Electronic Supplementary Information for

Selective conformational control by excitation of NH imino vibrational antennas

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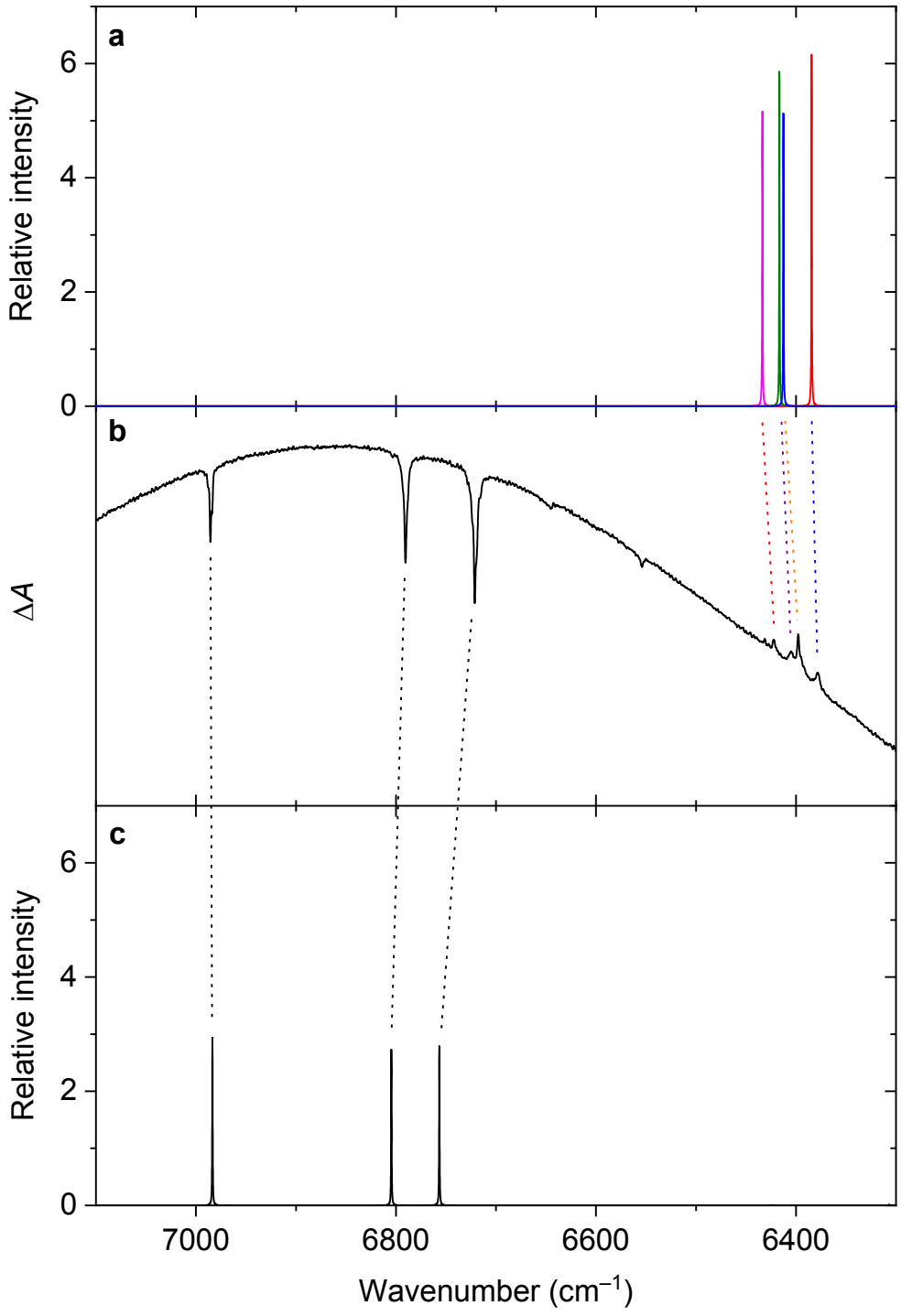

Figure S1. (**a**) Simulated spectra of the **aC** (red), **aT** (green), **sC** (pink), and **sT** (blue) imino-thiol isomers of thioacetamide. (**b**) Experimental near-IR spectrum showing changes induced by UV irradiation of thioacetamide monomers isolated in an argon matrix at 11 K (λ = 265 nm). Growing bands show upwards. (**c**) Simulated spectrum of the **Tn** tautomer. The simulated spectra are based on the unscaled anharmonic vibrational frequencies and anharmonic IR intensities computed at the B3LYP/6-311++G(3df,3pd) level of theory.

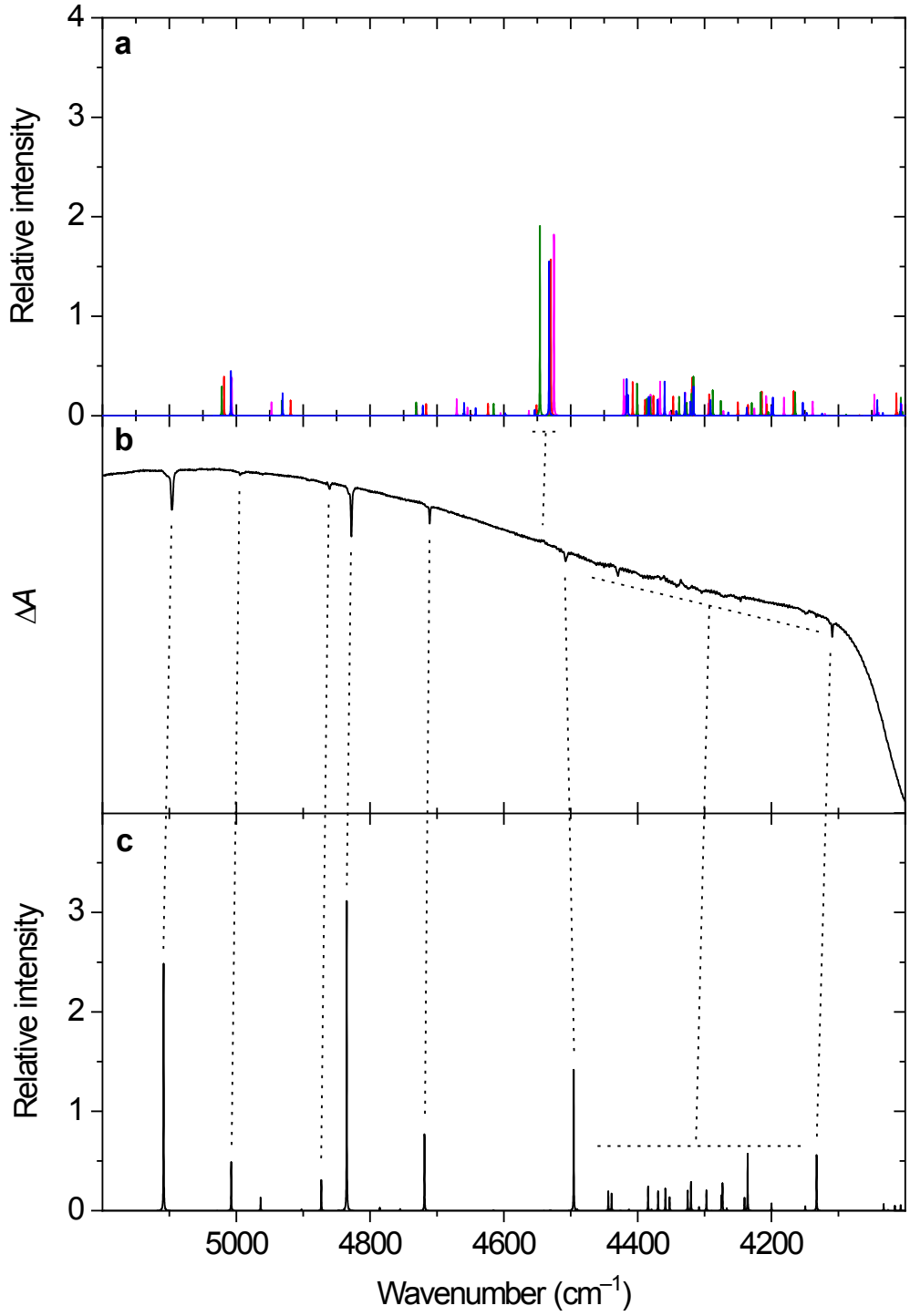

Figure S2. (**a**) Simulated spectra of the **aC** (red), **aT** (green), **sC** (pink), and **sT** (blue) imino-thiol isomers of thioacetamide. (**b**) Experimental near-IR spectrum showing changes induced by UV irradiation of thioacetamide monomers isolated in an argon matrix at 11 K (λ = 265 nm). Growing bands show upwards. (**c**) Simulated spectrum of the **Tn** conformer. The simulated spectra are based on the unscaled anharmonic vibrational frequencies and anharmonic IR intensities computed at the B3LYP/6-311++G(3df,3pd) level of theory.

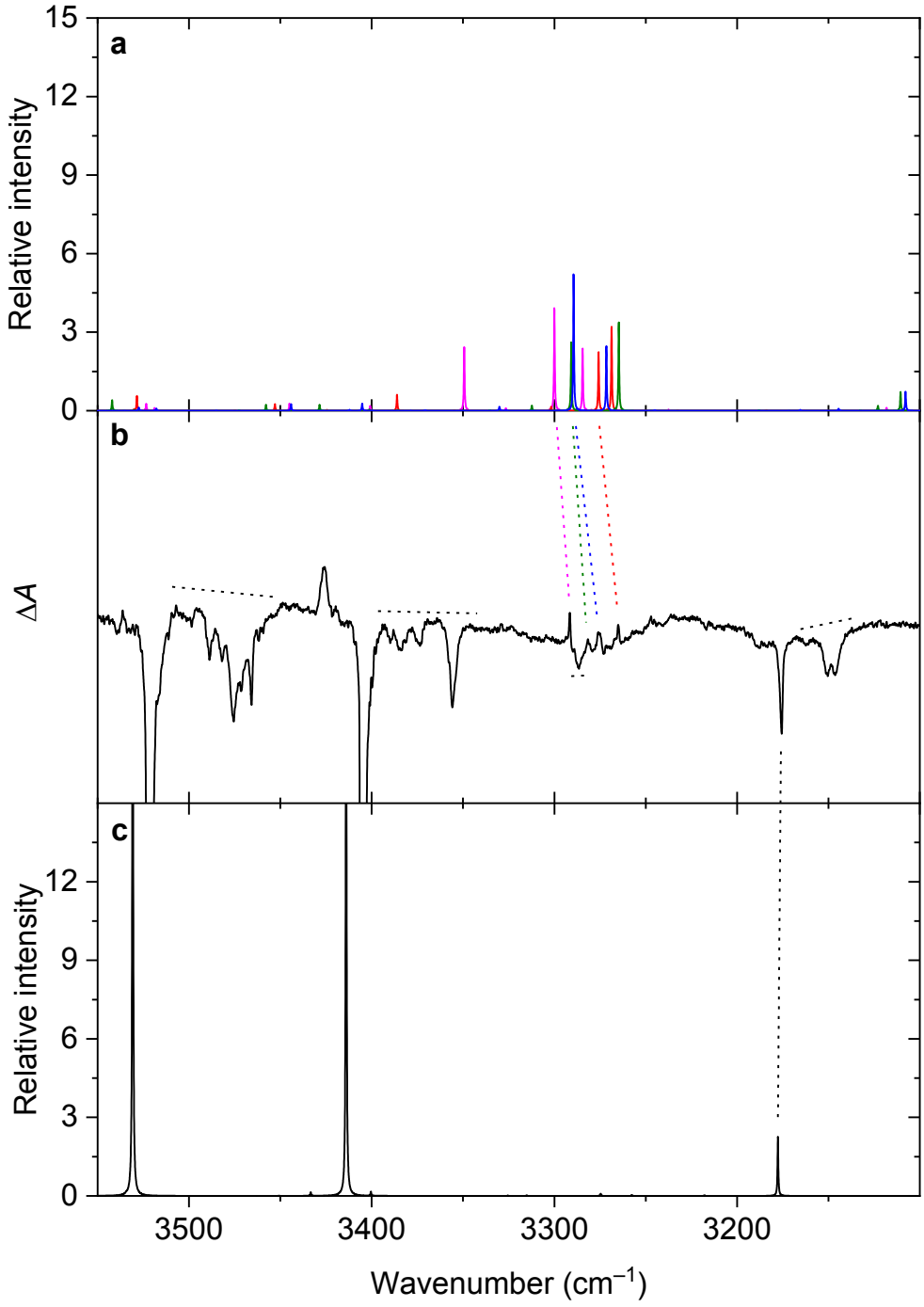

Figure S3. (**a**) Simulated spectra of the **aC** (red), **aT** (green), **sC** (pink), and **sT** (blue) imino-thiol isomers of thioacetamide. (**b**) Experimental mid-IR spectrum showing changes induced by UV irradiation of thioacetamide monomers isolated in an argon matrix at 11 K (λ = 265 nm). Growing bands show upwards. (**c**) Simulated spectrum of the **Tn** conformer. The simulated spectra are based on the unscaled anharmonic vibrational frequencies and anharmonic IR intensities computed at the B3LYP/6-311++G(3df,3pd) level of theory.

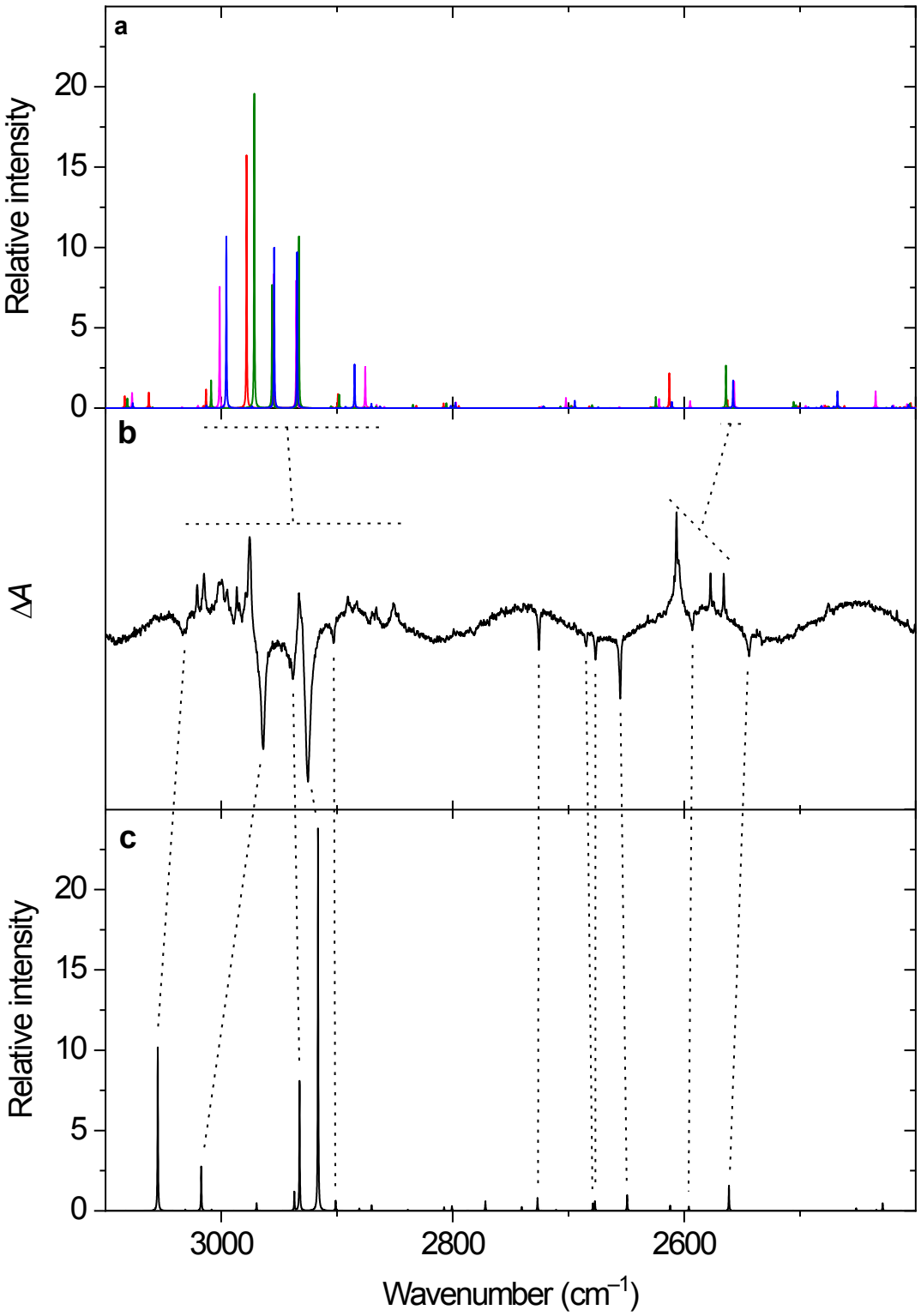

Figure S4. (**a**) Simulated spectra of the **aC** (red), **aT** (green), **sC** (pink), and **sT** (blue) imino-thiol isomers of thioacetamide. (**b**) Experimental mid-IR spectrum showing changes induced by UV irradiation of thioacetamide monomers isolated in an argon matrix at 11 K (λ = 265 nm). Growing bands show upwards. (**c**) Simulated spectrum of the **Tn** conformer. The simulated spectra are based on the unscaled anharmonic vibrational frequencies and anharmonic IR intensities computed at the B3LYP/6-311++G(3df,3pd) level of theory.

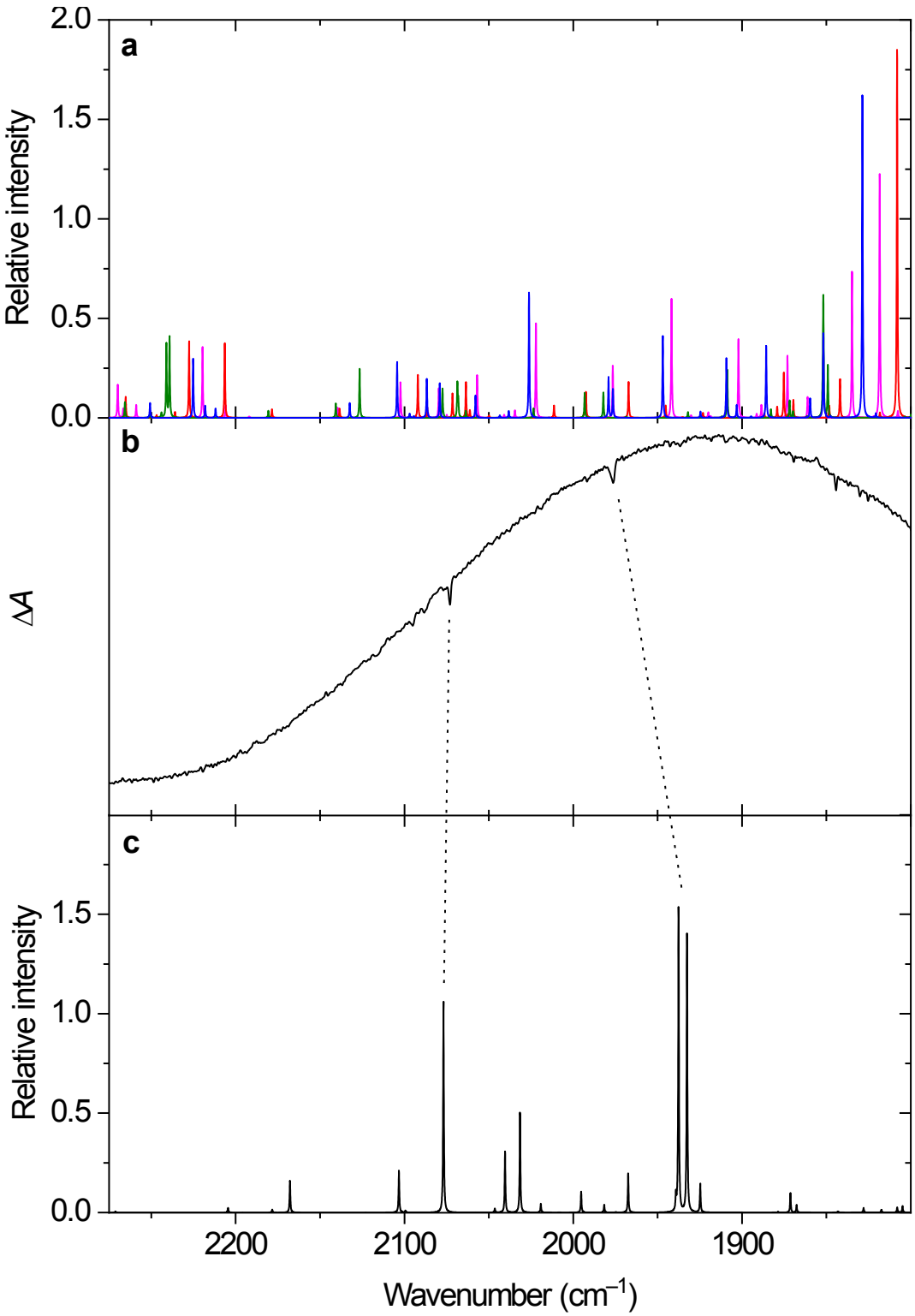

Figure S5. (**a**) Simulated spectra of the **aC** (red), **aT** (green), **sC** (pink), and **sT** (blue) imino-thiol isomers of thioacetamide. (**b**) Experimental mid-IR spectrum showing changes induced by UV irradiation of thioacetamide monomers isolated in an argon matrix at 11 K (λ = 265 nm). Growing bands show upwards. (**c**) Simulated spectrum of the **Tn** conformer. The simulated spectra are based on the unscaled anharmonic vibrational frequencies and anharmonic IR intensities computed at the B3LYP/6-311++G(3df,3pd) level of theory.

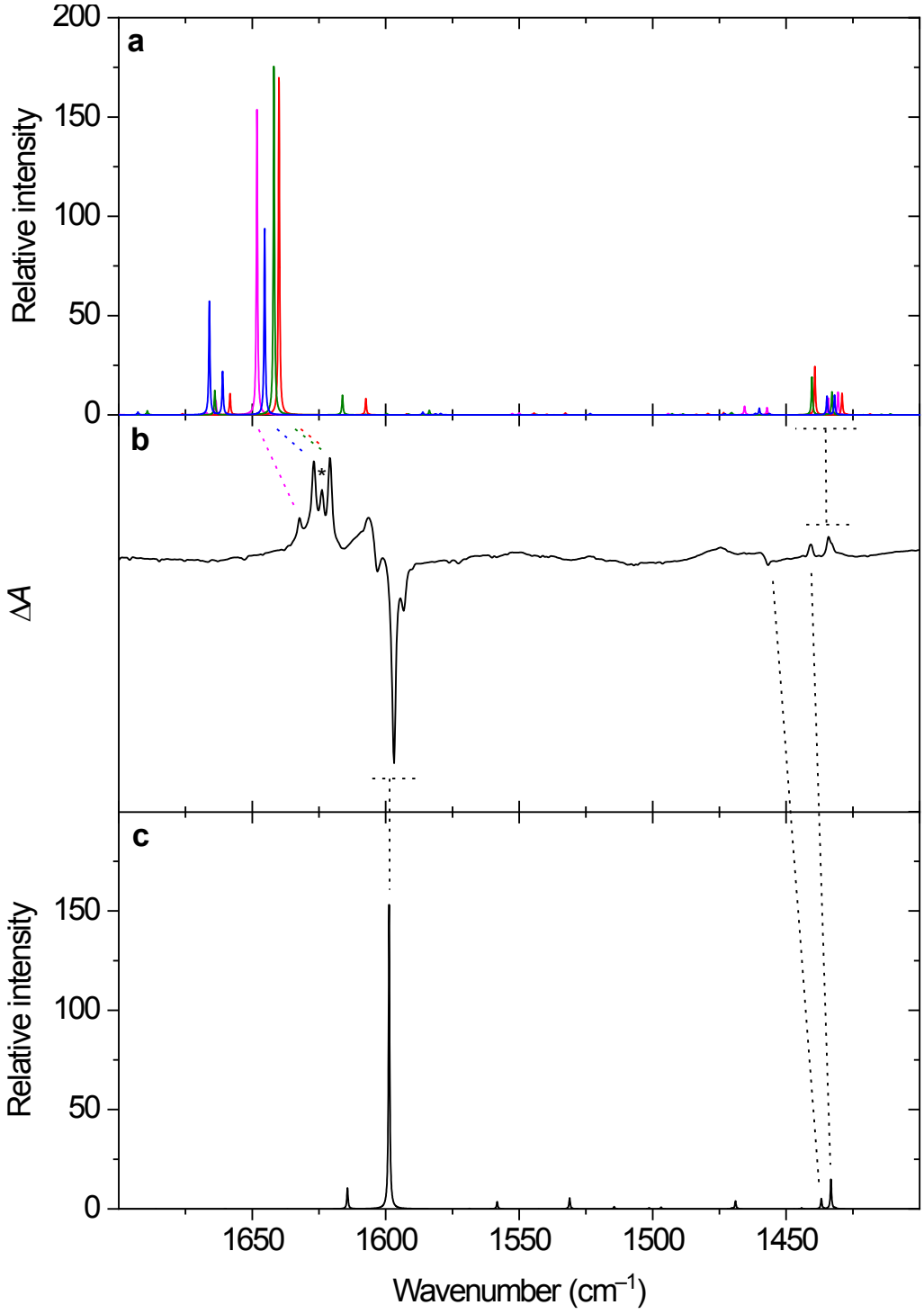

Figure S6. (**a**) Simulated spectra of the **aC** (red), **aT** (green), **sC** (pink), and **sT** (blue) imino-thiol isomers of thioacetamide. (**b**) Experimental mid-IR spectrum showing changes induced by UV irradiation of thioacetamide monomers isolated in an argon matrix at 11 K (λ = 265 nm). Growing bands show upwards. (**c**) Simulated spectrum of the **Tn** conformer. The simulated spectra are based on the unscaled anharmonic vibrational frequencies and anharmonic IR intensities computed at the B3LYP/6-311++G(3df,3pd) level of theory. The asterisk in panel (**b**) marks the band of the matrix-isolated monomeric H_2O impurity.

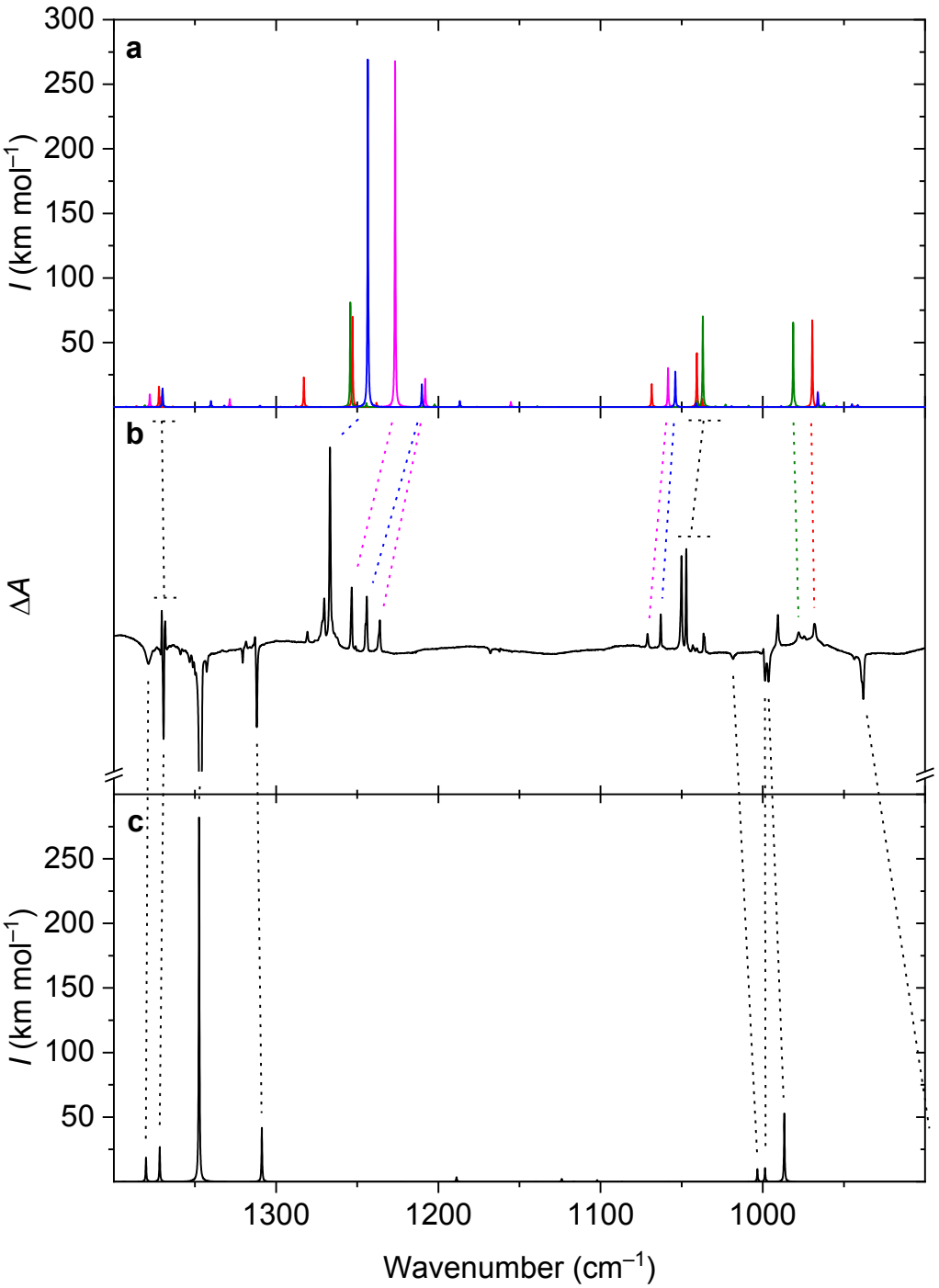

Figure S7. (**a**) Simulated spectra of the **aC** (red), **aT** (green), **sC** (pink), and **sT** (blue) imino-thiol isomers of thioacetamide. (**b**) Experimental mid-IR spectrum showing changes induced by UV irradiation of thioacetamide monomers isolated in an argon matrix at 11 K (λ = 265 nm). Growing bands show upwards. (**c**) Simulated spectrum of the **Tn** conformer. The simulated spectra are based on the unscaled anharmonic vibrational frequencies and anharmonic IR intensities computed at the B3LYP/6-311++G(3df,3pd) level of theory.

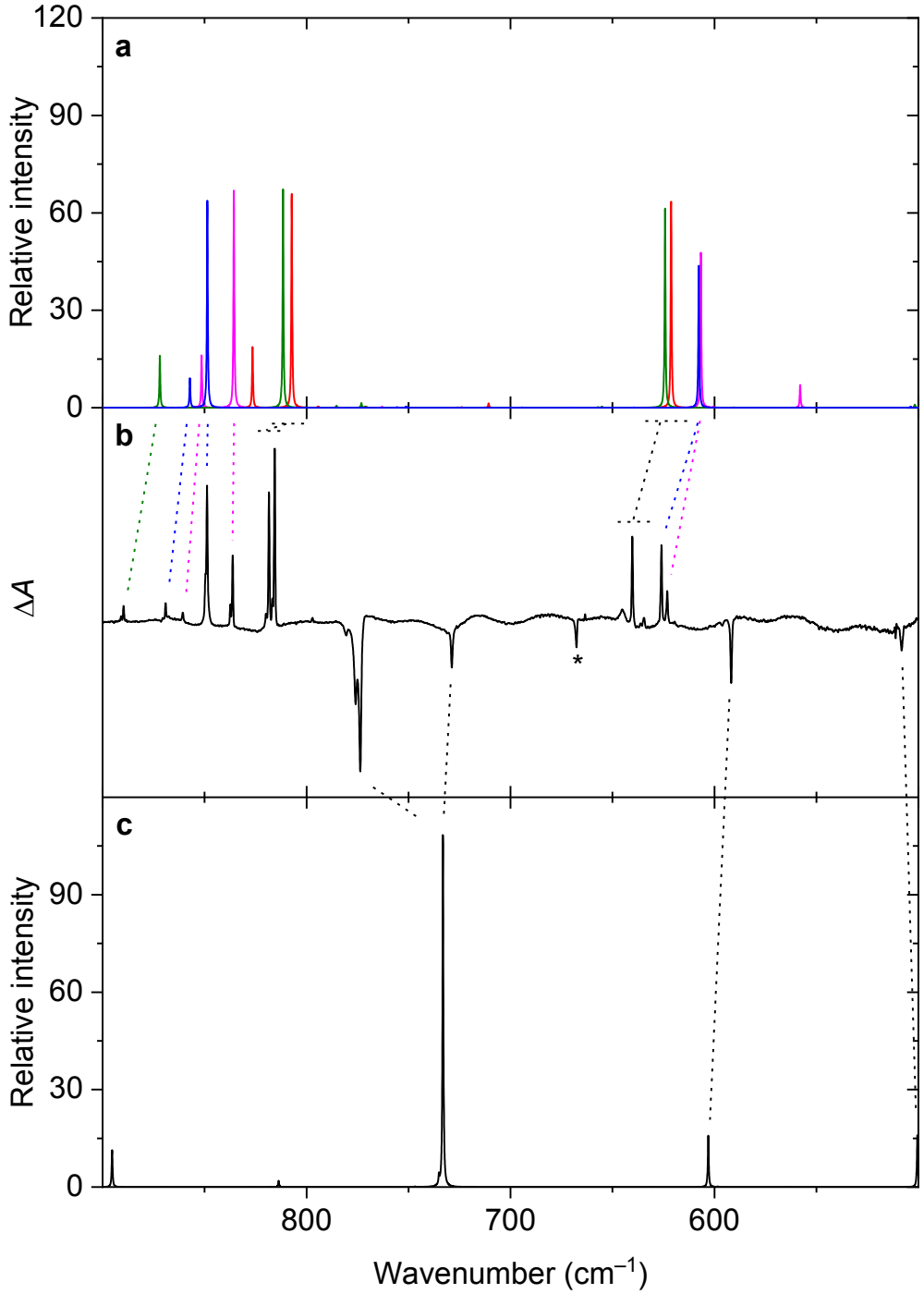

Figure S8. (**a**) Simulated spectra of the **aC** (red), **aT** (green), **sC** (pink), and **sT** (blue) imino-thiol isomers of thioacetamide. (**b**) Experimental mid-IR spectrum showing changes induced by UV irradiation of thioacetamide monomers isolated in an argon matrix at 11 K (λ = 265 nm). Growing bands show upwards. (**c**) Simulated spectrum of the **Tn** conformer. The simulated spectra are based on the unscaled anharmonic vibrational frequencies and anharmonic IR intensities computed at the B3LYP/6-311++G(3df,3pd) level of theory. The asterisk marks the signal of the not perfectly compensated atmospheric CO_2 molecule.

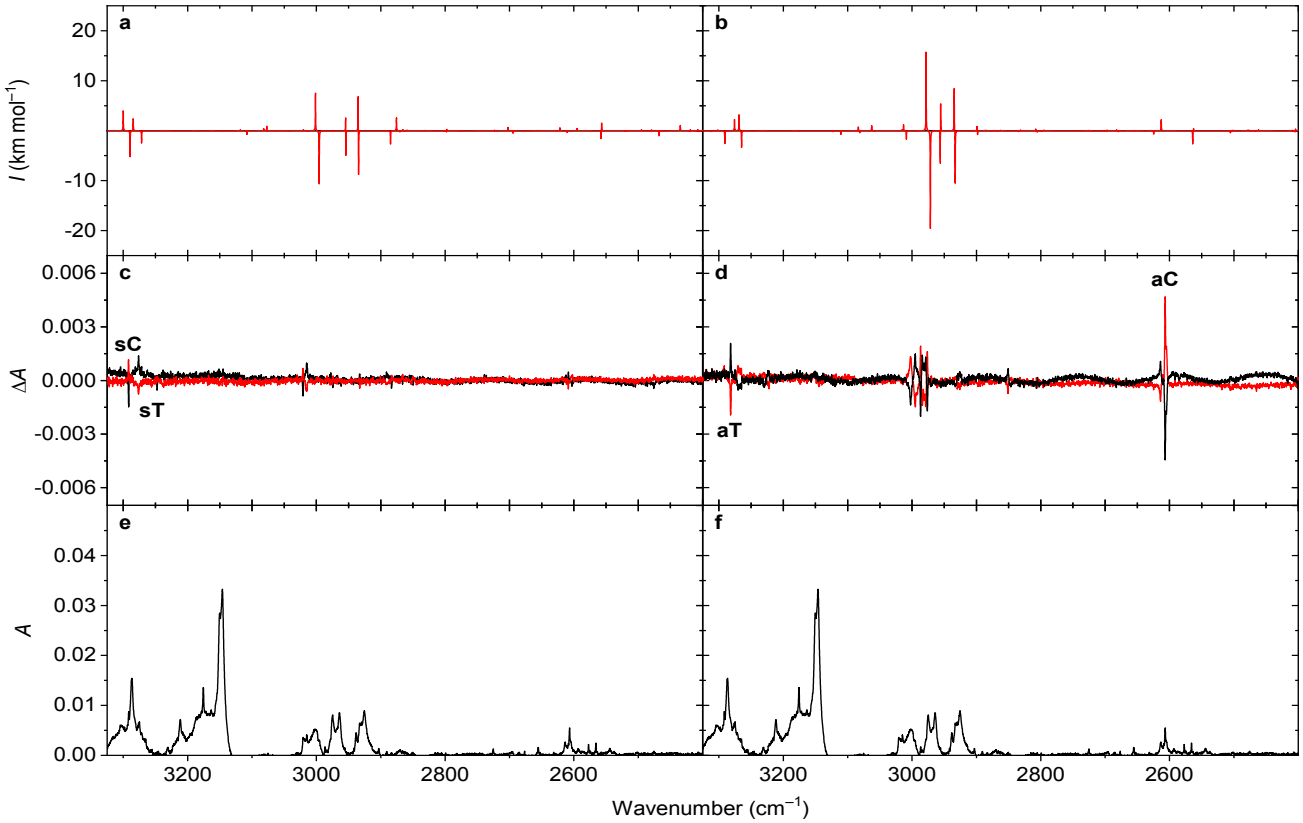

Figure S9. Simulated difference spectra of the *syn* (**a**) and *anti* (**b**) isomers; the growing bands are those of the **sC** and **aC**, respectively. (**c**) Experimental difference spectra of the *syn* isomers upon near-IR irradiation of 6422 cm^{-1} (black) and 6398 cm^{-1} (red). (**d**) Experimental difference spectra of the *anti* isomers upon near-IR irradiation of 6378 cm^{-1} (black) and 6405 cm^{-1} (red) (**e**, **f**) Mid-IR spectrum of the UV-irradiated sample. All panels visualize the spectral region of 3325–2575 cm^{-1}; the labels in panels (**c**) and (**d**) show the most intense bands of the respective isomers in the region.

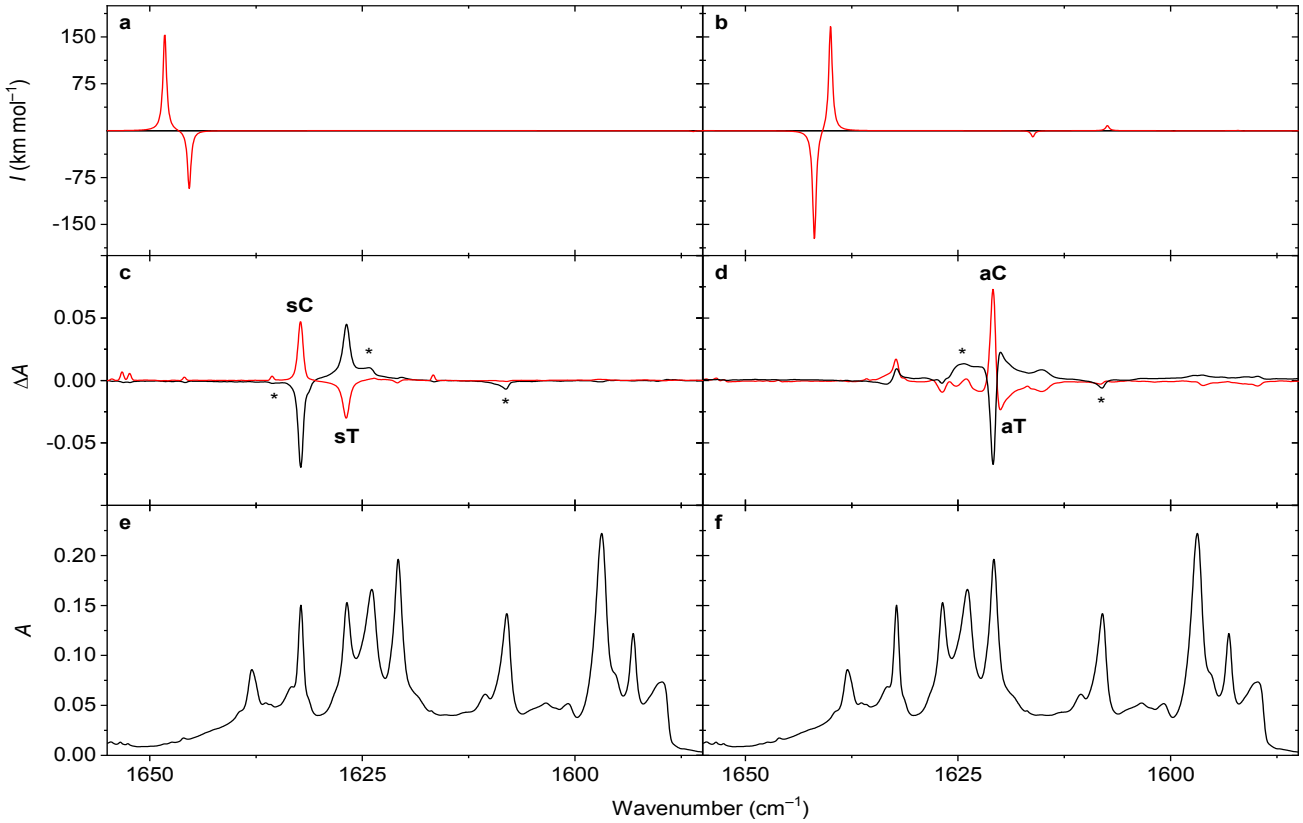

Figure S10. Simulated difference spectra of the *syn* (**a**) and *anti* (**b**) isomers; the growing bands are those of the **sC** and **aC**, respectively. (**c**) Experimental difference spectra of the *syn* isomers upon near-IR irradiation of 6422 cm^{-1} (black) and 6398 cm^{-1} (red). (**d**) Experimental difference spectra of the *anti* isomers upon near-IR irradiation of 6378 cm^{-1} (black) and 6405 cm^{-1} (red) (**e**, **f**) Mid-IR spectrum of the UV-irradiated sample. All panels visualize the spectral region of 1655–1585 cm^{-1}; the labels in panels (**c**) and (**d**) show the most intense bands of the respective isomers in the region. The asterisks in panels (**c**) and (**d**) mark the bands belonging to the matrix-isolated monomeric H_2O impurity.

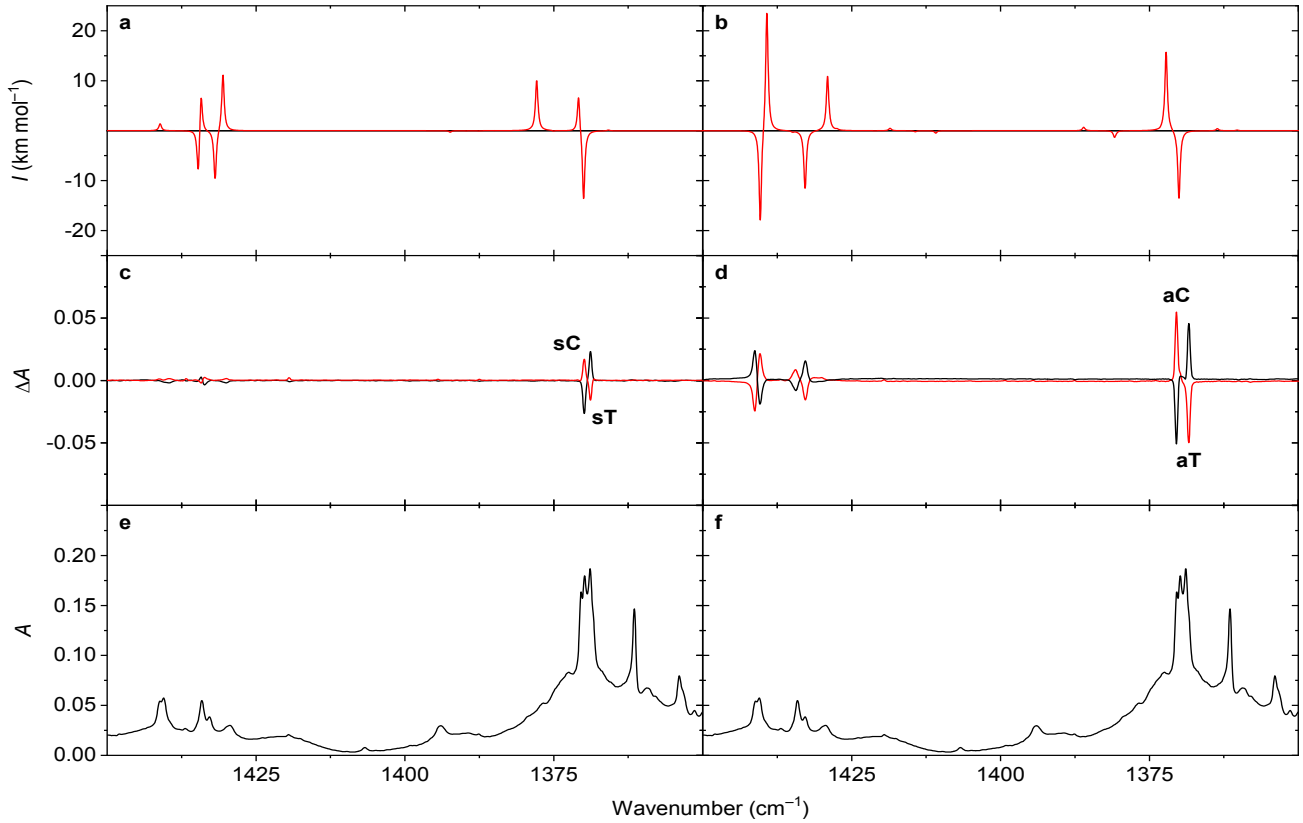

Figure S11. Simulated difference spectra of the *syn* (**a**) and *anti* (**b**) isomers; the growing bands are those of the **sC** and **aC**, respectively. (**c**) Experimental difference spectra of the *syn* isomers upon near-IR irradiation of 6422 cm^{-1} (black) and 6398 cm^{-1} (red). (**d**) Experimental difference spectra of the *anti* isomers upon near-IR irradiation of 6378 cm^{-1} (black) and 6405 cm^{-1} (red) (**e**, **f**) Mid-IR spectrum of the UV-irradiated sample. All panels visualize the spectral region of 1450–1300 cm^{-1}; the labels in panels (**c**) and (**d**) show the most intense bands of the respective isomers in the region.

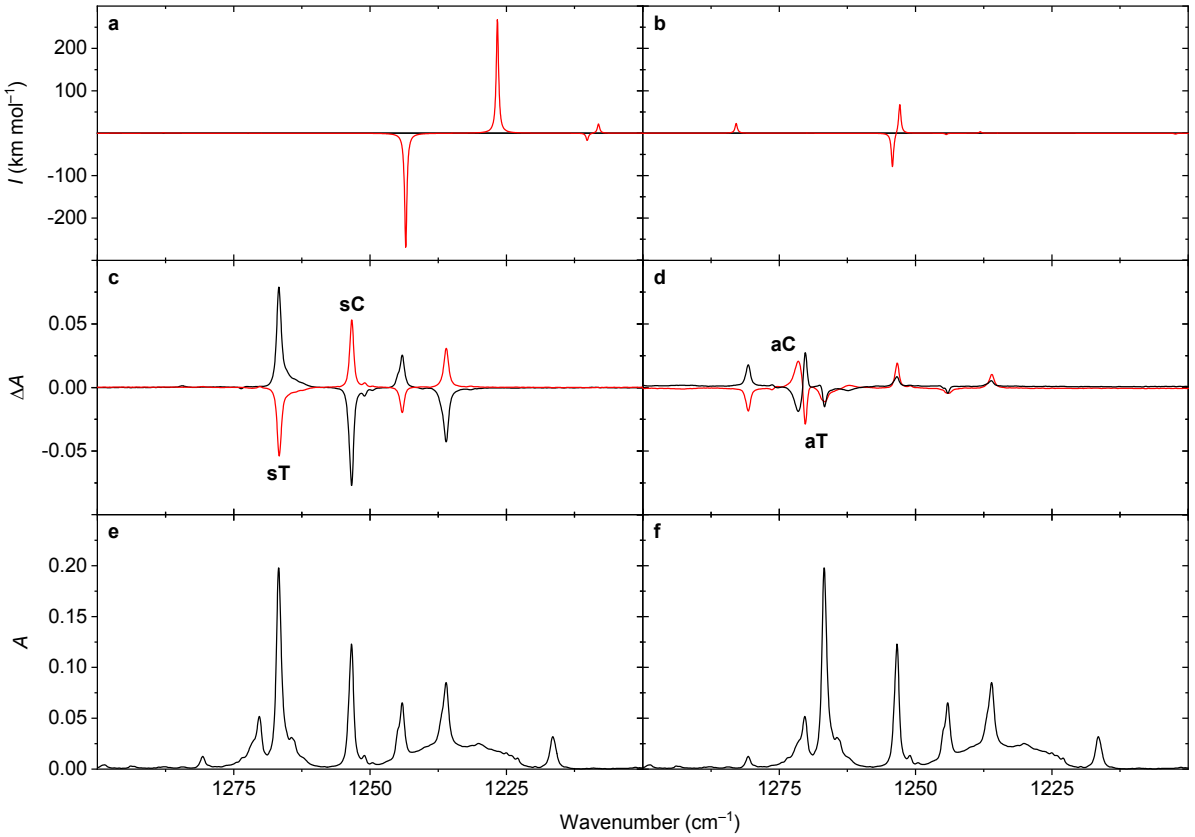

Figure S12. Simulated difference spectra of the *syn* (**a**) and *anti* (**b**) isomers; the growing bands are those of the **sC** and **aC**, respectively. (**c**) Experimental difference spectra of the *syn* isomers upon near-IR irradiation of 6422 cm^{-1} (black) and 6398 cm^{-1} (red). (**d**) Experimental difference spectra of the *anti* isomers upon near-IR irradiation of 6378 cm^{-1} (black) and 6405 cm^{-1} (red) (**e**, **f**) Mid-IR spectrum of the UV-irradiated sample. All panels visualize the spectral region of 1300–1200 cm^{-1}; the labels in panels (**c**) and (**d**) show the most intense bands of the respective isomers in the region.

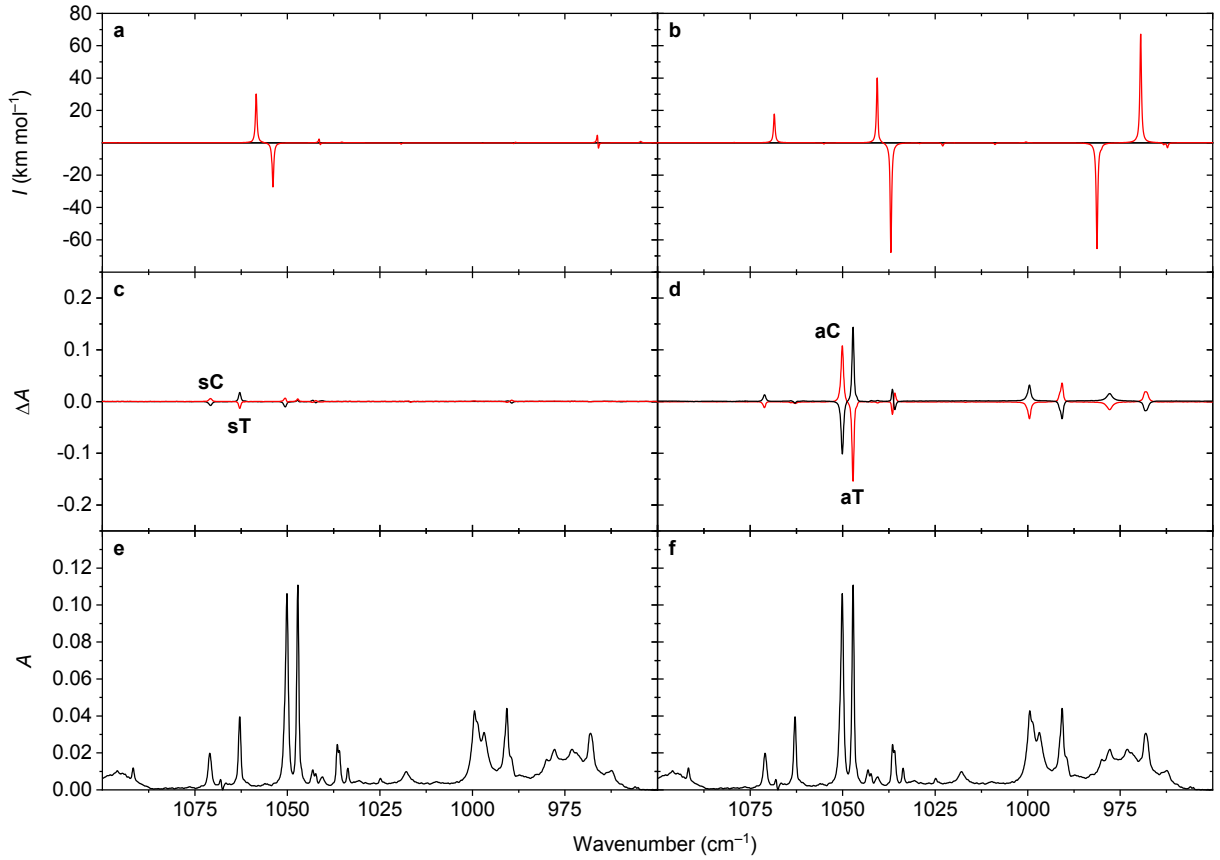

Figure S13. Simulated difference spectra of the *syn* (**a**) and *anti* (**b**) isomers; the growing bands are those of the **sC** and **aC**, respectively. (**c**) Experimental difference spectra of the *syn* isomers upon near-IR irradiation of 6422 cm^{-1} (black) and 6398 cm^{-1} (red). (**d**) Experimental difference spectra of the *anti* isomers upon near-IR irradiation of 6378 cm^{-1} (black) and 6405 cm^{-1} (red) (**e**, **f**) Mid-IR spectrum of the UV-irradiated sample. All panels visualize the spectral region of 1100–950 cm^{-1}; the labels in panels (**c**) and (**d**) show the most intense bands of the respective isomers in the region.

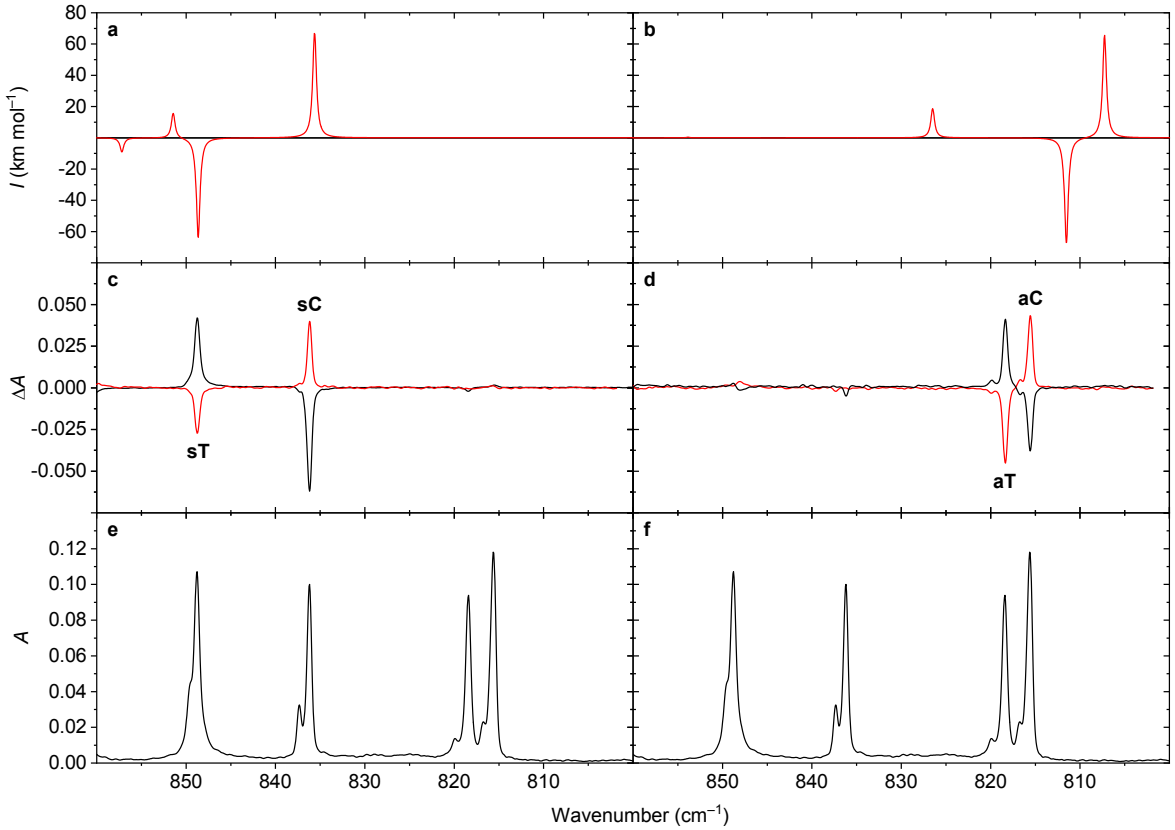

Figure S14. Simulated difference spectra of the *syn* (**a**) and *anti* (**b**) isomers; the growing bands are those of the **sC** and **aC**, respectively. (**c**) Experimental difference spectra of the *syn* isomers upon near-IR irradiation of 6422 cm^{-1} (black) and 6398 cm^{-1} (red). (**d**) Experimental difference spectra of the *anti* isomers upon near-IR irradiation of 6378 cm^{-1} (black) and 6405 cm^{-1} (red) (**e**, **f**) Mid-IR spectrum of the UV-irradiated sample. All panels visualize the spectral region of 860–800 cm^{-1}; the labels in panels (**c**) and (**d**) show the most intense bands of the respective isomers in the region.

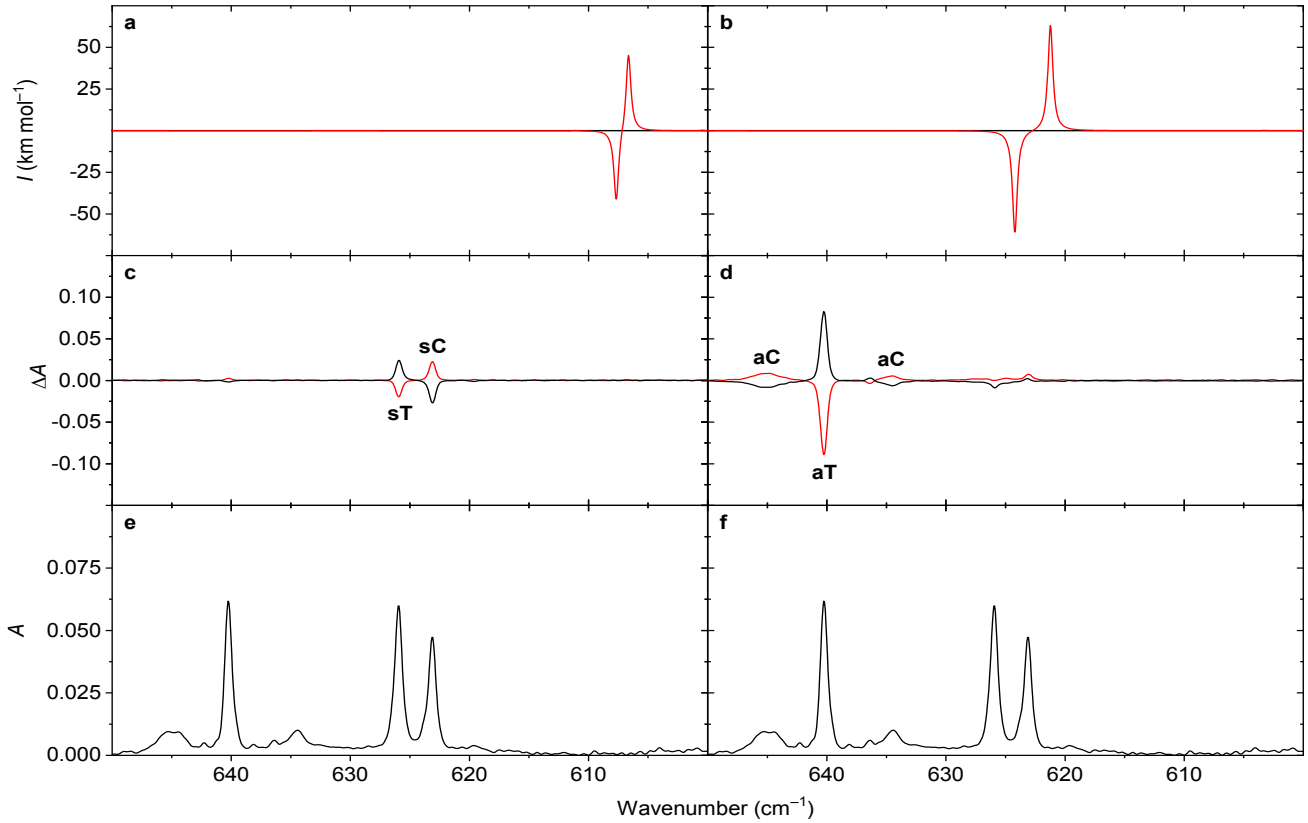

Figure S15. Simulated difference spectra of the *syn* (**a**) and *anti* (**b**) isomers; the growing bands are those of the **sC** and **aC**, respectively. (**c**) Experimental difference spectra of the *syn* isomers upon near-IR irradiation of 6422 cm^{-1} (black) and 6398 cm^{-1} (red). (**d**) Experimental difference spectra of the *anti* isomers upon near-IR irradiation of 6378 cm^{-1} (black) and 6405 cm^{-1} (red) (**e**, **f**) Mid-IR spectrum of the UV-irradiated sample. All panels visualize the spectral region of 650–600 cm^{-1}; the labels in panels (**c**) and (**d**) show the most intense bands of the respective isomers in the region

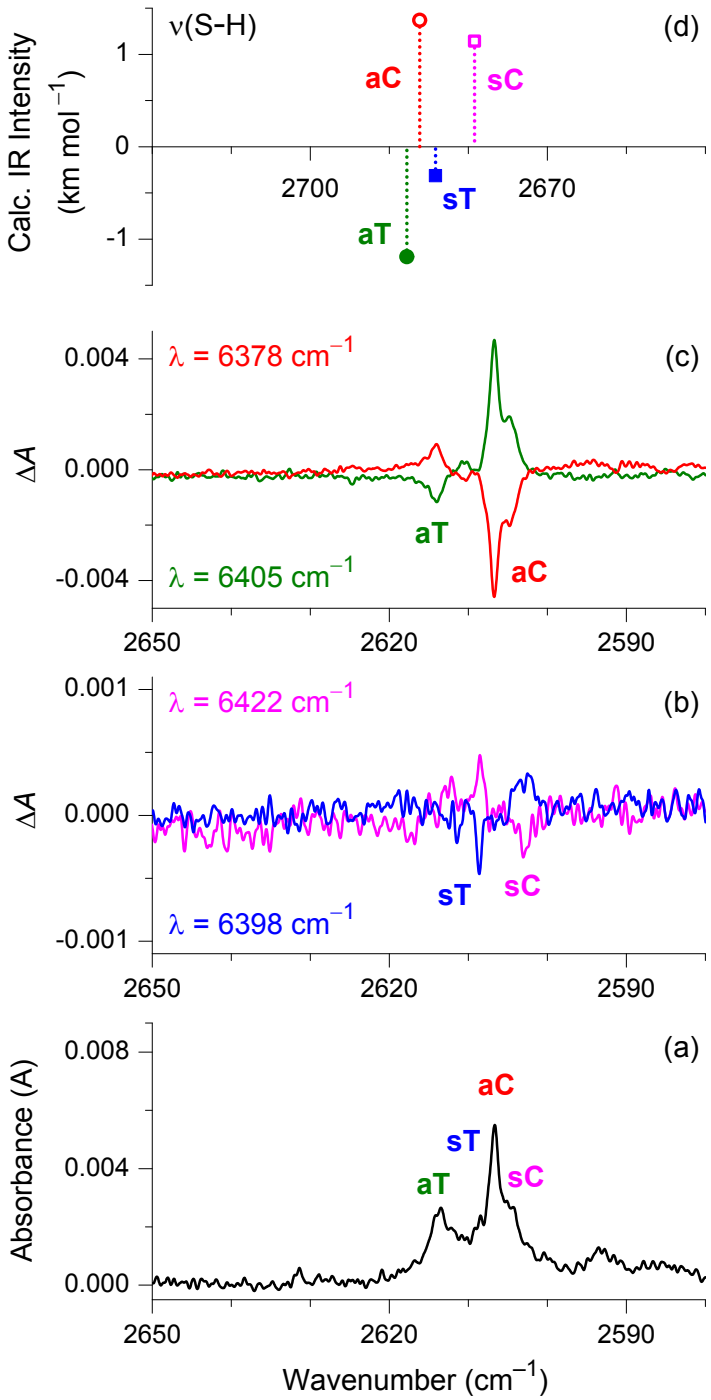

Figure S16. (**a**) Experimental mid-IR spectrum ν(SH) region, showing new bands of imino-thiol photoproducts growing upon UV irradiations of thioacetamide isolated in an argon matrix at 11 K; Experimental difference spectra showing changes in absorption (ΔA) upon subsequent irradiations of the sample with monochromatic near-IR laser light (**b**) at 6398 cm^{-1} (blue) or at 6422 cm^{-1} (pink); (**c**) at 6405 cm^{-1} (green) or at 6378 cm^{-1} (red); (**d**) harmonic wavenumbers (unscaled) and IR intensities of **sC** (pink, open squares) and **sT** (blue, closed squares), **aT** (green, closed circles), and **aC** (red, open circles) imino-thiol forms computed at the B3LYP/6-311++G(3df,3pd) level of theory. Intensities of **sT** and **aT** forms are multiplied by (−1).

Table S1. Assignment of the FT-IR data of the thiol tautomers upon irradiation on the sample isolated in Ar matrix.

Wavenumber (cm^{-1})		$I_{exp.}$[b]	$I_{theor.}$ (km mol^{-1})	Change upon irradiation of[c]					Symm.	Assignment[d]	
Exp.[a]	Theor.			UV	6405 cm^{-1}	6378 cm^{-1}	6422 cm^{-1}	6398 cm^{-1}			
6422	6434	0.3	4.0	+	N/A[c]	N/A[c]	N/A[c]	N/A[c]	A′	2ν(NH)	**sC**[e]
6405	6417	0.5	4.6	+	N/A[c]	N/A[c]	N/A[c]	N/A[c]	A′	2ν(NH)	**aT**[e]
6398	6413	0.3	4.0	+	N/A[c]	N/A[c]	N/A[c]	N/A[c]	A′	2ν(NH)	**sT**[e]
6378	6384	0.7	5.0	+	N/A[c]	N/A[c]	N/A[c]	N/A[c]	A′	2ν(NH)	**aC**[e]
4543	4546–4525	N/A	1	+	N/A	N/A	N/A	N/A	N/A	N/A	‘thiols’[f]
3292	3300	1.7	3.1	+	0	0	–	+	A′	ν(NH)	**sC**
3282	3291	1.0	2.1	+	–	+	0	0	A′	ν(NH)	**aT**
3276	3289	2.4	4.1	+	0	0	+	–	A′	ν(NH)	**sT**
3268	3276	1.9	1.8	+	+	–	0	0	A′	ν(NH)	**aC**
3248	3285	0.8	1.9	+	0	0	–	+	A′	2ν(C=N)	**sC**
3021	3001	1.6	6.0	+	0	0	–	+	A′	$\nu_{as}(CH_3)$	**sC**
3015	2996	3.1	8.4	+	0	0	–	+	A′	$\nu_{as}(CH_3)$	**sT**
3002,	2971	N/A	15	+	–	+	0	0	A′	$\nu_{as}(CH_3)$[d]	
2987,	2956	N/A	6.0	+	–	+	0	0	A″	$\nu_{as}(CH_3)$[d]	**aT**
2976, 2851	2933	N/A	8.4	+	–	+	0	0	A′	$\nu_{s}(CH_3)$[d]	

2995,	2978	N/A	12	+	–	–	0	0	A′	$\nu_{as}(CH_3)^d$	
2984, 2981,	2956	N/A	5.2	+	–	–	0	0	A″	$\nu_{as}(CH_3)^d$	**aC**
2979	2935	N/A	6.8	+	–	–	0	0	A′	$\nu_{s}(CH_3)^d$	
2883,	2954	N/A	6.6	+	0	0	–	+	A″	$\nu_{as}(CH_3)^d$	**sC**
2866	2935	N/A	6.3	+	0	0	–	+	A′	$\nu_{s}(CH_3)^d$	
2933,	2954	N/A	7.9	+	0	0	–	+	A″	$\nu_{as}(CH_3)^d$	**sT**
2891	2937	N/A	7.7	+	0	0	–	+	A′	$\nu_{s}(CH_3)^d$	
2614	2564	0.7	2.1	+	–	+	0	0	A′	ν(SH)	**aT**
2609	2558	0.7	1.4	+	0	0	+	–	A′	ν(SH)	**sT**
2607	2563	5.2	0.4	+	+	–	0	0	A′	ν(SH)	**aC**
2603	2557	3.1	1.3	+	0	0	–	+	A′	ν(SH)	**sC**
2476	2435	0.6	0.8	+	0	0	–	+	A′	2β(NH)	**sC**
2416	2404	0.3	0.2	+	+	–	0	0	A″	$\rho(CH_3)+\beta_s(CH_3)$	**aC**
1632	1648	130	122	+	0	0	–	+	A′	ν(C=N)	**sC**
1627	1645	168	74	+	0	0	+	–	A′	ν(C=N)	**sT**
1621	1642	145	139	+	+	+	0	0	A′	ν(C=N)	**aT**
1620sh	1640	65	134	+	–	–	0	0	A′	ν(C=N)	**aC**
1441	1440	20	15	+	–	+	0	0	A′	$\beta_{as}(CH_3)$	**aT**
1440	1439	26	19	+	+	–	0	0	A′	$\beta_{as}(CH_3)$	**aC**
1434,	1429	36	8.6	+	+	–	0	0	A″	$\beta_{as}(CH_3)$	**aC**[g]

1430											
1433	1433	29	9.0	+	–	+	0	0	A″	$\beta_{as}(CH_3)$	**aT**^{g}
1371	1372	31	12	+	+	–	0	0	A′	$\beta_{s}(CH_3)$	**aC**
1370sh	1371	56	6.0	+	0	0	–	+	A′	$\beta_{s}(CH_3)$	**sC**
1368	1370	51	11	+	0	0	+	–	A′	$\beta_{s}(CH_3)$	**sT**
1368sh	1370	32	11	+	–	+	0	0	A′	$\beta_{s}(CH_3)$	**aT**
1318	N/A	N/A	N/A	+	–	+	0	0	N/A	N/A	**aT**
1313	N/A	N/A	N/A	+	+	–	0	0	N/A	N/A	**aC**
1281	1254	42	64	+	–	+	0	0	A′	β(NH)	**aT**
1272sh	1253	41	55	+	+	–	0	0	A′	β(NH)	**aC**
1270	1244	10	2.5	+	–	+	0	0	A′	2ν(C–S)?	**aT**
1267	1243	244	212	+	–	+	+	–	A′	β(NH)	**sT**
1254	1227	107	211	+	+	–	–	+	A′	β(NH)	**sC**
1244	1210	54	14	+	–	+	+	–	A′	2ν(C–S)	**sT**
1236	1208	74	17	+	+	–	–	+	A′	2ν(C–S)	**sC**
1072sh	N/A	N/A	N/A	+	–	+	0	0	N/A	N/A	**aT**
1070	1058	4.8	24	+	0	0	–	+	A′	$\rho(CH_3)$	**sC**
1063	1054	29	22	+	–	0	+	–	A′	$\rho(CH_3)$	**sT**
1051sh	N/A	N/A	N/A	+	0	0	–	+	N/A	N/A	**sC**
1050	1041	77	33	+	+	–	0	0	A′	$\rho(CH_3)$	**aC**

1047	1037	68	55	+	–	+	0	0	A′	ρ(CH_3)	**aT**
1043, 1041	1042	8.3	2.3	+	0	0	+	–	A″	ρ(CH_3)	**sT**
1042sh	1042	2.8	3.0	+	0	0	–	+	A″	ρ(CH_3)	**sC**
1037	1040	12	3.8	+	–	+	0	0	A″	ρ(CH_3)	**aT**
1036	1037	15	5.0	+	+	–	0	0	A″	ρ(CH_3)	**aC**
1000sh	981	19	51	+	–	+	0	0	A′	ν(C–C)?	**aT**
991	969	38	53	+	+	–	0	0	A′	ν(C–C)?	**aC**
978	981	16	51	+	–	+	0	0	A′	ν(C–C)	**aT**
968	969	20	53	+	+	–	0	0	A′	ν(C–C)	**aC**
891, 890	872	9.0	13	+	–	+	0	0	A′	β(SH)	**aT**
869	857	8.0	7.1	+	0	0	+	–	A′	β(SH)	**sT**
860	851	10	13	+	0	0	–	+	A′	β(SH)	**sC**
850sh, 849	849	108	50	+	0	0	+	–	A″	τ(NH)	**sT**
849	827	N/A	15	+	+	–	0	0	A′	β(SH)	**aC**
837, 836	836	64	53	+	0	0	–	+	A″	τ(NH)	**sC**
820, 818	812	65	53	+	–	+	0	0	A″	τ(NH)	**aT**
817, 816	807	83	52	+	+	–	0	0	A″	τ(NH)	**aC**
645, 635	621	30	50	+	+	–	0	0	A′	ν(C–S)	**aC**
640	624	36	49	+	–	+	0	0	A′	ν(C–S)	**aT**

626	608	43	35	+	0	0	+	–	A′	ν(C–S)	**sT**
623	607	32	37	+	0	0	–	+	A′	ν(C–S)	**sC**
446	446	11	5.1	+	+	–	0	0	A′	β(NCS)	**aC**
443	437	11	12	+	0	0	–	+	A′	β(NCS)	**sC**
431	430	2.2	1.7	+	–	+	0	0	A′	β(NCS)	**aT**
421	5.4	416	13	+	0	0	+	–	A′	β(NCS)	**sT**

[a] sh: shoulder

[b] Normalized experimental band areas. The values were obtained by multiplying the integrated band areas with the sum of the theoretical IR intensities then divided by the sum of the experimental band areas.

[b] –/+: decrease/increase of signal, 0: no change upon irradiation

[c] ν: stretching, β: bending, ρ: rocking, ω: wagging, τ: torsional, s: symmetric, as: antisymmetric vibrations, ?: tentative assignment.

[d] Spectral assignment made based on the results of near-IR irradiation experiments.

[e] Unequivocal assignment could not be done due to extensive overlap.

[f] Contribution from *syn*-thiols cannot be excluded.

For the Cartesian coordinates of the isomers at the B3LYP/6-311++G(3df,3pd) level of theory, please refer to the Electronic Supplementary Information of S. Góbi, C. M. Nunes, I. Reva, G. Tarczay and R. Fausto, *Phys. Chem. Chem. Phys.*, 2019, **21**, 17063–17071.

Table S2. Unscaled harmonic (E_{harm}, in cm^{-1}) and anharmonic (E_{anharm}, in cm^{-1}) frequencies and absolute harmonic (I_{harm}, in km mol^{-1}) and anharmonic (I_{anharm}, in km mol^{-1}) IR intensities of the **Tn** tautomer of thioacetamide as computed at the B3LYP/6-311++G(3df,3pd) level of theory.

Fundamental Bands				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
1(1)	3694.415	3530.798	37.285	24.599
2(1)	3564.732	3413.988	42.076	20.607
3(1)	3166.228	3017.297	1.524	2.173
4(1)	3021.311	2916.398	18.852	18.706
5(1)	1637.565	1598.735	154.992	121.347
6(1)	1481.547	1433.216	10.382	11.749
7(1)	1403.887	1371.743	38.282	21.159
8(1)	1376.526	1347.476	244.911	222.187
9(1)	1322.229	1308.790	40.785	32.914
10(1)	1021.885	998.631	24.153	8.344
11(1)	987.730	986.736	16.004	41.814
12(1)	732.480	735.087	7.616	2.219
13(1)	427.289	433.558	1.183	1.795
14(1)	378.204	382.911	1.983	2.081
15(1)	3071.695	2932.357	8.246	6.348
16(1)	1488.043	1436.821	8.218	4.100
17(1)	1037.639	1008.463	0.220	0.049
18(1)	612.911	603.021	5.330	12.508
19(1)	518.057	500.505	3.758	12.614
20(1)	337.277	327.222	157.389	141.700
21(1)	31.807	113.138	0.008	2.610
Overtones				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
1(2)	7388.831	6983.524		2.304
2(2)	7129.464	6756.629		2.200
3(2)	6332.455	5930.712		0.498
4(2)	6042.623	5735.997		0.166
5(2)	3275.129	3177.657		1.779
6(2)	2963.094	2838.727		0.057
7(2)	2807.773	2726.752		0.624
8(2)	2753.052	2678.871		0.354
9(2)	2644.459	2612.156		0.263

10(2)	2043.770	1995.308		0.083
11(2)	1975.459	1937.588		1.203
12(2)	1464.960	1468.979		3.147
13(2)	854.579	868.195		0.045
14(2)	756.408	766.603		0.003
15(2)	6143.391	5799.723		0.611
16(2)	2976.086	2880.742		0.119
17(2)	2075.277	2019.200		0.035
18(2)	1225.822	1188.788		2.810
19(2)	1036.114	1003.334		7.717
20(2)	674.555	733.109		85.209
21(2)	63.614	277.368		0.390
Combination Bands				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
2(1) 1(1)	7259.147	6804.575		2.144
3(1) 1(1)	6860.643	6548.364		0.000
3(1) 2(1)	6730.960	6431.414		0.000
4(1) 1(1)	6715.727	6423.664		0.005
4(1) 2(1)	6586.043	6306.707		0.014
4(1) 3(1)	6187.539	5892.698		0.065
5(1) 1(1)	5331.980	5108.627		1.951
5(1) 2(1)	5202.297	5007.559		0.385
5(1) 3(1)	4803.792	4615.771		0.006
5(1) 4(1)	4658.876	4490.475		0.012
6(1) 1(1)	5175.963	4963.644		0.105
6(1) 2(1)	5046.279	4846.745		0.004
6(1) 3(1)	4647.775	4438.984		0.136
6(1) 4(1)	4502.858	4308.273		0.031
6(1) 5(1)	3119.112	3031.051		0.064
7(1) 1(1)	5098.302	4902.505		0.011
7(1) 2(1)	4968.619	4785.467		0.023
7(1) 3(1)	4570.114	4384.466		0.192
7(1) 4(1)	4425.198	4274.601		0.117
7(1) 5(1)	3041.451	2969.493		0.379
7(1) 6(1)	2885.434	2800.700		0.231
8(1) 1(1)	5070.941	4872.883		0.243
8(1) 2(1)	4941.258	4755.138		0.014
8(1) 3(1)	4542.754	4358.598		0.176
8(1) 4(1)	4397.837	4235.615		0.453
8(1) 5(1)	3014.091	2936.856		0.921
8(1) 6(1)	2858.073	2771.802		0.474
8(1) 7(1)	2780.413	2710.710		0.052
9(1) 1(1)	5016.645	4834.883		2.454
9(1) 2(1)	4886.962	4718.703		0.605
9(1) 3(1)	4488.457	4325.188		0.158

9(1)	4(1)	4343.541	4199.951		0.059
9(1)	5(1)	2959.794	2901.160		0.503
9(1)	6(1)	2803.777	2740.419		0.197
9(1)	7(1)	2726.116	2677.130		0.473
9(1)	8(1)	2698.756	2649.296		0.779
10(1)	1(1)	4716.300	4530.232		0.004
10(1)	2(1)	4586.617	4412.925		0.012
10(1)	3(1)	4188.113	4006.874		0.046
10(1)	4(1)	4043.196	3889.925		0.091
10(1)	5(1)	2659.450	2596.027		0.213
10(1)	6(1)	2503.432	2428.543		0.377
10(1)	7(1)	2425.772	2367.405		0.479
10(1)	8(1)	2398.411	2338.437		0.307
10(1)	9(1)	2344.115	2304.875		0.353
11(1)	1(1)	4682.145	4495.577		1.114
11(1)	2(1)	4552.462	4379.292		0.010
11(1)	3(1)	4153.957	3988.096		0.008
11(1)	4(1)	4009.041	3861.758		0.015
11(1)	5(1)	2625.294	2561.363		1.222
11(1)	6(1)	2469.277	2401.760		0.021
11(1)	7(1)	2391.616	2339.257		0.338
11(1)	8(1)	2364.256	2311.707		0.134
11(1)	9(1)	2309.959	2271.254		0.004
11(1)	10(1)	2009.615	1967.450		0.156
12(1)	1(1)	4426.896	4266.721		0.019
12(1)	2(1)	4297.212	4149.483		0.036
12(1)	3(1)	3898.708	3752.915		0.003
12(1)	4(1)	3753.791	3627.101		0.016
12(1)	5(1)	2370.045	2333.095		0.177
12(1)	6(1)	2214.027	2167.833		0.127
12(1)	7(1)	2136.367	2103.267		0.167
12(1)	8(1)	2109.006	2076.871		0.833
12(1)	9(1)	2054.710	2040.394		0.241
12(1)	10(1)	1754.365	1732.972		1.273
12(1)	11(1)	1720.210	1703.600		2.367
13(1)	1(1)	4121.705	3965.015		0.005
13(1)	2(1)	3992.021	3847.561		0.278
13(1)	3(1)	3593.517	3450.764		0.008
13(1)	4(1)	3448.601	3325.497		0.010
13(1)	5(1)	2064.854	2031.528		0.395
13(1)	6(1)	1908.837	1867.658		0.030
13(1)	7(1)	1831.176	1804.905		0.025
13(1)	8(1)	1803.815	1775.016		0.046
13(1)	9(1)	1749.519	1742.112		0.020
13(1)	10(1)	1449.174	1431.385		0.113

13(1)	11(1)	1415.019	1402.929		0.045
13(1)	12(1)	1159.770	1168.185		0.022
14(1)	1(1)	4072.619	3915.660		0.045
14(1)	2(1)	3942.936	3797.990		0.053
14(1)	3(1)	3544.432	3400.425		0.123
14(1)	4(1)	3399.515	3274.657		0.068
14(1)	5(1)	2015.769	1981.648		0.031
14(1)	6(1)	1859.751	1817.420		0.011
14(1)	7(1)	1782.091	1755.275		0.106
14(1)	8(1)	1754.730	1726.857		0.039
14(1)	9(1)	1700.433	1689.747		0.029
14(1)	10(1)	1400.089	1380.210		14.543
14(1)	11(1)	1365.934	1351.856		0.214
14(1)	12(1)	1110.684	1116.510		0.086
14(1)	13(1)	805.493	817.585		0.057
15(1)	1(1)	6766.111	6464.045		0.000
15(1)	2(1)	6636.428	6347.044		0.000
15(1)	3(1)	6237.923	5945.572		0.102
15(1)	4(1)	6093.007	5712.270		0.266
15(1)	5(1)	4709.260	4530.787		0.002
15(1)	6(1)	4553.243	4352.253		0.107
15(1)	7(1)	4475.582	4297.225		0.161
15(1)	8(1)	4448.221	4273.118		0.215
15(1)	9(1)	4393.925	4240.324		0.102
15(1)	10(1)	4093.580	3928.636		0.022
15(1)	11(1)	4059.425	3902.321		0.023
15(1)	12(1)	3804.176	3667.722		0.000
15(1)	13(1)	3498.985	3365.914		0.001
15(1)	14(1)	3449.899	3315.116		0.017
16(1)	1(1)	5182.459	4975.110		0.000
16(1)	2(1)	5052.775	4858.120		0.001
16(1)	3(1)	4654.271	4443.942		0.153
16(1)	4(1)	4509.354	4320.356		0.227
16(1)	5(1)	3125.608	3042.418		0.001
16(1)	6(1)	2969.590	2870.094		0.275
16(1)	7(1)	2891.930	2807.484		0.167
16(1)	8(1)	2864.569	2787.045		0.006
16(1)	9(1)	2810.273	2751.604		0.003
16(1)	10(1)	2509.928	2434.003		0.057
16(1)	11(1)	2475.773	2412.784		0.005
16(1)	12(1)	2220.523	2178.348		0.012
16(1)	13(1)	1915.333	1878.640		0.003
16(1)	14(1)	1866.247	1827.980		0.018
16(1)	15(1)	4559.739	4369.489		0.154
17(1)	1(1)	4732.054	4542.814		0.000

17(1)	2(1)	4602.371	4425.723		0.003
17(1)	3(1)	4203.866	4025.717		0.008
17(1)	4(1)	4058.950	3895.734		0.152
17(1)	5(1)	2675.203	2609.753		0.000
17(1)	6(1)	2519.186	2438.450		0.015
17(1)	7(1)	2441.525	2378.384		0.211
17(1)	8(1)	2414.165	2353.912		0.045
17(1)	9(1)	2359.868	2317.111		0.002
17(1)	10(1)	2059.524	2008.182		0.000
17(1)	11(1)	2025.368	1977.296		0.000
17(1)	12(1)	1770.119	1746.235		0.026
17(1)	13(1)	1464.928	1444.188		0.330
17(1)	14(1)	1415.843	1393.669		0.143
17(1)	15(1)	4109.334	3936.388		0.053
17(1)	16(1)	2525.682	2451.412		0.135
18(1)	1(1)	4307.326	4132.558		0.442
18(1)	2(1)	4177.643	4015.484		0.040
18(1)	3(1)	3779.139	3619.763		0.000
18(1)	4(1)	3634.222	3494.383		0.001
18(1)	5(1)	2250.476	2204.511		0.019
18(1)	6(1)	2094.458	2036.280		0.000
18(1)	7(1)	2016.798	1974.772		0.002
18(1)	8(1)	1989.437	1945.326		0.000
18(1)	9(1)	1935.140	1924.744		0.114
18(1)	10(1)	1634.796	1599.940		0.001
18(1)	11(1)	1600.640	1568.640		0.119
18(1)	12(1)	1345.391	1338.187		0.000
18(1)	13(1)	1040.200	1037.173		0.042
18(1)	14(1)	991.115	986.555		0.001
18(1)	15(1)	3684.606	3534.411		0.032
18(1)	16(1)	2100.954	2046.448		0.015
18(1)	17(1)	1650.549	1614.328		8.250
19(1)	1(1)	4212.472	4032.260		0.055
19(1)	2(1)	4082.789	3914.670		0.025
19(1)	3(1)	3684.285	3516.826		0.000
19(1)	4(1)	3539.368	3392.720		0.005
19(1)	5(1)	2155.621	2099.407		0.007
19(1)	6(1)	1999.604	1930.896		0.001
19(1)	7(1)	1921.944	1871.320		0.077
19(1)	8(1)	1894.583	1843.131		0.004
19(1)	9(1)	1840.286	1808.053		0.020
19(1)	10(1)	1539.942	1496.820		0.641
19(1)	11(1)	1505.786	1470.374		0.287
19(1)	12(1)	1250.537	1235.701		0.001
19(1)	13(1)	945.346	934.954		0.007

19(1)	14(1)	896.261	883.910		0.001
19(1)	15(1)	3589.752	3433.367		0.111
19(1)	16(1)	2006.100	1939.183		0.060
19(1)	17(1)	1555.695	1514.415		0.861
19(1)	18(1)	1130.968	1102.068		0.989
20(1)	1(1)	4031.693	3825.554		0.003
20(1)	2(1)	3902.009	3719.570		0.443
20(1)	3(1)	3503.505	3342.690		0.001
20(1)	4(1)	3358.589	3217.881		0.016
20(1)	5(1)	1974.842	1932.593		1.101
20(1)	6(1)	1818.824	1758.361		0.018
20(1)	7(1)	1741.164	1695.861		0.009
20(1)	8(1)	1713.803	1660.253		0.077
20(1)	9(1)	1659.507	1644.720		0.005
20(1)	10(1)	1359.162	1323.918		0.018
20(1)	11(1)	1325.007	1310.913		0.006
20(1)	12(1)	1069.757	1060.293		0.031
20(1)	13(1)	764.567	755.084		0.001
20(1)	14(1)	715.481	702.128		0.018
20(1)	15(1)	3408.973	3257.519		0.023
20(1)	16(1)	1825.320	1767.892		0.065
20(1)	17(1)	1374.916	1330.238		0.006
20(1)	18(1)	950.188	895.337		8.923
20(1)	19(1)	855.334	813.700		1.541
21(1)	1(1)	3726.222	3671.667		0.026
21(1)	2(1)	3596.539	3545.102		0.006
21(1)	3(1)	3198.035	3111.772		0.000
21(1)	4(1)	3053.118	3008.355		0.065
21(1)	5(1)	1669.371	1716.102		0.083
21(1)	6(1)	1513.354	1531.105		4.335
21(1)	7(1)	1435.694	1501.315		0.353
21(1)	8(1)	1408.333	1467.028		0.001
21(1)	9(1)	1354.036	1431.589		0.222
21(1)	10(1)	1053.692	1115.974		0.022
21(1)	11(1)	1019.536	1087.103		0.114
21(1)	12(1)	764.287	871.098		0.020
21(1)	13(1)	459.096	564.176		0.024
21(1)	14(1)	410.011	510.246		0.000
21(1)	15(1)	3103.502	3054.861		8.026
21(1)	16(1)	1519.850	1558.261		2.801
21(1)	17(1)	1069.445	1123.932		1.668
21(1)	18(1)	644.718	746.837		0.118
21(1)	19(1)	549.864	598.342		0.132
21(1)	20(1)	369.084	367.334		0.203

Table S3. Unscaled harmonic (E_{harm}, in cm^{-1}) and anharmonic (E_{anharm}, in cm^{-1}) frequencies and absolute harmonic (I_{harm}, in km mol^{-1}) and anharmonic (I_{anharm}, in km mol^{-1}) IR intensities of the **aC** isomer of thioacetamide as computed at the B3LYP/6-311++G(3df,3pd) level of theory.

Fundamental Bands				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
1(1)	3455.068	3275.813	1.600	1.766
2(1)	3118.941	2978.127	11.769	12.468
3(1)	3035.015	2934.502	5.506	6.811
4(1)	2686.155	2562.644	1.370	0.392
5(1)	1680.886	1639.983	149.379	133.907
6(1)	1482.424	1439.240	22.693	19.241
7(1)	1406.182	1372.197	14.062	12.498
8(1)	1299.347	1252.891	69.282	55.360
9(1)	1070.337	1040.666	52.219	32.872
10(1)	996.465	969.477	53.511	52.971
11(1)	851.843	826.488	13.761	14.694
12(1)	636.633	621.233	49.157	49.960
13(1)	449.857	446.087	6.907	5.070
14(1)	325.300	323.712	4.344	4.355
15(1)	3095.049	2955.548	4.160	5.240
16(1)	1472.775	1429.048	11.582	8.562
17(1)	1063.927	1037.282	5.184	4.952
18(1)	828.737	807.255	53.977	51.706
19(1)	501.375	497.483	0.075	0.111
20(1)	339.808	348.833	18.091	17.956
21(1)	97.849	103.946	0.468	0.166
Overtones				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
1(2)	6910.136	6384.375		4.835
2(2)	6237.881	5881.345		0.487
3(2)	6070.030	5781.910		0.064
4(2)	5372.309	5018.358		0.312
5(2)	3361.772	3268.699		2.524
6(2)	2964.849	2873.263		0.029
7(2)	2812.365	2725.279		0.045
8(2)	2598.694	2501.560		0.087
9(2)	2140.674	2078.101		0.005
10(2)	1992.930	1945.234		0.049
11(2)	1703.686	1676.165		0.448
12(2)	1273.265	1238.130		2.701
13(2)	899.714	892.411		0.015
14(2)	650.600	648.107		0.045

15(2)	6190.097	5848.071		0.469
16(2)	2945.549	2831.485		0.128
17(2)	2127.855	2071.533		0.097
18(2)	1657.474	1607.438		6.539
19(2)	1002.750	1000.443		0.393
20(2)	679.615	710.741		1.081
21(2)	195.697	207.069		0.030
Combination Bands				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
2(1) 1(1)	6574.009	6254.405		0.014
3(1) 1(1)	6490.083	6184.504		0.005
3(1) 2(1)	6153.956	5826.128		0.107
4(1) 1(1)	6141.223	5838.315		0.005
4(1) 2(1)	5805.095	5540.670		0.002
4(1) 3(1)	5721.170	5471.399		0.000
5(1) 1(1)	5135.954	4918.823		0.121
5(1) 2(1)	4799.827	4623.665		0.093
5(1) 3(1)	4715.901	4551.235		0.083
5(1) 4(1)	4367.041	4206.791		0.091
6(1) 1(1)	4937.492	4716.195		0.094
6(1) 2(1)	4601.365	4407.470		0.265
6(1) 3(1)	4517.440	4329.490		0.081
6(1) 4(1)	4168.579	4003.147		0.003
6(1) 5(1)	3163.311	3083.409		0.589
7(1) 1(1)	4861.250	4648.107		0.009
7(1) 2(1)	4525.123	4346.867		0.150
7(1) 3(1)	4441.198	4293.117		0.169
7(1) 4(1)	4092.337	3934.673		0.003
7(1) 5(1)	3087.068	3013.143		0.911
7(1) 6(1)	2888.607	2807.916		0.234
8(1) 1(1)	4754.415	4529.838		1.235
8(1) 2(1)	4418.288	4235.037		0.085
8(1) 3(1)	4334.362	4166.850		0.194
8(1) 4(1)	3985.502	3820.960		0.031
8(1) 5(1)	2980.233	2899.249		0.692
8(1) 6(1)	2781.772	2697.210		0.116
8(1) 7(1)	2705.530	2629.118		0.053
9(1) 1(1)	4525.405	4316.194		0.002
9(1) 2(1)	4189.278	4013.258		0.177
9(1) 3(1)	4105.352	3947.376		0.162
9(1) 4(1)	3756.492	3603.197		0.017
9(1) 5(1)	2751.223	2682.047		0.091
9(1) 6(1)	2552.762	2476.087		0.080
9(1) 7(1)	2476.520	2409.559		0.068

9(1)	8(1)	2369.684	2286.505		0.231
10(1)	1(1)	4451.533	4250.202		0.107
10(1)	2(1)	4115.406	3953.033		0.051
10(1)	3(1)	4031.480	3882.405		0.045
10(1)	4(1)	3682.620	3528.506		0.443
10(1)	5(1)	2677.351	2612.883		1.716
10(1)	6(1)	2478.890	2413.525		0.048
10(1)	7(1)	2402.648	2343.962		0.344
10(1)	8(1)	2295.812	2227.581		0.303
10(1)	9(1)	2066.802	2011.382		0.049
11(1)	1(1)	4306.911	4113.392		0.002
11(1)	2(1)	3970.783	3815.432		0.036
11(1)	3(1)	3886.858	3745.473		0.012
11(1)	4(1)	3537.998	3386.146		0.480
11(1)	5(1)	2532.729	2478.210		0.109
11(1)	6(1)	2334.267	2276.465		0.023
11(1)	7(1)	2258.025	2206.469		0.296
11(1)	8(1)	2151.190	2092.045		0.170
11(1)	9(1)	1922.180	1875.237		0.178
11(1)	10(1)	1848.308	1808.104		1.455
12(1)	1(1)	4091.700	3897.333		0.001
12(1)	2(1)	3755.573	3599.226		0.052
12(1)	3(1)	3671.648	3530.097		0.029
12(1)	4(1)	3322.787	3184.031		0.018
12(1)	5(1)	2317.519	2265.139		0.060
12(1)	6(1)	2119.057	2061.248		0.030
12(1)	7(1)	2042.815	1992.452		0.102
12(1)	8(1)	1935.980	1879.188		0.044
12(1)	9(1)	1706.970	1658.323		8.395
12(1)	10(1)	1633.098	1592.078		0.337
12(1)	11(1)	1488.475	1456.977		0.450
13(1)	1(1)	3904.925	3721.894		0.120
13(1)	2(1)	3568.797	3424.400		0.025
13(1)	3(1)	3484.872	3354.769		0.012
13(1)	4(1)	3136.012	3008.662		0.042
13(1)	5(1)	2130.743	2086.479		0.041
13(1)	6(1)	1932.281	1886.759		0.017
13(1)	7(1)	1856.039	1818.308		0.021
13(1)	8(1)	1749.204	1704.627		0.809
13(1)	9(1)	1520.194	1483.637		0.130
13(1)	10(1)	1446.322	1418.553		0.378
13(1)	11(1)	1301.700	1282.891		18.103
13(1)	12(1)	1086.489	1068.484		14.003
14(1)	1(1)	3780.368	3599.428		0.047
14(1)	2(1)	3444.240	3301.765		0.122

14(1)	3(1)	3360.315	3232.577		0.015
14(1)	4(1)	3011.454	2885.400		0.086
14(1)	5(1)	2006.186	1967.216		0.143
14(1)	6(1)	1807.724	1764.694		0.057
14(1)	7(1)	1731.482	1695.794		0.012
14(1)	8(1)	1624.647	1581.560		0.240
14(1)	9(1)	1395.637	1363.577		0.330
14(1)	10(1)	1321.765	1297.174		0.214
14(1)	11(1)	1177.143	1160.392		0.093
14(1)	12(1)	961.932	943.209		0.434
14(1)	13(1)	775.157	770.783		0.280
15(1)	1(1)	6550.116	6231.332		0.002
15(1)	2(1)	6213.989	5906.485		0.222
15(1)	3(1)	6130.064	5777.513		0.152
15(1)	4(1)	5781.203	5518.332		0.000
15(1)	5(1)	4775.935	4597.793		0.008
15(1)	6(1)	4577.473	4381.199		0.079
15(1)	7(1)	4501.231	4318.314		0.283
15(1)	8(1)	4394.396	4214.525		0.191
15(1)	9(1)	4165.386	3995.032		0.045
15(1)	10(1)	4091.514	3929.164		0.023
15(1)	11(1)	3946.891	3792.699		0.005
15(1)	12(1)	3731.681	3577.210		0.017
15(1)	13(1)	3544.905	3401.636		0.009
15(1)	14(1)	3420.348	3279.540		0.013
16(1)	1(1)	4927.843	4704.686		0.001
16(1)	2(1)	4591.715	4388.828		0.127
16(1)	3(1)	4507.790	4319.070		0.183
16(1)	4(1)	4158.929	3991.725		0.001
16(1)	5(1)	3153.661	3072.607		0.003
16(1)	6(1)	2955.199	2862.781		0.064
16(1)	7(1)	2878.957	2794.772		0.100
16(1)	8(1)	2772.122	2686.852		0.000
16(1)	9(1)	2543.112	2465.193		0.050
16(1)	10(1)	2469.240	2400.382		0.026
16(1)	11(1)	2324.617	2265.231		0.025
16(1)	12(1)	2109.407	2049.910		0.009
16(1)	13(1)	1922.631	1874.703		0.005
16(1)	14(1)	1798.074	1753.757		0.014
16(1)	15(1)	4567.823	4376.519		0.157
17(1)	1(1)	4518.995	4311.019		0.000
17(1)	2(1)	4182.868	4011.696		0.019
17(1)	3(1)	4098.943	3940.880		0.198
17(1)	4(1)	3750.082	3599.874		0.000
17(1)	5(1)	2744.814	2677.821		0.012

17(1)	6(1)	2546.352	2471.929		0.017
17(1)	7(1)	2470.110	2404.248		0.248
17(1)	8(1)	2363.275	2294.241		0.032
17(1)	9(1)	2134.265	2077.293		0.000
17(1)	10(1)	2060.393	2010.056		0.000
17(1)	11(1)	1915.770	1872.747		0.013
17(1)	12(1)	1700.560	1658.542		0.001
17(1)	13(1)	1513.784	1483.630		0.083
17(1)	14(1)	1389.227	1360.269		0.097
17(1)	15(1)	4158.976	3986.703		0.056
17(1)	16(1)	2536.702	2461.612		0.116
18(1)	1(1)	4283.805	4068.377		0.006
18(1)	2(1)	3947.677	3785.402		0.001
18(1)	3(1)	3863.752	3715.168		0.000
18(1)	4(1)	3514.892	3369.768		0.001
18(1)	5(1)	2509.623	2446.616		0.000
18(1)	6(1)	2311.161	2246.835		0.011
18(1)	7(1)	2234.919	2178.507		0.034
18(1)	8(1)	2128.084	2063.558		0.141
18(1)	9(1)	1899.074	1848.325		0.048
18(1)	10(1)	1825.202	1781.667		0.020
18(1)	11(1)	1680.580	1643.155		0.013
18(1)	12(1)	1465.369	1427.478		0.156
18(1)	13(1)	1278.594	1252.793		0.027
18(1)	14(1)	1154.037	1131.058		0.002
18(1)	15(1)	3923.785	3761.606		0.072
18(1)	16(1)	2301.512	2235.925		0.023
18(1)	17(1)	1892.664	1841.917		0.153
19(1)	1(1)	3956.443	3772.112		0.001
19(1)	2(1)	3620.315	3474.919		0.013
19(1)	3(1)	3536.390	3405.854		0.003
19(1)	4(1)	3187.530	3060.258		0.000
19(1)	5(1)	2182.261	2138.446		0.037
19(1)	6(1)	1983.799	1935.286		0.003
19(1)	7(1)	1907.557	1869.578		0.071
19(1)	8(1)	1800.722	1754.636		0.011
19(1)	9(1)	1571.712	1539.688		0.193
19(1)	10(1)	1497.840	1473.416		0.899
19(1)	11(1)	1353.218	1333.511		0.024
19(1)	12(1)	1138.007	1117.597		0.005
19(1)	13(1)	951.232	943.959		0.008
19(1)	14(1)	826.675	821.644		0.002
19(1)	15(1)	3596.423	3452.947		0.201
19(1)	16(1)	1974.150	1923.120		0.020
19(1)	17(1)	1565.302	1536.939		0.032

19(1)	18(1)	1330.112	1311.664		0.078
20(1)	1(1)	3794.876	3622.909		0.000
20(1)	2(1)	3458.748	3326.088		0.006
20(1)	3(1)	3374.823	3257.290		0.004
20(1)	4(1)	3025.962	2904.000		0.054
20(1)	5(1)	2020.694	1993.652		0.018
20(1)	6(1)	1822.232	1789.136		0.001
20(1)	7(1)	1745.990	1720.946		0.002
20(1)	8(1)	1639.155	1606.911		0.000
20(1)	9(1)	1410.145	1388.666		0.017
20(1)	10(1)	1336.273	1324.534		0.068
20(1)	11(1)	1191.651	1187.330		0.106
20(1)	12(1)	976.440	963.189		0.002
20(1)	13(1)	789.665	794.370		0.261
20(1)	14(1)	665.107	672.314		0.022
20(1)	15(1)	3434.856	3304.423		0.001
20(1)	16(1)	1812.582	1777.333		0.009
20(1)	17(1)	1403.735	1386.035		0.552
20(1)	18(1)	1168.545	1158.396		0.185
20(1)	19(1)	841.183	853.879		0.303
21(1)	1(1)	3552.917	3380.510		0.000
21(1)	2(1)	3216.789	3080.957		0.237
21(1)	3(1)	3132.864	3015.339		0.102
21(1)	4(1)	2784.003	2664.344		0.005
21(1)	5(1)	1778.735	1747.768		0.002
21(1)	6(1)	1580.273	1544.432		0.733
21(1)	7(1)	1504.031	1479.288		0.509
21(1)	8(1)	1397.196	1362.455		0.012
21(1)	9(1)	1168.186	1142.318		0.000
21(1)	10(1)	1094.314	1079.280		0.127
21(1)	11(1)	949.691	947.731		0.038
21(1)	12(1)	734.481	723.968		0.127
21(1)	13(1)	547.706	549.427		0.024
21(1)	14(1)	423.148	426.970		0.089
21(1)	15(1)	3192.897	3062.610		0.771
21(1)	16(1)	1570.623	1532.704		0.760
21(1)	17(1)	1161.776	1136.811		0.036
21(1)	18(1)	926.586	909.916		0.149
21(1)	19(1)	599.224	603.222		0.130
21(1)	20(1)	437.656	461.903		0.165

Table S4. Unscaled harmonic (E_{harm}, in cm^{-1}) and anharmonic (E_{anharm}, in cm^{-1}) frequencies and absolute harmonic (I_{harm}, in km mol^{-1}) and anharmonic (I_{anharm}, in km mol^{-1}) IR intensities of the **aT** isomer of thioacetamide as computed at the B3LYP/6-311++G(3df,3pd) level of theory.

Fundamental Bands				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
1(1)	3469.687	3290.781	2.815	2.063
2(1)	3112.067	2971.486	14.532	15.406
3(1)	3032.604	2932.917	6.878	8.399
4(1)	2687.783	2563.948	1.191	2.066
5(1)	1682.463	1641.880	165.996	138.737
6(1)	1482.867	1440.343	17.698	15.000
7(1)	1403.497	1370.036	12.099	10.784
8(1)	1300.045	1254.228	61.041	63.799
9(1)	1065.693	1036.969	65.215	55.302
10(1)	1011.458	981.263	50.293	51.430
11(1)	896.739	871.941	12.720	12.594
12(1)	638.007	624.218	48.304	48.551
13(1)	433.679	429.636	3.069	1.741
14(1)	340.089	343.964	0.712	0.841
15(1)	3095.908	2956.097	4.687	6.031
16(1)	1475.226	1432.822	11.498	9.173
17(1)	1064.877	1040.296	5.285	3.763
18(1)	831.920	811.525	58.239	53.297
19(1)	506.892	501.774	0.994	0.764
20(1)	245.068	161.718	4.993	4.704
21(1)	164.289	151.412	0.098	0.211
Overtones				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
1(2)	6939.374	6416.591		4.604
2(2)	6224.133	5872.684		0.516
3(2)	6065.207	5776.617		0.066
4(2)	5375.566	5021.709		0.229
5(2)	3364.925	3264.758		2.671
6(2)	2965.734	2876.113		0.036
7(2)	2806.993	2721.137		0.062
8(2)	2600.090	2503.416		0.146
9(2)	2131.385	2076.736		0.004
10(2)	2022.917	1968.572		0.005
11(2)	1793.477	1743.381		4.176
12(2)	1276.014	1244.373		2.465
13(2)	867.358	859.115		0.015
14(2)	680.177	682.884		0.030

15(2)	6191.816	5848.925		0.465
16(2)	2950.451	2834.425		0.166
17(2)	2129.755	2077.456		0.116
18(2)	1663.839	1616.204		7.827
19(2)	1013.783	1008.836		0.855
20(2)	490.136	262.464		1.132
21(2)	328.578	285.739		0.021
Combination Bands				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
2(1) 1(1)	6581.754	6262.575		0.010
3(1) 1(1)	6502.290	6196.384		0.004
3(1) 2(1)	6144.670	5809.852		0.132
4(1) 1(1)	6157.470	5854.822		0.002
4(1) 2(1)	5799.850	5535.410		0.009
4(1) 3(1)	5720.387	5469.874		0.007
5(1) 1(1)	5152.149	4931.501		0.119
5(1) 2(1)	4794.529	4615.289		0.094
5(1) 3(1)	4715.066	4546.161		0.110
5(1) 4(1)	4370.246	4204.672		0.027
6(1) 1(1)	4952.554	4731.072		0.105
6(1) 2(1)	4594.934	4400.906		0.254
6(1) 3(1)	4515.471	4326.595		0.100
6(1) 4(1)	4170.650	4004.249		0.028
6(1) 5(1)	3165.330	3081.150		0.477
7(1) 1(1)	4873.183	4660.892		0.014
7(1) 2(1)	4515.563	4338.059		0.148
7(1) 3(1)	4436.100	4287.826		0.201
7(1) 4(1)	4091.280	3933.957		0.000
7(1) 5(1)	3085.959	3008.772		1.357
7(1) 6(1)	2886.364	2805.525		0.240
8(1) 1(1)	4769.732	4546.108		1.399
8(1) 2(1)	4412.112	4229.448		0.100
8(1) 3(1)	4332.649	4164.636		0.184
8(1) 4(1)	3987.828	3823.175		0.035
8(1) 5(1)	2982.508	2898.147		0.666
8(1) 6(1)	2782.912	2697.896		0.112
8(1) 7(1)	2703.542	2627.731		0.039
9(1) 1(1)	4535.380	4330.916		0.003
9(1) 2(1)	4177.759	4006.606		0.143
9(1) 3(1)	4098.296	3943.679		0.182
9(1) 4(1)	3753.476	3603.905		0.013
9(1) 5(1)	2748.155	2679.668		0.150
9(1) 6(1)	2548.560	2475.094		0.060
9(1) 7(1)	2469.189	2406.655		0.053

9(1)	8(1)	2365.738	2285.721		0.345
10(1)	1(1)	4481.145	4275.713		0.118
10(1)	2(1)	4123.525	3957.539		0.020
10(1)	3(1)	4044.062	3890.878		0.056
10(1)	4(1)	3699.241	3542.067		0.318
10(1)	5(1)	2693.921	2624.580		0.554
10(1)	6(1)	2494.325	2425.367		0.020
10(1)	7(1)	2414.955	2354.283		0.204
10(1)	8(1)	2311.503	2241.048		0.291
10(1)	9(1)	2077.151	2023.510		0.038
11(1)	1(1)	4366.425	4163.381		0.008
11(1)	2(1)	4008.805	3844.096		0.011
11(1)	3(1)	3929.342	3777.072		0.008
11(1)	4(1)	3584.522	3428.545		0.181
11(1)	5(1)	2579.201	2505.442		0.306
11(1)	6(1)	2379.606	2310.397		0.032
11(1)	7(1)	2300.235	2239.180		0.318
11(1)	8(1)	2196.784	2126.555		0.194
11(1)	9(1)	1962.431	1908.745		0.191
11(1)	10(1)	1908.197	1851.830		0.474
12(1)	1(1)	4107.694	3915.130		0.000
12(1)	2(1)	3750.074	3595.709		0.052
12(1)	3(1)	3670.611	3530.082		0.024
12(1)	4(1)	3325.790	3187.874		0.015
12(1)	5(1)	2320.470	2265.622		0.063
12(1)	6(1)	2120.874	2063.655		0.028
12(1)	7(1)	2041.504	1993.212		0.099
12(1)	8(1)	1938.052	1882.879		0.033
12(1)	9(1)	1703.700	1664.021		9.697
12(1)	10(1)	1649.465	1607.423		0.177
12(1)	11(1)	1534.746	1492.678		0.460
13(1)	1(1)	3903.366	3720.802		0.033
13(1)	2(1)	3545.746	3401.315		0.037
13(1)	3(1)	3466.283	3335.337		0.012
13(1)	4(1)	3121.462	2992.713		0.094
13(1)	5(1)	2116.142	2068.092		0.063
13(1)	6(1)	1916.546	1869.795		0.026
13(1)	7(1)	1837.176	1799.722		0.024
13(1)	8(1)	1733.724	1689.295		1.609
13(1)	9(1)	1499.372	1470.352		0.745
13(1)	10(1)	1445.137	1414.321		0.185
13(1)	11(1)	1330.418	1300.590		0.171
13(1)	12(1)	1071.686	1055.048		0.577
14(1)	1(1)	3809.776	3631.681		0.029
14(1)	2(1)	3452.155	3312.329		0.156

14(1)	3(1)	3372.692	3246.882		0.003
14(1)	4(1)	3027.872	2905.182		0.095
14(1)	5(1)	2022.551	1982.154		0.101
14(1)	6(1)	1822.956	1782.163		0.078
14(1)	7(1)	1743.585	1710.805		0.016
14(1)	8(1)	1640.134	1599.654		0.523
14(1)	9(1)	1405.781	1380.852		1.027
14(1)	10(1)	1351.547	1327.243		0.148
14(1)	11(1)	1236.827	1212.291		0.050
14(1)	12(1)	978.096	963.278		0.920
14(1)	13(1)	773.768	771.311		0.284
15(1)	1(1)	6565.595	6246.839		0.002
15(1)	2(1)	6207.975	5895.754		0.249
15(1)	3(1)	6128.512	5779.577		0.146
15(1)	4(1)	5783.691	5520.501		0.001
15(1)	5(1)	4778.370	4596.182		0.006
15(1)	6(1)	4578.775	4381.939		0.079
15(1)	7(1)	4499.404	4316.644		0.307
15(1)	8(1)	4395.953	4216.031		0.186
15(1)	9(1)	4161.601	3995.252		0.046
15(1)	10(1)	4107.366	3940.980		0.004
15(1)	11(1)	3992.647	3827.419		0.019
15(1)	12(1)	3733.915	3580.787		0.016
15(1)	13(1)	3529.587	3385.698		0.011
15(1)	14(1)	3435.997	3297.508		0.009
16(1)	1(1)	4944.912	4723.344		0.001
16(1)	2(1)	4587.292	4386.017		0.133
16(1)	3(1)	4507.829	4319.314		0.173
16(1)	4(1)	4163.009	3996.659		0.000
16(1)	5(1)	3157.688	3074.330		0.003
16(1)	6(1)	2958.093	2866.353		0.081
16(1)	7(1)	2878.722	2798.401		0.103
16(1)	8(1)	2775.271	2691.695		0.000
16(1)	9(1)	2540.918	2468.604		0.044
16(1)	10(1)	2486.684	2416.619		0.026
16(1)	11(1)	2371.964	2304.137		0.022
16(1)	12(1)	2113.233	2056.647		0.008
16(1)	13(1)	1908.905	1861.396		0.007
16(1)	14(1)	1815.314	1775.170		0.013
16(1)	15(1)	4571.134	4381.144		0.142
17(1)	1(1)	4534.564	4328.975		0.000
17(1)	2(1)	4176.944	4007.912		0.023
17(1)	3(1)	4097.481	3941.211		0.193
17(1)	4(1)	3752.661	3604.235		0.000
17(1)	5(1)	2747.340	2678.760		0.018

17(1)	6(1)	2547.745	2475.173		0.012
17(1)	7(1)	2468.374	2405.043		0.223
17(1)	8(1)	2364.923	2297.931		0.028
17(1)	9(1)	2130.570	2079.642		0.001
17(1)	10(1)	2076.336	2025.251		0.000
17(1)	11(1)	1961.616	1911.922		0.005
17(1)	12(1)	1702.885	1664.432		0.000
17(1)	13(1)	1498.557	1470.789		0.458
17(1)	14(1)	1404.966	1380.558		0.117
17(1)	15(1)	4160.785	3990.332		0.059
17(1)	16(1)	2540.103	2467.756		0.109
18(1)	1(1)	4301.606	4088.536		0.010
18(1)	2(1)	3943.986	3783.061		0.001
18(1)	3(1)	3864.523	3716.544		0.001
18(1)	4(1)	3519.703	3374.297		0.002
18(1)	5(1)	2514.382	2448.787		0.000
18(1)	6(1)	2314.787	2250.978		0.010
18(1)	7(1)	2235.416	2180.613		0.028
18(1)	8(1)	2131.965	2068.640		0.134
18(1)	9(1)	1897.612	1852.253		0.053
18(1)	10(1)	1843.378	1795.200		0.027
18(1)	11(1)	1728.658	1680.955		0.008
18(1)	12(1)	1469.927	1434.906		0.173
18(1)	13(1)	1265.599	1240.805		0.020
18(1)	14(1)	1172.008	1152.572		0.005
18(1)	15(1)	3927.828	3766.427		0.079
18(1)	16(1)	2307.145	2243.978		0.020
18(1)	17(1)	1896.797	1849.143		0.204
19(1)	1(1)	3976.578	3791.371		0.002
19(1)	2(1)	3618.958	3472.628		0.012
19(1)	3(1)	3539.495	3407.240		0.001
19(1)	4(1)	3194.675	3065.479		0.000
19(1)	5(1)	2189.354	2140.680		0.057
19(1)	6(1)	1989.759	1939.805		0.002
19(1)	7(1)	1910.388	1871.813		0.068
19(1)	8(1)	1806.937	1759.668		0.009
19(1)	9(1)	1572.584	1543.478		0.171
19(1)	10(1)	1518.350	1488.623		0.394
19(1)	11(1)	1403.630	1373.296		0.089
19(1)	12(1)	1144.899	1124.476		0.007
19(1)	13(1)	940.571	931.667		0.000
19(1)	14(1)	846.980	844.116		0.042
19(1)	15(1)	3602.800	3457.874		0.182
19(1)	16(1)	1982.117	1932.029		0.023
19(1)	17(1)	1571.769	1543.977		0.007

19(1)	18(1)	1338.811	1319.817		0.137
20(1)	1(1)	3714.755	3447.708		0.002
20(1)	2(1)	3357.135	3132.686		0.009
20(1)	3(1)	3277.672	3067.365		0.004
20(1)	4(1)	2932.851	2706.991		0.086
20(1)	5(1)	1927.531	1803.473		0.004
20(1)	6(1)	1727.935	1601.667		0.003
20(1)	7(1)	1648.565	1532.182		0.000
20(1)	8(1)	1545.113	1421.072		0.032
20(1)	9(1)	1310.761	1201.580		0.005
20(1)	10(1)	1256.527	1139.004		0.486
20(1)	11(1)	1141.807	1029.229		0.379
20(1)	12(1)	883.075	785.303		0.487
20(1)	13(1)	678.747	590.579		0.112
20(1)	14(1)	585.157	501.660		0.002
20(1)	15(1)	3340.976	3117.798		0.010
20(1)	16(1)	1720.294	1593.792		0.006
20(1)	17(1)	1309.946	1202.333		1.660
20(1)	18(1)	1076.988	980.073		1.131
20(1)	19(1)	751.960	657.036		0.146
21(1)	1(1)	3633.976	3441.682		0.000
21(1)	2(1)	3276.356	3122.906		0.147
21(1)	3(1)	3196.893	3059.259		0.034
21(1)	4(1)	2852.072	2717.556		0.001
21(1)	5(1)	1846.752	1791.551		0.004
21(1)	6(1)	1647.156	1591.448		0.355
21(1)	7(1)	1567.786	1522.781		0.010
21(1)	8(1)	1464.334	1410.882		0.396
21(1)	9(1)	1229.982	1190.374		0.000
21(1)	10(1)	1175.747	1140.453		0.038
21(1)	11(1)	1061.028	1022.974		1.568
21(1)	12(1)	802.296	773.148		1.164
21(1)	13(1)	597.968	581.296		0.028
21(1)	14(1)	504.378	495.319		0.239
21(1)	15(1)	3260.197	3110.529		0.562
21(1)	16(1)	1639.515	1583.669		1.841
21(1)	17(1)	1229.167	1189.813		0.077
21(1)	18(1)	996.209	962.230		2.450
21(1)	19(1)	671.181	655.188		0.276
21(1)	20(1)	409.357	308.797		0.010

Table S5. Unscaled harmonic (E_{harm}, in cm^{-1}) and anharmonic (E_{anharm}, in cm^{-1}) frequencies and absolute harmonic (I_{harm}, in km mol^{-1}) and anharmonic (I_{anharm}, in km mol^{-1}) IR intensities of the **sC** isomer of thioacetamide as computed at the B3LYP/6-311++G(3df,3pd) level of theory.

Fundamental Bands				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
1(1)	3481.372	3300.005	5.065	3.086
2(1)	3143.362	3001.404	4.662	5.982
3(1)	3038.754	2935.142	5.443	6.279
4(1)	2679.211	2556.881	1.144	1.298
5(1)	1693.593	1648.229	133.999	121.760
6(1)	1473.990	1430.558	11.875	9.030
7(1)	1405.603	1370.828	13.772	6.039
8(1)	1266.424	1226.639	233.967	210.598
9(1)	1078.989	1058.424	25.864	23.752
10(1)	996.465	966.179	9.078	9.416
11(1)	867.420	851.443	12.852	12.685
12(1)	616.223	606.647	42.333	37.482
13(1)	442.811	437.026	13.412	12.411
14(1)	328.244	325.305	2.818	2.967
15(1)	3093.430	2954.465	5.427	6.566
16(1)	1478.654	1434.216	12.157	6.638
17(1)	1069.535	1041.410	3.960	2.970
18(1)	855.485	835.624	54.406	52.829
19(1)	493.417	490.426	2.579	2.336
20(1)	278.579	277.706	8.031	9.390
21(1)	105.617	119.337	1.339	0.749
Overtones				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
1(2)	6962.743	6433.636		4.057
2(2)	6286.724	5915.741		0.556
3(2)	6077.508	5784.838		0.063
4(2)	5358.422	5006.709		0.300
5(2)	3387.185	3284.546		1.866
6(2)	2947.979	2831.278		0.040
7(2)	2811.205	2723.336		0.079
8(2)	2532.849	2434.644		0.828
9(2)	2157.978	2102.353		0.141
10(2)	1992.929	1941.769		0.474
11(2)	1734.839	1701.840		9.774
12(2)	1232.447	1208.106		17.392
13(2)	885.621	873.968		0.318
14(2)	656.488	651.277		0.002

15(2)	6186.860	5846.095		0.484
16(2)	2957.309	2865.815		0.161
17(2)	2139.070	2079.664		0.117
18(2)	1710.970	1667.111		0.860
19(2)	986.834	988.403		0.390
20(2)	557.158	557.960		5.497
21(2)	211.234	249.970		0.004
Combination Bands				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anharm}
2(1) 1(1)	6624.733	6301.309		0.003
3(1) 1(1)	6520.125	6212.035		0.011
3(1) 2(1)	6182.116	5871.927		0.091
4(1) 1(1)	6160.582	5856.829		0.001
4(1) 2(1)	5822.573	5558.104		0.003
4(1) 3(1)	5717.965	5469.020		0.000
5(1) 1(1)	5174.964	4947.418		0.106
5(1) 2(1)	4836.954	4654.391		0.066
5(1) 3(1)	4732.347	4562.637		0.040
5(1) 4(1)	4372.804	4207.885		0.157
6(1) 1(1)	4955.361	4730.229		0.076
6(1) 2(1)	4617.351	4420.897		0.288
6(1) 3(1)	4512.744	4321.324		0.099
6(1) 4(1)	4153.201	3987.446		0.003
6(1) 5(1)	3167.582	3081.799		0.281
7(1) 1(1)	4886.974	4670.473		0.130
7(1) 2(1)	4548.964	4366.404		0.270
7(1) 3(1)	4444.356	4294.312		0.094
7(1) 4(1)	4084.813	3927.425		0.003
7(1) 5(1)	3099.195	3020.139		0.120
7(1) 6(1)	2879.592	2797.368		0.268
8(1) 1(1)	4747.796	4525.116		1.432
8(1) 2(1)	4409.786	4225.626		0.058
8(1) 3(1)	4305.178	4138.371		0.111
8(1) 4(1)	3945.635	3782.567		0.022
8(1) 5(1)	2960.017	2875.613		2.013
8(1) 6(1)	2740.414	2656.108		0.051
8(1) 7(1)	2672.027	2594.904		0.347
9(1) 1(1)	4560.361	4351.819		0.030
9(1) 2(1)	4222.351	4046.202		0.165
9(1) 3(1)	4117.743	3962.889		0.169
9(1) 4(1)	3758.200	3609.016		0.049
9(1) 5(1)	2772.582	2702.201		0.505
9(1) 6(1)	2552.979	2479.319		0.130
9(1) 7(1)	2484.592	2419.102		0.118

9(1)	8(1)	2345.414	2269.839		0.120
10(1)	1(1)	4477.836	4271.810		0.037
10(1)	2(1)	4139.826	3974.752		0.041
10(1)	3(1)	4035.219	3884.395		0.045
10(1)	4(1)	3675.676	3523.399		0.209
10(1)	5(1)	2690.057	2621.739		0.437
10(1)	6(1)	2470.454	2402.406		0.033
10(1)	7(1)	2402.067	2340.437		0.345
10(1)	8(1)	2262.889	2191.963		0.005
10(1)	9(1)	2075.454	2022.098		0.377
11(1)	1(1)	4348.791	4151.662		0.011
11(1)	2(1)	4010.781	3853.208		0.026
11(1)	3(1)	3906.174	3763.439		0.015
11(1)	4(1)	3546.631	3400.840		0.146
11(1)	5(1)	2561.012	2495.001		0.114
11(1)	6(1)	2341.409	2279.573		0.040
11(1)	7(1)	2273.022	2219.623		0.281
11(1)	8(1)	2133.844	2074.912		0.012
11(1)	9(1)	1946.409	1902.115		0.310
11(1)	10(1)	1863.884	1818.434		0.964
12(1)	1(1)	4097.595	3906.906		0.413
12(1)	2(1)	3759.585	3607.308		0.030
12(1)	3(1)	3654.977	3518.868		0.082
12(1)	4(1)	3295.434	3163.489		0.018
12(1)	5(1)	2309.816	2258.933		0.051
12(1)	6(1)	2090.213	2034.553		0.030
12(1)	7(1)	2021.826	1976.550		0.104
12(1)	8(1)	1882.648	1834.820		0.580
12(1)	9(1)	1695.213	1662.343		0.014
12(1)	10(1)	1612.688	1575.270		0.070
12(1)	11(1)	1483.643	1457.150		2.898
13(1)	1(1)	3924.182	3736.859		0.020
13(1)	2(1)	3586.173	3438.574		0.006
13(1)	3(1)	3481.565	3349.347		1.918
13(1)	4(1)	3122.022	2994.199		0.002
13(1)	5(1)	2136.403	2086.025		0.021
13(1)	6(1)	1916.800	1867.499		0.003
13(1)	7(1)	1848.413	1807.720		0.018
13(1)	8(1)	1709.235	1663.617		5.660
13(1)	9(1)	1521.800	1489.630		0.163
13(1)	10(1)	1439.275	1408.114		0.027
13(1)	11(1)	1310.230	1287.851		0.711
13(1)	12(1)	1059.034	1035.300		0.350
14(1)	1(1)	3809.616	3624.501		0.014
14(1)	2(1)	3471.606	3326.557		0.075

14(1)	3(1)	3366.998	3237.560		0.034
14(1)	4(1)	3007.455	2882.188		0.042
14(1)	5(1)	2021.837	1976.562		0.104
14(1)	6(1)	1802.234	1756.583		0.024
14(1)	7(1)	1733.847	1694.985		0.037
14(1)	8(1)	1594.669	1551.304		0.025
14(1)	9(1)	1407.233	1377.863		7.898
14(1)	10(1)	1324.709	1296.690		0.037
14(1)	11(1)	1195.664	1176.137		0.200
14(1)	12(1)	944.468	930.342		0.076
14(1)	13(1)	771.055	762.970		0.239
15(1)	1(1)	6574.802	6254.662		0.000
15(1)	2(1)	6236.792	5939.644		0.172
15(1)	3(1)	6132.184	5768.894		0.200
15(1)	4(1)	5772.641	5511.519		0.000
15(1)	5(1)	4787.023	4604.934		0.021
15(1)	6(1)	4567.420	4368.681		0.130
15(1)	7(1)	4499.033	4317.467		0.220
15(1)	8(1)	4359.855	4181.315		0.144
15(1)	9(1)	4172.419	4005.189		0.088
15(1)	10(1)	4089.895	3927.030		0.031
15(1)	11(1)	3960.850	3806.154		0.002
15(1)	12(1)	3709.654	3561.492		0.043
15(1)	13(1)	3536.241	3391.589		0.008
15(1)	14(1)	3421.674	3280.085		0.020
16(1)	1(1)	4960.026	4734.087		0.000
16(1)	2(1)	4622.016	4417.526		0.158
16(1)	3(1)	4517.408	4329.101		0.184
16(1)	4(1)	4157.865	3991.075		0.001
16(1)	5(1)	3172.247	3085.588		0.002
16(1)	6(1)	2952.644	2859.157		0.062
16(1)	7(1)	2884.257	2798.255		0.112
16(1)	8(1)	2745.079	2660.363		0.000
16(1)	9(1)	2557.644	2481.649		0.025
16(1)	10(1)	2475.119	2403.011		0.020
16(1)	11(1)	2346.074	2285.060		0.023
16(1)	12(1)	2094.878	2040.919		0.012
16(1)	13(1)	1921.465	1870.906		0.003
16(1)	14(1)	1806.899	1760.681		0.014
16(1)	15(1)	4572.085	4380.638		0.166
17(1)	1(1)	4550.907	4339.451		0.019
17(1)	2(1)	4212.897	4039.529		0.021
17(1)	3(1)	4108.289	3947.541		0.205
17(1)	4(1)	3748.746	3598.266		0.000
17(1)	5(1)	2763.128	2690.930		0.002

17(1)	6(1)	2543.525	2465.105		0.030
17(1)	7(1)	2475.138	2407.491		0.193
17(1)	8(1)	2335.960	2266.636		0.037
17(1)	9(1)	2148.524	2093.361		0.005
17(1)	10(1)	2066.000	2012.274		0.000
17(1)	11(1)	1936.955	1891.313		0.016
17(1)	12(1)	1685.758	1648.561		0.002
17(1)	13(1)	1512.346	1478.636		0.077
17(1)	14(1)	1397.779	1365.824		0.131
17(1)	15(1)	4162.965	3989.616		0.077
17(1)	16(1)	2548.190	2470.816		0.088
18(1)	1(1)	4336.857	4120.066		0.016
18(1)	2(1)	3998.847	3836.883		0.001
18(1)	3(1)	3894.239	3746.842		0.000
18(1)	4(1)	3534.696	3392.759		0.000
18(1)	5(1)	2549.078	2480.835		0.002
18(1)	6(1)	2329.475	2265.533		0.005
18(1)	7(1)	2261.088	2205.937		0.049
18(1)	8(1)	2121.910	2056.944		0.169
18(1)	9(1)	1934.474	1888.515		0.051
18(1)	10(1)	1851.950	1807.594		0.011
18(1)	11(1)	1722.905	1685.001		0.008
18(1)	12(1)	1471.709	1441.104		1.096
18(1)	13(1)	1298.296	1272.424		0.041
18(1)	14(1)	1183.729	1161.640		0.000
18(1)	15(1)	3948.915	3789.042		0.085
18(1)	16(1)	2334.140	2270.127		0.023
18(1)	17(1)	1925.020	1873.088		0.246
19(1)	1(1)	3974.789	3789.047		0.006
19(1)	2(1)	3636.779	3491.333		0.006
19(1)	3(1)	3532.171	3402.322		0.008
19(1)	4(1)	3172.628	3047.290		0.000
19(1)	5(1)	2187.010	2139.583		0.040
19(1)	6(1)	1967.407	1918.547		0.007
19(1)	7(1)	1899.020	1861.148		0.083
19(1)	8(1)	1759.842	1713.909		0.013
19(1)	9(1)	1572.406	1545.014		0.126
19(1)	10(1)	1489.882	1465.576		3.442
19(1)	11(1)	1360.837	1342.269		0.022
19(1)	12(1)	1109.640	1096.277		0.010
19(1)	13(1)	936.228	927.772		0.029
19(1)	14(1)	821.661	816.503		0.005
19(1)	15(1)	3586.847	3445.002		0.215
19(1)	16(1)	1972.072	1919.968		0.022
19(1)	17(1)	1562.952	1533.892		0.022

19(1)	18(1)	1348.902	1328.566		5.014
20(1)	1(1)	3759.950	3576.882		0.003
20(1)	2(1)	3421.941	3277.930		0.004
20(1)	3(1)	3317.333	3189.636		0.002
20(1)	4(1)	2957.790	2823.259		0.000
20(1)	5(1)	1972.171	1930.196		0.010
20(1)	6(1)	1752.568	1707.869		0.008
20(1)	7(1)	1684.181	1648.340		0.000
20(1)	8(1)	1545.003	1504.829		0.001
20(1)	9(1)	1357.568	1328.864		0.001
20(1)	10(1)	1275.043	1251.091		0.097
20(1)	11(1)	1145.998	1130.279		0.132
20(1)	12(1)	894.802	888.970		0.000
20(1)	13(1)	721.390	712.565		0.112
20(1)	14(1)	606.823	600.469		0.166
20(1)	15(1)	3372.009	3231.977		0.014
20(1)	16(1)	1757.233	1711.048		0.022
20(1)	17(1)	1348.114	1318.636		0.003
20(1)	18(1)	1134.064	1117.407		0.135
20(1)	19(1)	771.996	764.429		0.052
21(1)	1(1)	3586.988	3418.371		0.001
21(1)	2(1)	3248.979	3118.207		0.088
21(1)	3(1)	3144.371	3033.830		0.037
21(1)	4(1)	2784.828	2673.023		0.000
21(1)	5(1)	1799.209	1770.533		0.001
21(1)	6(1)	1579.606	1550.005		0.726
21(1)	7(1)	1511.219	1494.151		0.495
21(1)	8(1)	1372.041	1344.495		0.072
21(1)	9(1)	1184.606	1170.219		0.028
21(1)	10(1)	1102.081	1093.551		0.044
21(1)	11(1)	973.036	976.944		0.006
21(1)	12(1)	721.840	725.790		0.091
21(1)	13(1)	548.427	554.142		0.015
21(1)	14(1)	433.861	443.537		0.004
21(1)	15(1)	3199.047	3077.050		0.746
21(1)	16(1)	1584.271	1552.602		0.496
21(1)	17(1)	1175.152	1155.293		3.152
21(1)	18(1)	961.102	954.509		0.685
21(1)	19(1)	599.034	611.111		0.149
21(1)	20(1)	384.196	404.297		0.451

Table S6. Unscaled harmonic (E_{harm}, in cm^{-1}) and anharmonic (E_{anharm}, in cm^{-1}) frequencies and absolute harmonic (I_{harm}, in km mol^{-1}) and anharmonic (I_{anharm}, in km mol^{-1}) IR intensities of the **sT** isomer of thioacetamide as computed at the B3LYP/6-311++G(3df,3pd) level of theory.

Fundamental Bands				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anarm}
1(1)	3466.499	3289.488	4.648	4.107
2(1)	3136.961	2995.619	6.441	8.386
3(1)	3036.968	2934.482	6.385	7.676
4(1)	2684.153	2557.785	0.314	1.350
5(1)	1690.374	1645.350	139.120	73.668
6(1)	1474.512	1431.872	8.187	7.878
7(1)	1403.857	1369.986	12.347	11.169
8(1)	1283.256	1243.449	229.864	211.895
9(1)	1076.784	1053.917	23.930	21.590
10(1)	995.972	966.037	7.271	8.690
11(1)	875.549	857.188	7.768	7.104
12(1)	621.902	607.671	33.465	34.609
13(1)	421.153	416.251	14.473	12.672
14(1)	334.562	336.971	0.926	0.684
15(1)	3093.399	2954.296	6.161	7.867
16(1)	1481.126	1434.706	11.969	7.405
17(1)	1070.886	1041.181	4.536	2.277
18(1)	870.304	848.646	49.856	50.092
19(1)	497.010	489.759	3.875	3.032
20(1)	203.364	87.783	16.509	10.897
21(1)	170.380	149.972	0.000	3.907
Overtones				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anarm}
1(2)	6932.998	6412.596		4.039
2(2)	6273.922	5906.125		0.592
3(2)	6073.935	5781.449		0.065
4(2)	5368.305	5008.038		0.354
5(2)	3380.748	3271.538		1.937
6(2)	2949.024	2833.202		0.012
7(2)	2807.713	2721.684		0.098
8(2)	2566.513	2467.605		0.820
9(2)	2153.569	2104.342		0.221
10(2)	1991.944	1946.926		0.326
11(2)	1751.099	1716.607		7.598
12(2)	1243.804	1210.177		13.884
13(2)	842.306	832.224		0.011
14(2)	669.125	670.012		0.053

15(2)	6186.797	5845.451		0.487
16(2)	2962.251	2870.279		0.215
17(2)	2141.772	2079.087		0.137
18(2)	1740.608	1692.818		1.120
19(2)	994.020	988.808		0.478
20(2)	406.727	79.144		0.614
21(2)	340.761	283.317		0.028
Combination Bands				
Mode (Quanta)	E_{harm}	E_{anharm}	I_{harm}	I_{anarm}
2(1) 1(1)	6603.460	6284.940		0.004
3(1) 1(1)	6503.467	6199.610		0.010
3(1) 2(1)	6173.928	5860.363		0.104
4(1) 1(1)	6150.652	5846.343		0.012
4(1) 2(1)	5821.113	5553.365		0.007
4(1) 3(1)	5721.120	5468.101		0.007
5(1) 1(1)	5156.873	4930.757		0.177
5(1) 2(1)	4827.335	4642.174		0.061
5(1) 3(1)	4727.342	4553.896		0.047
5(1) 4(1)	4374.527	4200.160		0.070
6(1) 1(1)	4941.011	4721.126		0.078
6(1) 2(1)	4611.473	4416.422		0.288
6(1) 3(1)	4511.480	4320.813		0.110
6(1) 4(1)	4158.664	3989.607		0.031
6(1) 5(1)	3164.886	3076.464		0.233
7(1) 1(1)	4870.356	4659.466		0.103
7(1) 2(1)	4540.817	4359.780		0.270
7(1) 3(1)	4440.824	4291.283		0.122
7(1) 4(1)	4088.009	3927.680		0.000
7(1) 5(1)	3094.231	3012.828		0.132
7(1) 6(1)	2878.368	2797.813		0.263
8(1) 1(1)	4749.755	4532.376		1.221
8(1) 2(1)	4420.217	4236.879		0.065
8(1) 3(1)	4320.224	4153.122		0.103
8(1) 4(1)	3967.409	3801.011		0.095
8(1) 5(1)	2973.630	2884.818		2.128
8(1) 6(1)	2757.768	2674.278		0.038
8(1) 7(1)	2687.113	2610.683		0.296
9(1) 1(1)	4543.283	4342.365		0.037
9(1) 2(1)	4213.745	4041.824		0.122
9(1) 3(1)	4113.752	3962.132		0.177
9(1) 4(1)	3760.937	3611.817		0.011
9(1) 5(1)	2767.158	2694.569		0.368
9(1) 6(1)	2551.296	2481.469		0.114
9(1) 7(1)	2480.641	2420.130		0.115

9(1)	8(1)	2360.041	2286.644		0.092
10(1)	1(1)	4462.471	4264.596		0.026
10(1)	2(1)	4132.933	3970.961		0.017
10(1)	3(1)	4032.940	3883.969		0.052
10(1)	4(1)	3680.125	3527.443		0.097
10(1)	5(1)	2686.346	2617.973		0.029
10(1)	6(1)	2470.484	2405.638		0.031
10(1)	7(1)	2399.829	2341.612		0.262
10(1)	8(1)	2279.228	2211.929		0.037
10(1)	9(1)	2072.756	2026.181		0.495
11(1)	1(1)	4342.048	4147.323		0.022
11(1)	2(1)	4012.510	3853.287		0.005
11(1)	3(1)	3912.517	3766.896		0.003
11(1)	4(1)	3559.702	3405.210		0.218
11(1)	5(1)	2565.924	2492.742		0.036
11(1)	6(1)	2350.061	2287.830		0.043
11(1)	7(1)	2279.406	2225.213		0.234
11(1)	8(1)	2158.806	2096.939		0.017
11(1)	9(1)	1952.334	1909.231		0.237
11(1)	10(1)	1871.522	1828.665		1.279
12(1)	1(1)	4088.401	3897.627		0.394
12(1)	2(1)	3758.863	3602.739		0.022
12(1)	3(1)	3658.869	3517.874		0.067
12(1)	4(1)	3306.054	3165.338		0.022
12(1)	5(1)	2312.276	2250.716		0.059
12(1)	6(1)	2096.414	2038.197		0.027
12(1)	7(1)	2025.758	1976.485		0.113
12(1)	8(1)	1905.158	1851.818		0.335
12(1)	9(1)	1698.686	1666.059		45.105
12(1)	10(1)	1617.874	1579.411		0.520
12(1)	11(1)	1497.451	1461.499		0.551
13(1)	1(1)	3887.652	3704.716		0.047
13(1)	2(1)	3558.114	3412.120		0.027
13(1)	3(1)	3458.121	3326.492		0.017
13(1)	4(1)	3105.306	2973.433		0.092
13(1)	5(1)	2111.527	2057.893		0.089
13(1)	6(1)	1895.665	1847.647		0.007
13(1)	7(1)	1825.010	1786.084		0.023
13(1)	8(1)	1704.410	1661.091		17.253
13(1)	9(1)	1497.938	1473.030		0.450
13(1)	10(1)	1417.125	1389.714		0.034
13(1)	11(1)	1296.703	1272.870		0.085
13(1)	12(1)	1043.055	1019.267		0.630
14(1)	1(1)	3801.061	3623.479		0.003
14(1)	2(1)	3471.523	3330.101		0.118

14(1)	3(1)	3371.530	3245.002		0.016
14(1)	4(1)	3018.715	2892.619		0.067
14(1)	5(1)	2024.936	1979.089		0.160
14(1)	6(1)	1809.074	1767.390		0.036
14(1)	7(1)	1738.419	1704.389		0.046
14(1)	8(1)	1617.819	1577.517		0.083
14(1)	9(1)	1411.347	1387.671		0.045
14(1)	10(1)	1330.534	1309.931		0.872
14(1)	11(1)	1210.112	1192.604		0.027
14(1)	12(1)	956.464	939.937		0.051
14(1)	13(1)	755.715	751.179		0.228
15(1)	1(1)	6559.898	6243.985		0.000
15(1)	2(1)	6230.359	5931.700		0.188
15(1)	3(1)	6130.366	5768.248		0.206
15(1)	4(1)	5777.551	5512.477		0.001
15(1)	5(1)	4783.773	4598.084		0.020
15(1)	6(1)	4567.911	4370.200		0.127
15(1)	7(1)	4497.255	4316.510		0.232
15(1)	8(1)	4376.655	4197.933		0.143
15(1)	9(1)	4170.183	4006.679		0.099
15(1)	10(1)	4089.371	3928.161		0.010
15(1)	11(1)	3968.948	3811.274		0.011
15(1)	12(1)	3715.300	3562.434		0.040
15(1)	13(1)	3514.552	3370.678		0.014
15(1)	14(1)	3427.961	3289.451		0.012
16(1)	1(1)	4947.625	4726.280		0.000
16(1)	2(1)	4618.086	4414.526		0.160
16(1)	3(1)	4518.093	4329.496		0.179
16(1)	4(1)	4165.278	3994.534		0.000
16(1)	5(1)	3171.500	3081.678		0.001
16(1)	6(1)	2955.638	2862.877		0.084
16(1)	7(1)	2884.982	2801.681		0.121
16(1)	8(1)	2764.382	2679.722		0.000
16(1)	9(1)	2557.910	2485.727		0.019
16(1)	10(1)	2477.098	2410.402		0.030
16(1)	11(1)	2356.675	2293.614		0.011
16(1)	12(1)	2103.028	2043.501		0.010
16(1)	13(1)	1902.279	1850.556		0.006
16(1)	14(1)	1815.688	1772.787		0.012
16(1)	15(1)	4574.524	4383.415		0.150
17(1)	1(1)	4537.385	4328.850		0.020
17(1)	2(1)	4207.847	4033.528		0.023
17(1)	3(1)	4107.854	3945.459		0.202
17(1)	4(1)	3755.039	3598.902		0.000
17(1)	5(1)	2761.260	2684.140		0.004

17(1)	6(1)	2545.398	2466.641		0.021
17(1)	7(1)	2474.743	2406.300		0.163
17(1)	8(1)	2354.142	2283.264		0.039
17(1)	9(1)	2147.670	2094.410		0.007
17(1)	10(1)	2066.858	2014.397		0.001
17(1)	11(1)	1946.435	1894.633		0.006
17(1)	12(1)	1692.788	1649.263		0.000
17(1)	13(1)	1492.039	1460.050		2.683
17(1)	14(1)	1405.448	1375.020		0.108
17(1)	15(1)	4164.285	3989.309		0.082
17(1)	16(1)	2552.012	2470.740		0.077
18(1)	1(1)	4336.803	4124.322		0.017
18(1)	2(1)	4007.265	3844.065		0.001
18(1)	3(1)	3907.271	3757.768		0.000
18(1)	4(1)	3554.456	3405.680		0.003
18(1)	5(1)	2560.678	2487.894		0.003
18(1)	6(1)	2344.816	2279.873		0.004
18(1)	7(1)	2274.160	2218.056		0.048
18(1)	8(1)	2153.560	2086.772		0.154
18(1)	9(1)	1947.088	1903.146		0.051
18(1)	10(1)	1866.276	1820.687		0.017
18(1)	11(1)	1745.853	1702.770		0.000
18(1)	12(1)	1492.206	1456.299		0.535
18(1)	13(1)	1291.457	1264.753		0.025
18(1)	14(1)	1204.866	1183.444		0.001
18(1)	15(1)	3963.702	3801.862		0.091
18(1)	16(1)	2351.429	2284.574		0.020
18(1)	17(1)	1941.190	1885.679		0.284
19(1)	1(1)	3963.509	3778.329		0.008
19(1)	2(1)	3633.971	3484.867		0.006
19(1)	3(1)	3533.978	3399.531		0.005
19(1)	4(1)	3181.162	3047.456		0.000
19(1)	5(1)	2187.384	2132.442		0.059
19(1)	6(1)	1971.522	1919.433		0.005
19(1)	7(1)	1900.866	1859.635		0.077
19(1)	8(1)	1780.266	1729.990		0.011
19(1)	9(1)	1573.794	1545.365		0.102
19(1)	10(1)	1492.982	1466.298		0.013
19(1)	11(1)	1372.559	1347.387		0.020
19(1)	12(1)	1118.912	1095.957		0.008
19(1)	13(1)	918.163	905.745		0.040
19(1)	14(1)	831.572	824.338		0.002
19(1)	15(1)	3590.409	3444.117		0.199
19(1)	16(1)	1978.136	1924.629		0.025
19(1)	17(1)	1567.896	1532.591		0.114

19(1)	18(1)	1367.314	1340.180		3.697
20(1)	1(1)	3669.863	3378.560		0.003
20(1)	2(1)	3340.325	3082.821		0.006
20(1)	3(1)	3240.331	2997.980		0.004
20(1)	4(1)	2887.516	2626.732		0.018
20(1)	5(1)	1893.738	1734.161		0.003
20(1)	6(1)	1677.876	1518.927		0.002
20(1)	7(1)	1607.220	1458.047		0.000
20(1)	8(1)	1486.620	1331.938		0.993
20(1)	9(1)	1280.148	1141.169		0.011
20(1)	10(1)	1199.336	1059.690		0.171
20(1)	11(1)	1078.913	945.025		1.842
20(1)	12(1)	825.266	694.196		0.087
20(1)	13(1)	624.517	503.883		0.251
20(1)	14(1)	537.926	421.358		0.137
20(1)	15(1)	3296.762	3041.994		0.004
20(1)	16(1)	1684.489	1523.389		0.503
20(1)	17(1)	1274.250	1126.267		0.065
20(1)	18(1)	1073.668	941.470		1.268
20(1)	19(1)	700.374	571.146		0.013
21(1)	1(1)	3636.879	3440.559		0.000
21(1)	2(1)	3307.341	3144.444		0.061
21(1)	3(1)	3207.348	3062.449		0.013
21(1)	4(1)	2854.533	2708.936		0.000
21(1)	5(1)	1860.754	1794.054		0.002
21(1)	6(1)	1644.892	1581.209		0.392
21(1)	7(1)	1574.237	1521.512		0.013
21(1)	8(1)	1453.637	1392.394		0.254
21(1)	9(1)	1247.165	1202.660		0.015
21(1)	10(1)	1166.352	1127.417		0.013
21(1)	11(1)	1045.930	1006.975		0.011
21(1)	12(1)	792.282	755.610		0.141
21(1)	13(1)	591.534	564.941		0.012
21(1)	14(1)	504.943	486.039		0.061
21(1)	15(1)	3263.779	3107.803		0.576
21(1)	16(1)	1651.506	1586.109		1.125
21(1)	17(1)	1241.266	1186.751		3.723
21(1)	18(1)	1040.684	997.230		0.239
21(1)	19(1)	667.390	639.346		0.071
21(1)	20(1)	373.744	227.411		0.023