

Supporting Information for:

Time-Resolved Photodetachment Anisotropy:

Gas-Phase Rotational and Vibrational Dynamics of

the Fluorescein Anion.

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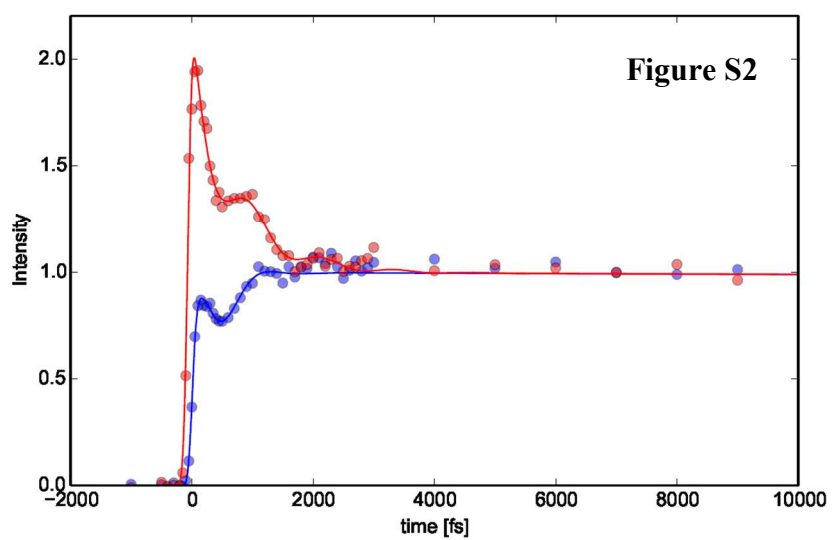
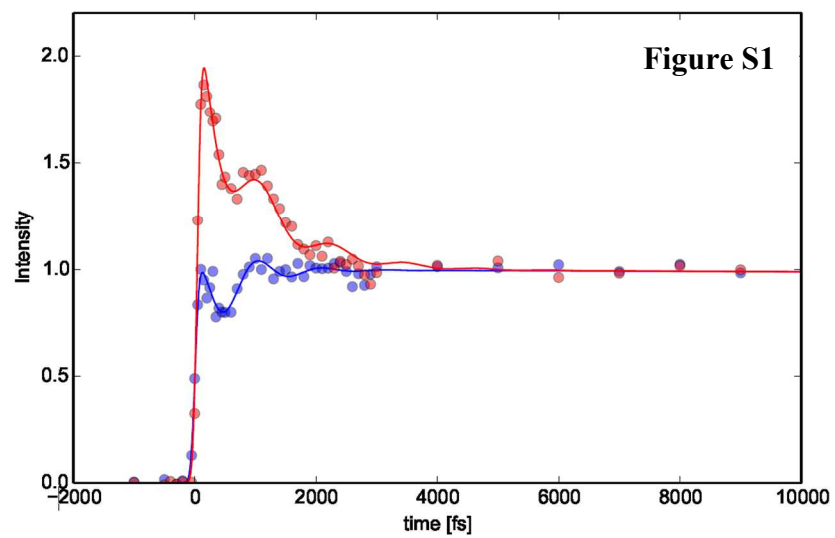
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Temperature dependence of time-resolved photodetachment

Figures S1 and S2 shows the dynamics of the total photoelectron signal (normalized to unity at long times) of parallel (red) and perpendicular (blue) relative pump-probe polarizations. In Figure S1, the fluorescein anion is produced “cold” which is close to room temperature (~ 300 K), while in Figure S2, fluorescein is produced “hot” by ejecting the anion from the trap with a higher voltage such that some collisional activation occurs. Comparison between the two graphs clearly shows that the rotational dephasing dynamics for the cold fluorescein are slower than for the hot fluorescein as one might expect because less rotational levels contribute to the wavepacket.

We have fitted these data sets, much in the same way as we fitted the dynamics shown in the manuscript. The parallel and perpendicular data were fitted to a single exponential decay and rise, respectively, modulated by a damped cosine oscillation and convoluted with the 130 fs instrument response function. The oscillation frequency, phase and amplitude was set fixed between all 4 data sets, while its damping was free to change between the hot and cold TR-PA dynamics. Similarly, the single exponential was fixed between parallel and perpendicular data sets but allowed to vary between hot and cold. The only free parameters were t_0 , which changed slightly from day to day and the amplitude of the decays. The fitting results reveal that the rotational dephasing times are $\tau_r(\text{hot}) = 730$ fs and $\tau_r(\text{cold}) = 960$ fs. This clearly shows that, when the ion is cooled, the dynamics are slowed, in accord with expectations.



Computational details and additional results

Details of the calculations were given in the main manuscript. The ground electronic state in its equilibrium geometry is ~ 300 meV lower in energy than when in the S_1 equilibrium geometry. In our experiment, the trapped ions have a maximum temperature of ~ 500 K (although are typically colder), which corresponds to several hundred of meV of internal energy, meaning that the initial photoexcitation ensemble will contain molecules with a distribution of ϕ values. Assuming a simple two-level Boltzmann model convoluted with the ω B97XD calculated oscillator strengths, we predict that, for every molecule photoexcited at the distorted S_1 geometry, there will be ~ 1600 photoexcited at the S_0 equilibrium geometry. Thus, photoexcitation will almost exclusively involve fluorescein molecules with $\phi \sim 90^\circ$.

At the S_0 equilibrium geometry, photoexcitation to S_1 involves a $\pi^*_{\text{LUMO}} \leftarrow \pi_{\text{HOMO}}$ transition, in which both orbitals are predominantly localized on the xanthene group. The $(\pi^*)_{\text{LUMO}}$ does not interact with any π^* orbitals on the benzoic acid group due to incompatible symmetry with $\phi \sim 90^\circ$. The calculated photoexcitation energy of 3.0 eV (2.8 eV with CAM-B3LYP) disagrees with the gas-phase absorption maximum of 2.4 eV (520 nm), and may reflect inadequacies in the level of electronic structure theory. Unfortunately, the size of this system means it is not computationally feasible to increase the level of theory at this time. The principal motion in geometrical relaxation of the nascent S_1 state involves rotation of the benzoic acid group with respect to the xanthene group, reaching a minimum energy geometry with $\phi \sim 53^\circ$. During this geometrical rotation, the occupied π^* orbital on the xanthene group can now mix with π^* orbitals on the benzoic acid group and induce charge-transfer character.

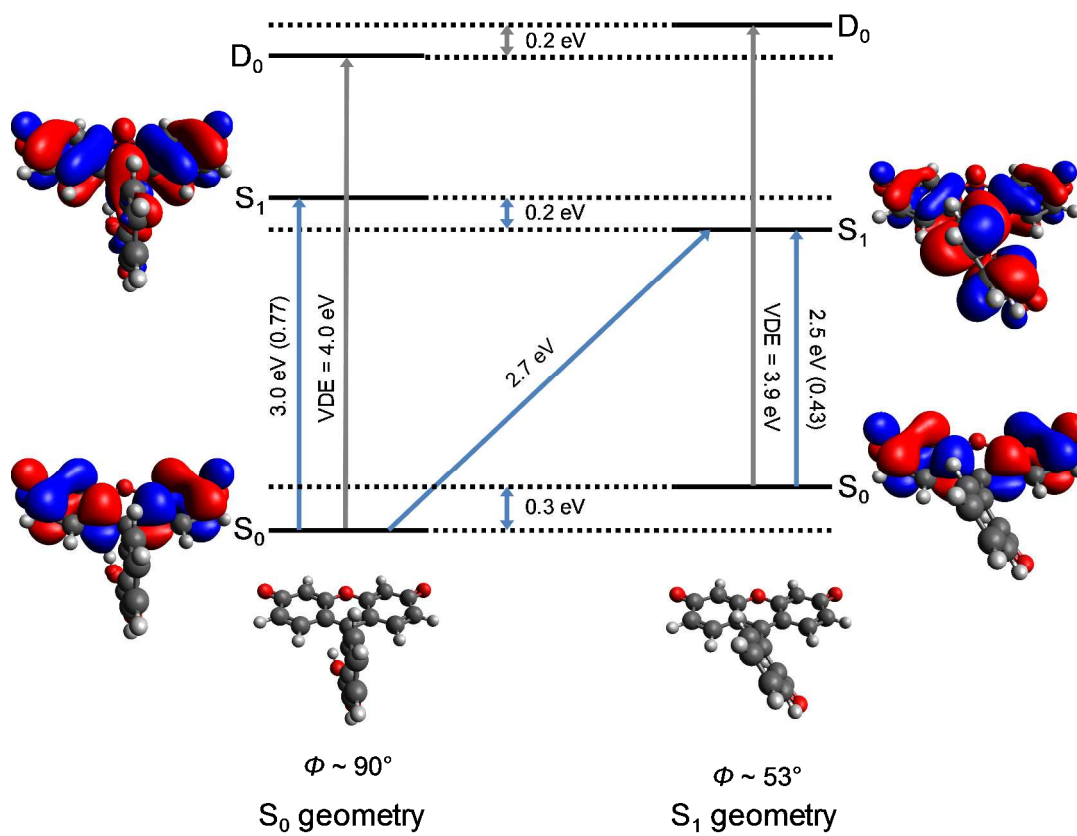
Calculation of the S_0 vibrational frequencies indicates six modes with frequencies less than 100 cm^{-1} . Of these modes, the 22 cm^{-1} vibration (corresponding to a vibrational period of ~ 0.7

ps) is the only mode whose major motion is internal rotation about the ϕ co-ordinate. The minor motion is a slight twisting of the xanthene plane. We have also calculated the excited state (S_1) frequencies and again, six modes with frequencies less than 100 cm^{-1} are recovered. Note that all frequencies calculated were real. The mode corresponding to the ϕ torsion co-ordinate was found to be the lowest in energy at 35.6 cm^{-1} . This is in excellent agreement with measurements (32 cm^{-1}) and we assign the observed oscillation primarily to a torsional motion about ϕ .

The calculations indicate that formation of the S_2 excited state, which involves a xanthene group to benzoic group charge-transfer transition in either the S_0 or S_1 geometries, has excitation energies (oscillator strengths in parentheses) of 3.4 eV ($f \sim 0.01$) and 3.3 eV ($f \sim 0.23$), respectively. That is, although the S_2 state may be (vertically) situated in energy close to the probe photon, these calculations support that the S_2 state is optically dark.

Finally, the rotational constants for $[\text{fl-H}]^-$ in the S_0 geometry were calculated to be $I_z = 3.616 \times 10^{-44}\text{ kg m}^2$, $I_y = 3.670 \times 10^{-44}\text{ kg m}^2$, and $I_x = 5.918 \times 10^{-44}\text{ kg m}^2$.

Figure S3



S₀ optimized geometry (ωB97XD//6-31++G(d,p))

O,0.0045118678,-0.0045191135,-0.0193821195
C,1.3682701984,-0.0035402971,-0.0167257453
C,1.9965097926,-0.0373329684,1.1954002772
H,1.4154579707,-0.0657813916,2.1103423849
C,-0.722295819,0.0550580301,-1.1727662453
C,-2.0815619825,0.0763585611,-1.0569216284
H,-2.5475251347,0.0482487998,-0.0784517431
C,-0.0479037102,0.0914727384,-2.4403863044
C,1.3450160794,0.0825796784,-2.4583387956
C,2.0803032707,0.0330249936,-1.2617684787
C,-0.8806030977,0.1337358615,-3.609273277
H,-0.3981083598,0.1506036768,-4.5830168702
C,-2.2339209623,0.1543283781,-3.5202499006
H,-2.8565038942,0.1849749052,-4.4093491929
C,3.5136979232,0.0515898579,-1.1785140862
H,4.0816831986,0.0934642687,-2.1049030879
C,4.1610043657,0.0191227985,0.0148029093
H,5.2454510757,0.0332195819,0.0672103979
C,3.4420329505,-0.0277328469,1.2931578225
O,4.0475351514,-0.0525602581,2.3802708741
C,-2.9327463584,0.1321813201,-2.2288840724
O,-4.1744426428,0.1608222375,-2.1611410485
C,2.074418944,0.1498547321,-3.7603776057
C,2.3523183823,1.4221850531,-4.271298853
H,2.032351017,2.2881437142,-3.699904382
C,3.0166028888,1.5814809231,-5.481134167
H,3.2254253551,2.5795173403,-5.8546396371
C,3.4065668319,0.4589983991,-6.2100109278
H,3.9212909385,0.5701504023,-7.1592980812
C,3.1269112661,-0.8086210587,-5.7184105289
H,3.4038904106,-1.6967863207,-6.2758047492
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C,2.2350650626,-2.4194779455,-4.0882280489
O,2.2424024236,-3.3059112497,-4.9134916565
O,2.0515780025,-2.717180974,-2.8003432686
H,2.0885688604,-1.9380720733,-2.2193896069

S₁ optimized geometry (ωB97XD//6-31++G(d,p))

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H,1.3622834958,0.5373414593,2.140366357
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C,-2.0254669154,-0.0841243009,-1.0325053981
H,-2.4952453722,0.0159373645,-0.0604130448
C,0.0253841748,-0.1339048612,-2.3938041349
C,1.455870444,-0.0317598091,-2.4393504326
C,2.1262233418,0.1223696111,-1.1857948124
C,-0.8057041289,-0.2625780494,-3.5552231092
H,-0.3243467722,-0.3118440407,-4.5261951939
C,-2.1621792672,-0.3160039274,-3.4803189149
H,-2.7702726857,-0.4186821128,-4.3734421596
C,3.5552591181,0.1020131446,-1.0458653938
H,4.1482456249,-0.0731439807,-1.9377888152
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O,3.9795782003,0.6865855972,2.4800575096
C,-2.8694212543,-0.242860411,-2.1986694339
O,-4.1108681383,-0.2988437072,-2.1295475428
C,2.2032509329,0.0473827392,-3.6972174632
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C,3.6209286834,1.4597292417,-5.1072277497
H,4.1889908863,2.3771232993,-5.2320778468
C,3.4872545696,0.5527704371,-6.1767312655
H,3.9604578199,0.7535757318,-7.132739067
C,2.7573716169,-0.604507825,-5.990562043
H,2.6626027664,-1.336796293,-6.7857685435
C,2.1354132884,-0.9028838598,-4.7624584682
C,1.5620441271,-2.2729589143,-4.6656636843
O,1.3537890513,-2.9765521196,-5.6363937343
O,1.3195846508,-2.7818267949,-3.4386994157
H,1.519839711,-2.1331361072,-2.7489367773