

Supporting Information

The rotational diffusion time constants can be approximately calculated assuming the molecule as an asymmetric ellipsoid with three semi-axes $a \neq b \neq c$ and a molecular volume of $V = \frac{4}{3}\pi abc$ dissolved in acetonitrile- d_3 (viscosity $\eta = 0.345 \text{ cP}^1$) at room temperature ($T = 298.15 \text{ K}$). The molecular volume of 3-HF can be estimated as the sum of all its atom increments² to $V = 200 \text{ \AA}^3$. Since it is a planar molecule in the investigated tautomer state, the shortest semi-axis c can be taken as the van der Waals radius of carbon 1.7 \AA .³ The molecular structure of 3-HF suggests an axis ratio of $a:b = 1:0.55$ (orientations of a, b, c chosen like principal axes of inertia, see Figure S1) giving $a = 7.1 \text{ \AA}$ and $b = 3.9 \text{ \AA}$. Rotational diffusion constants can be either estimated using slip boundary conditions,⁴⁻⁶ meaning that for the solute molecule to move, solvent molecules must be pushed out of the way, or using stick boundary condition,⁷⁻⁹ meaning neighboring solvent molecules move in a correlated manner with the solute. The resulting rotational diffusion time constants using slip boundary conditions range from 8 to 17 ps (the friction coefficients were estimated as the mean values of the friction coefficients for axis ratios 1:0.6:0.2 and 1:0.5:0.2),⁶ whilst they vary between 21 and 45 ps for the same model system in stick condition.

The S_0 - S_1 transition dipole moment lies in the molecular plane and forms an angle of 14° with the longest molecular axis according to our quantum chemical calculations. The moment is approximately pointing from the center of mass towards the phenyl moiety. Assuming that the tautomer excited state absorption transition dipole is also in this plane only three time constant contribute to $r(t)$ due to vanishing direction cosines. With an experimentally determined angle of $\approx 25^\circ$ between pumped S_0 - S_1 and probed tautomer excited state absorption transition dipole moments the angle of the latter formed with the longest molecular axes a is either $\beta = -11^\circ$ or 39° . Given the orientation of pumped and probed transition dipole moments the amplitudes of the three exponentials contributing to $r(t)$ can be calculated. The resulting amplitudes and time constants are listed in Table S1 for slip and stick boundary conditions. Despite the under/overestimated rotational diffusion time constants these results suggest that the two time constants contributing significantly to $r(t)$ only slightly differ, consistent with the experimental observations.

time constants / ps	slip condition			stick condition		
	15	17	8	45	39	21
$\beta = 39^\circ$	0.15	0.15	-0.01	0.15	0.14	0.01
$\beta = -11^\circ$	-0.05	0.23	0.11	-0.05	0.34	$\ll 0.01$

Table S1 Amplitudes and time constants of the exponentials contributing to the anisotropy transient $r(t)$ estimated for 3-HF in ACN- d_3 with slip and stick boundary condition. β denotes the possible orientations of the tautomer excited state absorption transition dipole relative to the longest molecular axis a (cf. Figure S1). The sum of each amplitude-triplet corresponds, except for rounding errors, to $r(0) = 0.29$, arising from an angle θ of about 25° between pumped and probed transition dipole moments.

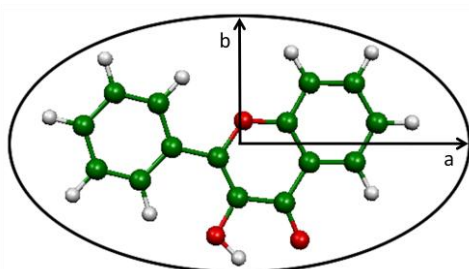


Figure S1 Molecular structure of 3-HF with ellipsoid used for the estimate of rotational diffusion time constants. The semi-axes are $a = 7.1 \text{ \AA}$, $b = 3.9 \text{ \AA}$ and $c = 1.7 \text{ \AA}$ (axis c perpendicular to the plane of the molecule).

The slip boundary condition has been found to give good agreement for small molecules in noninteracting solvents,^{7, 10, 11} which holds also true for 3-HF in acetonitrile- d_3 since the observed time constant of 22 ps is relatively well predicted in slip boundary condition. The rotational diffusion constant resulting from a sphere with the same molecular volume is $\tau = \frac{kT}{\eta V} = 17 \text{ ps}$ (stick boundary conditions) with k the Boltzmann constant.

References

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