Electronic Supplementary Material (ESI) for Faraday Discussions.
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Supplementary Material for
On the Importance of Initial Conditions in Excited-State Dynamics

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1. Correlation Energy Correction

The correction is based on the difference of bond dissociation energies (BDE) between low level (in this case FOMO-CASCI) and high-level method (we used CCSD(T)). For a molecule A-B, BDE can be obtained as energy differences between the energies of the fragments and the molecule

$$BDE = E_A + E_B - E_{AB}\,. \tag{1}$$

We add an empirical potential term into the FOMO-CASCI Hamiltonian that depends solely on the distance of the dissociating atom from the central atom. The empirical potential is tuned so that the FOMO-CASCI + CEC reproduces the experimental or high-level theory BDEs and is applied to both ground and all excited states. The potential is a switching function, for which we have chosen a simple polynomial

$$E_{corr} = a(r - r_0)^2 + b(r - r_0)^4\,. \tag{2}$$

This function resembles the dissociation curve with a sigmoid-like shape. It is applied in finite interval $\langle r_0; r_{dis} \rangle$, where it has a smooth first derivative and is constant outside of the interval. It follows that

$$E_{corr} = \begin{cases} 0 \ \forall\, r \in \langle 0; r_0 \rangle \\ a(r - r_0)^2 + b(r - r_0)^4 \ \forall\, r \in \langle r_0; r_{dis} \rangle \\ \Delta E \ \ \forall\, r \in \langle r_{dis}; \infty \rangle. \end{cases} \tag{3}$$

We obtained the empirical constants by calculating the dissociation curve at the

FOMO-CASCI level. Parameters r_0 and r_{disoc} are chosen arbitrarily but the latter should correspond to a geometry where the dissociation is essentially completed. The empirical constants a and b are obtained via the following conditions:

1. The potential at r_{dis} must equal to the difference between the experimental (or high-level theory) and theoretically computed bond dissociation energies ΔE:

$$E_{corr}(r_{dis}) = \Delta E \tag{4}$$

2. The potential has zero first derivative at $r = r_{\mathrm{dis}}$:

$$\frac{dE_{corr}(r_{dis})}{dr} = 0 = 2a(r - r_0) + 4b(r - r_0)^3 \tag{5}$$

Note that the corresponding conditions for the other side of the potential (*i.e.*, for $r = r_0$) are fulfilled by construction. For our simulations of the CF_2Cl_2 molecule, the energy difference ΔE was set as a difference between the CCSD(T) and FOMO-CASCI values for dissociation energy, 1.13 eV. Other parameters are: $r_0 = 1.9$ Å, $r_{dis} = 3.4$ Å, $a = 10.3366 \cdot 10^{-3}\, eV \cdot Å^{-2}$, $b = 6.4323 \cdot 10^{-4} eV \cdot Å^{-4}$.

2. Experimental spectrum of the CF_2Cl_2 together with reflection principle estimate of the spectrum based on reflection principle with QT based density.

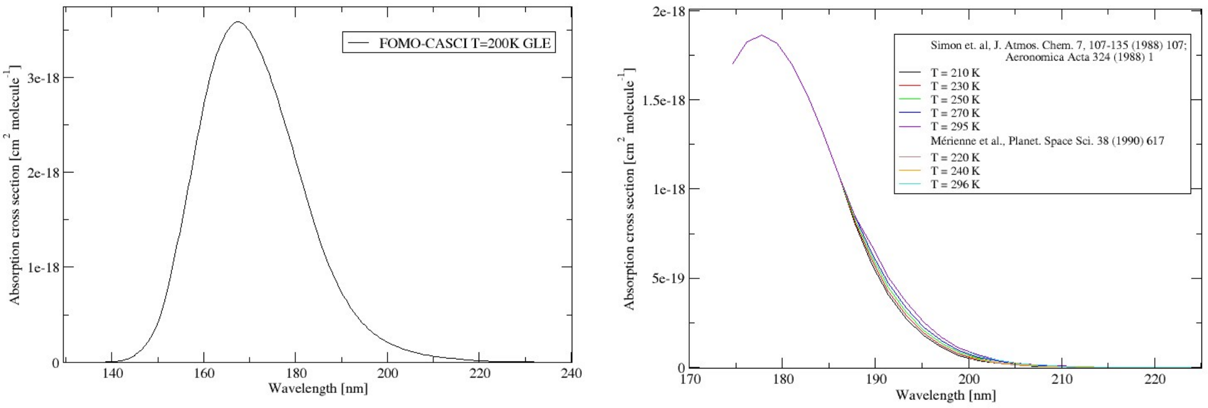

Figure S1. The distribution of the excitation energies of the CF_2Cl_2 molecule along the ground state GLE trajectory at the B3LYP/6-31+g* level. We also show the experimental UV absorption spectrum cross section with temperature dependence.

3. Potential energy scan for CF_2Cl_2 molecule.

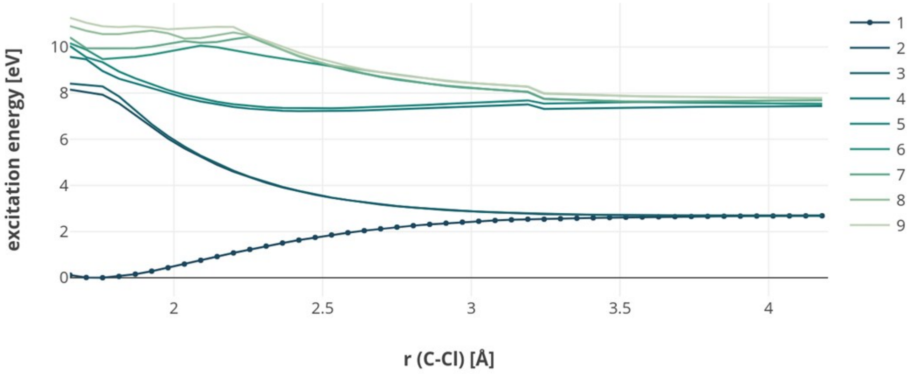

Figure S2. The first 9 singlet state energy curves for one Cl atom dissociation. The rigid scan along the C-Cl bond was performed at the FOMO-CASCI[12/8] 6-31+g*.

4. Distribution of chlorine velocities along C-Cl bond.

The CF_2Cl_2 dissociation takes place on a steep potential energy surface and we do not need worry too much of the proper sampling of the momenta in the present case. Still, there are some interesting issues. In the one dimensional case, the molecular dynamics with Lagrange multipliers should impose a condition of zero initial velocity. This is not entirely consistent with the sampling based on the filtering of the Wigner function according to equation (22). It is therefore interesting to look at the distribution of the relative velocities along the C-Cl bond in the multidimensional case. Figure S3 shows such a comparison for the points generated by the filtering of the Wigner function against the data obtained from the molecular dynamics with Lagrange multiplier constraint. We observe that the two sets of data are rather similar.

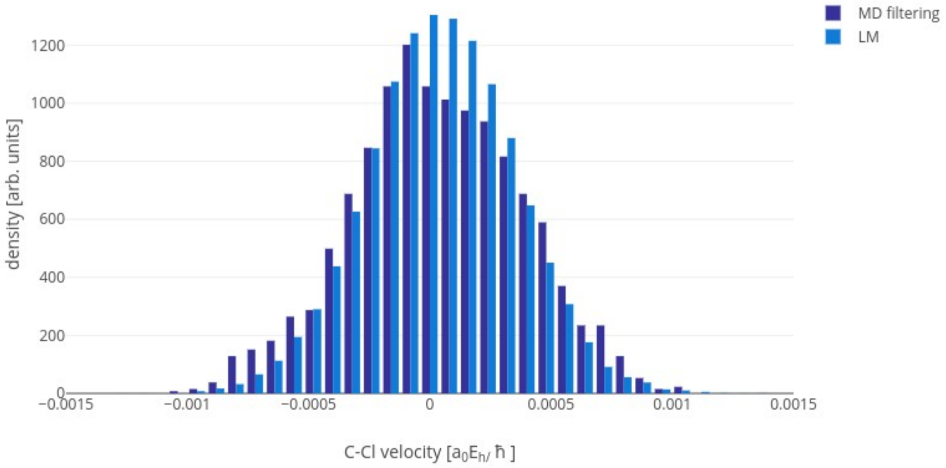

Figure S3. Distribution of Cl velocities projected onto C-Cl bonds derived from either (*i*) unconstrained MD simulations for selected points fulfilling the resonance condition (*MD filtering*), or (*ii*) for MD simulation with Lagrange multipliers (*LM*).

5. GLE input matrices adaptation

In order to damp the high artificial frequencies coming from the numerical noise from Lagrange multipliers, we had to adapt the GLE input matrices for quantum thermostat. In Generalized Langevin Equation[1], two additional forces are acting on a particle: random forces and drift forces. Technically, the drift matrix Γ is written in a form

$$\Gamma = \begin{pmatrix} \gamma_{pp} & \gamma_{ps}^{T} \\ \gamma_{sp} & \Gamma_{ss} \end{pmatrix},$$

coupling set of auxiliary momenta, **s**, to a system momentum, p. This matrix corresponds to a memory kernel[2]

$$K(t) = 2\gamma_{pp}\delta(t) - \gamma_{ps}^{T} e^{-|t|\gamma_{ss}} \gamma_{sp}$$

Fourier transformation of this kernel $K(\omega)$ shows the effect of the drift matrix on different normal modes in the system. We can additively expand this kernel by so called δ-like memory kernels defined by matrix form[3]

$$\Gamma_{\delta} = \begin{pmatrix} 0 & \sqrt{\frac{\gamma}{2\pi}} & \sqrt{\frac{\gamma}{2\pi}} \\ -\sqrt{\frac{\gamma}{2\pi}} & \Delta\omega & \omega_0 \\ -\sqrt{\frac{\gamma}{2\pi}} & -\omega_0 & \Delta\omega \end{pmatrix}$$

γ, $\Delta\omega$ and ω_0 are input parameters, set so that the GLE thermostat acts only in desired range of frequencies, peaking at ω_0, having width of $\Delta\omega$ and strength γ. This matrix itself corresponds to kernel $K(\omega) = 2\gamma \frac{\Delta\omega + {\omega_0}^2 + \omega^2 \quad 1 \qquad \Delta\omega}{\left(\omega + {\omega_0}^2\right) + \Delta\omega^{2\pi}\left(\omega - {\omega_0}^2\right) + \Delta\omega^2}$, which for small $\Delta\omega$ corresponds to δ-like shape: $K(\omega) \approx \gamma \frac{\Delta\omega}{\left(\omega - {\omega_0}^2\right) + \Delta\omega^2}$. Let us imagine that we already have a Γ matrix, which we need to combine with Γ_δ. We construct a new matrix in following way

$$\Gamma_{ex} = \begin{pmatrix} \gamma_{pp} & \gamma_{ps}^T & \sqrt{\frac{\gamma}{2\pi}} & \sqrt{\frac{\gamma}{2\pi}} \\ \gamma_{sp} & \Gamma_{ss} & 0 & 0 \\ -\sqrt{\frac{\gamma}{2\pi}} & 0 & \Delta\omega & \omega_0 \\ -\sqrt{\frac{\gamma}{2\pi}} & 0 & -\omega_0 & \Delta\omega \end{pmatrix}$$

One can verify that this will not affect the original kernel in any way except additional term in form of the delta thermostat. We can do this multiple times, always setting the cross elements to zero. Also we expand the second input (covariance) matrix, responsible for random forces acting on the particle, with zero values. This implies that only drift will be applied to the target region of frequencies, effectively setting their temperature to 0 K. In our work, we damped the region of 20 000–50 000 cm^{-1}, which we achieved by combining three kernels centered at three different frequencies $\omega_0 =$ 30000 cm^{-1}, 50000 cm^{-1} and 80000 cm^{-1} with $\Delta\omega = 5000$ cm^{-1} and 1/γ = 0.001 a.u.

References

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