Attar, L. Piticco, and S. R. Leone, *J. Chem. Phys.* **141**, 164308 (2014).
- ⁷¹D. Geißler, B. J. Pearson, and T. Weinacht, *J. Chem. Phys.* **127**, 204305 (2007).
- ⁷²Z.-H. Liu, Y.-Q. Wang, J.-J. Ma, L. Wang, and G. Z. He, *Chem. Phys. Lett.* **383**, 198–202 (2004).
- ⁷³M. Satta, P. Bolognesi, A. Cartoni, A. R. Casavola, D. Catone, P. Markus, and L. Avaldi, *J. Chem. Phys.* **143**, 244312 (2015).
- ⁷⁴Z. Wei, L. Tian, J. Li, Y. Lu, M. Yang, and Z.-H. Loh, *J. Phys. Chem. Lett.* **9**, 5742–5747 (2018).
- ⁷⁵W. M. Kwok and D. L. Phillips, *J. Chem. Phys.* **104**, 2529–2540 (1996).
- ⁷⁶A. T. N. Kumar, F. Rosca, A. Widom, and P. M. Champion, *J. Chem. Phys.* **114**, 701–724 (2001).
- ⁷⁷A. Saenz, *Phys. Rev. A* **61**, 051402 (2000).
- ⁷⁸T. Ergler, B. Feuerstein, A. Rudenko, K. Zrost, C. D. Schröter, R. Moshhammer, and J. Ullrich, *Phys. Rev. Lett.* **97**, 103004 (2006).
- ⁷⁹E. Goll, G. Wunner, and A. Saenz, *Phys. Rev. Lett.* **97**, 103003 (2006).
- ⁸⁰B. J. Pearson, S. R. Nichols, and T. Weinacht, *J. Chem. Phys.* **127**, 131101 (2007).
- ⁸¹S. R. Nichols, T. C. Weinacht, T. Rozgonyi, and B. J. Pearson, *Phys. Rev. A* **79**, 043407 (2009).
- ⁸²H. J. Zeiger, J. Vidal, T. K. Cheng, E. P. Ippen, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* **45**, 768–778 (1992).