

Supplementary material

Energy-dependent timescales in the dissociation of diiodothiophene dication

Iodine 4d photoelectron spectrum

The I 4d photoelectron spectrum, shown in Fig. 1, was analyzed by least-squares curve fitting using Voigt profiles. Voigt profile is defined as a convolution of a Gaussian (in this case describing instrumental broadening) and a Lorentzian (describing the lifetime broadening). The Gaussian and Lorentzian full widths at half maximum (FWHM), obtained from the fit, were 152 and 268 meV, respectively. The latter value is much larger than the expected lifetime width of less than 100 meV [1], for the reasons discussed below.

The fit resulted in the binding energies as $E_b(4d_{3/2}) = 58.59$ eV and $E_b(4d_{5/2}) = 56.86$ eV, with the spin-orbit splitting as 1.73 eV. These values can be compared with the ones by Karlsson *et al.* [1], who reported for the HI molecule, $E_b(4d_{3/2}) = 59.25$ eV and $E_b(4d_{5/2}) = 57.49$ eV and the s-o splitting 1.76 eV. Single Voigt profiles resulted in a poor fit to the data, therefore a vibrational progression of three profiles was used. The vibrational spacing of 213 meV was obtained as a common value in both the $4d_{5/2}$ and $4d_{3/2}$ profiles, which is close to the C=C bond stretching frequency. The likely C-I bond stretching excitations are of lower frequency and would be contained under a single Voigt profile, accounting for the additional broadening.

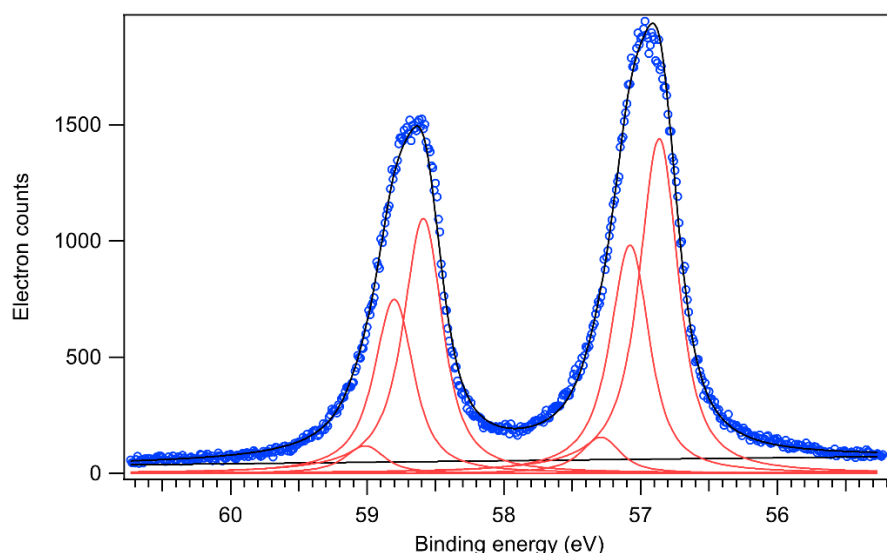


Figure 1. Iodine 4d photoelectron spectrum of 2,5-diiodothiophene, measured at $h\nu=85$ eV. Continuous lines show a least-squares curve fitting decomposition.

Stochastic charge-hopping molecular mechanics model

The initial planar geometry of the 2,5 diiodothiophene molecule is given in Table I. The initial distribution of the two positive charges is a representation of the Auger decay final state. The probability of creating a vacancy at a neutral atom was taken as proportional to its number of valence electrons, N_{val} , when randomly assigning the positive charges. The molecular bonds between atoms are represented by Morse potential energy curves in the form:

$$E_{pot,ij} = D_{ij} [1 - e^{-\alpha_{ij}(R_{ij}-R_e)}]^2$$

where the depth of the potential well was for the different bonds: $D_{CH}=411$ kJ/mol, $D_{CC}=418$ kJ/mol, $D_{CS}=272$ kJ/mol, $D_{CI}=172$ kJ/mol. Allocating positive charges to atoms i and j was taken to weaken the bond, with the modified well depth as

$$D_{ij}^* = D_{ij} \frac{N_{val,i} - Q_i + N_{val,j} - Q_j}{N_{val,i} + N_{val,j}}$$

The equilibrium bond lengths were obtained from the initial geometry (Table I). The width parameter

$$\alpha_{ij} = \frac{E_{v,ij}}{\hbar} \sqrt{\frac{\mu_{ij}}{2D_{ij}}}$$

where μ is the reduced mass of atoms i,j and the vibrational constants of the bond stretching were taken as: $E_{v,CH}=0.372$ eV, $E_{v,CC}=0.185$ eV, $E_{v,CS}=0.086$, $E_{v,Cl}=0.074$ eV.

Bending vibrations of bond angles θ_{ijk} were accounted for by a common torsional force constant $k_{bend}=0.025$ eV/rad in a harmonic potential

$$E_{bend,ijk} = \frac{1}{2} k_{bend} \Delta\theta_{ijk}^2$$

The same force constant was used in an optional planar force field term, in which case the angle θ was between the plane of the initial geometry and a bond ij , and the harmonic force was acting to resist turning the bonds from the plane. In addition, a nonbonding “hard repulsion sphere” potential was included preventing the approach of atoms that were not connected by bonds:

$$E_{rep,i}(R, R < R_{rep}) = \frac{1}{2} k_{rep} (R - R_{rep})^2,$$

with force constant $k_{rep}=2000$ N/m at distances $R < R_{rep}$, $R_{rep}=2$ Å.

Before integrating the equations of motion, individual atoms were assigned randomized initial velocities, resulting in the total kinetic energy of E_{int} , with the constraint that the translational velocity of the total system remains zero. The equations of motion were then integrated up to the time limit T_{max} that varied between 1.5 and 5 ps dependent on the internal energy E_{int} . During the integration, the positive unit charges were allowed to hop across the bonds. The probability of a successful hop was dependent on:

a) The distance between atoms. The over-the-barrier model [2] was used and, in the present case, the maximum allowed charge per atom was $+e$. The critical distance of positive charge hop from the positively charged atom i to neutral atom j is:

$$R_{crit,ij} = \frac{e^2}{\pi\epsilon_0 I E_j}$$

R_{crit} values for hops to neutral atoms are given in Table I.

b) The Mulliken charges Q_{Mul} of the atoms in the molecule in doubly charged state, in the neutral ground geometry. The values used in the model we obtained by GAMESS using the SPK-DZP basis set and are listed in Table I. In a potential charge hop, the charge was relocated across a bond between a charged atom i and neutral atom j , regardless of its initial location. The the charge $+e$ was randomly localized the on either i or j , with the weight dependent on the Mulliken charge of j . The algorithm was tuned to give the time-averaged charge distribution on atom i as $Q_i = +e(Q_{Mul,i} + Q_{tot}/N)$, where Q_{tot} is the total charge of the molecule and N is the number of atoms.

c) A charge hopping frequency parameter that determined, how many hop attempts were made at each iteration step. The parameter was chosen to give the average hopping frequency of $\approx 10^{15} s^{-1}$.

d) The hydrogen atoms were excluded from receiving charge initially or during the hops. This limit was imposed for practical reasons, as the experiment did not cover pathways with proton emission.

After the time T_{\max} , integration was continued until 100 ps, but now treating each fragment as a point charge. This post-propagation was to ensure the correct values of the final momenta of particles.

Table I. Atom-specific parameters used in the point-charge model.

Atom	N_{val}	$x(\text{\AA})$	$y(\text{\AA})$	$Q_{\text{Mul}}(e)$	$R_{\text{crit}}(\text{\AA})$	IE(eV)
I	7	-3.256	0.519	-0.15	5.51	10.45
I	7	3.256	0.519	-0.15	5.51	10.45
S	6	0.000	1.256	0.52	5.59	10.30
C	4	-0.712	-1.212	-0.18	4.44	12.97
C	4	0.712	-1.212	-0.18	4.44	12.97
C	4	-1.230	0.065	-0.24	4.44	12.97
C	4	1.230	0.065	-0.24	4.44	12.97
H	1	-1.315	-2.112	0.31	4.23	13.60
H	1	1.315	-2.112	0.31	4.23	13.60

Example molecular dynamics trajectory

An example of a simulated trajectory that corresponds to the three-body reaction

$\text{RI}_2^{++} \rightarrow \text{RI}^+ + \text{I}^+ \rightarrow \text{R}^+ + \text{I}^+ + \text{I}$, is shown in the attached animation, "Movie_Eint7_Ropens_planar.mp4". The animation depicts the charge hopping as red coloring of the atoms with positive charge. The particular trajectory was generated with the initial internal energy of 7 eV and it shows first a separation of charged iodine fragment, then the ring opening and a separation of the neutral iodine in about 1.5 ps after the first event.

References

1. Karlsson, L, *et al.* J. Phys. B: At. Mol. Opt. Phys. **22**, 3001–3009 (1989).
2. Boll, R., *et al.* Struct. Dyn. **3**, 043207 (2016).