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SUPPLEMENTARY MATERIAL

# Time-resolved photoelectron imaging of iodide-nitromethane ($I^- \cdot CH_3NO_2$) photodissociation dynamics

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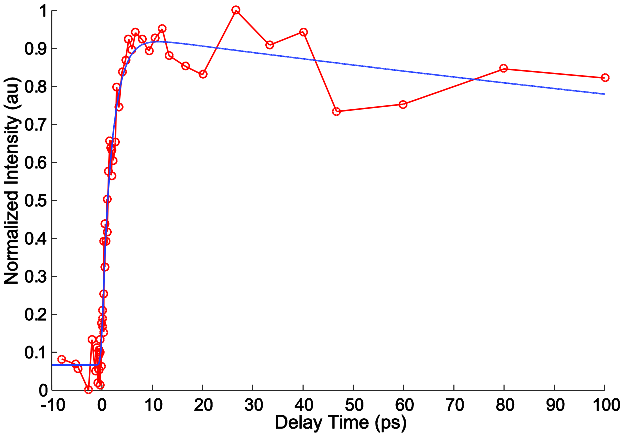

Figure S1. Normalized integrated intensity of feature C for long time delays from excitation at 3.56 eV vs. delay time. The rise time for feature C is 2.1 ± 0.2 ps and the decay time is on the order of ns.

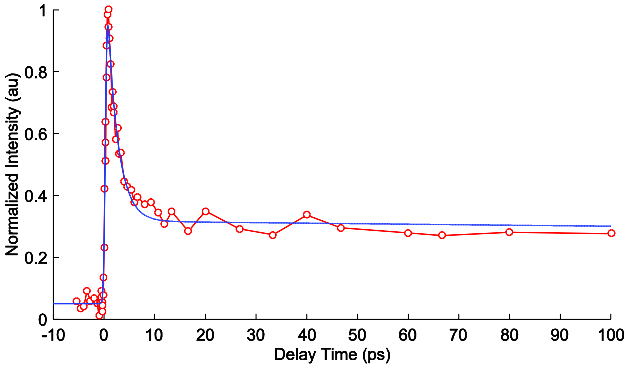

Figure S2. Normalized integrated intensity of feature E from excitation at 3.56 eV vs. delay time. The rise time for feature E is 0.33 ± 0.15 ps and the bi-exponential decay times are 2.2 ± 0.3 ps and 1100 ± 700 ps.

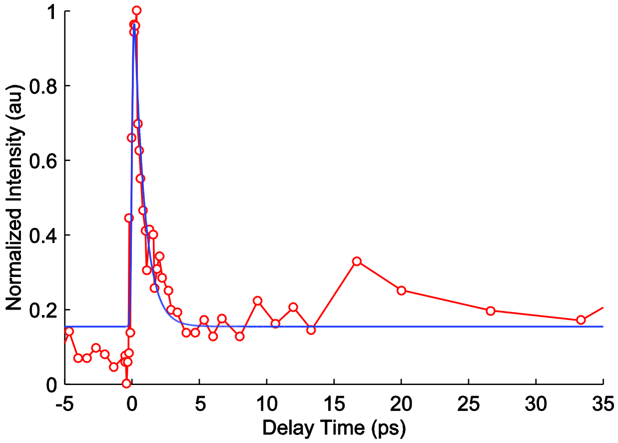

Figure S3. Normalized integrated intensity of feature G from excitation at 3.56 eV vs. delay time. The rise time for feature G is cross-correlation limited, and the decay time is 0.88 ± 0.22 ps.

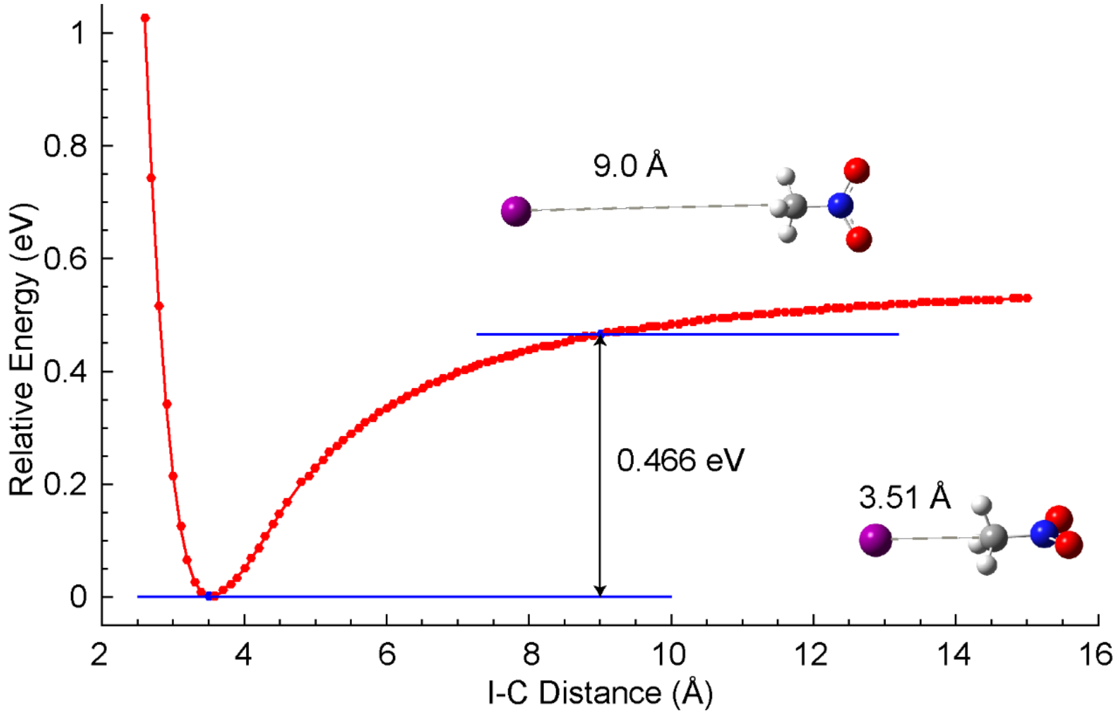

Figure S4. Potential energy curve calculated by geometry optimization at frozen I-C distances. The calculations were performed at the MP2/aug-cc-pVDZ(-pp) level of theory. All energies are ZPE corrected.

## Theoretical Methods

The potential energy surface for the unimolecular decomposition of electronic ground state $I^{-}\cdot CH_3NO_2$ to form $I^{-}$ was calculated at the MP2 level with an augmented Dunning basis set aug-cc-pVDZ for C, H, O, and N, with an expanded basis set with an increased set of diffuse functions for iodide, MP2/aug-cc-pVDZ(-pp)[1] using the Gaussian 09 computing package.[2] By scanning along the iodide-nitromethane stretching coordinate and optimizing the structure geometry and frequencies in 0.1 Å intervals from 2.5 Å to 15 Å, the potential energy surface was found to be barrierless.

As the potential is barrierless, variational transition state theory was used to calculate the transition state by calculating the rate constant *k(E)* using Equation 4 for each optimized distance to determine the minimum rate constant. The reactant species and transition state structures, frequencies, and energies were optimized at the MP2/aug-cc-pVDZ(-pp) level of theory. The calculated vibrational frequencies were scaled using a scaling factor of 0.9615 for MP2 calculations to account for anharmonicities.[3] The Beyer-Swinehart direct count algorithm[4] with the Stein-Rabinovitch modification[5] was employed to calculate the density of states for the reactant and sum of states for the transition state to determine the RRKM rate constant for unimolecular dissociation from the calculated frequencies and energy. The iodide-nitromethane low energy interaction modes involving rotation of iodide relative to the C-N nitromethane bond in-plane and out-of-plane were best treated as hindered rotational motions, as well as the methyl rotor mode in nitromethane, which is a free rotor in the neutral species but a hindered rotor in the anion due to the interaction between the methyl group and pyramidalized nitro group. The barrier height and symmetry for hindered rotors was calculated by performing relaxed potential energy scans at the MP2/aug-cc-pVDZ(-pp) level in 10° increments along the rotational motion. Using this variational approach, the transition state was calculated to be when the iodide-nitromethane I-C distance is 9.0 Å. The energy barrier $E_0$ between the reactant and the transition state was calculated to be 0.467 eV, and 0.466 eV when corrected for ZPEs. Additionally, the $I^{-}\cdot CH_3NO_2 \rightarrow HI + CH_2NO_2^{-}$ decay channel was calculated to have a reaction energy of 2.6 eV at the MP2/aug-cc-pVDZ(-pp) level.

Table S1. Beyer-Swinehart calculated densities and sums of states for the $I^{-}\cdot CH_3NO_2$ ground state and transition state including treatment of low-frequency hindered internal rotational modes.

| Ground state density (/cm$^{-1}$) | Transition state sum | $k_{RRKM}(E)$ (1/s) | Lifetime (fs) |
|---|---|---|---|
| $5.97326 \times 10^{5}$ | $6.78309 \times 10^{7}$ | $3.40441 \times 10^{12}$ | 294 |

Table S2. $I^{-}\cdot CH_3NO_2$ calculated vibrational frequencies (cm$^{-1}$) at the optimized, ground state geometry. Calculation performed at the MP2/aug-cc-pVDZ(-pp) level of theory. The modes in boldface type correspond to the $I^{-}\cdots CH_3NO_2$ intermolecular stretch and bends.

| | | |
|---|---|---|
| 27.4 | **55.4** | **59.2** |
| **75.2** | 479.5 | 593.9 |
| 658.2 | 925.2 | 1092.6 |
| 1107.5 | 1358.4 | 1430.0 |
| 1443.0 | 1454.6 | 1725.1 |
| 3131.2 | 3242.2 | 3281.0 |

# References

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