Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

The Role of Dispersion and Anharmonic Corrections in Conformational Analysis of Flexible Molecules: the Allyl Group Rotamerization of Matrix Isolated Safrole

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C3C10C13C15		**C6C5O18C20**		**Conformer name**	
-119.6	AC-	-10.5	D-	SF1a	AC-D-
-119.8	AC-	10.4	D+	SF1b	AC-D+
120.2	AC+	-10.8	D-	SF2a	AC+D-
120.4	AC+	10.6	D+	SF2b	AC+D+
1.9	SP	-10.4	D-	SF3a	SPD-
1.8	SP	10.8	D+	SF3b	SPD+

AC-anticlinal, SP- synperiplanar, D- distorted.

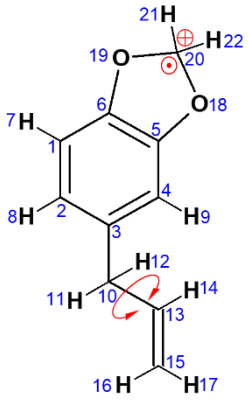


Figure S1. The key torsional angles and alternative names for SF conformers.

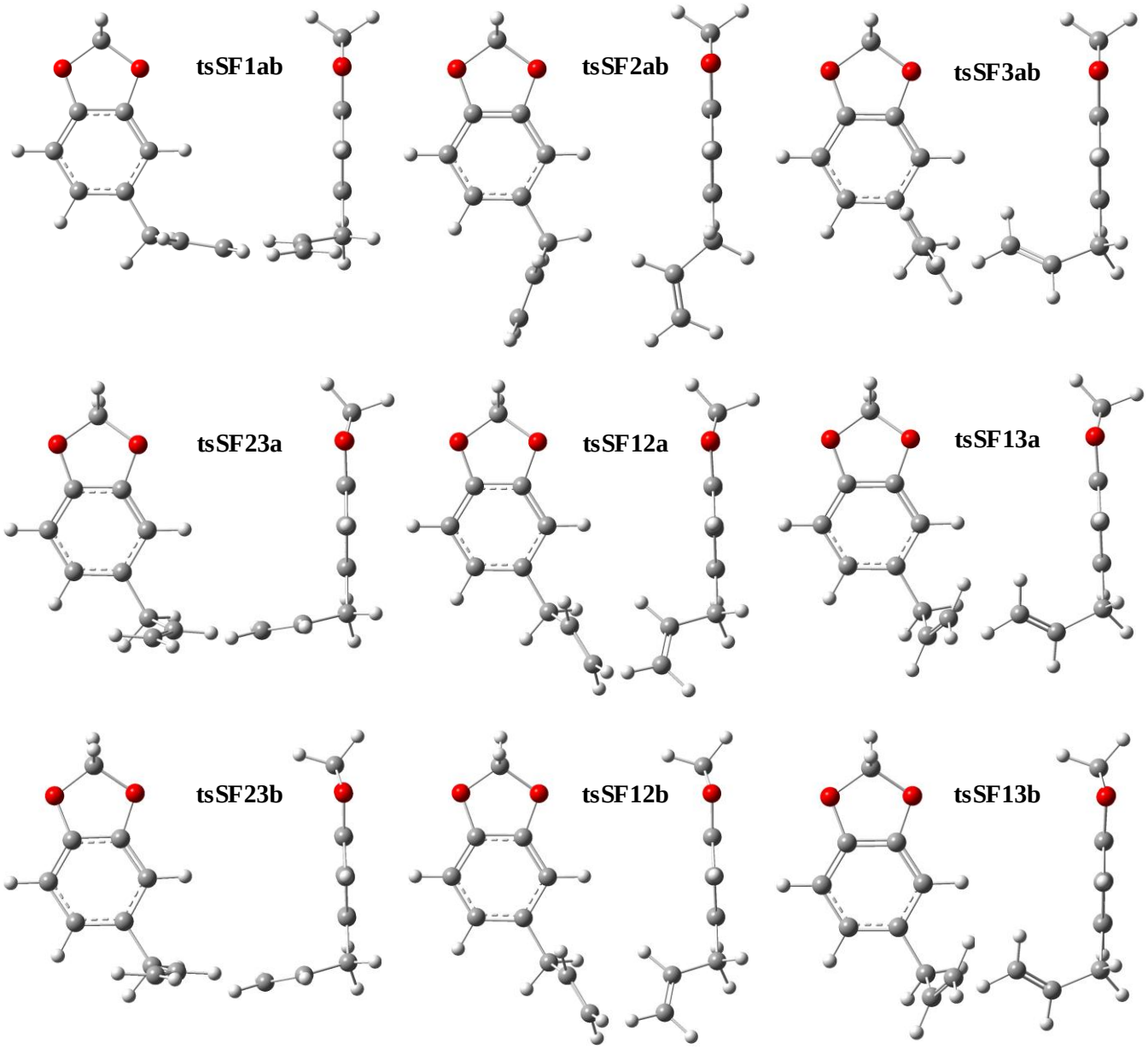


Figure S2. B2PLYP-D3/SNSD optimized structures of the SF transition states.

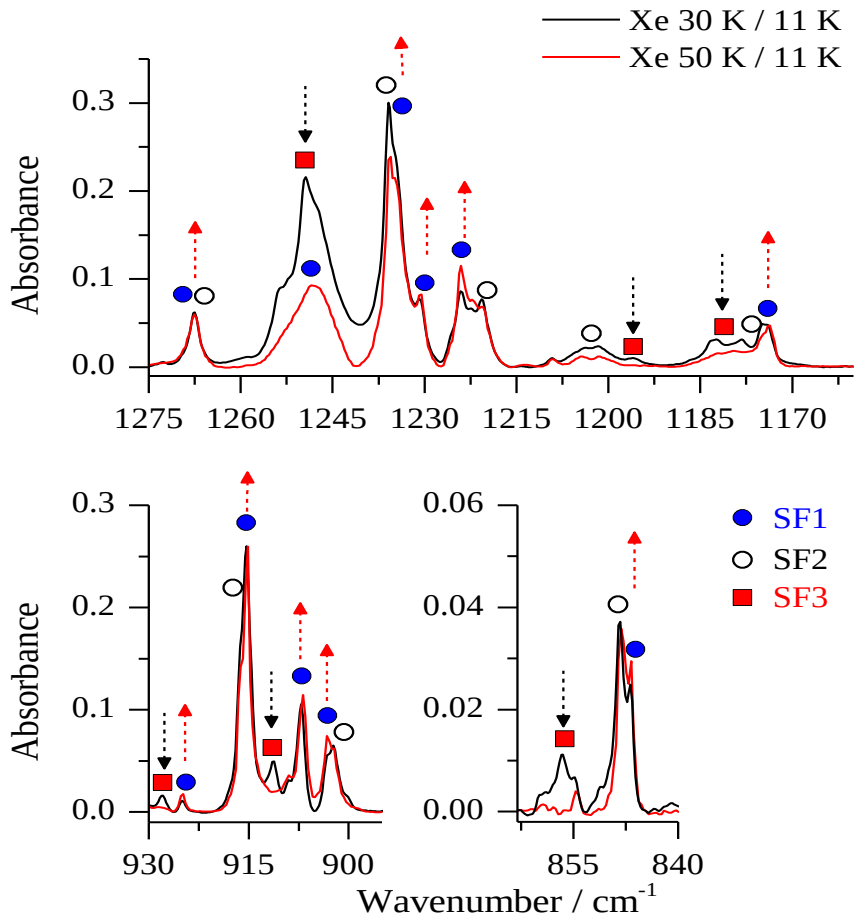
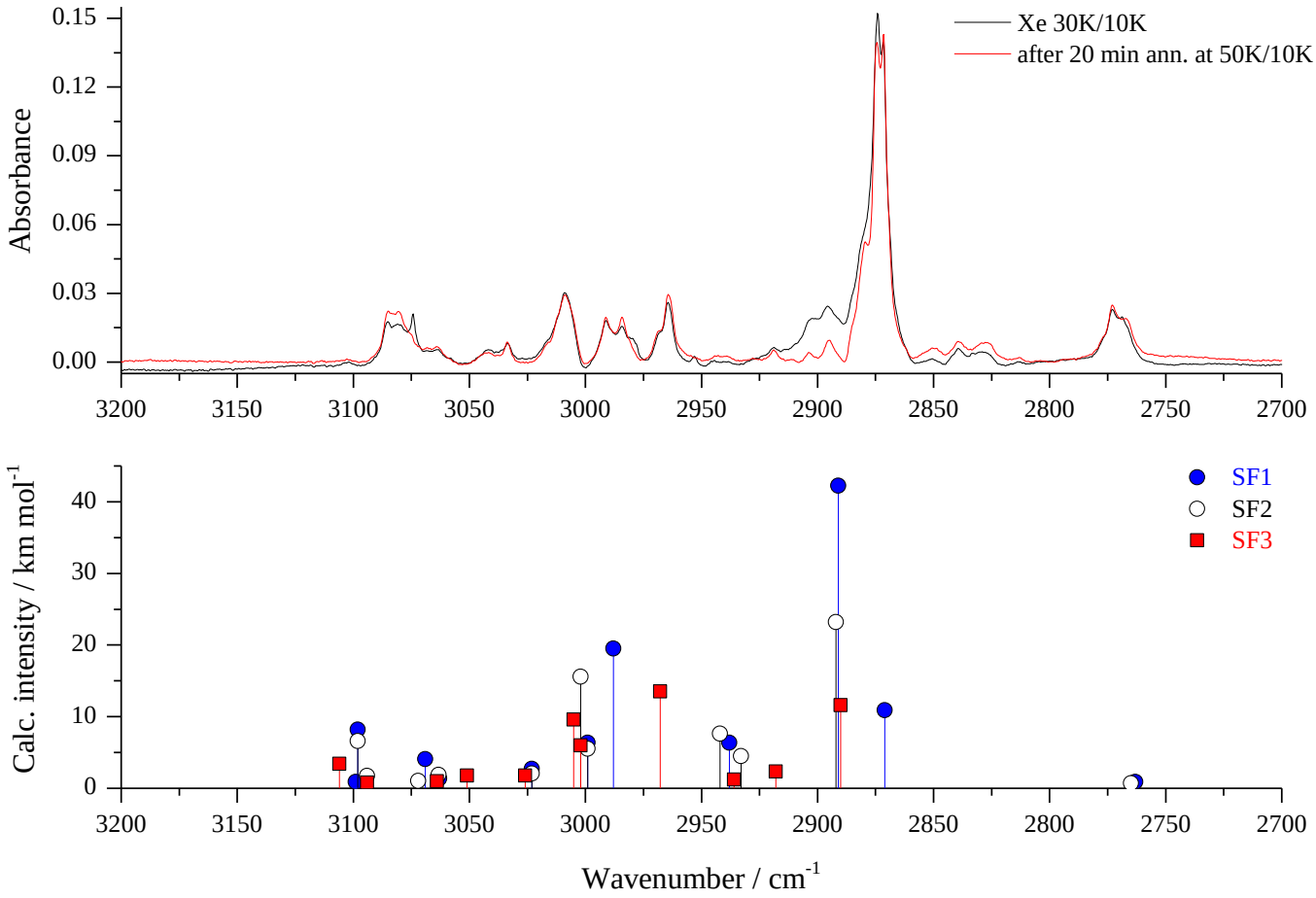
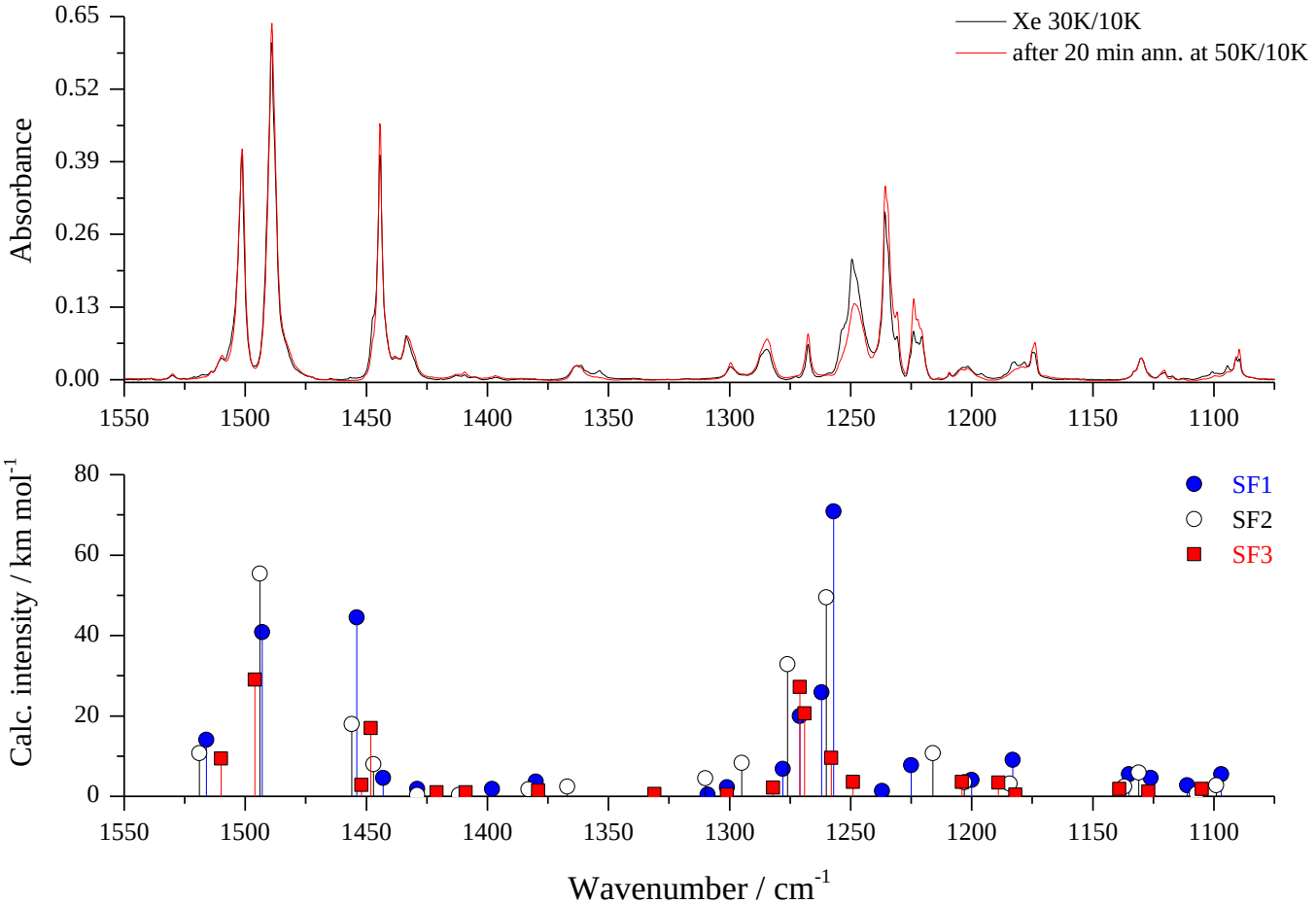


Figure S3. Selected regions of the experimental SF spectra of SF/Xe matrix deposited at 30 K and 50 K.


Absorbance
0.15
0.12
0.09
0.06
0.03
0.00
3200
3150
3100
3050
3000
2950
2900
2850
2800
2750
2700
Xe 30K/10K
after 20 min ann. at 50K/10K
Calc. intensity / km mol-1
40
30
20
10
0
SF1
SF2
SF3
Wavenumber / cm-1


Absorbance
0.65
0.52
0.39
0.26
0.13
0.00
1550
1500
1450
1400
1350
1300
1250
1200
1150
1100
Xe 30K/10K
after 20 min ann. at 50K/10K
Calc. intensity / km mol-1
80
60
40
20
0
SF1
SF2
SF3
Wavenumber / cm-1

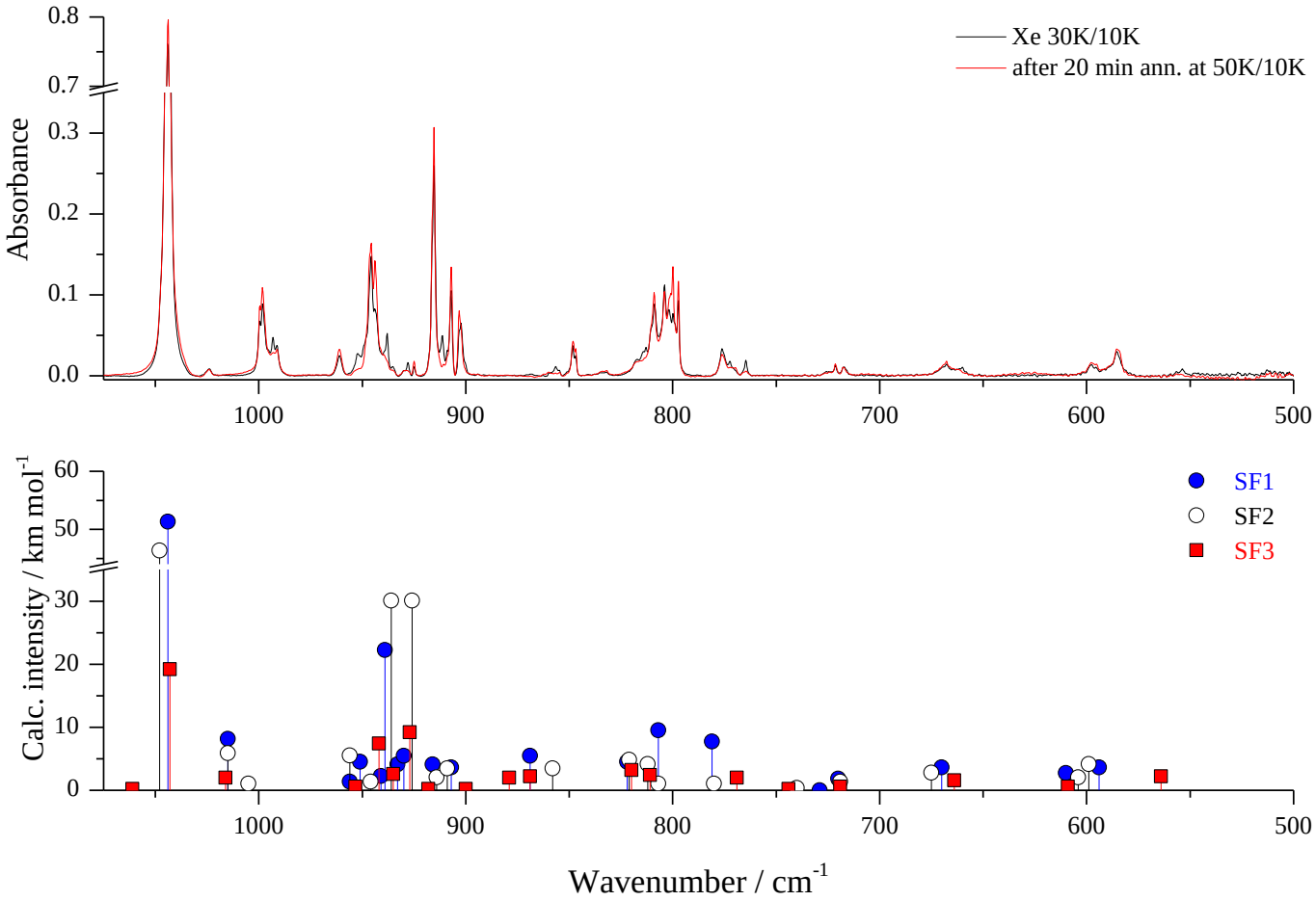
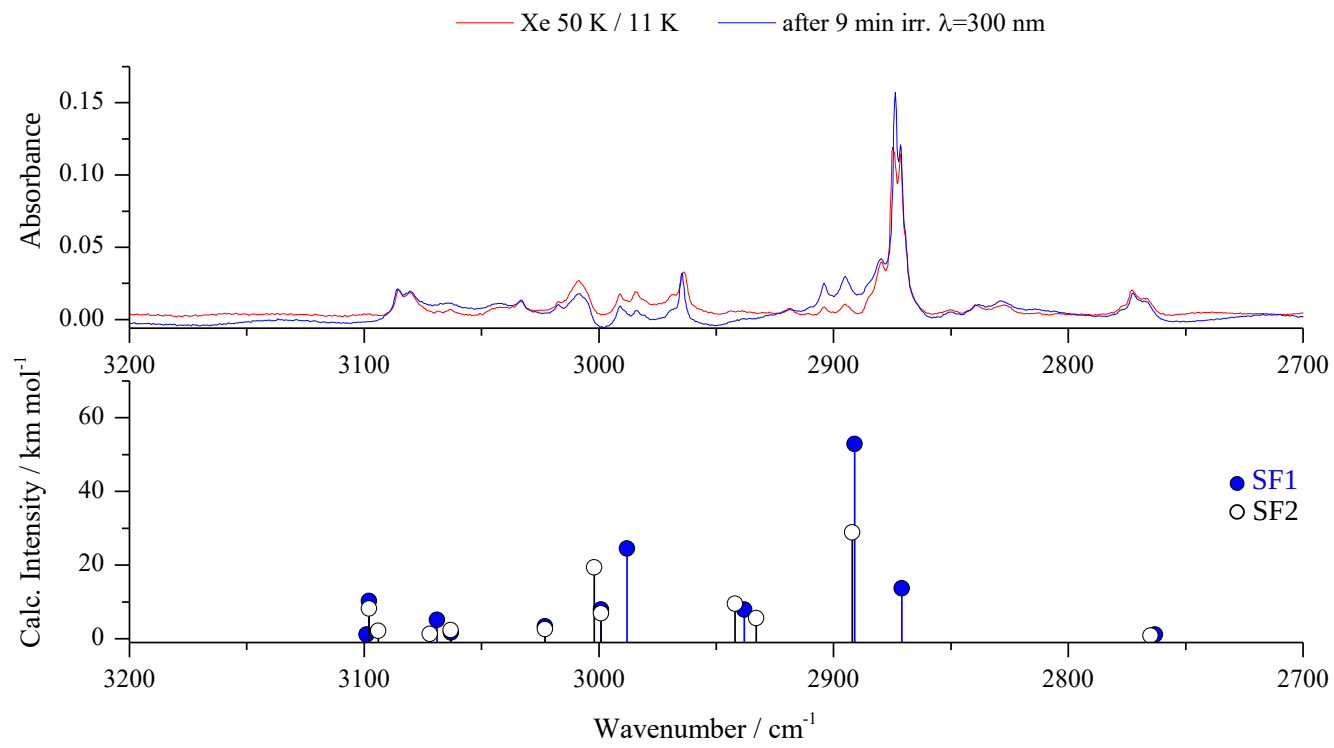
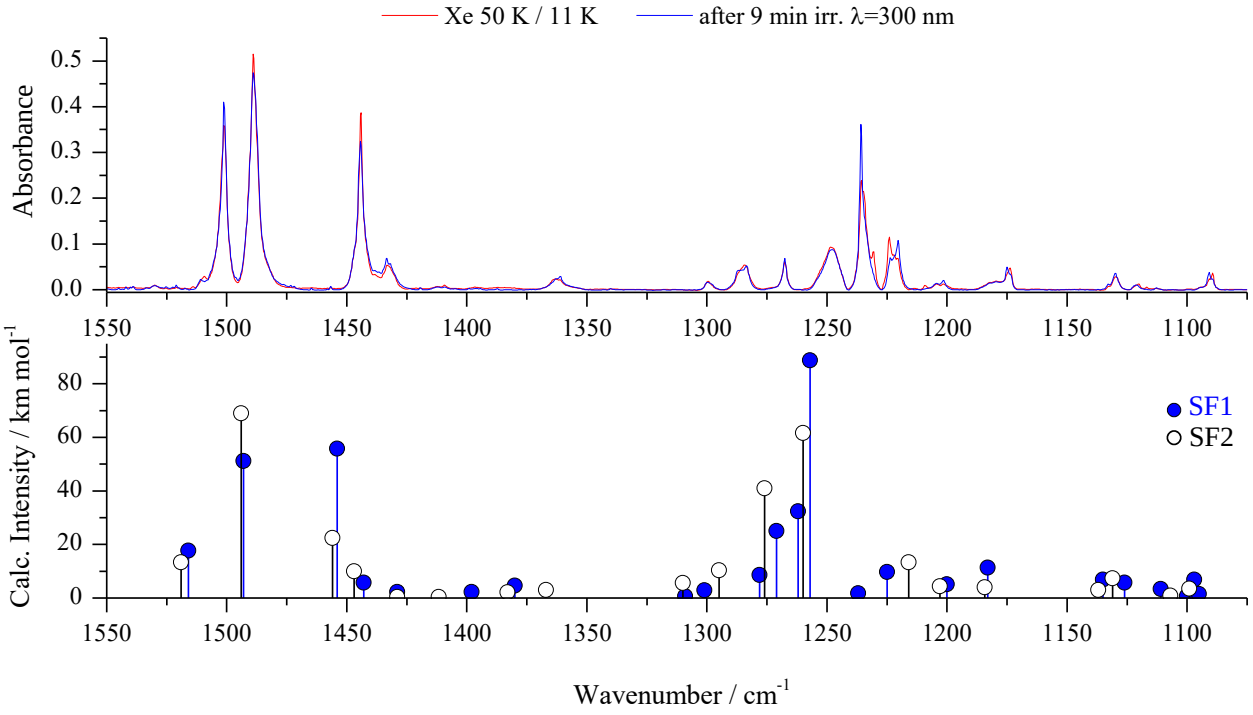


Figure S4. The experimental SF spectra (upper panel): freshly deposited SF/Xe matrix at 30 K (black traces) and the matrix deposited at 30 K after annealing to 50 K (red traces) compared to the GVPT2 spectra of SF conformers weighted by their abundances (45% SF1, 34% SF2, 21% SF3, lower panel).


Xe 50 K / 11 K
after 9 min irr. λ=300 nm
Absorbance
0.15
0.10
0.05
0.00
3200
3100
3000
2900
2800
2700
Calc. Intensity / km mol-1
60
40
20
0
SF1
SF2
Wavenumber / cm-1


Xe 50 K / 11 K
after 9 min irr. λ=300 nm
Absorbance
0.5
0.4
0.3
0.2
0.1
0.0
1550
1500
1450
1400
1350
1300
1250
1200
1150
1100
Calc. Intensity / km mol-1
80
60
40
20
0
SF1
SF2
Wavenumber / cm-1

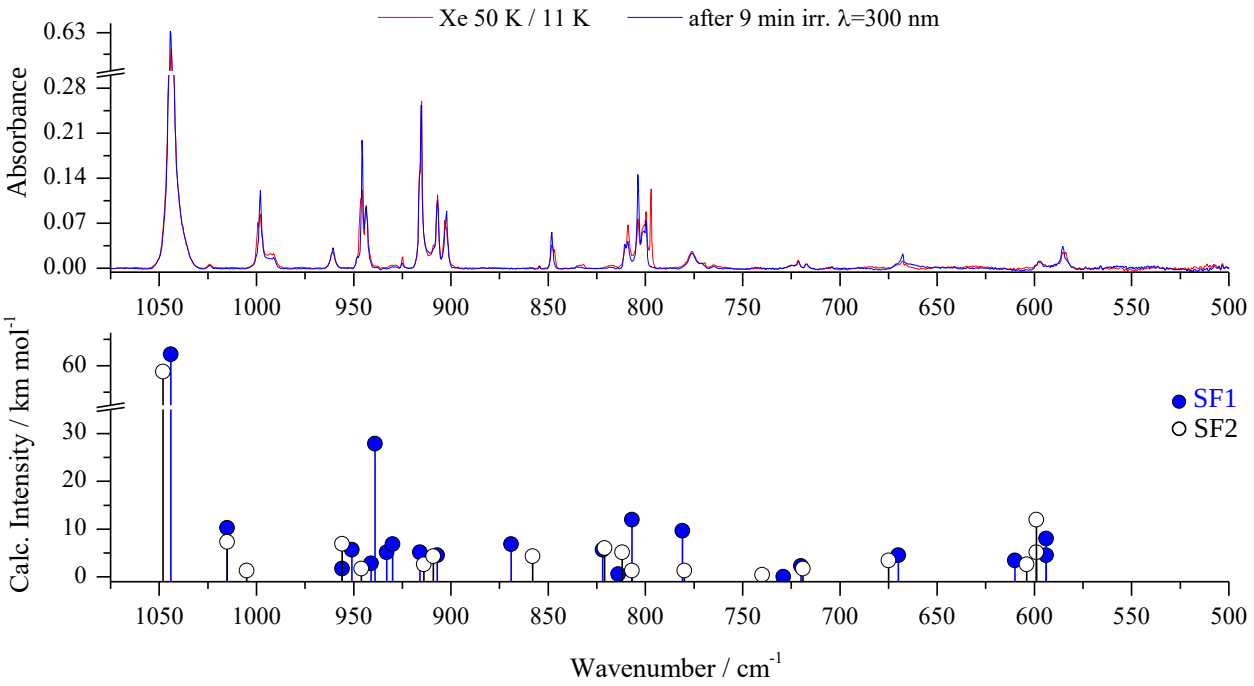


Figure S5. The experimental SF spectra (upper panel): freshly deposited at 50 K SF/Xe matrix (red traces) and the same matrix after 9 min of irradiation at 300 nm (blue traces) compared to the GVPT2 spectra of SF conformers weighted by their abundances (57% SF1, 43% SF2, lower panel).