Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Single- and multi-photon-induced ultraviolet excitation and photodissociation of CH_3I probed by coincident ion momentum imaging

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1. Comparing different models for evaluating the delay dependent KER

To test how sensitive the Coulomb explosion simulations are to the detailed shape of the PECs used for modeling the neutral dissociation dynamics, we compare the results obtained using the calculated PEC for the $^3Q_0$ state by Alekseyev *et al.* [14] with the predictions of two simplified models often used in literature. These models either assume that the dissociating fragments travel with constant velocities [27, 32, 38, 39] or that the velocity rises exponentially towards its asymptotic value [74]. Figure S1(a) and Fig. S1(b) are a reproduction of the plots from the main text, while Fig. S1(c) and Fig. S1(d) present the calculated velocity and C-I internuclear distances associated with these simplifying models for the $^3Q_0$ state. Close agreement is observed between the exponential rise velocity model and the model based on the Alekseyev PECs [14] except for short delays, where a single exponential function does not describe well the shape of the $^3Q_0$ PEC.

Figure S2 shows the comparison of the three models to the experimental data, assuming a purely Coulombic di-cationic PEC, i.e., that the value of E_{CE} can be calculated using the Coulomb repulsion energy of two point charges separated by the C-I distance. As expected, the three models agree with the experimental data at large delays (or internuclear distances), but a discernible mismatch is observed within the first ~100 fs, where the KER is overestimated by all three models. While the constant velocity model clearly overestimates the internuclear separation at any given time, which is expected given the rather crude approximation that fragments instantaneously reach their asymptotic KER, the exponential-rise velocity model resembles the PEC-based model much better, with only slight deviations in the velocity values at short delays between ~20 to ~50 fs. This deviation is attributed to the shape of the $^3Q_0$ PEC, which a single exponential function cannot fully describe. The electronic structure calculations by Alekseyev *et al.* [14] showed that this state has a shallow minimum of about 0.1 eV, which lies at larger internuclear distances than the Franck-Condon region.

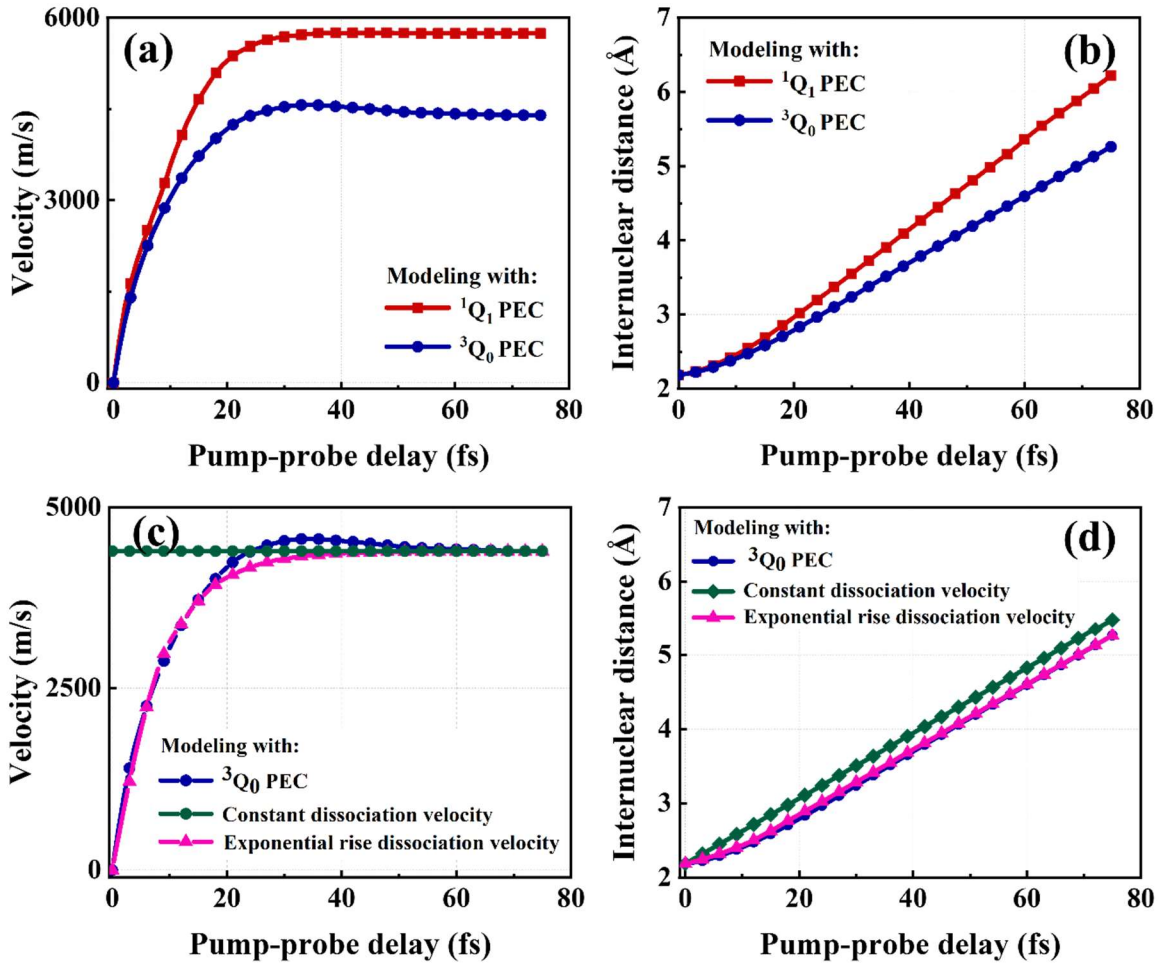

Figure S1: Time-dependence of the **(a)** relative CH_3-I velocity and **(b)** C-I internuclear distance determined for the dissociative PECs of the $^3Q_0$ and $^1Q_1$ states reported by Alekseyev *et al*. [14]. Comparison of the **(c)** velocity and **(d)** C-I internuclear distance for dissociation on the $^3Q_0$ surface resulting from different approximations for the PEC (see text above).

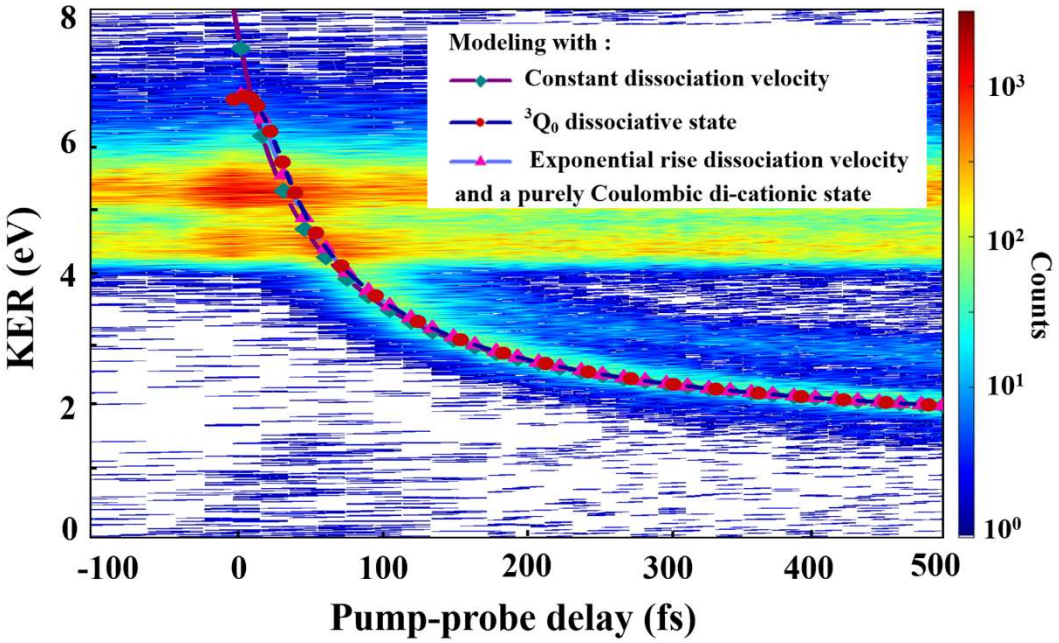

Figure S2: Comparison of the Coulomb explosion simulations for different approximations of the dissociation on the $^3Q_0$ state with the experimental delay-dependent KER of the $CH_3^+ + I^+$ channel. The experimental data is the same as shown in Fig. 3. For all three simulations, the final di-cationic state accessed by the probe pulse is assumed to be purely Coulombic.

2. Experimental signatures of the potential well in low-lying PECs of CH_3I^{2+}

The lowest potential energy curve of the iodomethane di-cation, CH_3I^{2+}, shown in Fig. 1 of the main article, leads to a clear signature in the time-dependent KER as discussed in the main text. In addition, that potential well can be observed as an enhancement in the time dependence of the CH_3I^{2+} yield, shown in Fig. S3. The lifetimes of the (CH_3I^{2+}) v=0 and v=1 vibrational states are about 2 s and 75 μs, respectively, according to our phase-amplitude [77] calculations (for zero angular momentum). Therefore, these are the CH_3I^{2+} states detected as di-cations, while, in contrast, the v=2-4 vibrational states decay rapidly (i.e., in a few ns or ps), and thus are detected as $CH_3^+ + I^+$ coincidence events. We expect that some CH_3I^{2+} (v=0,1) should be populated by the NIR-probe pulse, and thus produce a delay independent CH_3I^{2+} yield. However, at very short time delays, we expect an enhancement due to ionization of the dissociating CH_3I A-band into $CH_3 + I$ as described in the main article, but once the CH_3–I gained sufficient kinetic energy to overcome the barrier, estimated above to take about 13 fs, the metastable CH_3I^{2+} production should close. The measured CH_3I^{2+} yield as a function of time delay, shown in Fig S3, exhibits a narrow enhancement peak around t=0, which corroborates our expectations above and is consistent with the time-dependent KER signature presented in the main article. Note that our time resolution does not permit probing the expected 13 fs time scale for this channel closing. However, the width of the enhancement peak, 42 fs, is consistent with the duration of our laser pulses and serves also as a verification of our cross-correlation measurements.

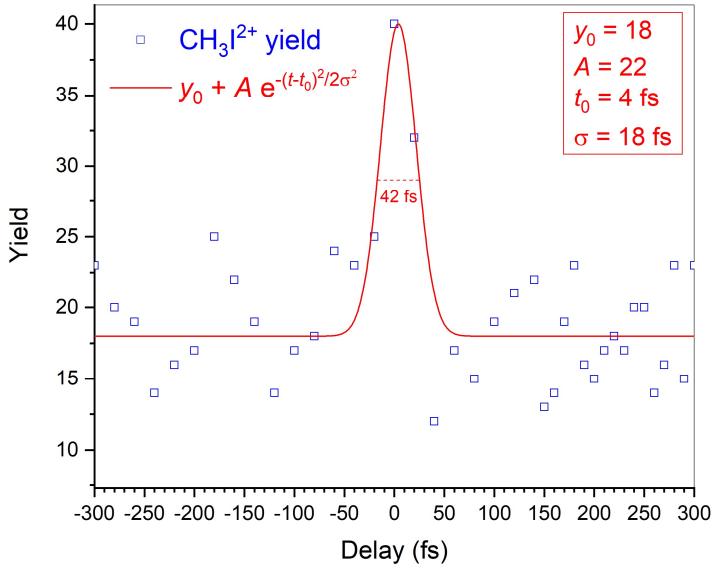

Figure S3: CH_3I^{2+} yield as a function of delay (blue squares) together with a Gaussian fit to the data (red line). The width of this enhancement peak is consistent with our cross-correlation measurements of the pump and probe pulses.

References

[77] E.Y. Sidky and I. Ben-Itzhak, "Phase-amplitude method for calculating resonance energies and widths for one-dimensional potentials", Phys. Rev. A **60**, 3586 (1999).