Supporting Online Material

The supporting on-line material contains:

- A Table with the CC2/cc-pVTZ calculated harmonic wavenumbers compared to the experimental values of tryptamine A. Furthermore, approximate descriptions of the modes and the calculated oscillator strengths in km/mol for all modes are given.
- A Table with the vibrational wavenumbers and Duschinsky matrix for the low frequency vibrations of the A conformer of tryptamine calculated at the CC2/cc-pVTZ level of theory.
- A Figure with the displacement vectors of the normal modes of tryptamine.
- A Figure with the IR-ID spectra of all other conformers.
- A figure with a FC simulation of the R2PI spectrum after pumping IR resonances of the A conformer at 341.5 cm^{-1}.

Table S1: Harmonic vibrational frequencies and oscillator strengths of tryptamine A calculated at the CC2/cc-pVTZ level of theory, along with the approximate description of the modes and the experimental values. ^{a} from Ref. [1] ^{b} this publication

Mode	ν [cm^{-1}]	I [km/mol]	Description	Exp.	Mode	ν	I [km/mol]	Description	Exp.
1	44.8	1.28123	τ_1	43^a	34	1150.0	1.523870	18a	1155^a
2	83.6	1.23459	β_1	81^a	35	1171.8	0.487759	9a	1138^a
3	135.7	3.18774	τ_2	133^a	36	1180.5	0.102449	NH_2 twist	1194^a
4	177.9	1.76047	10b	177^a	37	1220.2	2.680435	CH_2 twist	1228^a
5	219.2	11.05047	10a	215^a	38	1244.0	11.262858	13	
6	240.9	19.75197	$N_{inv}/\tau_1/\tau_3$	237^b	39	1279.9	4.60635	3	1294^a
7	265.7	33.20797	$\gamma NH/\tau_3$	268^b	40	1315.7	3.81878	18b	1326^a
8	332.3	47.00850	$N_{inv}/\tau_1/\tau_3$	341.5^b	41	1340.9	2.16207	$C_\beta H_2$ twist	1334^a
9	384.6	22.49646	$N_{inv}/\tau_1/\tau_2$	387^b	42	1361.2	1.74642	$C_\alpha H_2$ bend	1361^a
10	425.1	5.56796	16b	422^b	43	1376.1	13.84470	3/νCC	
11	462.1	6.58679	4	454^b	44	1380.1	10.10924	$C_\beta H_2$ wag	
12	476.6	19.72806	9b	468^b	45	1425.0	46.43047	δ CH, NH	1421^a
13	538.5	2.02159	CCN bend		46	1446.2	5.31395	δ NH	
14	570.9	1.29528	6a		47	1476.4	5.19797	$C_\alpha H_2$ bend	1462^a
15	581.6	10.17618	6b	569^a	48	1483.5	6.36950	19a	
16	639.7	0.40608	γNH		49	1514.7	5.05619	CCC bend	1512^a
17	705.9	0.17446	16a		50	1523.5	3.52947	$C_\beta H_2$ bend	1521^a
18	740.1	4.53353	18		51	1586.2	4.21056	νCC	
19	747.9	73.38435	11		52	1613.4	0.36652	8a	1598^a
20	774.4	4.88340	γCH		53	1653.8	30.18284	NH_2 bend	1631^a
21	799.7	6.46777	1		54	1658.3	2.88088	8b	
22	840.8	1.11881	17a	847^a	55	2951.7	44.82044	$\nu_s C_\beta H$	
23	845.5	49.00812	17b		56	3021.1	24.52387	$\nu_s C_\alpha H$	
24	879.9	6.88880	$C_\alpha H_2$ twist		57	3048.7	50.35626	$\nu_{as} C_\beta H$	
25	892.1	41.24889	5	875^a	58	3068.1	19.64459	$\nu_{as} C_\alpha H$	
26	913.1	2.35243	12		59	3163.2	2.61424	ν_{as}CH	
27	919.5	8.50358	NH_2 wag		60	3169.5	1.03134	ν_sCH	
28	947.4	0.06897	$C_\alpha H_2$ wag		61	3179.4	20.47852	ν_{as}CH	
29	1025.3	3.03033	18b	1015^a	62	3190.5	15.35401	ν_sCH	
30	1036.5	6.66141	CH_2 twist		63	3245.7	0.06675	ν_{py} CH	
31	1093.0	12.22130	NH_2 twist	1091^a	64	3487.9	1.52794	$\nu_s NH_2$	
32	1098.7	22.16356	δ CH, NH		65	3567.6	2.96235	$\nu_{as} NH_2$	
33	1108.5	4.46519	$C_\alpha H_2$ wag	1131^a	66	3669.8	83.83458	ν_{py} NH	

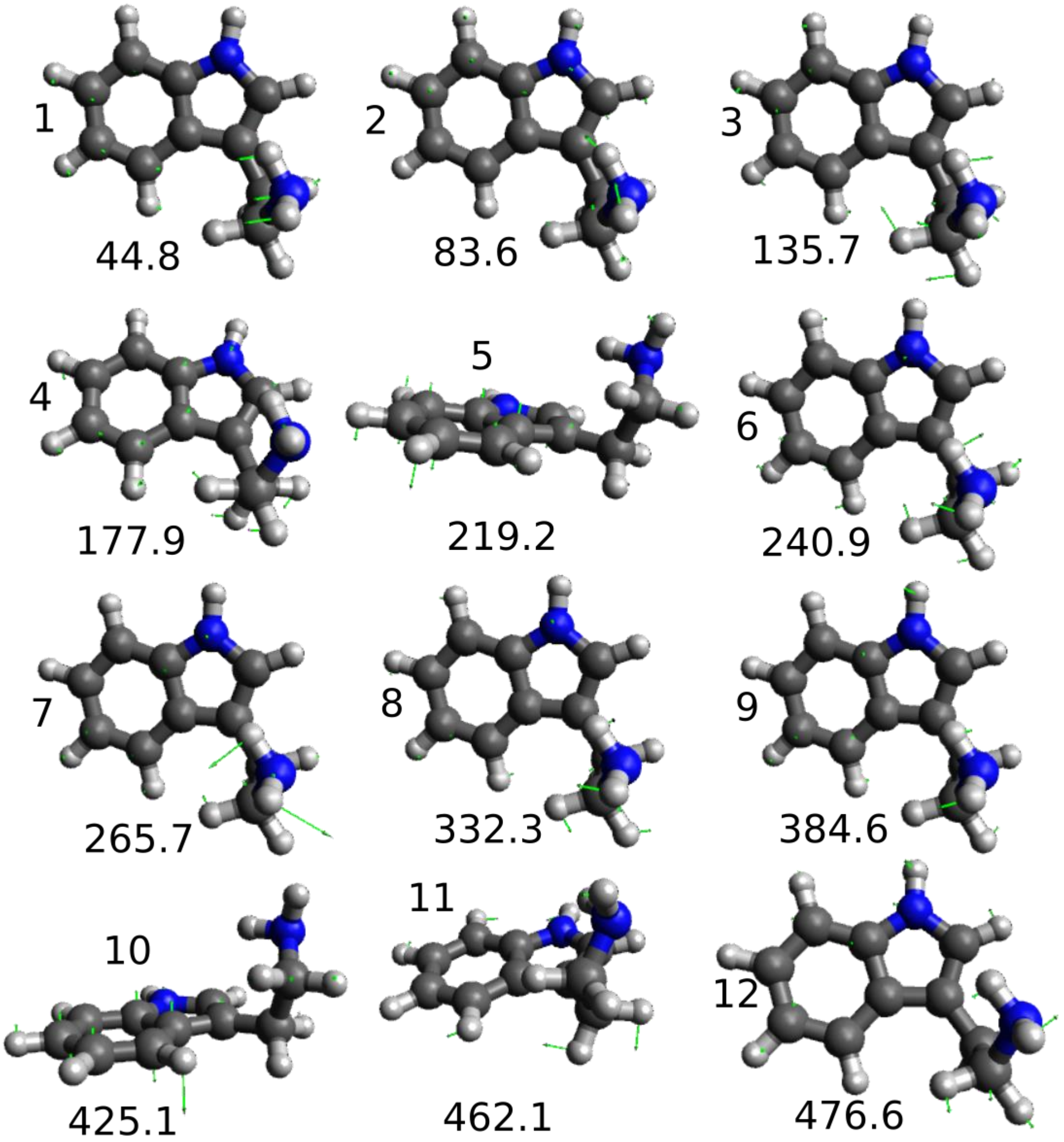

Figure S1: Displacement vectors of the twelve lowest wavenumber vibrations of tryptamine from a normal mode analysis using the CC2/cc-pVTZ optimized geometry. The mode numbering is according to Tables S1 and S2.

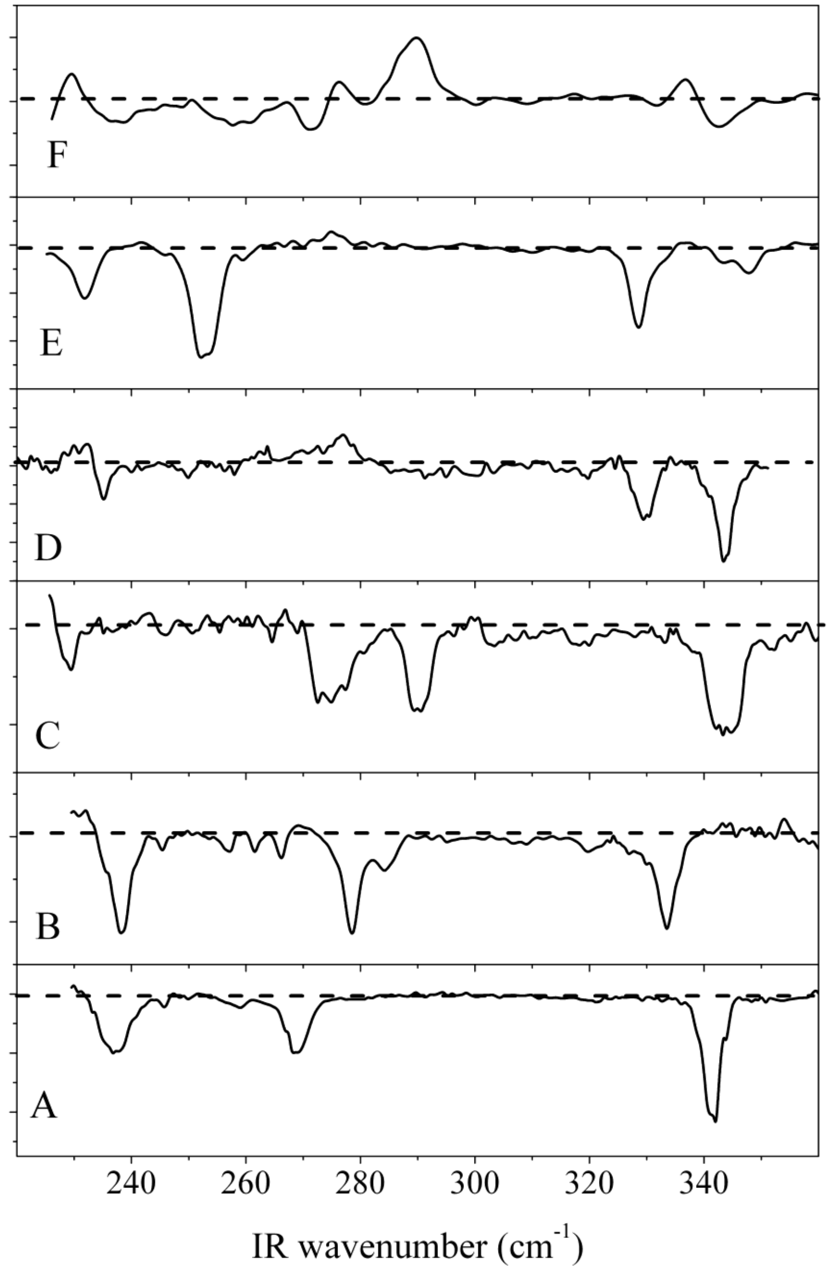

Figure S2: IR-ID spectra of the six conformers (A-F) of tryptamine obtained using a laser desorption source. Solid tryptamine was mixed with graphite powder and applied on a solid graphite bar. A pulsed YAG laser operating at 1064 nm (Polaris Pulsed Nd:YAG Laser, NewWave Research) with a pulse energy of about 1.5 mJ was used to desorb unfragmented tryptamine molecules from the graphite bar. The desorbed molecules are entrained in a supersonic pulsed molecular beam of argon, from a pulsed valve (Jordan) at a backing pressure of 3 bar. In the molecular beam, tryptamine is cooled towards its vibrational ground state and the different conformers of tryptamine are frozen out, depending on their relative energy and the barriers separating the conformer minima. The relative intensity of the conformer origins in the R2PI spectra depend on the temperature and on the relaxation in the beam. For weak conformers, we could enhance the signal by using a laser desorption source. However, all spectra involving only the A conformer in the main paper were taken using the thermal source.

Table S2: Vibrational wavenumbers and Duschinsky matrix for the low frequency vibrations of the A conformer of tryptamine calculated at the CC2/cc-pVTZ level of theory. In the second row the S_1 wavenumber is given, in the second column the S_0 wavenumber. The primed vibrational quantum numbers refer to the excited state vibrations, the doubly primed to the ground state.

	S_1	1^t	2^t	3^t	4^t	5^t	6^t	7^t	8^t	9^t	10^t	11^t	12^t
S_0		40.8	78.9	120.8	158.7	163.9	229.2	237.6	279.0	307.6	343.9	378.7	458.4
1^{tt}	44.8	-0.992	0.065	0.053	0.020	-0.002	-0.009	0.032	0.010	0.006	-0.007	0.016	0.011
2^{tt}	83.6	-0.065	-0.991	0.046	-0.077	-0.038	0.003	0.002	-0.007	-0.015	0.008	-0.019	-0.000
3^{tt}	135.7	0.062	0.011	0.938	0.301	0.113	0.038	0.068	0.009	0.006	0.001	0.017	-0.006
4^{tt}	177.9	0.009	0.091	0.313	-0.791	-0.457	-0.214	0.053	0.053	-0.022	-0.027	0.026	-0.029
5^{tt}	219.2	0.006	-0.011	-0.042	0.488	-0.835	-0.137	-0.120	-0.032	0.114	0.040	0.075	-0.002
6^{tt}	240.9	0.017	0.009	-0.045	-0.023	-0.215	0.661	0.709	-0.012	0.024	-0.032	0.034	0.011
7^{tt}	265.7	0.026	-0.023	-0.082	0.144	0.096	-0.635	0.629	0.381	0.048	0.086	-0.042	-0.002
8^{tt}	332.3	-0.007	0.007	0.017	-0.045	-0.031	0.280	-0.233	0.723	0.207	0.501	-0.185	-0.043
9^{tt}	384.6	-0.014	0.029	0.013	0.009	-0.053	-0.057	0.098	-0.398	-0.393	0.602	-0.532	-0.105
10^{tt}	425.1	0.002	-0.006	0.005	-0.088	0.107	-0.069	0.071	-0.392	0.754	0.417	0.221	-0.019
11^{tt}	462.1	-0.008	-0.002	-0.016	0.028	0.003	0.014	0.001	0.017	0.071	-0.143	-0.061	-0.948
12^{tt}	476.6	-0.001	-0.005	-0.011	-0.007	0.010	0.006	-0.012	0.009	0.085	-0.141	-0.128	-0.109

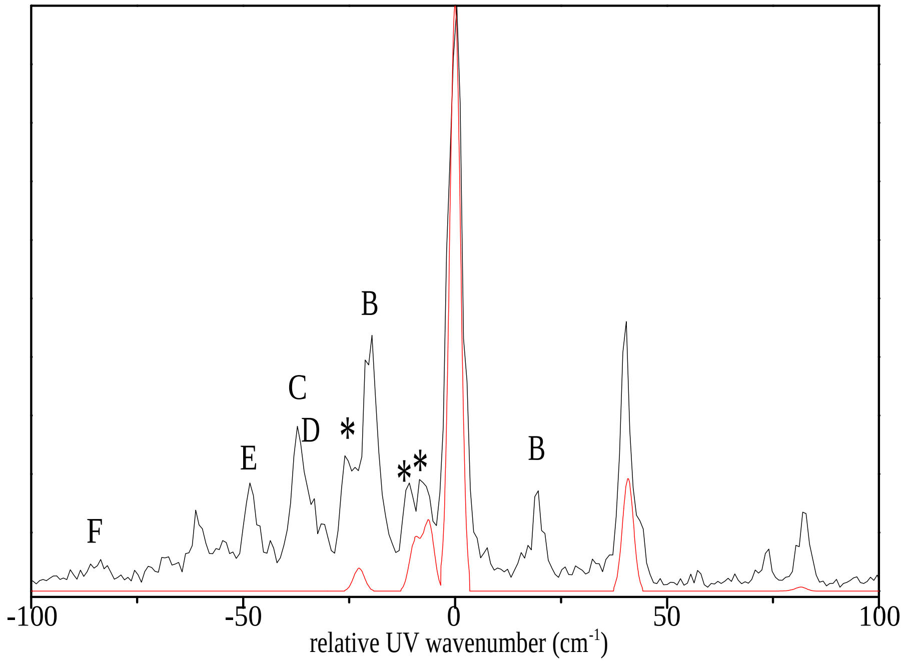

Figure S3: R2PI spectrum of tryptamine after pumping IR resonances of the A conformer at 341.5 cm^{-1} (black trace) along with a Franck-Condon simulation using the vibrationless origin and the vibration 8 as ground state levels. For details of the simulation see text. The bands marked with * are those, that appear only upon concerted action of IR and UV radiation. IR pulse energy used here is 0.54 mJ.

References

[1] M. Schmitt, K. Feng, M. Böhm, and K. Kleinermanns, *J. Chem. Phys.*, 2006, **125**, 144303(1–9).