Excited state dynamics of CH₂I₂ and CH₂Brl studied with UV pump VUV probe photoelectron spectroscopy

Cite as: J. Chem. Phys. 150, 174201 (2019); https://doi.org/10.1063/1.5086665 Submitted: 21 December 2018 . Accepted: 08 April 2019 . Published Online: 07 May 2019

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Cite as: J. Chem. Phys. 150, 174201 (2019); doi: 10.1063/1.5086665 Submitted: 21 December 2018 • Accepted: 8 April 2019 • Published Online: 7 May 2019

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ABSTRACT

We compare the excited state dynamics of diiodomethane (CH_2I_2) and bromoiodomethane (CH_2BrI) using time resolved photoelectron spectroscopy. A 4.65 eV UV pump pulse launches a dissociative wave packet on excited states of both molecules and the ensuing dynamics are probed via photoionization using a 7.75 eV probe pulse. The resulting photoelectrons are measured with the velocity map imaging technique for each pump-probe delay. Our measurements highlight differences in the dynamics for the two molecules, which are interpreted with high-level *ab initio* molecular dynamics (trajectory surface hopping) calculations. Our analysis allows us to associate features in the photoelectron spectrum with different portions of the excited state wave packet represented by different trajectories. The excited state dynamics in bromoiodomethane are simple and can be described in terms of direct dissociation along the C–I coordinate, whereas the dynamics in diiodomethane involve internal conversion and motion along multiple dimensions.

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I. INTRODUCTION

The excited state dynamics of photoexcited halogenated methanes are important for atmospheric photochemistry and understanding the concerted electron and nuclear dynamics of small polyatomic systems.^{1,2} They serve as a homologous family of molecules, where one can study systematic differences in the dynamics of structurally similar molecules.³ We study the excited state dynamics of diiodomethane, CH_2I_2 , and bromoiodomethane,

CH₂BrI, after pumping with UV-light at 267 nm. These two molecules have previously been the subject of intense theoretical and experimental studies.^{4–22} However, femtosecond time resolved studies of the dissociation dynamics following UV excitation have been limited. The dissociation dynamics of CH₂BrI excited with UV pump pulses at ~270 nm [near the center of the A band, assigned to a n(I) $\rightarrow \sigma^*$ (C–I) transition] have been studied with Coulomb explosion imaging, core level transient extreme ultraviolet absorption spectroscopy, and resonance enhanced multiphoton ionization



FIG. 1. UV absorption spectra for CH_2I_2 and CH_2BrI . The UV pump pulse spectrum is also shown for comparison.

in conjunction with velocity map imaging.^{5,23,24} The steep excited state potential energy surface at the Franck Condon point leads to rapid C–I dissociation (~50 fs) and substantial rotational motion of the CH₂Br radical.

Figure 1 shows the absorption spectra for the two molecules in the region surrounding the pump pulse central wavelength.²⁵ Excitation of both molecules in the deep UV (~250–320 nm) leads to breaking of the C–I bond, but the initial dynamics leading to the fission are expected to be different, given the differences in the symmetries and electronic structures (e.g., slope of the excited state at the Franck Condon point) for the two molecules. By comparing time resolved photoelectron spectroscopy (TRPES)²⁶ with trajectory surface hopping calculations of the dynamics,²⁷ we show that the initial dynamics leading to dissociation are manifested in the time-dependent photoelectron spectrum (PES), and the agreement between experiment and theory allows us to interpret the dynamics in detail.

II. EXPERIMENT

Using laser pulses in the vacuum ultraviolet (VUV) as a probe of molecular dynamics is attractive because the photon energy can be chosen to lie just below the ionization potential (IP) of the ground state (typically between 8 and 12 eV), but above the ionization potential for the majority of excited states (typically less than 8 eV). This enables one to probe the neutral excited state dynamics over a broad range of energies without windowing effects (probe photon energy insufficient to ionize the evolving excited state wave packet) while remaining blind to the ground state (whose ionization yield would typically saturate the detector). Using a weak field (singlephoton) interaction as a probe has the advantage that the measurement observable can be calculated and compared in detail with data. One drawback of using the VUV as a probe is that most organic molecules have strong absorption cross sections in the VUV. The oscillator strengths of these transitions can be larger than those of the lower lying neutral excited states that one wishes to study. Near zero time delay, it can be difficult to distinguish UV driven dynamics from VUV driven dynamics. In order to disentangle the UV and the VUV excited dynamics, it is important to accurately determine timezero (i.e., the temporal overlap of the pump and probe laser pulses). We determine time-zero of our system by looking at the nonresonant 1 + 1' photoionization of Xe, which is also used to determine

the impulse response function (IRF) of our system [measured to be about 75 fs Full Width at Half Maximum (FWHM)]. By fitting the Xe data with a Gaussian, we can accurately determine a time-zero for the experiment. Appendix A contains details on the time-zero determination. We calibrated the energies measured with our velocity map imaging (VMI) spectrometer by using three photon ionization of Xe with the UV pulses. In Appendixes B and C, a detailed analysis of the CH_2I_2 data is performed to evaluate the contribution of VUV pumped dynamics probed by the UV pulse at small positive time delays (i.e., where the center of the UV pulse precedes the center of the VUV pulse, but where there is still some overlap between the pulses).

The VUV probe is the fifth harmonic (160 nm, 7.75 eV) of a Ti:sapphire laser system generated through noncollinear four-wavemixing of the fundamental (800 nm, 1.55 eV) and third harmonic (267 nm, 4.65 eV) in an argon gas cell.²⁸ The details of this VUV generation setup can be found in Refs. 29 and 30. The third harmonic of the Ti:sapphire laser system is directed through a prism compressor system and used as the UV pump for the molecular systems studied here.

The velocity map imaging (VMI) spectrometer system, described by Forbes et al.,²⁹ consists of a source and a separate interaction chamber. The sample gases, typically 2% of the molecule of interest seeded in He through the use of a bubbler, were introduced into the spectrometer by means of a pulsed molecular beam. The beam was produced by a 1 kHz Even-Lavie pulsed valve, which was heated to 60 °C throughout the experiments in order to prevent clustering. The molecular beam was expanded through a 250 μ m conical nozzle into a source chamber typically held at a base pressure of 1×10^{-6} Torr. The beam was then skimmed, to yield a beam with an estimated diameter of around 1 mm, before entering an interaction chamber along the spectrometer Time-of-Flight (ToF) axis, typically held at a base pressure of 1×10^{-8} Torr, and intersected, at 90°, by the copropagating pump and probe laser pulses. Photoelectrons produced from the pump-probe laser interaction were focused using electrostatic lenses onto a conventional microchannel plate (MCP) and a phosphor-based detector setup, and the images were recorded using a charge coupled device (CCD) camera.

III. CALCULATIONS

In order to carry out the excited-state dynamics simulations, we used the ab initio molecular dynamics program SHARC (Surface Hopping including ARbitrary Couplings),^{31,32} interfaced with Molcas 8.0.³³ The electronic structure calculations for both neutral molecules were performed with MS-CASPT2(12,8)/ano-rccvdzp (multistate complete active space perturbation theory second order) based on SA(5/4)-CASSCF(12,8) (complete active space selfconsistent field with 12 electrons in 8 orbitals), where the stateaveraging included 5 singlet/4 triplet states for CH₂I₂ and 3 singlet/4 triplet states for CH₂BrI. The IPEA shift was set to zero, as this was found to improve the results in combination with the small double- ζ basis set.³⁴ However, in order to avoid intruder states and ensure a stable propagation in the dynamics simulations, an imaginary shift of 0.3 hartree was added.³⁵ In order to account for scalar-relativistic effects, the second-order Douglas-Kroll-Hess (DKH) Hamiltonian³⁶ was employed while spin-orbit couplings (SOCs) were computed with the restricted active space state

interaction RASSI³⁷ and atomic mean field integral AMFI³⁸ formalisms. The dynamics were run employing the velocity-Verlet algorithm with a time step of 0.5 fs for the nuclear dynamics and a time step of 0.02 fs for the propagation of the electronic wavefunction, using the "local diabatization" formalism.³⁹ Energy conservation during a surface hop was ensured by scaling of the full velocity vectors, which is an approximation compared to scaling along the nonadiabatic coupling vectors. This approximation was necessary here since the nonadiabatic coupling vectors were not available for our level of theory. The transition probabilities between states of the same multiplicity are hence taken into account with the help of wavefunction overlap calculations. We employed an energy-based decoherence correction with a parameter of 0.1 hartree.⁴⁰ Other, more involved approaches to decoherence correction like the augmented version of Subotnik and co-workers⁴¹ do not improve the quality of the results in our experience in systems like the present ones, where the frequency of hopping is comparably low. The initial geometries and velocities for the trajectories were sampled from a Wigner distribution of the harmonic ground state potential. In this way, 10 000 geometries were produced for each molecule, and

a single-point calculation at the MS-CASPT2(12,8) level of theory was performed at each of these to obtain the state energies and oscillator strengths. The initial excited states were selected stochastically,⁴² restricting the excitation energy window to energies around our pump pulse. The ionization probability along the trajectories was obtained in an approximate manner from Dyson norm calculations,⁴³ using our WFOverlap code⁴⁴ in a postprocessing step. The necessary wavefunctions for the neutral and ionized molecule were obtained at steps of 2.5 fs along the precomputed trajectories from MS-CASPT2(12,8)/ano-rcc-vdzp or MS-CASPT2(11,8)/anorcc-vdzp calculations including altogether 5 singlets, 9 doublets, 4 triplets, and 4 quartets as well as all possible SOCs for CH₂I₂ and 3 singlets, 4 doublets, and 4 triplets as well as all SOCs for CH₂BrI. A single time step of the neutral molecule's dynamics took about 1 h on a single core (Intel Xeon E5-2650 v3). The ionization simulation was carried out as postprocessing for every fifth time step, requiring approximately 5 min per point. Since initial wavefunctions were taken from the previous time step, intermittent points were recalculated with CASSCF requiring approximately 2 min, respectively.



FIG. 2. Time resolved photoelectron spectra: (a) CH₂I₂ measured, (b) CH₂I₂ calculated, (c) CH₂BrI measured, and (d) CH₂BrI calculated. The x-axis represents the pumpprobe delay (UV pump, VUV probe for positive delays). The y-axis is the electron Kinetic Energy Release (KER). All spectra are normalized with their own peak values.

IV. RESULTS

Figure 2 shows the measured and calculated photoelectron spectra as a function of pump-probe delay for CH_2I_2 and CH_2BrI . Panels (a) and (b) show the measurements and calculations, respectively, for CH_2I_2 , while panels (c) and (d) show measurements and calculations for CH_2BrI . The calculated results have been convolved with the IRF of the system to facilitate comparison with the experiment. From earlier results,⁷ we estimate that the VUV absorption cross section. This means that near time-zero, where the pump and probe pulses overlap, the signal comes from a combination of both UV pumped and VUV pumped excited state dynamics. In order to highlight the UV driven dynamics that have contributions from VUV driven dynamics near time-zero, we multiply the signal level at positive pump-probe delays (i.e., outside the temporal overlap of the pump and probe pulses) by a factor of 2.5.

There is a good agreement between the experimental and calculated TRPES. For CH_2I_2 , they both have a main peak near zero delay at about 2.5 eV, corresponding to ionization from the Franck-Condon region to low-lying states of the cation. As there is rapid motion of the wave packet on the excited state, and the low-lying states of the cation are close in energy, one cannot resolve the ionization to different cationic states, which one can see in examining the calculations.⁴⁵ In both the calculated and measured spectra, the higher energy peak disappears in about 60 fs and there is a lower energy tail that persists out past 100 fs.

For CH₂BrI, the calculations and measurements show two peaks at time-zero separated by ~0.9 eV. These two peaks originate from photoionization correlating to two different final cationic states after initial photoexcitation with the UV pulse. The calculations and the experiments both show a rapid decay of the two peaks in under 60 fs without a low energy (<0.5 eV) tail, consistent with previous measurements of direct dissociation (DD) using core to valence extreme ultraviolet transient absorption spectroscopy that found a C–I dissociation time of about 45 fs.²³

V. DISCUSSION

Before interpreting the measurements with the aid of the calculations, we assess the extent to which excited state dynamics driven by the VUV pulse contribute to the photoelectron spectrum at short positive delays. The experimental yield including both UV and VUV pumping is modeled. The overall molecular decay is modeled with a sum of two exponential decays (one for positive and one for negative delays with decay times based on fits to the data), with the VUV signal having four times the amplitude of the UV dynamics based on the estimated ratio of the absorption cross sections.⁷ (We do not know the ionization cross sections for UV vs VUV excitation, and thus, we took them to be equal as the simplest approximation.) The modeled dynamics are then convolved with the IRF of the apparatus. In order to assess the importance of UV driven dynamics in the data, the model described here is compared with the one that does not include UV driven dynamics-one with an exponential decay only for negative times, convolved with the IRF for the apparatus using the same decay time as before. The two results are shown in Fig. 3(a). Together with the two models, the experimental CH₂I₂ TRPES data integrated from 0 to 0.5 eV are shown. This



FIG. 3. (a) The convolution of the IRF and an exponential decay model of the photoelectron yield for both UV and VUV driven dynamics (solid red line) and with only VUV driven dynamics (dashed black line) plotted alongside the experimental CH_2I_2 TRPES data integrated from 0 to 0.5 eV (open diamonds). (b) Decomposition of the exponential decay model shown as the solid red line in panel (a). The model consists of two exponential decays (one for positive and one for negative delays) and is represented here by the dashed black curve. The UV driven dynamics signal has an amplitude of 1/4 and a decay constant of 30 fs, and the VUV driven dynamics signal has an amplitude of 1 and a decay constant of 47 fs. The combination of these are convolved with the measured IRF (dotted black curve) to model the experiment. The model convolved with the IRF is represented by the solid red curve as it is in panel (a).

energy region was chosen because it is the one with the largest contribution to the dynamics at longer positive time delays. It is clear that the data are only consistent with the model which includes both VUV and UV driven dynamics contributing to the photoelectron yield, and not consistent with the model which contains only VUV driven dynamics, particularly for positive delays beyond 50 fs.

Figure 3(b) shows the individual components used in this simple model of the molecular dynamics signal. Further analysis of the UV vs VUV driven dynamics contributions to the signal are given in Appendices A–C.

Given the agreement between the measured and calculated TRPES, and having established that the measurements contain information on the UV driven dynamics, we now examine the calculation results in more detail for insights into the dissociation dynamics. Figure 4 shows the potential energy as a function of C–I distance for several neutral and ionic states, as well as the state populations vs time after the pump pulse for both CH_2I_2 and CH_2BrI . In panels (a) and (b), the calculated potential energy of the molecule is plotted as (one of) the C–I bond(s) is stretched and all of the





other bonds are kept fixed. While some earlier work on CH_2BrI with excitation at 266 nm found evidence of C–Br bond fission as well as C–I fission,²³ C–I bond fission dominated (with a ratio of about 5:1), and the other work making use of excitation at 271 nm measured only C–I bond fission.⁵ Our calculations found evidence of C–Br fission, but only for about 5% of the trajectories, and the evolution of the TRPES was similar to that calculated for C–I fission. Thus, our measurements are not able to separately track C–Br fission.

Figure 4 illustrates a number of important points. First, absorption of a pump photon with an energy about 4.65 eV leads to excitation of a cluster of excited states. In CH₂BrI, these are all directly dissociative states, whereas in CH₂I₂, it is a mixture of bound and dissociative states. As illustrated in panels (c) and (d), in CH₂BrI, internal conversion plays a minor role as the molecule dissociates, whereas in CH₂I₂, there is significant internal conversion that takes place prior to dissociation. As the molecule dissociates in states 2 through 8 or 9 through 12, the ionization potential increases such that the probe pulse cannot ionize the molecule, leading to a decay of the photoelectron spectrum. The ionization potentials for I/I* and CH₂I radical are above our employed photon energy. (The IP of the CH₂I radical is 8.4 eV; the IP of I is 10.5 eV.)⁴⁶ CH₂I₂ molecules remaining in states 13-17 are energetically capable of being ionized and, thus, may be responsible for the tail in the photoelectron spectrum for CH₂I₂. This naturally leads to the question of whether the tail in the photoelectron spectrum for CH2I2 can be associated with particular trajectories in the calculations.

In order to determine whether the low energy tail in the photoelectron spectrum (PES) for CH_2I_2 is associated with a particular

motion of the molecule, we examined the trajectories for correlations between the low energy tail in the PES and motion along different degrees of freedom in the molecule. Since there is sufficient energy on the excited state for dissociation of a single C-I bond but not both, we looked specifically at symmetric stretching of the C-I bonds and constructed a scatter plot such that one axis is the integral of the low energy tail in the PES, while the other axis is the absolute difference between the C-I bond lengths (which is small for symmetric stretching and large for stretching of a single C-I bond). This is shown in Fig. 5. The values on each axis are averaged over the dynamics. Each point on the plot corresponds to a different trajectory. As is evident from the graph, trajectories which give rise to a significant tail in the photoelectron spectrum tend to have small average differences between the two C-I bond lengths (corresponding to symmetric C-I stretching). Conversely, large average differences in the C-I bond lengths, which correspond to dissociation, are associated with small yields in the photoelectron spectrum. Thus, one can associate the tail in the PES with the symmetric C-I stretching that does not lead directly to dissociation.

In order to illustrate the points discussed above, in Fig. 6, we plot the C–I distance for both bonds, along with the populated state index, and the potential energy for two complementary trajectories shown in the scatter plot—one which corresponds to the maximum low energy yield in the PES (labeled SS) and the other which corresponds to the minimum (labeled DD). These two trajectories show very different behavior. For the one with the low photoelectron yield, one of the C–I bonds remains roughly constant, while the other one stretches significantly. The asymmetric C–I stretching is also



FIG. 5. Scatter plot illustrating the correlation between the photoelectron yield and symmetric C–I stretching in CH₂I₂. The x-axis represents the absolute difference between the C–I bond lengths averaged over all delays, while the y-axis represents the photoelectron yield from 0–0.5 eV averaged over all delays. Each point on the graph represents a different trajectory. Two trajectories are selected for further analysis below and marked with a red diamond and blue square. Symmetric Stretch (SS) and Direct Dissociation (DD) are used to label these two trajectories.

associated with internal conversion and rapid potential energy loss, as illustrated in panels (c) and (d), while the symmetric C–I stretching is associated with less internal conversion and energy loss. In contrast, the calculations for CH_2BrI indicate that there is not much



FIG. 6. C–I bond lengths [panels (a) and (b)], electronic states [panel (c)], and potential energies [panel (d)] as a function of time for two trajectories chosen from the scatter plot in Fig. 5—square and diamond symbols in Fig. 5. Again, Symmetric Stretch (SS) and Direct Dissociation (DD) are used to label the two trajectories.

internal conversion (see panel (d) of Fig. 4), but rather direct dissociation which proceeds without competing stretching of both carbon halogen bonds.

Earlier work comparing dynamics following excitation at 268 nm in CH_2BrI and CH_2ICl^{24} interpreted their measurements in terms of dissociation on multiple states in conjunction with internal conversion. While they observed small differences in the measured dissociation times, they did not see evidence for simultaneous stretching of the carbon halogen bonds leading to a delayed dissociation as we observe in CH_2I_2 . Future work with a slightly higher probe photon energy could allow for following of the directly dissociative portions of the wave packet in both molecules out to larger C–I bond lengths and improved time resolution would allow for following the internal conversion dynamics near the Franck-Condon region in greater detail, with less contribution from VUV driven dynamics.

VI. CONCLUSION

In conclusion, the photodissociation dynamics of CH₂BrI and CH₂I₂ excited with deep UV radiation at 267 nm are measured using VUV driven photoionization and velocity map imaging of the photoelectrons. The measurements are interpreted with the aid of trajectory surface hopping calculations. The dynamics for the two molecules are observed to be different. In CH2BrI, dissociation proceeds directly, consistent with earlier time resolved measurements.^{5,23,24} In contrast, the dissociation of CH₂I₂ involves both internal conversion and motion along multiple dimensions. An analysis of the trajectories calculated for CH_2I_2 shows that one can associate a feature in the TRPES (low energy electrons at pumpprobe delays greater than 50 fs) with specific trajectories (the ones which correspond to symmetric stretching of the C-I bonds in the initial dynamics). These results clearly demonstrate the relevance of specific trajectories from surface hopping calculations in rationalizing features of the measured observables and offers promise for using a combination of multichannel measurements (such as TRPES) and trajectory surface hopping calculations to follow nonlocal dynamics in polyatomic molecules.

ACKNOWLEDGMENTS

We gratefully acknowledge support from the Department of Energy under Award No. DEFG02-08ER15984. This project was partly supported by the Government of Hungary and the European Regional Development Fund under Grant No. VEKOP-2.3.2-16-2017-00015. The computational results presented have been achieved, in part, using the Vienna Scientific Cluster (VSC). R.F. acknowledges a research scholarship from the Engineering and Physical Sciences Research Council (EPSRC).

APPENDIX A: IMPULSE RESPONSE FUNCTION AND ZERO TIME DELAY DETERMINATION

Nonresonant 1 + 1' photoionization of Xe was used to determine the IRF and time-zero of the experiment. The time resolved photoelectron spectrum of Xe is shown in Fig. 7. It is evident that there is a slight asymmetry to the data (a slight diagonal tilt with

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respect to delay) that indicates there is a slight chirp (time varying frequency) in our VUV probe pulse.

The data in Fig. 7 were integrated over kinetic energy release (KER) and fit to a Gaussian in order to determine the FWHM of the impulse response function (IRF) for the system and an accurate time-zero (where the pump and probe pulses are maximally overlapped). The result of this integration and the subsequent fitting can be seen in Fig. 8.

From this fitting, the FWHM of the IRF was determined to be ~75 fs, and the time-zero was determined to correspond to the location of the delay stage at which the integrated Xe yield was maximum.

APPENDIX B: DETAILS ON VUV PUMPED CONTRIBUTIONS TO DYNAMICS AT SHORT POSITIVE TIME DELAYS

As our interpretation of the measurements relies heavily on the low energy tail observed in the CH_2I_2 TRPES, we provide additional evidence for the significance of this feature in our measurements. The first is simply a slightly different view of the TRPES, where we allow the color axis to saturate. This is shown in Fig. 9. The presence of electrons between 0 and 0.5 eV for positive delays beyond 40 fs is clearer here than in Fig. 2.

A more rigorous test of this low energy tail is provided by a bootstrapping analysis, which allows us to determine the statistical



FIG. 8. Gaussian fit to the energy integrated Xe time resolved photoelectron spectrum.



FIG. 9. TRPES for CH_2I_2 with saturated colormap in order to highlight low energy electrons for positive time delays.

significance of the electrons measured in a given energy bin for each delay. At each time delay, 20 photoelectron spectra are measured in the experiment. This dataset is resampled 20 times, 20 spectra each time, using a standard bootstrapping method. This process generates 20 bootstrapped photoelectron spectra. Each bootstrapped spectrum is analyzed to calculate the photoelectron yield between 0 and 0.5 eV, and the standard deviation of the 20 results is taken as the standard error. Figure 10(a) shows the photoelectron yield as a function of pump-probe delay for electrons below 0.5 eV along with error bars determined by the bootstrapping analysis. Panel (b) shows the yield and error as separate curves as a function of delay. Panel (c) shows the ratio of the yield and uncertainty, demonstrating a signal to noise of greater than 5 over the relevant range of delays.



FIG. 10. Error analysis for low energy photoelectron yield. (a) Photoelectron yield as a function of pump-probe delay for electrons below 0.5 eV along with error bars determined by the bootstrapping analysis. (b) Yield and error as separate curves as a function of delay. (c) Ratio of the yield and uncertainty, demonstrating a signal to noise of greater than 5 over the relevant range of delays.

APPENDIX C: EVOLUTION OF THE TRPES NEAR ZERO TIME DELAY

In order to further evaluate the contribution of the VUV driven dynamics to the TRPES near zero time delay, we consider the evolution of the TRPES as a function of delay near time-zero. Figure 11 shows the photoelectron spectrum for a few time delays for CH₂I₂. The spectra for small negative and positive delays (e.g., -26 fs and +23 fs) show some similarities and differences, consistent with static calculations of the photoelectron spectrum that we carried out for VUV + UV and UV + VUV. They all show a broad distribution of photoelectrons between 0 and 3 eV, with a relatively sharp cutoff around 3 eV, as one would expect based on the difference between the sum of the UV and VUV photon energies (~12.5 eV) and the ground state ionization potential (~9.5 eV). The broad distribution from 0 to 3 eV is a result of ionization to a mixture of low lying ionic states and conversion of potential energy to vibrational kinetic energy on the excited state. While there are clearly differences in the spectra for positive and negative delays, the similarities provide some rationale for the agreement of the calculations including only UV driven dynamics with the measurements which include both UV and VUV driven dynamics near time-zero. The similarities in the photoelectron spectra for VUV + UV vs UV + VUV can be understood in terms of the fact that at our photon energies, the VUV absorption spectrum is dominated by Rydberg states that are correlated with the same four lowest states of the cation that contribute to the spectrum produced in our calculations which include UV excitation (see Fig. 3 in Ref. 7). The differences in the spectrum for positive and negative delays can be attributed to some dynamics on the excited neutral states as well as different weightings of the ionic states involved for UV vs VUV pumping.

In addition to examining the TRPES for both sides of time-zero, we calculated the photoelectron spectrum due to VUV pump, UV probe. The spectra were calculated with MS-CASPT2(12,10) for 14 singlets and 12 triplets and MS-CASPT2(11,10) for 9 doublets and 4 quartets with MOLCAS 8.0. We used an ano-rcc-vdzp basis set augmented with diffuse functions for Rydberg orbitals according to the



FIG. 11. Photoelectron spectra for CH_2I_2 for several different delays near zero time delay.



FIG. 12. Photoelectron spectrum for CH₂I₂ as calculated for a δ function pulse. (a) lonization from state 16, i.e., the most highly populated state after UV excitation (4.65 eV), to different ionic channels (blue to pink peaks correspond to D0, D1, ..., while their sum is plotted as a black line). (b) lonization from state 40, i.e., excitation with the VUV-photon energy of 7.75 eV. Note that less structure than in the experimental spectra is visible due to the limited number of geometries (here 99) and the artificial Gaussian broadening of 0.3 eV.

scheme proposed by Kaufmann *et al.*⁴⁷ The single point calculations including Dyson norm computations for the 84 states were carried out for 99 geometries from the afore-mentioned Wigner distribution. For the UV + VUV spectrum, we considered the Dyson norms between the neutral state 16 (which is the most populated state in the UV excitation with 4.65 eV) and all possible ionic states. The VUV + UV spectrum stems from the Dyson norms between the neutral state 40 (most populated in VUV excitation with 7.7 eV) and all possible ionic states. The resulting stick spectra were convoluted with Gaussians (FWHM 0.3 eV), respectively. The results of these calculations are shown in Fig. 12. They show that the photoelectron spectra for VUV + UV and UV + VUV both populate a combination of the four lowest ionic states (D0, D1, D2, and D3). Ionization to states higher than D3 (leading to the peak near zero energy) is likely due to a slight redshift in the calculations. Features between 0.5 and 2 eV are absent in the static calculated spectra but are present in Fig. 2 as a result of dynamics and temporal broadening (mimicking the finite duration of the laser pulses). These calculations indicate that the VUV + UV and the UV + VUV pathways produce similar features in the TRPES.

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