Supporting Information: Characterizing Mode Anharmonicity and Huang–Rhys Factors Using Models of Femtosecond Coherence Spectra

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S1 Derivation of Morse Oscillator ω-Only FCS Expression

The Morse oscillator potential energy function can be written as

$$\hat{V}(x) = D_e \left(1 - e^{-a(x-x_e)}\right)^2 , \tag{S1}$$

where x_e is the equilibrium bond distance, D_e is the well depth, and a is inversely related to the width of the potential well.

For a mass μ, the expression for the Morse oscillator FCS includes a useful dimensionless quantity $\lambda = \frac{\sqrt{2\mu D_e}}{a\hbar}$, the displacement, $\Delta = x_e' - x_e$, the effective natural frequency of the oscillator, $\omega_0^{\text{eff}} = \sqrt{\frac{2D_e a^2}{\mu}}$, the effective classical turning point of the $n = 0$ eigenfunction, $x_0^{\text{eff}} = \sqrt{\frac{\hbar}{\mu\omega_0^{\text{eff}}}}$, and, finally, the normalized displacement $\tilde{\Delta} = \Delta/x_0^{\text{eff}}$. With these definitions, one can derive that $a\Delta = \tilde{\Delta}\lambda^{-\frac{1}{2}}$.

The Franck–Condon factors for the case of identical but displaced Morse potentials are given by[S1]

$$\mathrm{FC}_{n,m}^{\mathrm{MO}} = N_{m,\lambda} N_{n,\lambda} \zeta^{\lambda-n-\frac{1}{2}} \left(\frac{2}{1+\zeta}\right)^{\xi} \sum_{k,k'=0}^{n,m} \left[\frac{(-1)^{k+k'}}{k!k'!} \begin{pmatrix} \xi + n \\ m - k' \end{pmatrix} \begin{pmatrix} \xi + m \\ n - k \end{pmatrix} \zeta^k \left(\frac{2}{1+\zeta}\right)^{k+k'} \Gamma(\eta) \right] , \tag{S2}$$

where n and m index the excited-state and ground-state vibrational eigenfunctions, respectively, and where we have defined variables

$$\zeta = e^{-\tilde{\Delta}/\sqrt{\lambda}} \tag{S3a}$$

$$\eta = 2\lambda - n - m + k + k' - 1 \tag{S3b}$$

$$\xi = 2\lambda - m - n - 1, \tag{S3c}$$

where we use binomial coefficients given by

$$\begin{pmatrix} a \\ b \end{pmatrix} = \frac{\Gamma(a+1)}{\Gamma(b+1)\Gamma(a-b+1)}, \tag{S4}$$

and where an auxiliary function is

$$N_{n,\lambda} = \left(\sum_{j=0}^{n} \frac{\Gamma(2\lambda - 2n - 1 + j)}{j!} \right)^{-1/2} . \tag{S5}$$

The energy levels are given by,[S2]

$$E_j = \hbar\omega_0^{\text{eff}} \left(\left(j + \frac{1}{2} \right) - \frac{1}{2\lambda} \left(j + \frac{1}{2} \right)^2 \right) . \tag{S6}$$

The parameter λ enumerates the number of bound energy levels.

Previously[S3] we calculated the wavepacket oscillations at every ω_2 value,

$$\begin{aligned} M(\omega;\omega_2) = \sum_{n',n,m}^{n,\lambda,\lambda} & \mathrm{FC}^{\mathrm{MO}}_{n,m} \mathrm{FC}^{\mathrm{MO}}_{n',m} \mathrm{FC}^{\mathrm{MO}}_{n,0} \mathrm{FC}^{\mathrm{MO}}_{n',0} \left[\frac{1}{\omega - \omega_{n',m} + i\gamma/2} - \frac{1}{\omega - \omega_{n,m} - i\gamma/2} \right] \\ & \times \left(\frac{1}{(\omega_2 - \omega_{n',n})^2 - \gamma_2} \right), \end{aligned} \tag{S7}$$

where γ_2 sets the width of each peak as a function of ω_2 and each $\mathrm{FC}^{\mathrm{MO}}_{i,j}$ is given by Eqn. (S2). To create the ω-only Morse oscillator FCS expression for $\omega_2 = \omega_0^{\text{msrd}}$, we set $n' = 1$ and $n = 0$, which is given by

$$M(\omega;\omega_0^{\text{msrd}}) = \sum_{m}^{\lambda} A_{\text{MO}}(\lambda, \tilde{\Delta}, m) \left[\frac{1}{\omega - \omega_{1,m} + i\gamma/2} - \frac{1}{\omega - \omega_{0,m} - i\gamma/2} \right], \tag{S8}$$

where $A_{\text{MO}}(\lambda, \tilde{\Delta}, m)$ represents the dependency of the product of Franck–Condon coefficients on fundamental microscopic parameters λ and $\tilde{\Delta}$. The Franck–Condon factors can be expanded for n and n' and then simplified. We use algebra and various Gamma-function identities to find that

$$\mathrm{FC}^{\mathrm{MO}}_{0,0} = \zeta^{\lambda-\frac{1}{2}} \left(\frac{2}{1+\zeta}\right)^{2\lambda-1} \tag{S9}$$

and

$$\mathrm{FC}^{\mathrm{MO}}_{1,0} = \sqrt{\frac{(2\lambda-2)(2\lambda-3)}{2\lambda-1}}\zeta^{\lambda-\frac{3}{2}} \left(\frac{2}{1+\zeta}\right)^{2\lambda-2} \left(\frac{1-\zeta}{1+\zeta}\right), \tag{S10}$$

to produce

$$\mathrm{FC}^{\mathrm{MO}}_{0,0}\mathrm{FC}^{\mathrm{MO}}_{1,0} = \zeta^{2\lambda-2} \left(\frac{2}{1+\zeta}\right)^{4\lambda-3} \sqrt{\frac{(2\lambda-2)(2\lambda-3)}{2\lambda-1}} \left(\frac{1-\zeta}{1+\zeta}\right). \tag{S11}$$

This expression contains no Gamma functions.

Similarly, we can combine the third and fourth coefficients, $\mathrm{FC}^{\mathrm{MO}}_{0,m}$ and $\mathrm{FC}^{\mathrm{MO}}_{1,m}$, to yield

$$\begin{aligned}\mathrm{FC}^{\mathrm{MO}}_{0,m}\mathrm{FC}^{\mathrm{MO}}_{1,m} = & \frac{1}{(2\lambda-2)\sqrt{2\lambda-3}\Gamma(2\lambda-3)} N^2_{m,\lambda}\zeta^{2\lambda-2}\left(\frac{2}{1+\zeta}\right)^{4\lambda-2m-3} \\ & \times \sum_{k'=0}^{m}\Big[S(k')\,(2\lambda-m+k'-2)\Big] \\ & \times \sum_{k''=0}^{m}\left[S(k'')\left(2\lambda-2-\frac{2\zeta}{1+\zeta}(2\lambda-m+k''-2)\right)\right],\end{aligned} \tag{S12}$$

where we have defined the auxiliary counting function

$$S(j) = \frac{(-1)^j}{j!}\begin{pmatrix}2\lambda-m-1\\ m-j\end{pmatrix}\left(\frac{2}{1+\zeta}\right)^j \Gamma\left(2\lambda-m+j-2\right). \tag{S13}$$

Although the pair of summations in Eqn. (S12) cannot be simplified further, they can be computed synchronously in a single `for` loop for increased speed.

Finally, we can produce the total product of the four Franck–Condon factors as

$$\begin{aligned} A_{\mathrm{MO}}(\lambda,\tilde{\Delta},m) = N_{m,\lambda}^{2}\zeta^{4\lambda-4}\left(\frac{2}{1+\zeta}\right)^{8\lambda-2m-6} & \frac{1}{\sqrt{(2\lambda-1)(2\lambda-2)}\Gamma(2\lambda-3)}\left(\frac{1-\zeta}{1+\zeta}\right) \\ \times \sum_{k'=0}^{m} & \left[S(k')\,(2\lambda-m+k'-2)\right] \\ \times \sum_{k''=0}^{m} & \left[S(k'')\left(2\lambda-2-\frac{2\zeta}{1+\zeta}(2\lambda-m+k''-2)\right)\right]. \end{aligned} \tag{S14}$$

In this approximation, we derive that the measured oscillation frequency, ω_0^{msrd} can be used to compute

$$\omega_0^{\mathrm{eff}} = \frac{\lambda\omega_0^{\mathrm{msrd}}}{\lambda-1}. \tag{S15}$$

S2 Franck–Condon Coefficients for Displaced Harmonic Oscillators of Unequal Curvatures

Iachello and Ibrahim[S1] present the Franck–Condon factors for the displaced harmonic oscillator model when the ground-state and excited-state potentials have distinct curvatures, α and α', respectively. Here we re-write their expression in our notation as,

$$
\begin{aligned}
\mathrm{FC}^{\mathrm{HO}}_{n,m}(\tilde{\Delta},\epsilon) = e^{-\frac{\epsilon^2\tilde{\Delta}^2}{2(1+\epsilon^2)}} \left(\frac{\epsilon\cdot m!n!}{2^{m+n-1}}\right)^{1/2} \left(\frac{1}{1+\epsilon^2}\right)^{(m+n+1)/2} & \times \sum_{l=0}^{\min[m,n]} \frac{1}{l!}\left(-\frac{1+\epsilon^2}{\epsilon^2\tilde{\Delta}^2}\right)^{l} \\
\times \frac{1}{4}\sum_{j=l}^{m}\sum_{j'=l}^{n} \Bigg[\Big((-1)^{(m-j)}+1\Big)\Big((-1)^{(n-j')}+1\Big)(-1)^{j'} & \\
\times \frac{(\epsilon^2-1)^{(m-j)/2}(1-\epsilon^2)^{(n-j')/2}}{(1+\epsilon^2)^{(j+j')/2}} \frac{\epsilon^{2j'+j}(2\tilde{\Delta})^{j+j'}}{(\frac{m-j}{2})!(\frac{n-j'}{2})!(j-l)!(j'-l)!}\Bigg]. & \qquad \text{(S16)}
\end{aligned}
$$

where $\alpha_{\pm}^2 = \alpha^2 \pm \alpha'^2$, we have replaced the 'modulo 2' notation of Ref. [S1] with flip-flop factors in the sums over j and j', and where we use dimensionless parameters $\epsilon = \alpha/\alpha'$ and $\tilde{\Delta} = \alpha'\Delta$.

In Fig. (S1) we present simulated FCS spectra for the conditions of ϵ=1.1, ω_{0e}=9, γ/ω_{0e}=1, ω_{eg}=400, and $\tilde{\Delta} \in \{0.1, 0.5, 1.0, 2.0\}$. In all cases, the FCS computed for $\epsilon \neq 1$ yields more asymmetry of the two main peaks than for the corresponding $\epsilon = 1$ FCS.

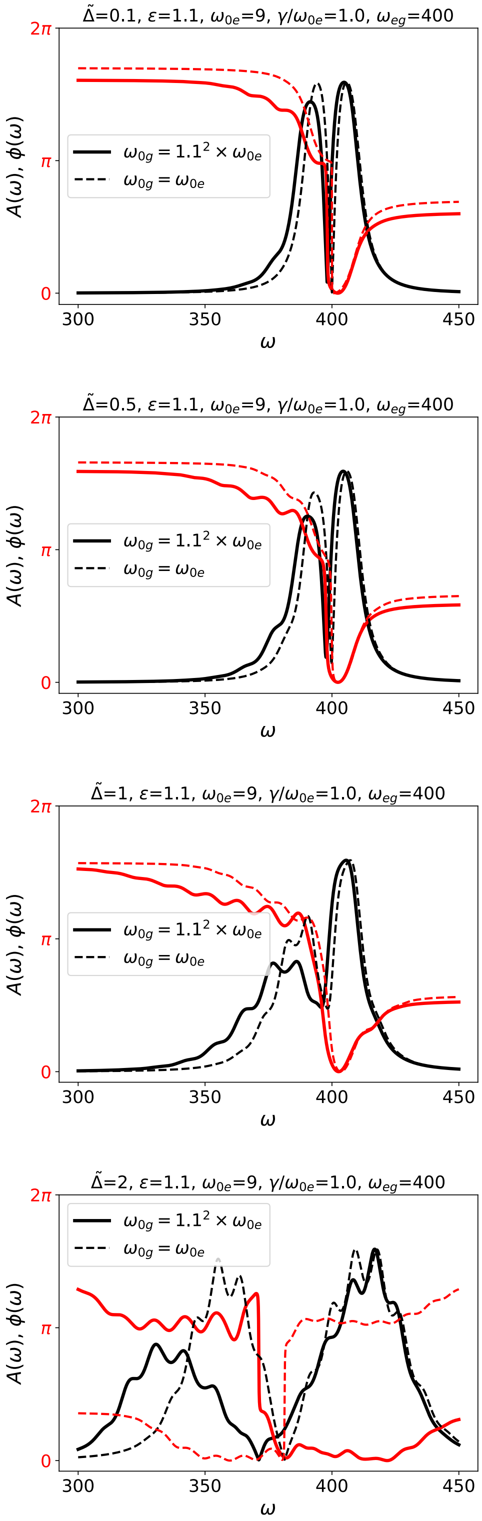

Figure S1: Simulation results for the DHO model in which the ground-state and excited-state potentials have distinct curvatures.

S3 Detailed Measurement & Fit Results

In Tables (S1) and (S3), we present the quantitative fit results—with standard deviations arising from confidence intervals of the fits—for, respectively, three modes of rhodamine 101 and cresyl violet.

Table S1: Fit results of rhodamine 101. Frequency values are in units of THz.

	harmonic model			**anharmonic model**			
$\boldsymbol{\omega_0/(2\pi)}$	$\boldsymbol{\mathcal{S}}$	$\boldsymbol{\gamma/\omega_0}$	$\boldsymbol{\omega_{eg}/(2\pi)}$	$\boldsymbol{\mathcal{S}_{\mathrm{eff}}}$	$\boldsymbol{\lambda}_{\mathrm{min}}$	$\boldsymbol{\gamma/\omega_0}$	$\boldsymbol{\omega_{eg}/(2\pi)}$
6.3	0.45±0.09	2.72±0.25	515.0±0.5	1.80±0.10	11	2.26±0.02	523.7±0.0
7.0	0.41±0.07	2.97±0.19	515.0±0.4	1.56±0.01	11	2.31±0.02	522.3±0.1
12.4	0.93±0.02	0.94±0.06	534.0±0.2				

Table S2: Fit results of two fundamental modes of rhodamine 101 to unequal-curvature harmonic model. Frequency values are in units of THz.

	unequal-curvature harmonic model			
$\boldsymbol{\omega_0/(2\pi)}$	$\boldsymbol{\mathcal{S}}$	$\boldsymbol{\epsilon}$	$\boldsymbol{\gamma/\omega_0}$	$\boldsymbol{\omega_{eg}/(2\pi)}$
6.3	0.14±0.01	2.10±0.01	2.26±0.01	533.6±0.1
7.0	0.70±0.01	1.15±0.01	1.06±0.13	522.7±0.1

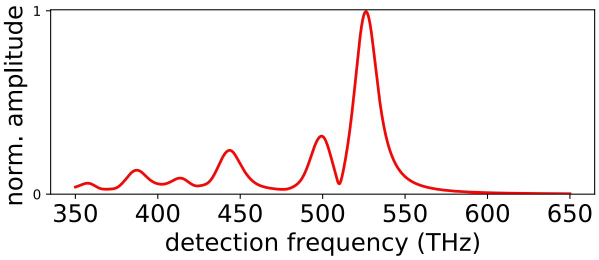

Figure S2: Results of extending the unequal-curvature harmonic model fit of the 6.3 THz mode to detection frequency values beyond those of the measurement to reveal peaks at lower frequencies arising from the extremely large ϵ value.

Table S3: Fit results of cresyl violet. Frequency values are in units of THz. The value of $\boldsymbol{\mathcal{S}}_{\text{eff}}$ for the 22.0 THz mode arises from a negative $\tilde{\Delta}$ value.

	harmonic model			**anharmonic model**			
$\boldsymbol{\omega_0/(2\pi)}$	$\boldsymbol{\mathcal{S}}$	$\boldsymbol{\gamma/\omega_0}$	$\boldsymbol{\omega_{eg}/(2\pi)}$	$\boldsymbol{\mathcal{S}_{\text{eff}}}$	$\boldsymbol{\lambda}_{\text{min}}$	$\boldsymbol{\gamma/\omega_0}$	$\boldsymbol{\omega_{eg}/(2\pi)}$
15.6	0.25±0.01	0.85±0.02	487.3±0.1	0.32±0.02	8	0.94±0.01	487.3±0.1
17.6	0.24±0.01	0.89±0.02	488.4±0.1	0.15±0.02	6	1.25±0.02	487.6±0.1
22.0	0.01±0.01	0.89±0.01	492.3±0.0	0.20±0.14	8	0.90±0.01	492.2±0.0

Table S4: Fit results of cresyl violet to unequal-curvature harmonic model. Frequency values are in units of THz. The error estimate of ∞ for the Huang–Rhys factor of the 22.0 THz mode results from a division by zero.

	unequal-curvature harmonic model			
$\boldsymbol{\omega_0/(2\pi)}$	$\boldsymbol{\mathcal{S}}$	$\boldsymbol{\epsilon}$	$\boldsymbol{\gamma/\omega_0}$	$\boldsymbol{\omega_{eg}/(2\pi)}$
15.6	0.27±0.01	0.98±0.01	0.82±0.02	486.6±0.2
17.6	0.22±0.02	1.09±0.01	0.87±0.02	491.9±0.3
22.0	0.01±∞	0.95±0.01	0.98±0.01	489.9±0.4

S4 Quantum-Chemical Computations of Rhodamine 101

We used density functional theory (DFT) for geometry optimizations and harmonic frequency calculations of the electronic ground state of rhodamine 101, and we performed time-dependent DFT (TDDFT) for S_1 excited-state geometries and vibrational frequencies using the same level of theory as the ground state. We performed calculations at both the M05-2X/6-311+G(d,p) and B3LYP/6-311+G(d,p) level of theory for comparison.[S4,S5] The applied polarizable continuum model (PCM) approximated a methanol solvent environment. We report the zwitterionic form of rhodamine 101 here, however structures protonated at the carboxylate yielded similar geometry changes. Franck–Condon vibronic simulations used the geometries and frequencies from the S_0 and S_1 rhodamine structures. By inspection of the computed geometries, see Fig. (S3), the significant geometric changes associated with the S_0–S_1 transition resulted in non-negligible Duschinsky mixing and ultimately unreliable vibronic results. Specifically, the o-benzoic acid side group tilts perpendicular relative to the xanthene core, with the carbonyl group of the benzoic acid also rotating slightly relative to the plane of the aromatic ring to which it is attached. We performed all quantum-chemical calculations using the Gaussian 16 suite.[S6]

Table S5: Optimized S_0 and S_1 geometries of rhodamine 101

	M05-2X						B3LYP					
	S_0			S_1			S_0			S_1		
	Cartesian Coordinates (Å)			Cartesian Coordinates (Å)			Cartesian Coordinates (Å)			Cartesian Coordinates (Å)		
Atom	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
O	-0.08185	-1.66038	-0.07268	-0.19764	-1.66456	-0.14481	0.00350	-1.67037	-0.04149	-0.17611	-1.65593	-0.06697
O	0.82227	3.95684	2.74885	2.13789	3.37917	2.28913	-0.03167	4.10491	2.81969	2.01422	3.50403	2.39893
O	0.14246	1.89113	2.19998	0.35575	2.01930	2.36162	-0.01256	1.93244	2.23345	0.26475	2.08829	2.41978
N	4.62854	-1.96748	-0.04959	4.50798	-2.12098	-0.09780	4.74823	-1.85974	-0.01367	4.55570	-2.13066	-0.11669
N	-4.80317	-1.73315	-0.01298	-4.92121	-1.57482	0.03807	-4.74283	-1.88470	-0.05462	-4.93212	-1.62104	0.02245
C	3.50776	-1.22637	-0.14459	3.42121	-1.33058	-0.20205	3.59940	-1.14029	-0.10535	3.45207	-1.33090	-0.20433
C	-3.64418	-1.03946	-0.08883	-3.74954	-0.90657	-0.05503	-3.59359	-1.15394	-0.12723	-3.74837	-0.93739	-0.06893
C	2.23409	-1.84259	-0.09019	2.11097	-1.90108	-0.14997	2.33509	-1.78922	-0.05107	2.14448	-1.89990	-0.11552
C	-2.40312	-1.71806	-0.03357	-2.51330	-1.62475	-0.03808	-2.32744	-1.79506	-0.04082	-2.50777	-1.64296	-0.01478
C	3.60696	0.20134	-0.31058	3.56934	0.08611	-0.36385	3.65876	0.29301	-0.26082	3.59702	0.08473	-0.38472
C	-3.66898	0.39413	-0.22096	-3.73265	0.52398	-0.15679	-3.65618	0.27848	-0.28316	-3.74375	0.49196	-0.19760
C	1.11897	-1.03393	-0.15022	1.02931	-1.05872	-0.20549	1.19335	-1.00801	-0.11647	1.05068	-1.04895	-0.16218
C	-1.24745	-0.96745	-0.11966	-1.34394	-0.91683	-0.15648	-1.18753	-1.00913	-0.11240	-1.33138	-0.91792	-0.12095

Continued on next page

Atom	M05-2X						B3LYP					
	S_0			S_1			S_0			S_1		
	Cartesian Coordinates (Å)			Cartesian Coordinates (Å)			Cartesian Coordinates (Å)			Cartesian Coordinates (Å)		
	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
C	2.11110	-3.33871	0.02533	1.93710	-3.39034	-0.03839	2.25207	-3.29269	0.06838	1.96868	-3.39126	0.02212
C	-2.32279	-3.21563	0.12709	-2.48058	-3.12322	0.11057	-2.21469	-3.29439	0.12680	-2.46757	-3.14356	0.15404
C	4.59223	-3.42705	0.03641	4.41201	-3.57617	-0.00917	4.75129	-3.32612	0.06922	4.45996	-3.58774	0.00353
C	-4.79517	-3.19190	-0.08389	-4.95549	-3.03210	-0.03430	-4.70483	-3.35057	-0.07554	-4.96046	-3.08362	-0.00740
C	5.97090	-1.39160	0.06107	5.86957	-1.59194	-0.01431	6.08093	-1.24278	0.06335	5.92181	-1.59559	-0.09518
C	-6.10769	-1.08416	-0.13212	-6.20469	-0.88232	-0.04085	-6.06643	-1.27427	-0.22737	-6.22045	-0.93994	-0.12174
C	1.18131	0.37236	-0.27576	1.13654	0.35178	-0.32313	1.21573	0.40591	-0.24363	1.15537	0.35915	-0.29762
C	-1.23636	0.43725	-0.24420	-1.28636	0.49779	-0.27398	-1.21333	0.40161	-0.24741	-1.28482	0.49527	-0.25791
C	3.33761	-3.99181	-0.59934	3.14109	-4.09141	-0.65325	3.49832	-3.93612	-0.53929	3.16431	-4.12662	-0.58153
C	-3.62498	-3.75646	0.70024	-3.78078	-3.63080	0.71670	-3.50512	-3.88076	0.69622	-3.77395	-3.67228	0.74258
C	4.97385	0.81798	-0.41743	4.95279	0.66270	-0.46073	5.00733	0.96321	-0.35827	4.97843	0.67269	-0.52051
C	-4.99170	1.11089	-0.31223	-5.02943	1.28797	-0.17331	-4.99790	0.96325	-0.41863	-5.04764	1.25195	-0.26065
C	5.93409	0.06141	0.49173	5.89331	-0.14187	0.42787	6.02653	0.21384	0.49910	5.97358	-0.13132	0.31604
C	-6.06786	0.32658	0.42326	-6.11246	0.50867	0.55794	-6.09422	0.16089	0.27763	-6.17083	0.47927	0.42717
C	-0.00681	1.11303	-0.28861	-0.03444	1.15119	-0.36306	0.00160	1.12014	-0.27395	-0.02654	1.16364	-0.32912
C	2.47295	0.95232	-0.35516	2.45419	0.87650	-0.41197	2.49764	1.01386	-0.31001	2.47257	0.87756	-0.41982
C	-2.49513	1.08411	-0.27889	-2.53329	1.17756	-0.24587	-2.49540	1.00332	-0.32460	-2.54102	1.15840	-0.27274
C	0.02974	2.58139	-0.52422	0.05226	2.62068	-0.50933	-0.00085	2.59460	-0.52418	0.05337	2.63643	-0.49070
C	0.25579	3.51528	0.49066	0.61726	3.43748	0.48079	-0.01169	3.55755	0.50065	0.56649	3.48545	0.51430
C	-0.14550	3.00842	-1.84176	-0.39980	3.20188	-1.69849	0.00694	3.00817	-1.86410	-0.35923	3.19986	-1.71027
C	0.30456	4.86787	0.15909	0.72803	4.80781	0.24948	-0.01449	4.91226	0.14758	0.65462	4.85963	0.25993
C	-0.09952	4.36035	-2.15520	-0.31019	4.57193	-1.90556	0.00410	4.36050	-2.19542	-0.28575	4.57126	-1.93849
C	0.42591	3.08345	1.94762	1.08223	2.88665	1.82822	-0.01945	3.16579	1.98445	0.98955	2.97263	1.89608
C	0.12580	5.29429	-1.14984	0.25761	5.37960	-0.92577	-0.00682	5.31902	-1.18285	0.22296	5.40776	-0.94521
H	2.03202	-3.62940	1.07655	1.84186	-3.67174	1.01478	2.16375	-3.58163	1.12329	1.86820	-3.65461	1.08336
H	1.20065	-3.67195	-0.46884	1.01584	-3.68915	-0.53363	1.35101	-3.65619	-0.42749	1.04048	-3.70099	-0.45947
H	-2.12313	-3.67934	-0.84276	-2.32692	-3.57950	-0.87191	-1.99361	-3.75784	-0.84276	-2.28420	-3.61255	-0.82147
H	-1.48428	-3.46677	0.77485	-1.62821	-3.40651	0.72545	-1.36969	-3.53044	0.77619	-1.62188	-3.41976	0.78601
H	4.65947	-3.72457	1.08733	4.45564	-3.86672	1.04643	4.85414	-3.62455	1.12089	4.54669	-3.86076	1.06562
H	5.48152	-3.79911	-0.47261	5.29399	-3.98479	-0.50250	5.64249	-3.68016	-0.45547	5.32596	-4.01546	-0.50841
H	-4.74114	-3.51019	-1.13042	-4.93239	-3.34214	-1.08580	-4.67860	-3.70535	-1.11548	-4.95894	-3.42755	-1.05335
H	-5.73971	-3.54324	0.32541	-5.90137	-3.35746	0.39195	-5.63606	-3.70893	0.36625	-5.90370	-3.40375	0.43753
H	6.47914	-1.49234	-0.90219	6.34460	-1.70238	-0.99494	6.56982	-1.33170	-0.91556	6.36385	-1.72954	-1.09295
H	6.51602	-1.99322	0.78928	6.41259	-2.22329	0.68971	6.66986	-1.83106	0.77240	6.50188	-2.21328	0.59619
H	-6.82168	-1.69315	0.41953	-6.93293	-1.48985	0.49252	-6.78149	-1.88922	0.32276	-6.96684	-1.53777	0.40444
H	-6.41921	-1.06917	-1.18192	-6.51788	-0.82340	-1.09004	-6.35480	-1.30972	-1.28743	-6.50609	-0.92539	-1.18500
H	3.35404	-3.79341	-1.67257	3.17451	-3.89791	-1.72690	3.50473	-3.78108	-1.62299	3.17226	-3.99648	-1.66840
H	3.31910	-5.07070	-0.45524	3.07945	-5.16806	-0.50543	3.50438	-5.01395	-0.36289	3.10201	-5.19808	-0.38015
H	-3.72532	-3.46294	1.74645	-3.84617	-3.34249	1.76703	-3.60846	-3.60953	1.75154	-3.84853	-3.40368	1.80090
H	-3.64269	-4.84391	0.65033	-3.83133	-4.71673	0.65955	-3.48953	-4.97143	0.63816	-3.81112	-4.76181	0.67703
H	5.33022	0.74833	-1.44938	5.30313	0.60982	-1.49616	5.34648	0.96119	-1.40224	5.28980	0.64960	-1.57339
H	4.92126	1.87381	-0.15741	4.93222	1.71282	-0.17398	4.92454	2.00887	-0.05463	4.96620	1.72209	-0.21869
H	-4.88650	2.11760	0.08963	-4.87603	2.27020	0.27167	-4.93522	1.97711	-0.01684	-4.91862	2.24023	0.18712
H	-5.27900	1.20784	-1.36295	-5.34080	1.44661	-1.21013	-5.24875	1.06202	-1.48242	-5.31754	1.41908	-1.31175
H	6.94019	0.47324	0.43440	6.91431	0.22952	0.35979	7.02261	0.65091	0.40042	6.99256	0.23693	0.17890
H	5.59585	0.13247	1.52704	5.57341	-0.06852	1.46868	5.74262	0.27592	1.55452	5.72951	-0.03661	1.37882
H	-5.84543	0.29032	1.49123	-5.87188	0.43038	1.61960	-5.94114	0.17081	1.36153	-6.00349	0.44610	1.50839
H	-7.04419	0.79092	0.29450	-7.07822	1.00212	0.46343	-7.07817	0.59211	0.08001	-7.13623	0.96111	0.25781
H	2.55109	2.02656	-0.45991	2.57535	1.94556	-0.52098	2.55178	2.09145	-0.40601	2.59472	1.94604	-0.54478
H	-2.51854	2.16274	-0.36367	-2.52897	2.25764	-0.29991	-2.55292	2.08014	-0.42812	-2.55006	2.23837	-0.34859

Continued on next page

	M05-2X						B3LYP					
	S_0			S_1			S_0			S_1		
	Cartesian Coordinates (Å)			Cartesian Coordinates (Å)			Cartesian Coordinates (Å)			Cartesian Coordinates (Å)		
Atom	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
H	-0.31461	2.27427	-2.61910	-0.81651	2.56324	-2.46734	0.01519	2.26158	-2.65075	-0.73120	2.54596	-2.49189
H	0.48292	5.57630	0.95518	1.18336	5.42209	1.01403	-0.02275	5.63864	0.95050	1.06429	5.49938	1.03273
H	-0.23819	4.68009	-3.17880	-0.67055	5.00319	-2.82961	0.01030	4.66012	-3.23732	-0.61386	4.98018	-2.88771
H	0.16135	6.34895	-1.38655	0.33721	6.44739	-1.07898	-0.00912	6.37483	-1.43003	0.28753	6.47769	-1.11036

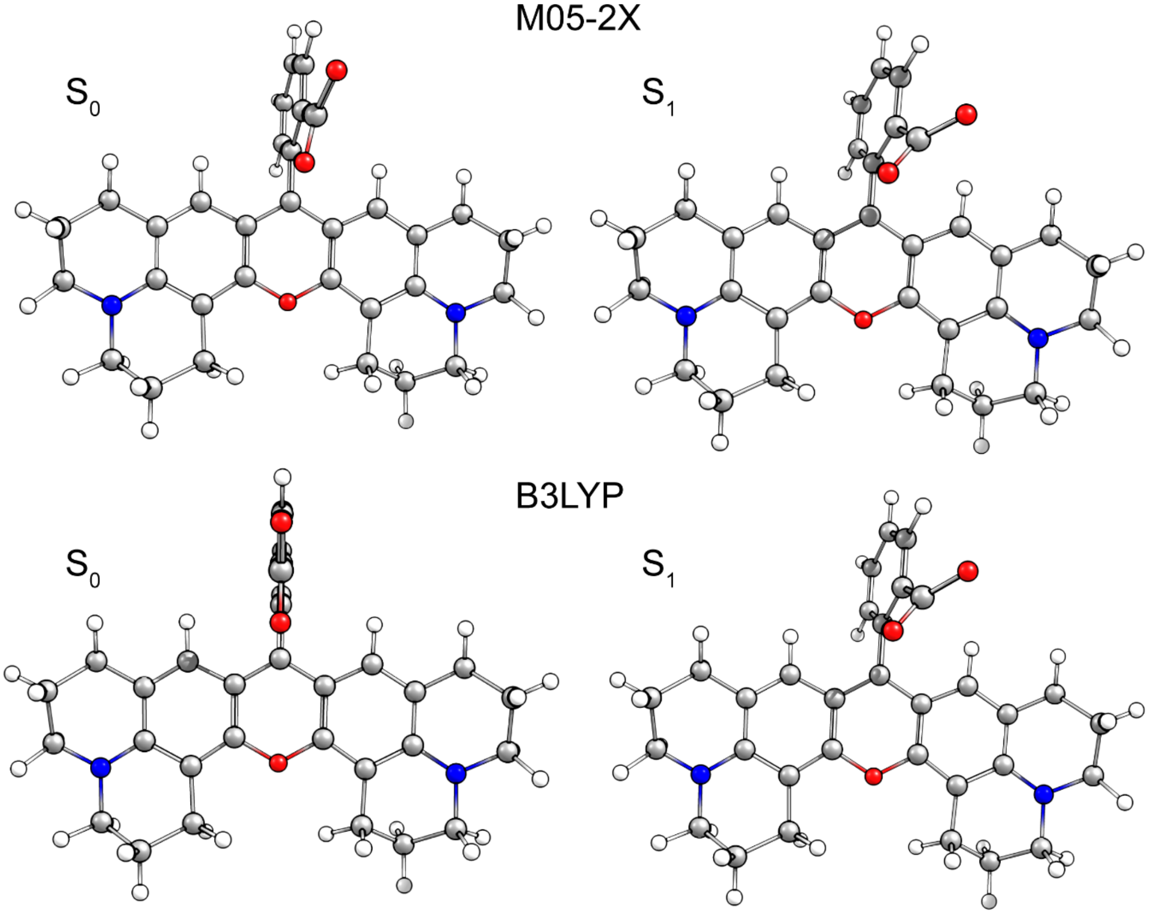

Figure S3: Optimized geometries of the zwitterionic form of rhodamine 101 calculated at the (top) M05-2X/6-311+G(d,p) and (bottom) B3LYP/6-311+G(d,p) level of theory.

S5 Quantum-Chemical Computations of Cresyl Violet

We performed quantum-chemical computations on cresyl violet similar to those described in Section (S4). We only used M05-2X/6-311++G(d,p), and the Franck–Condon vibronic computations finished successfully. Table (S6) displays the notable vibronic modes of cresyl violet arising from the quantum-chemical computations including eleven fundamentals and one overtone. These results, which used a polarizable continuum model (PCM) of methanol, are consistent with a more comprehensive computational study of cresyl violet in water.[S7] Huang–Rhys factors were extracted from vibronic simulations by Franck–Condon analysis of the intensity progression of each mode to determine their individual displacements and therefore Huang–Rhys factor.[S8,S9] We assigned the measured vibronic spectra to the calculated modes based on frequency. The calculated 35.7 and 42.2 THz modes were not assigned, as the measurements did not exhibit any reproducible vibronic bands at nearby frequencies.

Table S6: Huang–Rhys values ($\mathcal{S}$) of computed vibronic modes of cresyl violet and measured frequencies.

mode	**class**[a]	**frequency (THz)**	**measured frequency (THz)**	$\boldsymbol{\mathcal{S}}_{\mathbf{calc}}$
$\nu_{0,9}$	f	7.8	7.2	0.068
$\nu_{0,12}$	f	10.3	10.2	0.076
$\nu_{0,19}$	f	14.3	14.6	0.045
$\nu_{0,21}$	f	14.9	15.6	0.065
$\nu_{0,23}$	f	16.1	17.0	0.034
$\nu_{0,27}$	f	17.9	17.6	0.281
$\nu_{0,32}$	f	20.5	20.0	0.045
$\nu_{0,38}$	f	25.3	24.4	0.034
$\nu_{0,27}$	o	35.7		0.281
$\nu_{0,63}$	f	42.2		0.036
$\nu_{0,64}$	f	42.6	45.2	0.058
$\nu_{0,72}$	f	47.5	49.0	0.065

[a] f: fundamental, o: overtone

Table S7: Optimized S_0 and S_1 geometries of cresyl violet

Atom	S_0			S_1		
	Cartesian Coordinates (Å)			Cartesian Coordinates (Å)		
	X	Y	Z	X	Y	Z
C	−1.773 283	−0.812 503	−0.000 008	1.767 091	−0.819 125	0.000 127
C	−2.829 865	−1.756 089	−0.000 232	2.843 494	−1.753 425	0.000 147
C	−4.127 616	−1.346 585	−0.000 147	4.142 321	−1.346 439	0.000 112
C	−4.452 253	0.044 582	0.000 143	4.457 986	0.047 569	0.000 054
C	−3.421 723	0.999 955	0.000 105	3.407 902	1.000 579	0.000 052
C	−2.122 947	0.558 709	−0.000 090	2.114 557	0.566 867	0.000 099
O	−1.127 749	1.481 730	−0.000 318	1.130 861	1.511 491	0.000 142
C	0.155 967	1.092 052	−0.000 126	−0.163 535	1.079 316	0.000 064
C	0.456 137	−0.307 593	−0.000 106	−0.456 807	−0.308 332	0.000 062
N	−0.491 624	−1.213 301	−0.000 141	0.496 288	−1.262 132	0.000 128
C	1.858 337	−0.694 211	0.000 069	−1.847 854	−0.681 899	−0.000 033
C	1.119 772	2.064 371	−0.000 395	−1.133 355	2.049 145	0.000 027
C	2.474 734	1.699 667	0.000 214	−2.499 187	1.698 312	−0.000 020
C	2.862 464	0.292 876	0.000 000	−2.870 263	0.301 706	−0.000 097
C	3.544 650	−2.416 495	0.000 172	−3.524 666	−2.427 755	−0.000 204
C	2.216 135	−2.047 956	0.000 197	−2.197 764	−2.041 394	−0.000 081
C	4.209 457	−0.103 914	−0.000 083	−4.208 818	−0.116 707	−0.000 244
C	4.546 394	−1.440 739	−0.000 041	−4.533 031	−1.461 942	−0.000 293
N	3.396 900	2.653 515	0.000 381	−3.414 115	2.670 998	−0.000 020
N	−5.739 963	0.423 697	0.000 833	5.731 544	0.447 555	−0.000 070
H	3.126 264	3.623 006	0.000 060	−3.130 271	3.636 663	0.000 113
H	4.381 033	2.456 397	−0.000 093	−4.401 135	2.486 771	0.000 131
H	−6.479 561	−0.256 168	−0.001 057	6.486 671	−0.218 655	0.000 193
H	−5.996 972	1.394 771	−0.000 725	5.972 671	1.425 047	0.000 155
H	−4.931 801	−2.068 752	−0.000 421	4.947 484	−2.067 726	0.000 125
H	−2.570 600	−2.805 374	−0.000 362	2.586 246	−2.803 246	0.000 187
H	−3.635 763	2.058 996	−0.000 219	3.621 756	2.060 323	0.000 026
H	0.830 463	3.105 082	−0.000 534	−0.838 017	3.089 273	0.000 061
H	5.010 075	0.621 038	−0.000 129	−5.017 895	0.599 559	−0.000 338
H	5.586 990	−1.731 176	−0.000 229	−5.571 624	−1.760 031	−0.000 406
H	3.812 410	−3.463 643	0.000 379	−3.780 442	−3.477 747	−0.000 243
H	1.434 100	−2.792 150	0.000 328	−1.406 783	−2.775 953	−0.000 024

S6 Second Harmonic Generation - Frequency Resolved Optical Gating

We measured the pulse duration to be 8.8 fs by fitting the second-harmonic generation frequency-resolved optical gating signal (SHG-FROG) shown in Fig. (S4) to a Gaussian function.

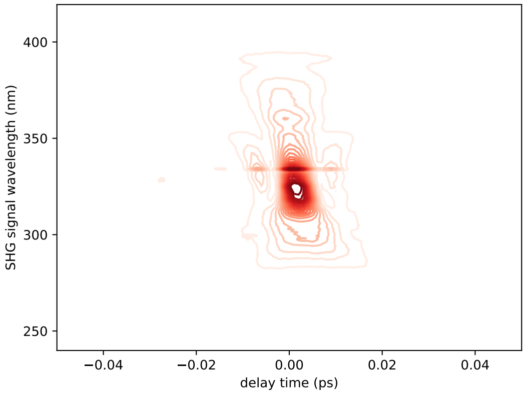

Figure S4: SHG-FROG yields a pulse duration of 8.8 fs.

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