

Coherent vibrational dynamics in molecular bond breaking: Methyl radical umbrella mode probed by femtosecond x-ray spectroscopy

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We report on the observation of coherent molecular vibrations in the methyl radical, which is produced by 267 nm photodissociation of methyl iodide. The radical is excited to high levels in its ν_2 “umbrella” vibrational mode by the dissociation, and the ensuing coherent vibrational dynamics are observed by measuring ultrafast time-dependent changes in the x-ray transition energy from the C 1s to the singly occupied valence orbital. Due to symmetry, the real-space vibrational motion appears predominantly in the x-ray energy shift at the difference frequencies of the ν_2 progression, although the fundamental frequencies of the ν_2 mode are also observed. By constructing a quantum-mechanical model of the dynamics, the coherent superposition is characterized and the real-space motion of the radicals is reconstructed. The retrieved trajectories are dominated by pronounced quantum beating governed by the high degree of coherent excitation and the strong negative anharmonicity of the ν_2 mode.

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Introduction. Impulsive excitations regularly induce coherent vibrational dynamics in molecules. While such an excitation is usually delivered to the system under study artificially, e.g., with a short laser pulse [1–4], it can occur more indirectly. The required “kick” can be derived, e.g., from a rapid change in geometry as it is intrinsic to Jahn-Teller distortion [5] or from the strong repulsive forces that photofragments experience in the breaking of a chemical bond (e.g., Refs. [6–8]). In this Letter, we address coherence in bond breaking by reporting on the observation of coherent activation of the ν_2 “umbrella” vibration of the methyl radical produced by the 267 nm photodissociation of methyl iodide, probed by ultrafast x-ray spectroscopy (cf. Refs. [5,9,10]). Previous ultrafast studies have approached the process from the perspective of the iodine atom, focusing on resolving the transition state region [11] or the conical intersection [1,12]. Selectively probing the methyl radical and its dynamics, this experiment provides a complement to these previous studies that allows vibrational coherence to be identified.

Experimental. The experimental apparatus is similar to that reported in Ref. [13], modified to initiate dynamics with

ultraviolet (UV) pump pulses. Briefly, we split off part of the incoming 35 fs pulses centered at 800 nm in the pump line and frequency double it to obtain 40 μ J of 400 nm light in a 200 μ m thick β -barium borate (BBO) crystal. This is then recombined with 750 μ J of 800 nm light in another BBO crystal (50 μ m thick) in vacuum to generate UV pulses of up to 20 μ J pulse energy with a spectral width of 3 nm, centered around 267 nm. Measured via a cross-correlation in argon gas, the apparatus has a temporal instrument response of 36 ± 6 fs and its spectral resolution is ~ 300 meV near 244 eV as measured via the static absorption of argon gas at its $L_{2,3}$ edge. Methyl iodide is obtained commercially at $>98\%$ purity and is used without further purification. The liquid readily forms sufficient vapor pressure for the experiment at room temperature and is introduced into a 4 mm long gas cell with 200 μ m openings, which forms the interaction region. The UV pump pulse and soft x-ray probe pulse cross in the gas cell at a small angle ($\sim 1^\circ$). An iris is positioned after the gas cell and set to block the UV light while transmitting the soft x-ray beam into the spectrometer assembly. Sequences of spectra are collected as a function of delay time, both with the pump beam irradiating the sample and with it blocked. The change in absorption due to the presence of the pump pulse is calculated as $\Delta OD = -\log_{10}(S_{on}/S_{off})$, where $S_{on/off}$ denotes spectra taken with the pump beam on and off, respectively. We chose time steps of $\Delta t = 10$ fs and a delay time range of approximately 2 ps. Individual delay scans recorded over the course of multiple days are aligned in time and averaged.

Coherent vibrations in methyl iodide photodissociation. In order to launch a coherent vibration, the excess kinetic energy

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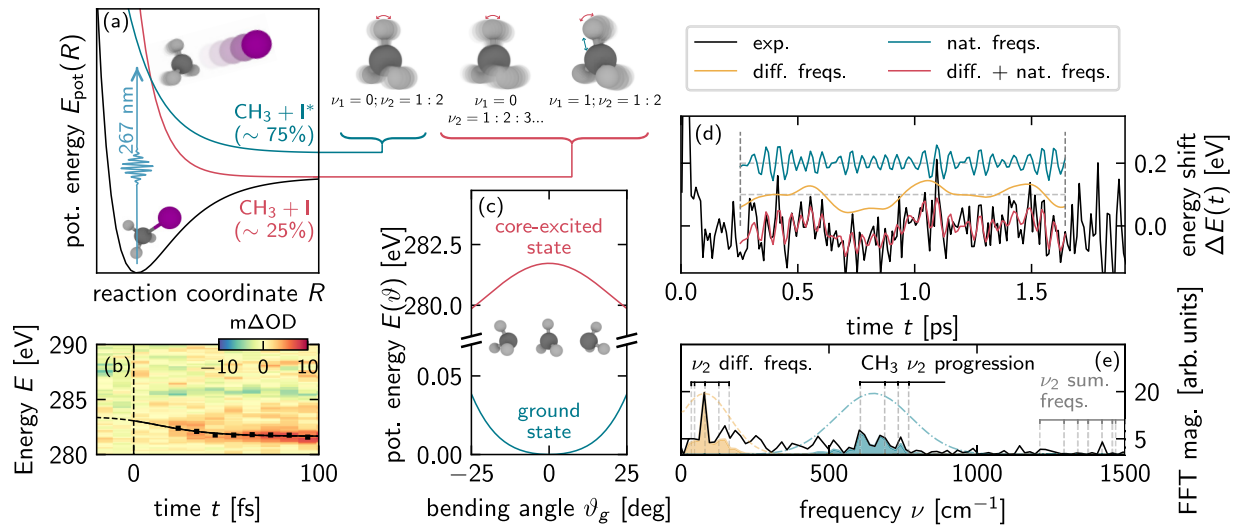


FIG. 1. (a) Dissociation of methyl iodide probed with femtosecond x-ray spectroscopy. Excitation via 267 nm radiation will promote the molecule onto its 3Q_0 surface (blue curve) from where it will evolve toward a conical intersection with the 1Q_1 surface (red). The two ensembles of radicals that are produced from the dissociation are shown as ball-and-stick models with their vibrational excitation indicated. (b) The first 100 fs of the transient absorption signal shows the radical peak initially appearing at 282.9 eV and moving to its dissociation limit value of 281.7 eV. Black dots are the peak position. We determine a time constant of 20.7 ± 5.4 fs by fitting an exponential decay convolved with a Gaussian function of 36 fs width for the instrument response (black curve). The depletion of the ground-state absorption near 286 eV is also visible. (c) Potential energy surfaces for the methyl radical along the ν_2 umbrella vibrational motion for the ground state and core-excited state as a function of the bending angle ϑ_g modeled here. (d) Energetic position of the radical peak as a function of pump-probe delay time (black) decomposed into the difference frequency component due to radicals excited only along the umbrella mode (yellow) and the fundamental frequencies (blue), which become visible due to symmetry breaking (see text). Beginning and end of the filtered data are cropped as these contain the time-domain image of the filter windows. The blue and yellow curves have been shifted up in energy for visual clarity. (e) Frequency-domain picture of what is shown in panel (d) with the filter windows indicated. A clear peak is seen in the region where the difference frequencies are expected (yellow, dashed), as well as a series of peaks that increase in amplitude again and closely resemble the fundamental ν_2 vibrational progression (blue, dash-dotted). Other features in the low-frequency region are due to noise and not associated with any significant signal.

in the dissociation has to be transferred to the emerging methyl radicals on a timescale shorter than a vibrational period. Photodissociation of methyl iodide in its A band near 270 nm occurs either on the strongly repulsive 3Q_0 surface (75% yield), which is initially populated by the UV pump pulse, or via a conical intersection to access the 1Q_1 surface (25% yield) that is approached within 15 ± 4 fs [1] [see Fig. 1(a)]. Radicals originating from the 3Q_0 surface are vibrationally excited up to $\nu_2 = 2$ and will leave behind electronically excited iodine atoms in the $^2P_{1/2}$ state (denoted as I^* channel), while for those that emerge via the 1Q_1 surface the energy partitioning forms the iodine atom's ground state ($^2P_{3/2}$, denoted as I channel), and the radical is excited up to $\nu_2 = 4$ [14–17] [see Fig. 1(a)]. We can assign a time constant to the dissociation process by tracking the initial energy shift of the characteristic $\text{C } 1s \rightarrow \text{SOMO}$ (singly occupied molecular orbital) x-ray absorption peak of the methyl radical and find that it reaches its dissociation-limit value of 281.7 eV within $\tau_d = 20.7 \pm 5.4$ fs [see Fig. 1(b) and Supplemental Material [18]]. Together with the temporal instrument response of $\tau_{\text{IRF}} = 36.0 \pm 6.4$ fs, this confines the duration of the impulse delivered to the methyl radicals in the experiment to an upper limit of 41.5 ± 6.2 fs or $\sim 75\%$ of the oscillation period of the $\nu_2 = 1 \rightarrow 0$ transition (55 fs). This suggests that coherent vibrational dynamics can in principle be induced via

bond breaking in the experiment. Ultrafast extreme-ultraviolet or soft x-ray spectroscopy resolves coherent molecular vibrations by measuring time-dependent changes in the x-ray transition energy as the molecule moves along a vibrational coordinate on the respective potential energy surfaces (cf. Refs. [1–4,12]). If the change in transition energy $E_{\text{cx}}(q)$ as a function of the reaction q coordinate can be approximated well by a linear function, then the energy shift will be directly proportional to the real-space motion along the trajectory $\langle q(t) \rangle$. The methyl radical's umbrella vibration, however, is completely symmetric with respect to its reaction coordinate (the bending angle ϑ_g , referenced to the planar geometry). As such, the change in transition energy $E_{\text{cx}}(\vartheta_g) \propto \vartheta_g^2 + \dots$ must be an even function of ϑ_g . The trajectory $\langle \vartheta_g(t) \rangle$, which oscillates at frequencies $\Delta\omega_{1 \rightarrow 0}, \Delta\omega_{2 \rightarrow 1}, \Delta\omega_{3 \rightarrow 2}, \dots$, if a coherent superposition of multiple vibrational states is formed, will be mapped onto an energy shift that oscillates at the sums and differences of these frequencies. Unless the symmetry of the radical's motion or that of its mapping onto the x-ray energy is broken, the fundamental frequencies will be quenched in the energy shift's frequency content. The implication for the experiment is that one signature of coherent ν_2 activation is slow oscillatory motion of the $\text{C } 1s \rightarrow \text{SOMO}$ energy with a period on the order of ~ 400 fs (80 cm^{-1} instead of $607 \text{ cm}^{-1}, 688 \text{ cm}^{-1}, \dots$ [19]) due to the difference frequencies, superimposed with a rapid oscillation due to

the sum frequencies with about 25 fs ($\sim 1300 \text{ cm}^{-1}$) period. Similar arguments regarding symmetry and the detection of mixing products of vibrational frequencies have been brought forward by Yatsushashi *et al.* [20] and Fuß *et al.* [21] (see also references therein), but in the context of ultrafast mass spectroscopy. Figures 1(d) and 1(e) show the evolution of the radical peak's position as a function of time after photodissociation as measured in the experiment and its Fourier transform, respectively. A broad feature with a strong peak near 80 cm^{-1} that lines up exactly with the difference frequency between the $\nu_2 = 2 \rightarrow 1$ and $1 \rightarrow 0$ transitions is clearly present [yellow shaded area in Fig. 1(e)], showing unambiguously that vibrational coherence in the umbrella mode up to at least $\nu_2 = 2$ is induced and is observable through the difference frequency signal. The rapidly oscillating sum frequencies, which would be found near 1300 cm^{-1} and above, are not observed in the experiment due to insufficient temporal resolution. Quite interestingly, there is also a series of peaks that precisely match the ν_2 umbrella progression at its fundamental frequency up to the $\nu_2 = 3 \rightarrow 2$ transition (shaded in blue). The appearance of these peaks requires the symmetry assumed in the discussion above to be broken, which is elaborated upon further in Sec. III B.

Two-channel model of coherent vibrational dynamics. In order to further corroborate that vibrational coherence is induced in the experiment and extract phase information that characterizes the quantum superpositions in which the umbrella mode is populated in both the I and I* channels, we construct a model based on a quartic vibrational potential $V_{\text{gs}}(\vartheta)$. The use of a quartic term was identified as an appropriate description of the umbrella mode in early studies of the methyl radical (e.g., Refs. [22–24]), as it captures the pronounced negative anharmonicity of the ν_2 mode well. Following Ragni *et al.* [25], the umbrella motion is described via the hyperangle ϑ that captures the motion along the true ν_2 bending angle ϑ_g and the small changes in the C–H bond length r_{CH} that accompany ν_2 activation [see the Supplemental Material [18] and Figs. 3(a) and 3(b)]. For the potential here, $V_{\text{gs}}(\vartheta) = E_1^{\text{gs}} \vartheta^2 + E_2^{\text{gs}} \vartheta^4$, and the parameters E_1^{gs} and E_2^{gs} are optimized such that the transition energies of the potential match tabulated values [19]. It is shown as the blue curve in Fig. 1(c). A coherent superposition

$$\psi(\vartheta, t) = \sum_{i=0}^{\nu_{\text{max}}} |a_i| \phi_i(\vartheta) e^{-i\omega_i t} e^{-i\varphi_i} \quad (1)$$

of its eigenfunctions $\phi_i(\vartheta)$, where a_i are the amplitudes, ω_i are the eigenenergies, and φ_i the individual phases, then describes the microscopic dynamics of the methyl radicals in which only the umbrella mode is activated. The displacement of the hyperangle $\vartheta_d = \vartheta - \vartheta_0$ is

$$\langle \vartheta_d(t) \rangle = 2 \sum_{i=1}^{\nu_{\text{max}}} |a_i| |a_{i-1}| \mu_{i,i-1} \cos(\Delta\omega_{i \rightarrow i-1} t + \Delta\varphi_{i,i-1}), \quad (2)$$

where $\mu_{i,j} = \langle \phi_i | \vartheta_d | \phi_j \rangle$, $\Delta\omega_{i \rightarrow j} = \omega_i - \omega_j$, $\Delta\varphi_{i,j} = \varphi_i - \varphi_j$, and $\vartheta_0 = \pi/2$ is the equilibrium angle in the hyperspherical coordinate system. With the appropriate phases and amplitudes, evaluating the energy of the core-excited state

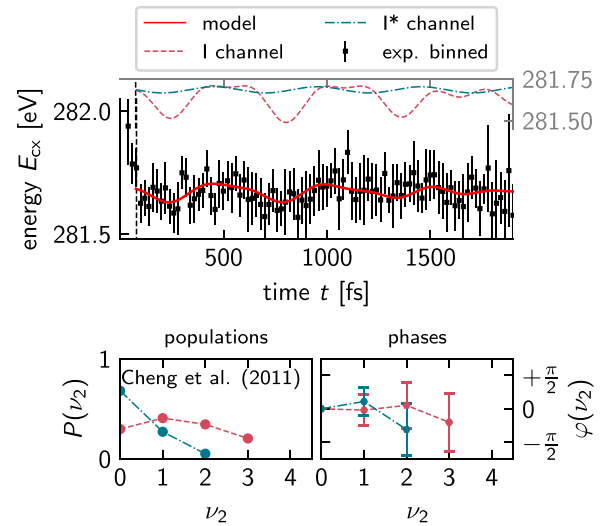


FIG. 2. Application of the two-channel model to the experiment using the populations reported by Cheng *et al.* [17]. The points in the top panel are the experimental data, where adjacent points have been binned for the fit. The bold red line is the fit of our model. In all panels, blue dash-dotted and red dashed lines indicate results for the I* and I channels, respectively. The individual energy shifts in the I and I* channels are also shown in the top panel on the detached gray set of axes. Their weighted sum $E_{\text{exp.}}(t) \approx \sigma_{\text{I}^*} E_{\text{cx}}^{\text{I}^*}(t) + (1 - \sigma_{\text{I}^*}) E_{\text{cx}}^{\text{I}}(t)$ yields the bold red line.

$E_{\text{cx}}(\langle \vartheta_d(t) \rangle) = V_{\text{ce}}(\langle \vartheta_d(t) \rangle) - V_{\text{gs}}(\langle \vartheta_d(t) \rangle)$ as a function of the trajectory of $\langle \vartheta_d(t) \rangle$ will describe the evolution of the energetic position of the radical peak in either the I or I* channel. In the experiment, these signals overlap, but the overall energetic position of the C 1s $\rightarrow$ SOMO peak moves as $E_{\text{exp.}}(t) \approx \sigma_{\text{I}^*} E_{\text{cx}}^{\text{I}^*}(t) + (1 - \sigma_{\text{I}^*}) E_{\text{cx}}^{\text{I}}(t)$, where $\sigma_{\text{I}^*} \approx 0.75$ is the branching ratio at the conical intersection [26,27]. We make the simplifying assumption that $E_{\text{cx}}(\vartheta_d) \approx E_0^{\text{cx}} + E_1^{\text{cx}} \vartheta_d^2$ is a good approximation for the dependency of the core-excited state energy on the bending angle, which is justified by the success of the model as seen below. The finite temporal resolution of the experiment is incorporated into the model by convolving $E_{\text{exp.}}(t)$ with a Gaussian function of 36 fs width. Using vibrational population data reported in the literature [14–17], the phases φ_i can then be determined via a nonlinear least-squares fit, which is restricted to pump-probe delays $\tau > 75$ fs, as the initial energy shift during the bond breaking is not accounted for in the model. In both channels, the phase φ_0 is fixed to $\varphi_0 = 0$. Using the parameters E_0^{cx} and E_1^{cx} from the fit, the core-excited potential energy surface $V_{\text{ce}}(\vartheta_g)$ along the umbrella motion is determined. It is shown in Fig. 1(c) as a red curve. A more detailed account of the fitting procedure is given in the Supplemental Material [18]. The result of this fit is shown in Fig. 2 using the population data of Ref. [17], and we find no significant differences using population data from other studies (see Refs. [15,16,26] and the Supplemental Material [18]). Despite its simplicity, the model captures the time dependence of the radical's x-ray absorption peak observed in the experiment very well and over the entire range of time delays. This confirms the model is an appropriate description of the microscopic dynamics for $t > 75$ fs, further strengthening the claim that coherent vibrational dynamics are induced

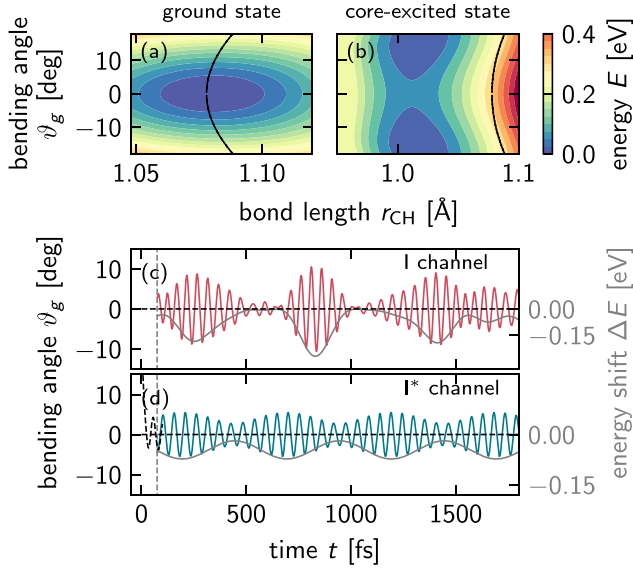


FIG. 3. (a), (b) Ground-state and core-excited state potential energy surfaces of Ekström *et al.* [28]. The path along which the real-space motion takes place is shown as black dashed lines. (c), (d) Reconstructed real-space motion of the methyl radicals with pure ν_2 activation along the angular coordinate ϑ_g . The radial coordinate r_{CH} follows from the black dashed lines in panels (a) and (b). The energy shift (see also Fig. 2) closely follows the envelope of the vibrational trajectory. The complex nature of the trajectory in the I channel is due to the pronounced beating resulting from the high degree of excitation. To a lesser, yet notable extent, such beating is also present in the I* channel trajectory. The black dashed line in panel (d) is a calculation by Hammerich *et al.* [29] for the I* channel radicals, which shows excellent agreement with our model.

via the dissociation of the molecular bond. As now the phases φ_i , the amplitudes a_i , and the frequencies ω_i are determined (lower panels in Fig. 2), the vibrational wavefunction [Eq. (1)] is characterized in its entirety for $t > 75$ fs in both dissociation channels. Therefore, the real-space motion of the radicals can be reconstructed.

We evaluate Eq. (2) and obtain the oscillatory trajectories shown in Figs. 3(c) and 3(d). The signal in the I channel is dominated by pronounced beating over the entire range of delay times, leading to large excursions of the bending angle near 250 fs, 830 fs, and 1.1 ps. While such beating is present also in the I* channel, it is to a much lesser degree and the angular displacement is overall smaller, in accord with the lower degree of vibrational excitation. Comparison with a calculation by Hammerich *et al.* [29] [black dashed line in Fig. 3(d)] for the I* channel radicals shows excellent agreement with the time dependency and magnitude of the angular displacement determined using our model. As we have approximated $E_{cx}(\vartheta_d) \approx E_0^{cx} + E_1^{cx} \vartheta_d^2$, we can now compare our value $E_1^{cx} = -9.0 \pm 2.2$ eV/rad² to quadratic expansions of energy curves calculated from first principles along the trajectory ($\langle \vartheta_g(t) \rangle$, $\langle r_{CH}(t) \rangle$). For the surfaces calculated by Ekström *et al.* [28], we find $E_1^{cx} = -2.89 \pm 0.01$ eV/rad², which is significantly smaller in magnitude than the value determined from the fit. Likewise, we find $E_1^{cx} = -3.2 \pm 0.1$ eV/rad² from a calculation of our own (see the Sup-

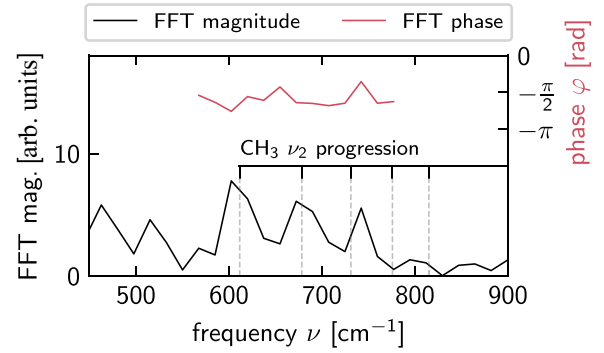


FIG. 4. Direct observation of the ν_2 vibrational progression mediated by symmetry breaking. The phase of this oscillation as determined via the Fourier transform (red) is essentially flat across this region. A slight detuning of the ν_2 vibration, due to the concurrent activity in the ν_1 mode, may be the reason for the third peak near 750 cm⁻¹ to appear at a slightly higher frequency (see text).

plemental Material [18]), which compares well to the value determined for the surfaces of Ekström *et al.* [28]. For all cited population data though, we find E_1^{cx} to have a negative sign from the fit, indicating that the core-excited state potential energy surface has a double-well structure as it was found in Ref. [28]. The discrepancies between the value of E_1^{cx} determined from the model fit and those determined from calculations may be due to how the overall energy shift $E_{exp}(t)$ is sampled in the experiment; the signals from the I and I* channels overlap energetically and cannot be accurately disentangled. The expression $E_{exp}(t) \approx \sigma_{I^*} E_{cx}^{I^*}(t) + (1 - \sigma_{I^*}) E_{cx}^I(t)$ we use for the peak position is only approximate. Despite discrepancies between the calculations and E_1^{cx} determined from the experiment using our model, it captures the essential aspects of the coherent dynamics of the methyl radical, i.e., the umbrella mode's pronounced anharmonicity, its symmetry, and the resulting mapping of the real-space coherent vibrational motion onto a slow oscillation of the observable energy shift.

Symmetry breaking and observation of fundamental frequencies. In the (r_{CH}, ϑ_g) plane, the methyl radical's umbrella mode moves along a trajectory of high symmetry [black curves in Figs. 3(a) and 3(b)] leading to the difference frequency signal discussed above, with expected quenching of signal near the fundamental frequencies. The peaks in the 500 – 800 cm⁻¹ region of the Fourier transform (Figs. 1(e) and 4), however, indicate the presence of a mechanism that breaks either the symmetry of the ν_2 motion itself or that of its mapping to the measured x-ray energy in either one or both of the dissociation channels. Symmetry breaking of the motion itself may be facilitated by the simultaneous activation of another vibrational mode. The I channel produces a small fraction [$\sim 12\%$ of its yield; see Fig. 1(a)] of radicals in which the symmetric CH stretch ν_1 mode is also activated [15] (albeit possibly not coherently in this experiment due to its high frequency and the timescale of bond breaking). If the resulting composite motion distorts the ideal quartic potential of the ν_2 mode, it would break the symmetry and could account for some of the observed fundamental vibrational progression, possibly with a slight detuning. The peak near 750 cm is in fact slightly offset from the frequency determined by

Oliveira *et al.* [19]. However, the comparably large magnitude of these peaks despite the small fraction of radicals with ν_1 activation is not accounted for. Another possible mechanism of transient symmetry breaking has been identified by Kosma *et al.* [30]. Briefly, the transition probability of the wave packet from the electronic ground state to the core-excited state may—depending on the launched wave packet phase—be favorable for bending angles near one of the two minima of the excited-state surface [Fig. 3(b)], if a small tunneling splitting is present, effectively breaking the symmetry on the timescale of the tunneling time. The splitting and associated tunneling time for the core-excited state of the methyl radical is 13.8 meV or 149 fs, respectively [28], i.e., roughly three times the period of the fundamental ν_2 vibration. Figure 4 shows the 500–800 cm^{-1} region of the x-ray energy shift's Fourier transform in more detail. Isolating the peaks with a Gaussian filter [blue curve in Figs. 1(d) and 1(e)] reveals the associated time-domain signal; the phase associated with it is essentially flat (red curve in Fig. 4). While the current results do not unambiguously identify the mechanism of symmetry breaking, it is a promising avenue for future exploration.

Conclusion. In conclusion, the photodissociation of methyl iodide is observed to produce methyl radicals with coherent vibrational excitation in the ν_2 umbrella mode. In our x-ray spectroscopy experiment, the radicals report on these coherent dynamics in a manner governed by their symmetry; the real-space vibrational motion is mapped onto an observable energy shift as slow oscillatory motion at the difference frequencies of the vibrational progression. By constructing a model of the coherent dynamics, the vibrational motion is retrieved. It is dominated by strong quantum beating due to the high degree of coherent vibrational excitation, albeit a detailed estimate of the degree of coherence is not yet possible. Mechanisms for symmetry breaking that facilitate the observation of the fundamental vibrational progression are also discussed. While the complex two-channel nature of methyl iodide photodisso-

ciation near the center of its A-band absorption is a challenge for the analysis in this specific experiment, the modeling presented could be applied to infer the curvature of core-excited potential energy surfaces in the future when the vibrational populations and frequencies are known.

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Data availability. The data that support the findings of this article are openly available [31].

- [1] K. F. Chang, H. Wang, S. M. Poullain, J. González-Vázquez, L. Bañares, D. Prendergast, D. M. Neumark, and S. R. Leone, Conical intersection and coherent vibrational dynamics in alkyl iodides captured by attosecond transient absorption spectroscopy, *J. Chem. Phys.* **156**, 114304 (2022).
- [2] J.-H. Ou, D. Hait, P. Rupprecht, J. E. Beetar, T. J. Martínez, and S. R. Leone, Attosecond probing of coherent vibrational dynamics in CBr_4 , *J. Phys. Chem. A* **128**, 9208 (2024).
- [3] P. Rupprecht, L. Aufleger, S. Heinze, A. Magunia, T. Ding, M. Rebholz, S. Amberg, N. Mollov, F. Henrich, M. W. Haverkort, C. Ott, and T. Pfeifer, Resolving vibrations in a polyatomic molecule with femtometer precision via X-ray spectroscopy, *Phys. Rev. A* **108**, 032816 (2023).
- [4] L. Barreau, A. D. Ross, V. Kimberg, P. Krasnov, S. Blinov, D. M. Neumark, and S. R. Leone, Core-excited states of SF_6 probed with soft-X-ray femtosecond transient absorption of vibrational wave packets, *Phys. Rev. A* **108**, 012805 (2023).
- [5] E. Ridente, D. Hait, E. A. Haugen, A. D. Ross, D. M. Neumark, M. Head-Gordon, and S. R. Leone, Femtosecond symmetry breaking and coherent relaxation of methane cations via X-ray spectroscopy, *Science* **380**, 713 (2023).
- [6] U. Banin and S. Ruhman, Ultrafast photodissociation of I_3 , coherent photochemistry in solution, *J. Chem. Phys.* **98**, 4391 (1993).
- [7] N. Pugliano, A. Z. Szarka, and R. M. Hochstrasser, Relaxation of the product state coherence generated through the photolysis of HgI_2 in solution, *J. Chem. Phys.* **104**, 5062 (1996).
- [8] M. T. Zanni, B. J. Greenblatt, A. V. Davis, and D. M. Neumark, Photodissociation of gas phase I_3^- using femtosecond photoelectron spectroscopy, *J. Chem. Phys.* **111**, 2991 (1999).
- [9] A. R. Attar, A. Bhattacharjee, C. D. Pemmaraju, K. Schnorr, K. D. Closser, D. Prendergast, and S. R. Leone, Femtosecond x-ray spectroscopy of an electrocyclic ring-opening reaction, *Science* **356**, 54 (2017).
- [10] A. Bhattacharjee and S. R. Leone, Ultrafast X-ray transient absorption spectroscopy of gas-phase photochemical reactions: A new universal probe of photoinduced molecular dynamics, *Acc. Chem. Res.* **51**, 3203 (2018).
- [11] A. R. Attar, A. Bhattacharjee, and S. R. Leone, Direct observation of the transition-state region in the photodissociation

- of CH_3I by femtosecond extreme ultraviolet transient absorption spectroscopy, *J. Phys. Chem. Lett.* **6**, 5072 (2015).
- [12] K. F. Chang, H. Wang, S. M. Poullain, D. Prendergast, D. M. Neumark, and S. R. Leone, Mapping wave packet bifurcation at a conical intersection in CH_3I by attosecond XUV transient absorption spectroscopy, *J. Chem. Phys.* **154**, 234301 (2021).
- [13] L. Barreau, A. D. Ross, S. Garg, P. M. Kraus, D. M. Neumark, and S. R. Leone, Efficient table-top dual-wavelength beamline for ultrafast transient absorption spectroscopy in the soft X-ray region, *Sci. Rep.* **10**, 5773 (2020).
- [14] A. T. J. B. Eppink and D. H. Parker, Energy partitioning following photodissociation of methyl iodide in the a band: A velocity mapping study, *J. Chem. Phys.* **110**, 832 (1999).
- [15] G. Li, H. J. Hwang, and H. C. Jung, High resolution kinetic energy by long time-delayed core-sampling photofragment translational spectroscopy, *Rev. Sci. Instrum.* **76**, 023105 (2005).
- [16] F. Aguirre and S. T. Pratt, Photoionization of vibrationally hot CH_3 and CF_3 , *J. Chem. Phys.* **122**, 234303 (2005).
- [17] M. Cheng, Z. Yu, L. Hu, D. Yu, C. Dong, Y. Du, and Q. Zhu, Vibrationally resolved photofragment translational spectroscopy of CH_3I from 277 to 304 nm with increasing effect of the hot band, *J. Phys. Chem. A* **115**, 1153 (2011).
- [18] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/32v3-tgfd> for extended experimental data, the anharmonic oscillator model, a more detailed account of the fitting procedure, estimation of the influence of other photoproducts, which includes Refs. [32–41].
- [19] A. M. Oliveira, Y.-J. Lu, J. H. Lehman, P. B. Changala, J. H. Baraban, J. F. Stanton, and W. C. Lineberger, Photoelectron spectroscopy of the methide anion: Electron affinities of $\bullet\text{CH}_3$ and $\bullet\text{CD}_3$ and inversion splittings of CH_3 and CD_3 , *J. Am. Chem. Soc.* **137**, 12939 (2015).
- [20] T. Yatsushashi, S. Trushin, W. Fuß, W. Rettig, W. Schmid, and S. Zilberg, Ultrafast charge transfer and coherent oscillations in 4-piperidino-benzonitrile, *Chem. Phys.* **296**, 1 (2004).
- [21] W. Fuß, W. E. Schmid, K. Kuttan Pushpa, S. A. Trushin, and T. Yatsushashi, Ultrafast relaxation and coherent oscillations in aminobenzonitriles in the gas phase probed by intense-field ionization, *Phys. Chem. Chem. Phys.* **9**, 1151 (2007).
- [22] H. W. Hermann and S. R. Leone, Photofragmentation dynamics of CH_3I at 248 and 266 nm: Vibrational distributions in the $\text{CH}_3(\nu_2)$ “umbrella” mode, *J. Chem. Phys.* **76**, 4766 (1982).
- [23] H. W. Hermann and S. R. Leone, Photofragment infrared emission spectroscopy: Vibrational progression and potential parameters of the $\text{CH}_3(\nu_2)$ “umbrella” mode, *J. Chem. Phys.* **76**, 4759 (1982).
- [24] C. Yamada, E. Hirota, and K. Kawaguchi, Diode laser study of the ν_2 band of the methyl radical, *J. Chem. Phys.* **75**, 5256 (1981).
- [25] M. Ragni, A. C. P. Bitencourt, F. V. Prudente, P. R. P. Barreto, and T. Posati, Umbrella motion of the methyl cation, radical, and anion molecules: I. potentials, energy levels and partition functions, *Eur. Phys. J. D* **70**, 60 (2016).
- [26] A. T. J. B. Eppink and D. H. Parker, Methyl iodide a-band decomposition study by photofragment velocity imaging, *J. Chem. Phys.* **109**, 4758 (1998).
- [27] S. H. Gardiner, M. L. Lipciuc, T. N. V. Karsili, M. N. R. Ashfold, and C. Vallance, Dynamics of the A-band ultraviolet photodissociation of methyl iodide and ethyl iodide via velocity-map imaging with “universal” detection, *Phys. Chem. Chem. Phys.* **17**, 4096 (2015).
- [28] U. Ekström, V. Carravetta, M. Alagia, M. Lavollée, R. Richter, C. Bolcato, and S. Stranges, The umbrella motion of core-excited CH_3 and CD_3 methyl radicals, *J. Chem. Phys.* **128**, 044302 (2008).
- [29] A. D. Hammerich, U. Manthe, R. Kosloff, H.-D. Meyer, and L. S. Cederbaum, Time-dependent photodissociation of methyl iodide with five active modes, *J. Chem. Phys.* **101**, 5623 (1994).
- [30] K. Kosma, S. A. Trushin, W. Fuß, W. E. Schmid, and B. M. R. Schneider, Photodissociation of group-6 hexacarbonyls: Observation of coherent oscillations in an antisymmetric (pseudorotation) vibration in $\text{Mo}(\text{CO})_5$ and $\text{W}(\text{CO})_5$, *Phys. Chem. Chem. Phys.* **12**, 13197 (2010).
- [31] C. A. Schröder, J. Hack, Z. J. L. E. Zhang, J. T. Kenyon, Q. Wang, H. Wang, D. Neumark, and S. Leone, Dataset for “Coherent vibrational dynamics in molecular bond breaking: Methyl radical umbrella mode probed by femtosecond X-ray spectroscopy”, Zenodo (2026), <https://doi.org/10.5281/zenodo.19776116>.
- [32] J. Finley, P.-Å. Malmqvist, B. O. Roos, and L. Serrano-Andrés, The multi-state CASPT2 method, *Chem. Phys. Lett.* **288**, 299 (1998).
- [33] G. C. King, M. Tronc, F. H. Read, and R. C. Bradford, An investigation of the structure near the $L_{2,3}$ edges of argon, the $M_{4,5}$ edges of krypton and the $N_{4,5}$ edges of xenon, using electron impact with high resolution, *J. Phys. B* **10**, 2479 (1977).
- [34] G. Li and H. J. Hwang, State-to-state correlated study of cd_3i photodissociation at 266 and 304 nm, *J. Chem. Phys.* **124**, 244306 (2006).
- [35] P.-o. Malmqvist and B. O. Roos, The CASSCF state interaction method, *Chem. Phys. Lett.* **155**, 189 (1989).
- [36] T. N. Olney, G. Cooper, and C. Brion, Quantitative studies of the photoabsorption (4.5–488 eV) and photoionization (9–59.5 eV) of methyl iodide using dipole electron impact techniques, *Chem. Phys.* **232**, 211 (1998).
- [37] I. Fdez. Galván, M. Vacher, A. Alavi, C. Angeli, F. Aquilante, J. Autschbach, J. J. Bao, S. I. Bokarev, N. A. Bogdanov, R. K. Carlson, *et al.*, OpenMolcas: From source code to insight, *J. Chem. Theory Comput.* **15**, 5925 (2019).
- [38] I. Powis, The unimolecular dissociation of electronic state-selected methyl iodide cations, *Chem. Phys.* **74**, 421 (1983).
- [39] V. Sauri, L. Serrano-Andrés, A. R. M. Shahi, L. Gagliardi, S. Vancocillie, and K. Pierloot, Multiconfigurational second-order perturbation theory restricted active space (RASPT2) method for electronic excited states: A benchmark study, *J. Chem. Theory Comput.* **7**, 153 (2011).
- [40] K. Hermann, L. Pettersson, M. Casida, C. Daul, A. Goursot, A. Koester, E. Proynov, A. St-Amant, D. Salahub, V. Carravetta, *et al.*, Stobe-demon version 3.3, 2014, <https://www.fhi.mpg.de/1022673/StoBe>.
- [41] K. Walter, R. Weinkauff, U. Boesl, and E. W. Schlag, Molecular ion spectroscopy: Mass selected, resonant two-photon dissociation spectra of CH_3I^+ and CD_3I^+ , *J. Chem. Phys.* **89**, 1914 (1988).