

Observation of conformation-specific pathways in the photodissociation of 1-iodopropane ions

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Many molecules can rotate freely around single bonds and thereby interconvert between different conformations, such as *gauche* and *anti* 1,2-disubstituted ethane, a classic example of conformational isomerism^{1–3}. Even though rotation occurs rapidly at room temperature, the product selectivity seen in some reactions has been explained by conformation-dependent reaction mechanisms^{4,5}: if reactant molecules differing only in their conformation are located at different positions on the reaction path, they may undergo different reactions. But a direct verification of this effect is difficult, because the energy barrier separating conformational isomers is so low that under ambient conditions reactants with more than one conformation will be present¹. But by using temperatures low enough to suppress the interconversion between different conformations, *gauche*-1-iodopropane ions and *anti*-1-iodopropane ions have been selectively generated⁶. Here we show that the kinetic energy released during the photodissociation of 1-iodopropane ions depends strongly on the conformation of the ions. Thermodynamic arguments and *ab initio* calculations indicate that this difference in kinetic energy release results from differences in the reaction mechanism, with *gauche*-1-iodopropane ions forming 2-propyl ions and *anti*-1-iodopropane ions forming protonated cyclopropane ions. These findings suggest that the well-known concept of conformation selection forms the basis of a simple scheme for reaction control, thus providing in some cases an attractive alternative for more involved schemes that utilize the phase and pulse shape of laser beams to control chemical reactions^{7–10}.

We have previously⁶ used mass-analysed threshold ionization¹¹ (MATI), a technique for generating state-selected molecular ions, to produce 1-iodopropane ions ($1\text{-C}_3\text{H}_7\text{I}^+$) with coherent vacuum-ultraviolet¹² (VUV) radiation (Fig. 1). The resonant nature of MATI and the very low temperature (rotational temperature ~ 35 K) of the molecular beam ensure that $1\text{-C}_3\text{H}_7\text{I}^+$ is in its ground vibronic state, with hardly any internal energy that could drive the interconversion between the *gauche* and *anti* forms of the ion. These two forms should therefore be considered as isomers, rather than conformers. Interconversion between the *gauche* and *anti* forms of $1\text{-C}_3\text{H}_7\text{I}^+$ can also be induced by collisions, but the very low pressure ($< 10^{-7}$ torr) in our experimental system precludes this process. Hence, we are able to produce ion beams containing only *gauche*- $1\text{-C}_3\text{H}_7\text{I}^+$ or only *anti*- $1\text{-C}_3\text{H}_7\text{I}^+$, by selectively tuning the wavelength of the ionizing VUV radiation (133.94 and 133.72 nm for the *gauche* and *anti* forms, respectively).

However, conformation-selective formation of ion beams does not guarantee the observation of a conformation-selective reaction, because the activation energy needed to initiate a reaction may also induce the interconversion between different conformations. We therefore used photoinduced excitation of the molecular ions to a repulsive electronic state, which ensures that subsequent dissociation occurs essentially immediately. This approach should prevent complications arising from interconversion between the conformations.

In our experiments, selective generation of either *gauche* or *anti* $\text{C}_3\text{H}_7\text{I}^+$ ions by a VUV laser pulse was followed about 100 ns later by

a second laser pulse in the visible wavelength region (480–700 nm), which excited the ions to their first excited electronic state¹³—according to our observations (see below), this excited state is repulsive with respect to the C–I bond. The C_3H_7^+ fragment ion produced in this photodissociation event was then accelerated orthogonal to the molecular beam/VUV direction, and detected by time-of-flight (TOF) mass spectrometry.

The TOF profiles of C_3H_7^+ changed with the polarization of the photodissociation laser, indicating that dissociation via the first excited state occurs very rapidly and hence anisotropically, as was intended. The anisotropy effect can be eliminated by recording a TOF profile at the laser polarization angle of 54.7° : the broadening of the profile recorded at this angle is then solely due to the centre-of-mass kinetic energy of the fragments, the kinetic energy release KER (ref. 14). Figure 2a shows the TOF profiles of C_3H_7^+ generated from *gauche* and *anti* $1\text{-C}_3\text{H}_7\text{I}^+$ by using a laser pulse with a wavelength of 607 nm and a polarization angle of 54.7° . The profile generated from the *gauche* isomer is significantly broader than that from the *anti* form, indicating that the photodissociation of the *gauche* form results in the release of a larger amount of kinetic energy. Figure 2b illustrates the KER distribution obtained from the TOF profiles with a method similar to that in ref. 15. These distributions yield average values of KER, $\langle T \rangle$, of 0.096 eV and 0.042 eV for the photodissociation at 607 nm of the *gauche* and *anti* forms of $\text{C}_3\text{H}_7\text{I}^+$, respectively.

We performed further photodissociation experiments using dissociating laser pulses with different wavelengths in the range 480–700 nm. Figure 2c shows the resulting plot of $\langle T \rangle$ obtained from these data as a function of photon energy. The figure also includes the KER measured by Brand *et al.*¹⁶ for the same reaction, using a photoionization technique that does not allow for state and conformation selections (see Fig. 2c). The data show that even when $\text{C}_3\text{H}_7\text{I}^+$ has an internal energy of only ~ 1.1 eV (so dissociation can occur only in the ground electronic state), the KER observed by Brand *et al.* is much larger than the KER we observe near the dissociation threshold (700 nm, 1.77 eV). This difference indicates that the dissociation events we probe do not involve the ground electronic state of $\text{C}_3\text{H}_7\text{I}^+$, and that our experimental set-up thus performs as planned.

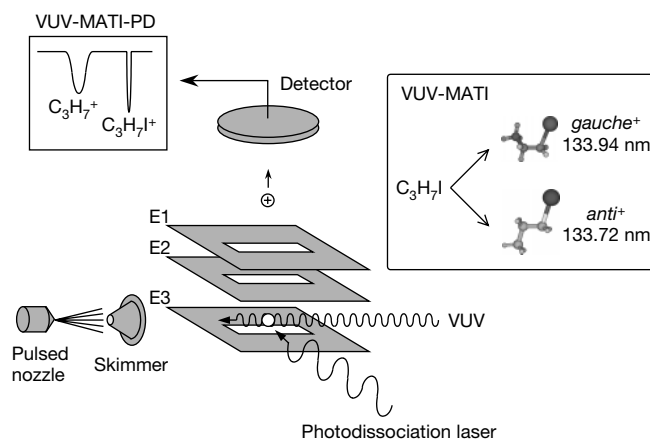


Figure 1 Experimental scheme. Vacuum-ultraviolet radiation (VUV) at a wavelength of ~ 134 nm is generated in a Kr cell by combining and focusing two laser beams at 212 and ~ 510 nm. This VUV is overlapped with the molecular beam in a collinear fashion. Electrode E3 is kept at -0.5 V, and other electrodes grounded at the time of the VUV pulse. After $20 \mu\text{s}$ delay, 930 and 1,200 V are applied to electrodes E2 and E3, respectively, for the pulsed-field ionization and acceleration. The *gauche* and *anti* isomers of $1\text{-C}_3\text{H}_7\text{I}^+$ are generated selectively by VUV-mass-analysed threshold ionization (VUV-MATI) at 133.94 and 133.72 nm, respectively (inset). About 100 ns after the ionization, the sample is irradiated by a second laser in the visible to induce photodissociation (PD).

The values obtained for the photodissociation of the *gauche* and *anti* forms of $C_3H_7I^+$ decrease almost linearly with photon energy and with similar slopes, but the absolute values obtained for the *gauche* isomer are always noticeably larger than those obtained for the *anti* form. Assuming that $\langle T \rangle$ depends linearly on the photon energy, an extrapolation of the data to $\langle T \rangle = 0$ yields dissociation threshold energies of 1.6 eV and 1.3 eV for *anti* $C_3H_7I^+$ and *gauche* $C_3H_7I^+$, respectively.

When trying to explain the conformation-specific differences in the photodissociation behaviour that we observe, we first note that the chemical composition of the reactants and products involved are identical. Assuming the reaction paths for the reactions involving the *gauche* and *anti* forms of $C_3H_7I^+$ are the same, the difference in the KER would have to be due to a significant difference in the internal energy of the photoexcited *gauche* and *anti* isomers. This, however, can be ruled out: the internal energy of the *anti* form exceeds that of the *gauche* form by ~ 0.015 eV (ref. 6), yet the latter releases more kinetic energy when dissociating. The significant difference in KER (Fig. 2b) and the difference in the dissociation threshold energies estimated from Fig. 2c thus seem to result from differences in the dissociation dynamics of the two $C_3H_7I^+$ forms (see, for example, ref. 17). The fact that the KER distributions for

gauche and *anti* $C_3H_7I^+$ (Fig. 2b) are conspicuously different and do not appear to be the superposition of two components also suggests that photoexcitation does not induce the interconversion of the two $C_3H_7I^+$ conformations, but that they move along different reaction paths. We can also exclude a photodissociation reaction mechanism that involves internal conversion to the ground state followed by dissociation. Such a mechanism would not be expected to lead to the conformation-specific differences we have observed in our data. This is because internal conversion to the ground state would yield $C_3H_7I^+$ species with a large amount of internal energy, and thus able to rapidly interconvert between the two different conformational states. These considerations, taken together, suggest that the reactions we have probed occur rapidly and anisotropically in an excited state that is repulsive, or the repulsive region of which is being probed in the present experiment.

To explain our observations, we consider the possible products that may be formed in our system. Simple C–I bond cleavage of 1- $C_3H_7I^+$ would generate 1- $C_3H_7^+$ and I, but 1- $C_3H_7^+$ is not a stable gas-phase species¹⁸. However, the 2-propyl cation (2- $C_3H_7^+$) and protonated cyclopropane (cyclo- $C_3H_7^+$) are stable species that are generated during the photodissociation of 1- $C_3H_7I^+$ (refs 19, 20). Consideration of the energies involved in the photodissociation process suggest that the iodine atom will be generated as one of the two possible ground-state spin–orbit doublets, $^2P_{3/2}$ or $^2P_{1/2}$. Plausible product combinations are therefore (1) 2- $C_3H_7^+$ + I ($^2P_{3/2}$), (2) 2- $C_3H_7^+$ + I ($^2P_{1/2}$), (3) cyclo- $C_3H_7^+$ + I ($^2P_{3/2}$), and (4) cyclo- $C_3H_7^+$ + I ($^2P_{1/2}$). The fact that the KER distributions in Fig. 2b do not appear as a superposition of two or more components indicates that the photoexcited *gauche* and *anti* 1- $C_3H_7I^+$ each dissociate to give only one of four possible product combinations. The estimated reaction enthalpies for the corresponding reactions are listed in Table 1. Our estimated dissociation threshold energies of 1.3 eV for *gauche*-1- $C_3H_7I^+$ and 1.6 eV for *anti*-1- $C_3H_7I^+$ suggest that the dissociation of these isomers involves the respective product channels (2) and (4), as these are associated with reaction enthalpies of 1.40 and 1.72 eV at 0 K, respectively (Table 1). That is, thermochemical analysis suggests that dissociation of the *gauche* isomer produces 2- $C_3H_7^+$ while the *anti* form generates the less-stable cyclo- $C_3H_7^+$ ion.

The potential energy diagram along the two reaction paths of 1- $C_3H_7I^+$ in the first excited electronic state ($n \leftarrow \sigma$ (C–I) character), obtained from *ab initio* calculations at the single excitation configuration interaction²¹ (CIS) level, is shown in Fig. 3. In accord with our earlier considerations, the calculated excited state is repulsive with respect to the C–I bond. The calculations show that as *gauche*-1- $C_3H_7I^+$ moves along the reaction path, the C–I bond is lengthened. About halfway along the reaction path, the hydrogen atom on C(2) that occupies the *anti* position with respect to the iodine atom

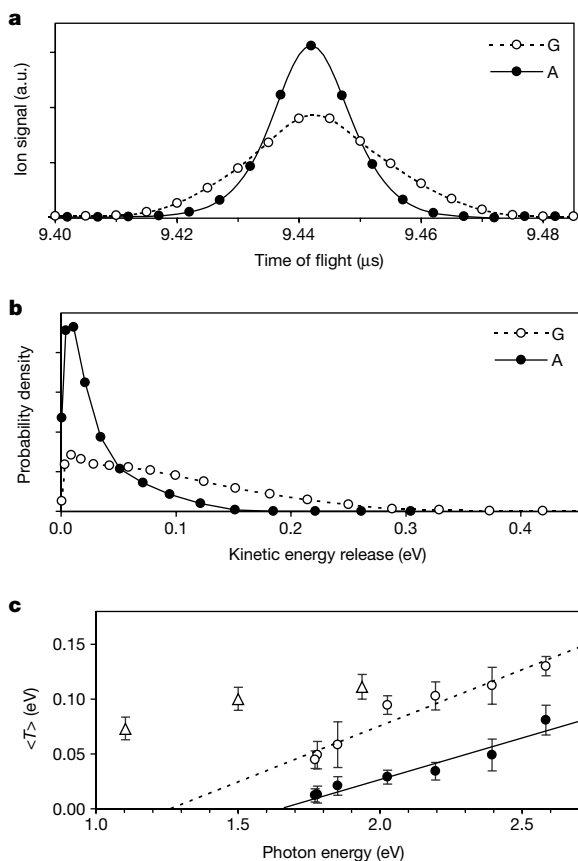


Figure 2 Time-of-flight profiles and kinetic energy releases. **a**, Time-of-flight profiles of $C_3H_7^+$ generated by photodissociation of the *gauche* (G; open circles) and *anti* (A; filled circles) isomers of 1- $C_3H_7I^+$ with 54.7° polarization of the photodissociation laser at 607 nm. Averages over 2,500 laser shots. **b**, Kinetic energy release (KER) distributions determined from **a**, *gauche* (open circles) and *anti* (filled circles) isomers. **c**, Average KER, $\langle T \rangle$, versus photon energy in the 480–700 nm range, for *gauche* (open circles) and *anti* (filled circles) isomers. Each point represents an average over ten measurements (± 2 s.d.), which, in turn, are averages over 250 laser shots. Values of $\langle T \rangle$ from the photoionization measurement of ref. 16 are shown as open triangles. a.u., arbitrary units.

Table 1 Enthalpies of formation and reaction at 0 K

System	$\Delta H_{f,0K}^0$ (eV)*	$\Delta H_{r,0K}^0$, <i>gauche</i> (eV)†	$\Delta H_{r,0K}^0$, <i>anti</i> (eV)†
Reactants			
1- $C_3H_7I^+$ (<i>gauche</i>)	9.170 \pm 0.040		
1- $C_3H_7I^+$ (<i>anti</i>)	9.186 \pm 0.040		
Products			
2- $C_3H_7^+$ + I ($^2P_{3/2}$)	9.627 \pm 0.039	0.457 \pm 0.056	0.442 \pm 0.056
2- $C_3H_7^+$ + I ($^2P_{1/2}$)	10.570 \pm 0.039	1.400 \pm 0.056	1.385 \pm 0.056
cyclo- $C_3H_7^+$ + I ($^2P_{3/2}$)	9.958 \pm 0.041	0.788 \pm 0.056	0.772 \pm 0.056
cyclo- $C_3H_7^+$ + I ($^2P_{1/2}$)	10.901 \pm 0.041	1.730 \pm 0.056	1.715 \pm 0.056

For products, the enthalpy of formation at 0 K is the sum of the enthalpies for the two products. Data for the reactants and 2- $C_3H_7^+$ (8.517 eV) are evaluated using thermochemical data²². Enthalpy of formation at 0 K of cyclo- $C_3H_7^+$, 8.847 eV, is evaluated using the *ab initio* results at the G2 level. The energy difference between the two fragment ions, 0.331 eV, is close to the *ab initio* result, 0.313 eV, at the MP4/6-311G** level (ref. 20). Using the enthalpy of formation of cyclo- $C_3H_7^+$ obtained from proton affinity measurement²³, 8.864 eV, the experimental difference becomes 0.347 eV, which is in agreement with the G2 result. Enthalpies of formation at 0 K of I ($^2P_{3/2}$) and I ($^2P_{1/2}$) are²⁴ 1.1107 and 2.0534 eV, respectively.

* Enthalpy of formation at 0 K.

† Enthalpy of reaction at 0 K.

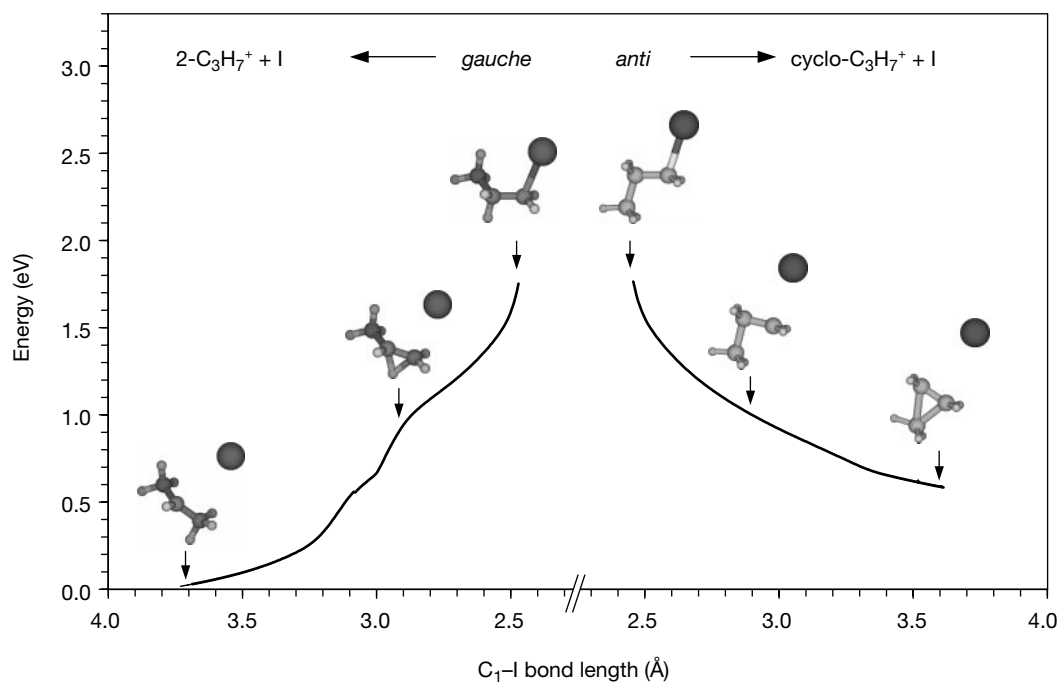


Figure 3 Potential energy along the reaction path. Changes in potential energies along the minimum energy paths for the dissociations of *gauche* and *anti* isomers in the first excited state were obtained by *ab initio* calculation at the CIS level. The 6-31G** basis set was used for carbons and hydrogens, while the LanL2DZ basis set was used for iodine. Equilibrium geometries of the *gauche* and *anti* isomers in the ground electronic state at the Hartree-Fock level were taken as the initial geometries of the photoexcited 1-C₃H₇I⁺.

moves to C(1), and finally 2-C₃H₇⁺ is formed. In the case of *anti*-1-C₃H₇I⁺, movement of the methyl group occupying the *anti* position to the iodine atom accompanies the C–I bond breaking, and finally cyclo-C₃H₇⁺ is formed. In both cases, an intramolecular S_N2-type rearrangement accompanies the C–I bond breaking. The substantial changes in the C₃H₇⁺ structure during C–I bond lengthening indicates that the reaction path is curved on the multidimensional potential energy surface. This might explain why the fraction of the available energy that is released as kinetic energy is rather small, compared to typical repulsive dissociation reactions (see, for example, refs 14, 15). The presence of shallow bound regions on the potential energy surface of the reaction would provide an alternative explanation for the small fraction of available energy being released as kinetic energy. But such an explanation would be in disagreement with the *ab initio* results. Considering all the evidence presented, the most plausible explanation for our experimental observations is provided by assuming conformation-specific differences in the photodissociation mechanism of 1-C₃H₇I⁺. □

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Then, the energies and gradients in the first excited state corresponding to the above configurations were calculated by CIS. Finally, the minimum energy paths from these configurations were calculated by the steepest descent method. The energy of the products, 2-C₃H₇⁺ + I[•], is taken as the zero of the energy scale. Some representative geometries are also drawn.

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Competing interests statement

The authors declare that they have no competing financial interests.

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