

Supporting Information

Ultrafast Dynamics of Hydrogen Bond Breaking and Making in the Excited State of Fluoren-9-one: Time-Resolved Visible Pump –IR Probe Spectroscopic Study

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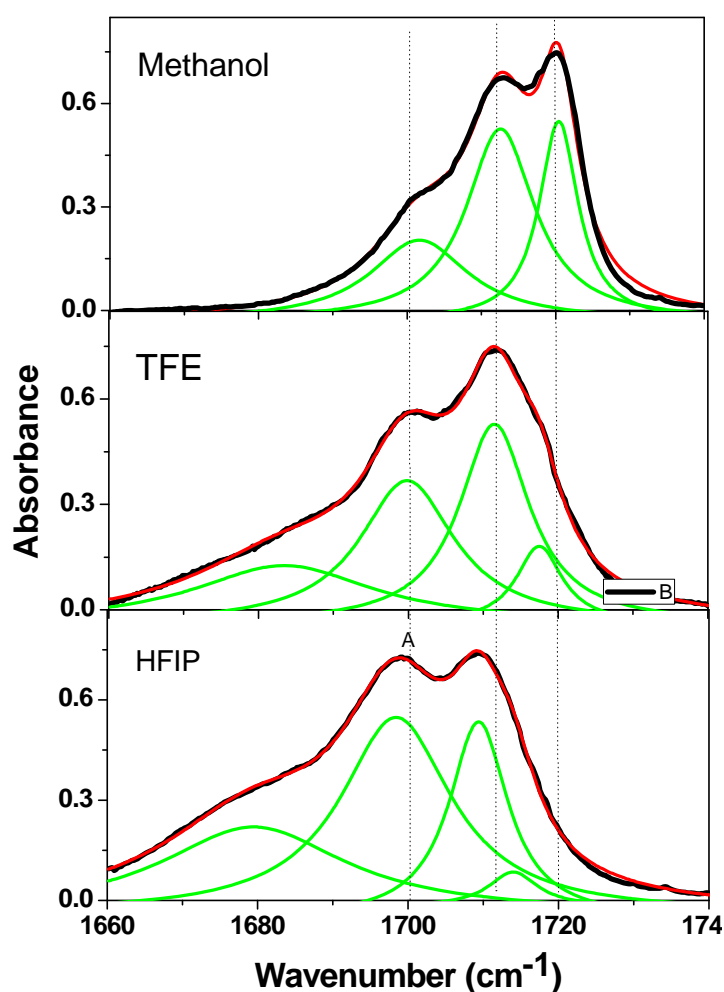


Figure S1: Deconvolution of the FTIR spectra assuming Lorentzian shapes of the IR absorption bands of the free C=O stretch and those engaged in hydrogen bond formation of different orders in the ground electronic state of FL in methanol, TFE and HFIP. The fitting parameters are given in the Table S1.

Table S1: C=O stretch frequencies (in cm^{-1}) and relative intensities of the peak corresponding to free C=O or two kinds of hydrogen bonded complexes derived by deconvolution of the FTIR spectra using Lorentzian functions as shown in Figure S1.

A. S_0 state:

Solvents	C=O stretching frequency (percent population)			
	Free	1: 1 Complex	1:2 Complex	Higher order complexes
Cyclohexane	1721.9 (100)	----	----	
CD ₃ CN	1718.2 (100)	-----	----	
CD ₃ OD	1720.4 (28)	1712.6 (45)	1701.6 (27)	
TFE	1717.5 (12)	1711.5 (35)	1699.8 (33)	1683.4 (20)
HFIP	1714 (2)	1709.4 (25)	1698.4 (45)	1679.5(28)

B. S_1 state

Solvents	C=O stretching frequency (percent population)		
	Free	1: 1 Complex	1:2 Complex
cyclohexane	1541.3 (100)	-----	-----
CD ₃ CN	1543.4 (100)	-----	-----
CD ₃ OD	1544.7 (79)	1529.4 (21)	
TFE	1548.8 (72)	1527.1 (28)	
HFIP	1548 (68)	1522.5 (32)	

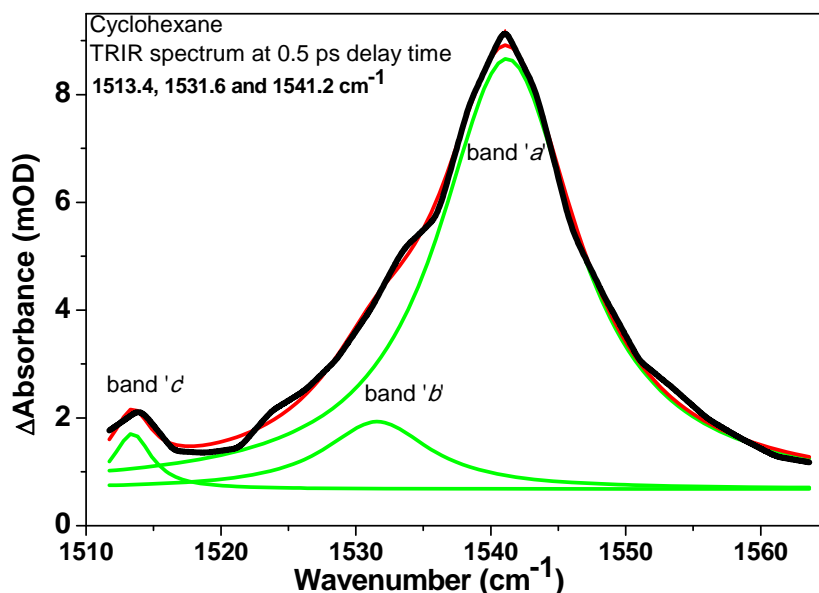


Figure S2: Deconvolution of TRIR spectrum of FL in cyclohexane recorded at 0.5 ps delay time following photoexcitation (Black line). The transient spectrum is deconvoluted using three Lorentzian bands (green lines). The red line is the sum spectra of the Lorentzian bands.

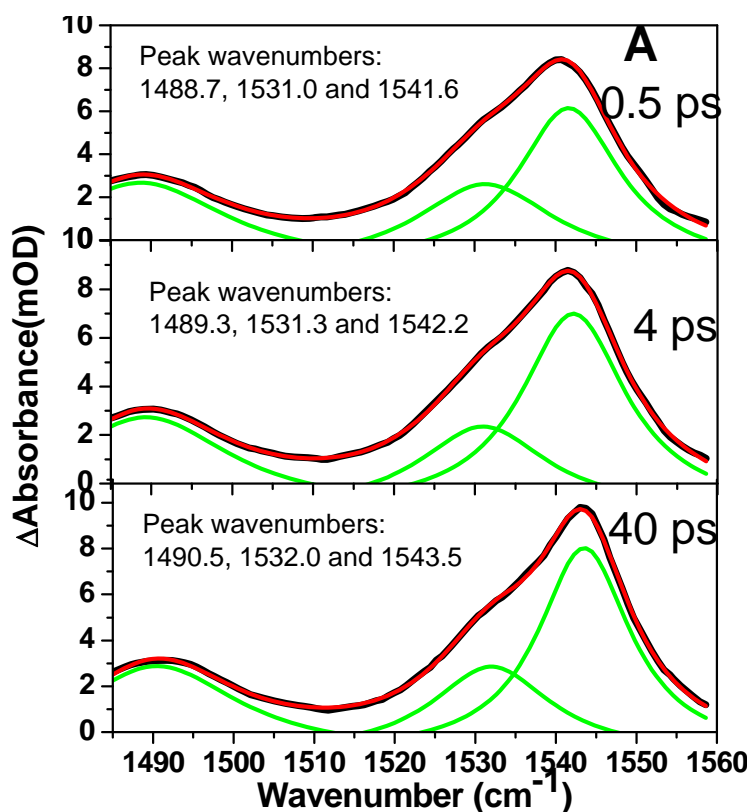


Figure S3: Deconvolution of TRIR spectra of FL in acetonitrile at different delay times after photoexcitation (black lines). Lorentzian deconvolutions are shown in green lines. Red lines are the sum spectra of the Lorentzian bands.

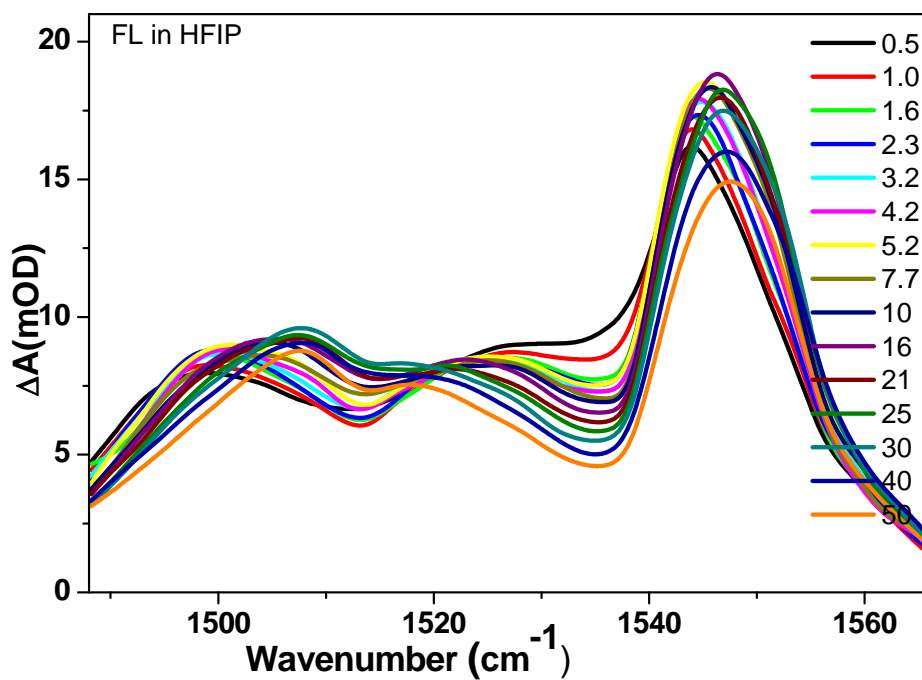


Figure S4: TRIR spectra recorded following photoexcitation of FL in HFIP to show the real changes of absorbance during evolution of the transient spectra.

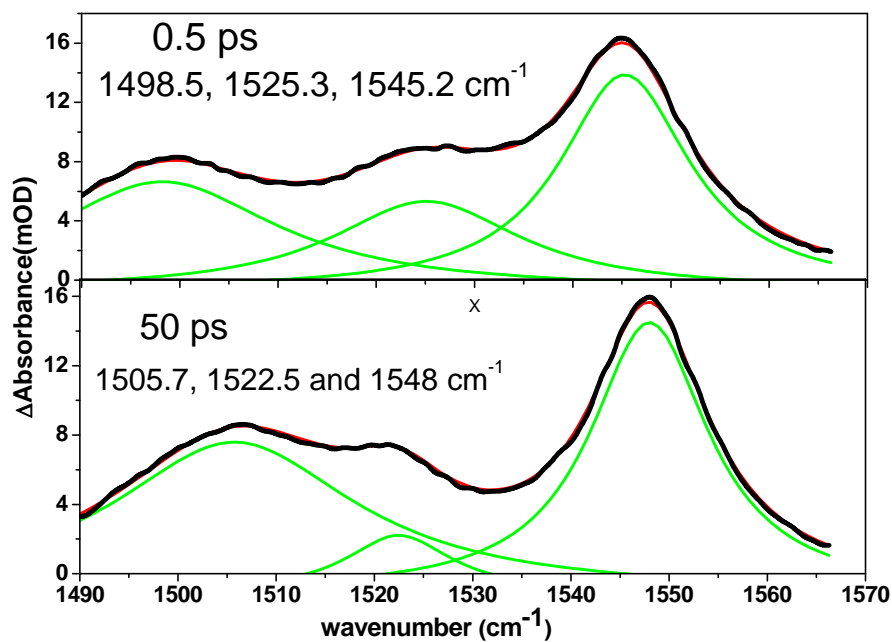


Figure S5: Deconvolution of TRIR spectra of FL in HFIPat 0.5 ps and at 50 ps after photoexcitation (black lines). Green curves represent Lorentzian deconvolution. Red lines are the sum spectra of the Lorentzian bands.

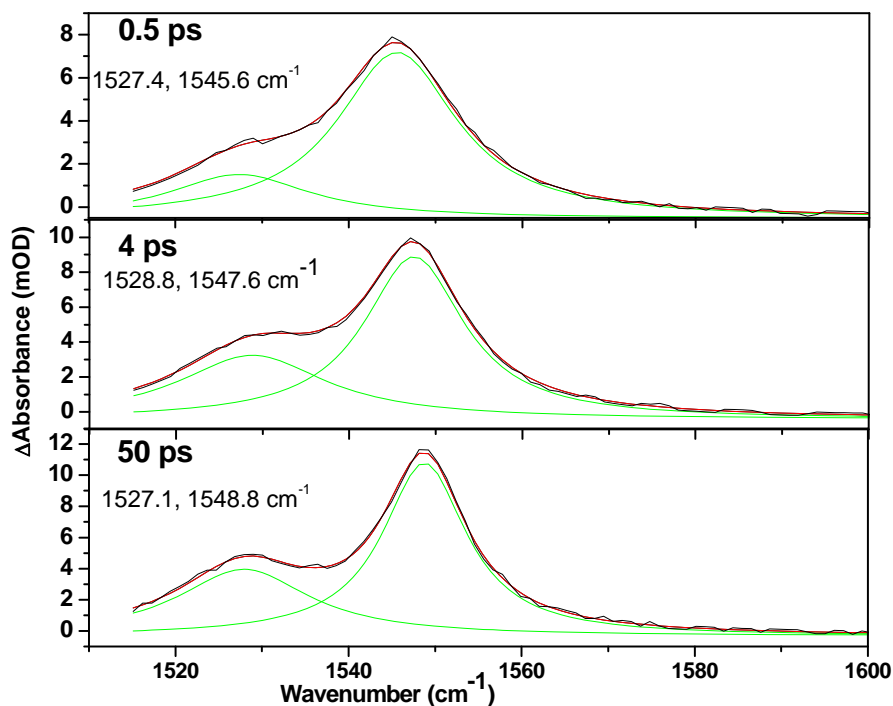


Figure S6: Deconvolution of TRIR spectra of FL in TFEat three delay times after photoexcitation (black lines). Green curves represent Lorentzian deconvolution. Red lines are the sum spectra of the Lorentzian bands.

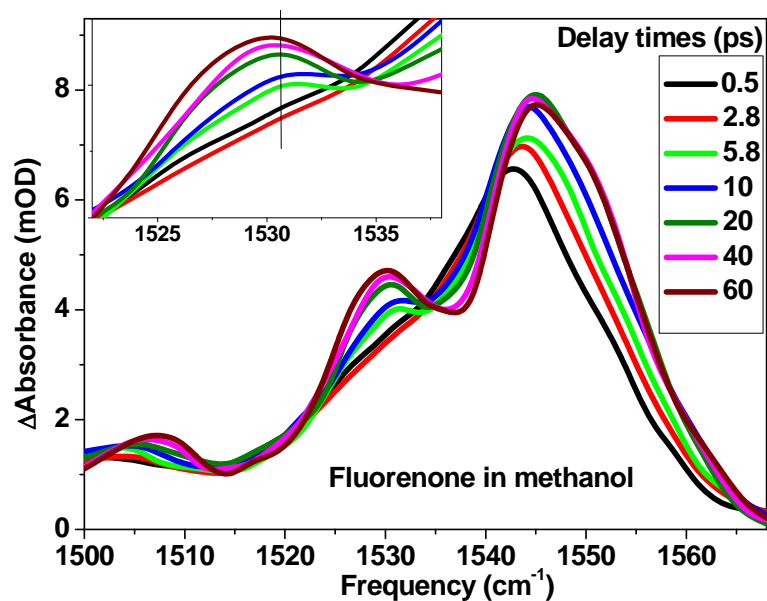


Figure S7: TRIR spectra recorded following photoexcitation of FL in CD₃OD to show the real changes of absorbance during evolution of the transient spectra.

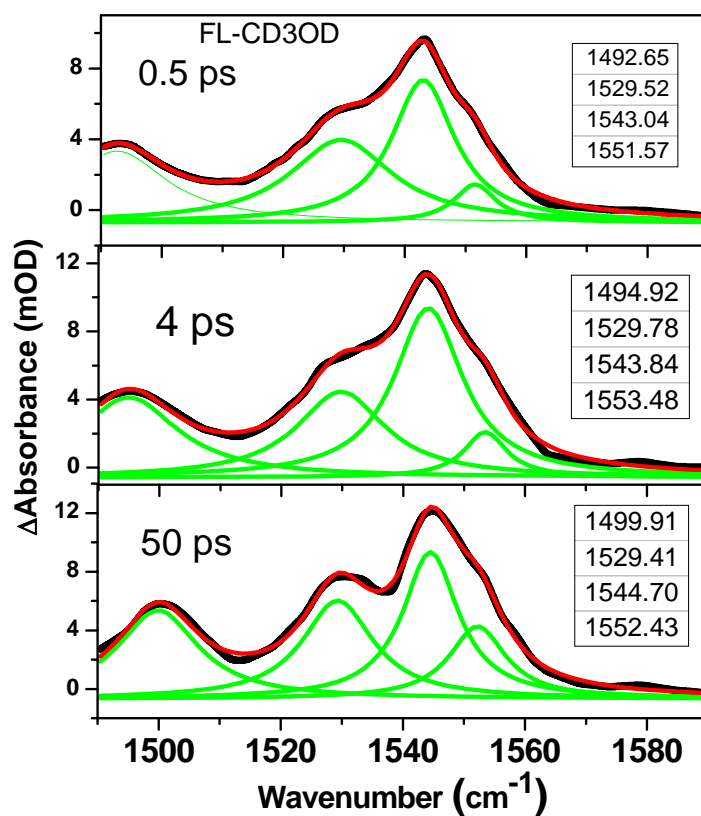


Figure S8: Deconvolution of TRIR spectra of FL in CD₃OD at 0.5 ps, 4 ps and 50 ps.

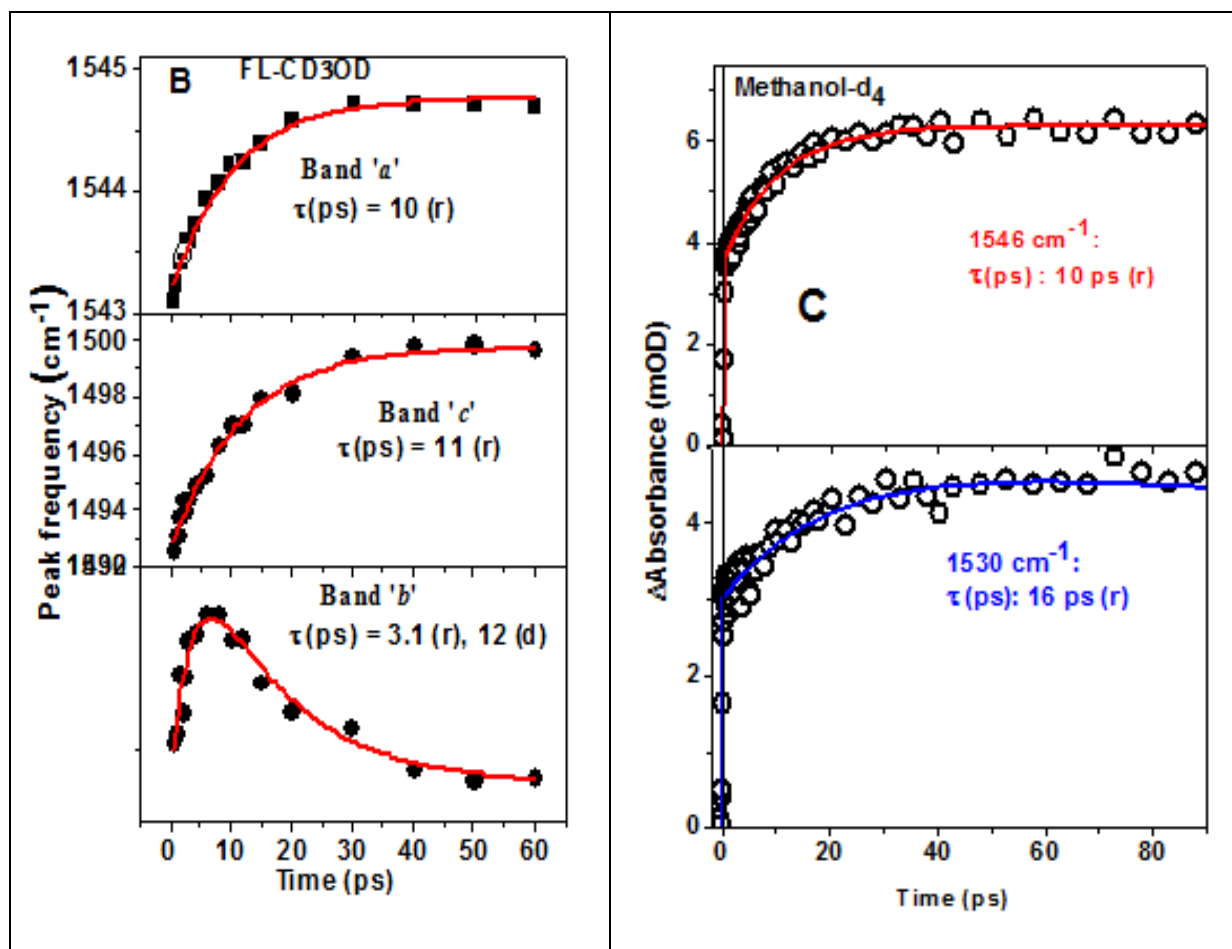


Figure S9: Peak shift dynamics for three bands in TRIR spectra and the temporal dynamics recorded at two selective frequencies following photoexcitation of FL in CD3OD.

$$F_{\text{Onsager}} = \frac{2(\epsilon - 1)(n^2 + 2)}{3(2\epsilon + n^2)} \quad (\text{S1})$$

Table S2: Solvent parameters

Solvent	ϵ	n	F_{ON}	α	Free C=O Stretch Frequency	
					S_0 state	S_1 state (vib. cooled)
Cyclohexane	2.02	1.43	0.45	0	1721.9	1541.5
Acetonitrile	37.5	1.34	1.20	0.19	1718.2	1543.1
Methanol	32.63	1.33	1.19	0.93	1720.4	1545.2
TFE	27	1.29	1.14	1.51	1717.5	1548.6
HFIP	16.7	1.28	1.09	1.96	1714	1548.0

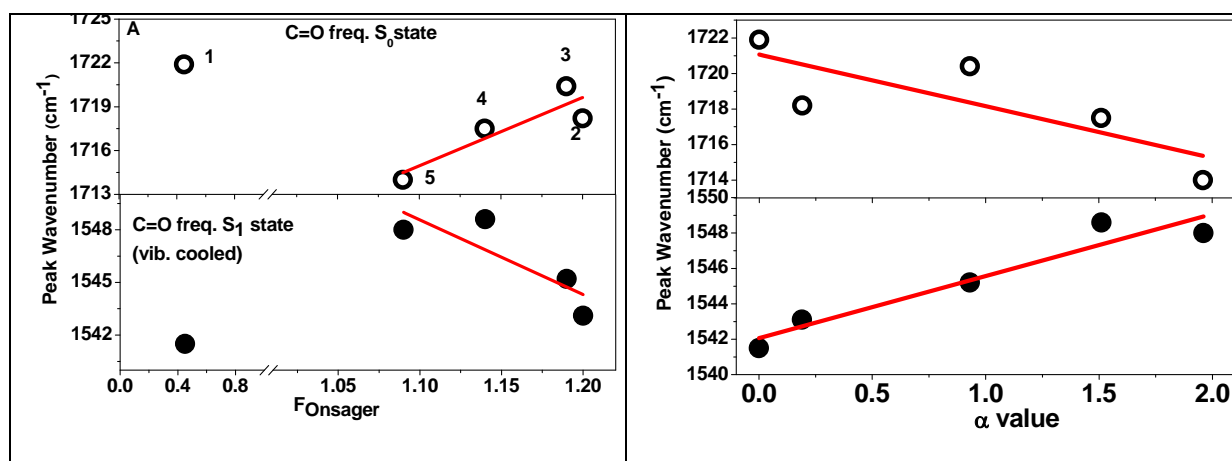


Figure S10: Correlation of the peak wave number of the free C=O stretching band with the Onsager factor of the solvent.