Supporting Information

Conformational Switching by Vibrational Excitation of a Remote NH Bond

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Table S1. Relative electronic ($\Delta E_{elec,}$ kJ mol^{-1}) and zero-point energies ($\Delta E_{0,}$ kJ mol^{-1}) calculated at different levels of theory, and equilibrium Boltzmann populations at 323 K (Pop., %) for the *syn* and *anti* conformers of 6-methoxyindole (6MOI).

Model Chemistry	Conformer	
	syn	*anti*
B3LYP/6-311++G(d,p)		
ΔE_{elec}	0.00	1.78
ΔE_0	0.00	1.72
Pop. (323K)[a]	65.5	34.5
MP2/6-311++G(d,p)		
ΔE_{elec}	0.00	3.11
Pop. (323K)	76.1	23.9
MP2/6-311++G(3df,3pd)		
ΔE_{elec}	0.00	2.90
Pop. (323K)	74.2	25.8
CC2/cc-pVTZ[b]		
ΔE_{elec}	0.00	3.23
ΔE_0	0.00	2.98
Pop. (323K)[a]	75.2	24.8

[a] Estimated from the relative zero-point energies. [b] Values from: Brand, C.; Oeltermann, O.; Wilke, M.; Schmitt, M. *J. Chem. Phys.* **2013**, *138*, 024321.

Table S2. Cartesian coordinates for the geometries of the *syn* conformer of 6MOI optimized at different levels of theory.

	B3LYP/6-311++G(d,p)			MP2/6-311++G(d,p)			MP2/6-311++G(3df,3pd)		
N	0.111333	2.348069	0.000000	0.111702	2.344535	0.000000	0.111001	2.334089	0.000000
C	-1.155909	2.912035	0.000000	-1.148368	2.912113	0.000000	-1.144047	2.899098	0.000000
C	-2.092493	1.916133	0.000000	-2.097159	1.909326	0.000000	-2.088317	1.900358	0.000000
C	-1.762038	-0.687919	0.000000	-1.769413	-0.697193	0.000000	-1.762421	-0.694564	0.000000
C	-0.789764	-1.668360	0.000000	-0.788078	-1.675991	0.000000	-0.786077	-1.669608	0.000000
C	0.584408	-1.333560	0.000000	0.590769	-1.339418	0.000000	0.586649	-1.334367	0.000000
C	1.001288	-0.007227	0.000000	1.009658	-0.009409	0.000000	1.004841	-0.010366	0.000000
C	0.000000	0.974259	0.000000	0.000000	0.971353	0.000000	0.000000	0.965991	0.000000
C	-1.382495	0.666206	0.000000	-1.387160	0.663190	0.000000	-1.382516	0.659682	0.000000
O	1.436588	-2.405927	0.000000	1.439081	-2.415711	0.000000	1.434855	-2.404405	0.000000
C	2.832561	-2.159156	0.000000	2.825205	-2.124236	0.000000	2.816164	-2.111836	0.000000
H	0.974280	2.864639	0.000000	0.978759	2.859945	0.000000	0.974284	2.847987	0.000000
H	-1.277747	3.983552	0.000000	-1.266408	3.987360	0.000000	-1.262042	3.969896	0.000000
H	-3.162214	2.056021	0.000000	-3.169153	2.053350	0.000000	-3.155894	2.044417	0.000000
H	-2.810411	-0.965484	0.000000	-2.820001	-0.977534	0.000000	-2.808540	-0.973545	0.000000
H	-1.052413	-2.719093	0.000000	-1.047177	-2.730749	0.000000	-1.044951	-2.719816	0.000000
H	2.047841	0.266571	0.000000	2.057528	0.270710	0.000000	2.049396	0.265138	0.000000
H	3.310354	-3.137819	0.000000	3.333669	-3.088145	0.000000	3.326952	-3.068842	0.000000
H	3.142464	-1.605962	0.894345	3.112748	-1.559699	0.895298	3.099645	-1.547469	0.890960
H	3.142464	-1.605962	-0.894345	3.112748	-1.559699	-0.895298	3.099645	-1.547469	-0.890960

Table S3. Cartesian coordinates for the geometries of the *anti* conformer of 6MOI optimized at different levels of theory.

	B3LYP/6-311++G(d,p)			MP2/6-311++G(d,p)			MP2/6-311++G(3df,3pd)		
N	0.113906	2.536759	0.000000	0.114438	2.537140	0.000000	0.116578	2.527646	0.000000
C	1.456360	2.886487	0.000000	1.451038	2.889718	0.000000	1.448415	2.876378	0.000000
C	2.221716	1.755041	0.000000	2.225620	1.748455	0.000000	2.217171	1.738427	0.000000
C	1.475970	-0.757138	0.000000	1.477367	-0.766318	0.000000	1.468828	-0.764106	0.000000
C	0.355560	-1.579537	0.000000	0.349256	-1.586053	0.000000	0.344526	-1.578049	0.000000
C	-0.942493	-1.025721	0.000000	-0.953139	-1.026743	0.000000	-0.951334	-1.019391	0.000000
C	-1.134074	0.353451	0.000000	-1.142086	0.355669	0.000000	-1.138717	0.357276	0.000000
C	0.000000	1.162288	0.000000	0.000000	1.163621	0.000000	0.000000	1.159435	0.000000
C	1.320102	0.633377	0.000000	1.322574	0.632175	0.000000	1.317266	0.628513	0.000000
O	-2.089783	-1.777793	0.000000	-2.105077	-1.773960	0.000000	-2.096713	-1.767170	0.000000
C	-1.980482	-3.192469	0.000000	-1.954177	-3.183702	0.000000	-1.945133	-3.172413	0.000000
H	-0.654349	3.185762	0.000000	-0.657269	3.186508	0.000000	-0.650618	3.176154	0.000000
H	1.750270	3.924257	0.000000	1.743348	3.931332	0.000000	1.741732	3.913116	0.000000
H	3.299989	1.722452	0.000000	3.306770	1.717799	0.000000	3.293909	1.706989	0.000000
H	2.465900	-1.200099	0.000000	2.468703	-1.213375	0.000000	2.455079	-1.211033	0.000000
H	0.491155	-2.652288	0.000000	0.485388	-2.661293	0.000000	0.475463	-2.649484	0.000000
H	-2.140989	0.753245	0.000000	-2.151662	0.757693	0.000000	-2.143015	0.760458	0.000000
H	-3.002500	-3.569108	0.000000	-2.965984	-3.589005	0.000000	-2.950690	-3.579866	0.000000
H	-1.462255	-3.556930	0.894025	-1.424226	-3.529446	0.895063	-1.415170	-3.514457	0.890718
H	-1.462255	-3.556930	-0.894025	-1.424226	-3.529446	-0.895063	-1.415170	-3.514457	-0.890718

Table S4. Results of the harmonic and anharmonic vibrational calculations carried out at the B3LYP/6-311++G(d,p) level for the fundamental transitions of the *anti* and *syn* conformers of 6MOI [E = vibrational energy, cm^{-1}; I = infrared intensity, km mol^{-1}].

Mode (Quanta)	*anti*				*syn*			
	E (harm)	E (anharm)	I (harm)	I (anharm)	E (harm)	E (anharm)	I (harm)	I (anharm)
1(1)	3675.546	3506.198	70.38	50.70	3674.631	3495.883	64.28	45.62
2(1)	3255.449	3135.532	2.54	2.39	3257.000	3121.576	2.06	3.97
3(1)	3235.337	3108.247	1.97	2.73	3235.781	3099.504	2.53	1.62
4(1)	3207.899	3072.477	9.29	9.13	3198.909	3080.296	6.77	31.12
5(1)	3187.959	3044.894	3.69	5.52	3194.315	3074.840	7.67	14.70
6(1)	3170.620	3016.897	10.85	15.40	3169.802	3034.836	9.52	11.64
7(1)	3127.240	2982.152	26.20	31.33	3128.890	2983.661	24.56	28.76
8(1)	3000.241	2821.836	70.75	55.25	2995.515	2816.950	58.26	50.59
9(1)	1670.893	1628.870	106.11	71.50	1663.812	1624.385	107.14	66.61
10(1)	1611.775	1575.952	14.39	9.21	1612.999	1576.910	8.76	5.83
11(1)	1551.398	1518.660	43.95	26.54	1545.809	1511.916	56.24	45.95
12(1)	1534.819	1498.114	41.96	43.19	1532.891	1498.917	27.68	21.21
13(1)	1504.955	1468.969	46.21	32.36	1505.550	1470.151	21.65	9.54
14(1)	1478.610	1446.360	4.58	5.99	1484.212	1452.333	44.45	26.67
15(1)	1470.321	1437.008	22.47	3.85	1471.555	1444.370	11.78	2.32
16(1)	1421.926	1384.224	12.81	5.21	1425.560	1387.471	16.87	7.19
17(1)	1375.674	1346.710	64.30	14.94	1371.549	1342.018	11.31	6.70
18(1)	1345.781	1318.489	32.88	26.46	1346.536	1320.867	5.30	3.37
19(1)	1308.235	1279.167	46.10	1.52	1316.557	1288.695	107.99	36.97
20(1)	1277.685	1253.989	123.09	76.19	1272.964	1254.772	93.87	63.72
21(1)	1224.424	1202.793	14.64	9.36	1226.833	1207.137	43.66	44.02
22(1)	1212.785	1186.640	40.89	43.70	1216.416	1193.761	31.25	29.83
23(1)	1179.338	1150.509	132.18	87.82	1180.801	1167.118	81.99	85.96
24(1)	1152.682	1134.698	7.88	12.10	1138.671	1124.562	20.60	18.97
25(1)	1106.286	1089.853	43.29	31.83	1101.853	1089.556	20.50	13.61
26(1)	1083.000	1060.990	16.05	20.65	1082.501	1059.214	14.88	4.49
27(1)	1056.796	1031.886	27.58	25.46	1055.109	1033.925	40.26	20.62
28(1)	947.414	932.885	5.20	3.33	959.557	944.327	17.59	11.30
29(1)	908.373	895.898	11.02	13.62	912.820	900.398	10.23	11.39
30(1)	798.040	792.687	2.48	6.44	809.823	804.405	10.42	17.02
31(1)	748.604	735.595	4.53	5.22	753.948	742.602	1.38	2.51
32(1)	628.605	618.987	14.48	13.06	603.115	594.564	5.48	6.30
33(1)	549.125	543.456	5.75	5.80	526.648	522.876	3.45	4.06
34(1)	421.047	417.600	0.04	0.09	463.400	455.542	7.31	2.88
35(1)	366.701	361.208	1.23	0.87	370.176	366.460	4.05	3.28

Table S4. Continued.

Mode (Quanta)	*anti*				*syn*			
	E (harm)	E (anharm)	I (harm)	I (anharm)	E (harm)	E (anharm)	I (harm)	I (anharm)
36(1)	224.928	230.081	4.14	3.46	210.754	210.665	1.26	1.17
37(1)	3056.913	2885.835	42.05	18.80	3050.405	2891.613	43.91	44.40
38(1)	1490.947	1455.035	8.46	5.63	1490.021	1460.735	8.77	2.72
39(1)	1165.645	1150.034	0.67	0.18	1168.154	1144.659	0.68	0.56
40(1)	930.765	943.858	1.48	0.48	951.155	978.128	0.19	0.10
41(1)	858.000	858.857	4.98	14.29	854.566	863.184	7.26	19.23
42(1)	840.336	843.827	29.09	20.20	820.189	823.573	58.57	52.51
43(1)	799.639	804.322	42.61	34.78	808.566	825.752	4.37	1.87
44(1)	760.633	740.710	2.98	2.94	757.863	763.082	13.45	2.11
45(1)	714.583	704.205	51.53	50.11	711.045	700.406	49.78	59.82
46(1)	634.668	629.550	7.15	8.49	631.260	640.768	8.44	5.17
47(1)	606.372	603.221	4.73	3.50	608.431	610.881	3.60	4.66
48(1)	439.721	438.394	9.83	9.58	435.354	448.347	10.98	8.59
49(1)	383.076	419.708	34.45	71.93	378.901	471.383	28.29	178.08
50(1)	318.870	357.031	41.65	8.39	326.624	400.822	43.94	0.49
51(1)	249.741	277.194	0.71	1.16	235.200	291.590	2.70	1.18
52(1)	218.860	231.556	3.80	6.04	233.308	246.243	3.02	9.08
53(1)	146.752	156.797	0.08	0.36	146.876	159.280	0.17	0.05
54(1)	57.778	79.919	5.79	5.50	79.185	84.141	2.94	3.23

Table S5. Results of the harmonic and anharmonic vibrational calculations carried out at the B3LYP/6-311++G(d,p) level for the overtone transitions of the *anti* and *syn* conformers of 6MOI [E = vibrational energy, cm^{-1}; I = infrared intensity, km mol^{-1}].

Mode (Quanta)	*anti*			*syn*		
	E (harm)	E (anharm)	I (anharm)	E (harm)	E (anharm)	I (anharm)
1(2)	7351.092	6873.031	3.514	7349.262	6848.405	3.320
2(2)	6510.899	6210.504	0.733	6514.000	6172.165	0.815
3(2)	6470.674	6151.730	0.940	6471.563	6126.714	0.915
4(2)	6415.799	6037.570	0.512	6397.819	6051.555	0.521
5(2)	6375.918	5964.895	0.705	6388.630	6066.918	0.600
6(2)	6341.241	5939.510	0.929	6339.603	6004.229	1.000
7(2)	6254.480	5854.714	0.664	6257.780	5856.625	0.660
8(2)	6000.481	5660.303	0.003	5991.029	5649.372	0.004
9(2)	3341.786	3253.736	0.201	3327.623	3246.124	0.101
10(2)	3223.550	3149.209	3.419	3225.998	3148.624	1.975
11(2)	3102.795	3025.148	0.181	3091.618	3017.000	0.212
12(2)	3069.638	2992.743	0.045	3065.782	2993.738	0.094
13(2)	3009.910	2951.800	0.253	3011.100	2954.522	0.309
14(2)	2957.219	2911.272	0.009	2968.425	2900.627	0.781
15(2)	2940.641	2867.423	4.982	2943.111	2899.129	0.592
16(2)	2843.851	2765.425	0.090	2851.119	2771.458	0.075
17(2)	2751.348	2690.006	0.325	2743.097	2680.741	0.112
18(2)	2691.562	2635.134	0.104	2693.072	2639.617	0.046
19(2)	2616.469	2554.673	0.440	2633.113	2574.366	0.392
20(2)	2555.370	2506.577	0.416	2545.927	2510.280	0.046
21(2)	2448.848	2404.289	0.045	2453.667	2412.979	0.234
22(2)	2425.570	2371.116	0.094	2432.833	2385.619	0.036
23(2)	2358.676	2298.076	0.019	2361.601	2333.428	0.176
24(2)	2305.364	2272.680	0.063	2277.342	2250.429	0.092
25(2)	2212.573	2182.486	0.112	2203.705	2178.752	0.177
26(2)	2165.999	2119.385	0.219	2165.003	2116.749	0.208
27(2)	2113.591	2059.708	1.621	2110.218	2061.992	2.211
28(2)	1894.828	1865.140	0.312	1919.113	1887.933	0.114
29(2)	1816.747	1793.329	0.035	1825.640	1800.737	0.037
30(2)	1596.080	1584.268	0.597	1619.645	1610.064	2.177
31(2)	1497.209	1470.879	0.266	1507.895	1485.305	2.370
32(2)	1257.210	1237.911	0.638	1206.229	1188.837	0.054
33(2)	1098.251	1086.948	0.031	1053.296	1044.490	28.755
34(2)	842.095	835.377	0.001	926.799	910.937	0.015
35(2)	733.401	723.445	0.006	740.352	732.809	0.000

Table S5. Continued.

Mode (Quanta)	*anti*			*syn*		
	E (harm)	E (anharm)	I (anharm)	E (harm)	E (anharm)	I (anharm)
36(2)	449.856	459.936	0.003	421.508	426.525	0.022
37(2)	6113.826	5731.749	0.532	6100.811	5737.135	0.468
38(2)	2981.895	2897.359	0.379	2980.042	2923.322	0.288
39(2)	2331.289	2297.764	0.007	2336.307	2285.732	0.003
40(2)	1861.530	1905.017	6.046	1902.311	1973.593	4.551
41(2)	1715.999	1724.769	6.630	1709.131	1737.254	6.406
42(2)	1680.672	1694.820	5.771	1640.378	1648.530	4.740
43(2)	1599.277	1611.596	2.892	1617.133	1665.887	3.450
44(2)	1521.266	1475.248	0.040	1515.727	1524.756	0.906
45(2)	1429.167	1406.703	5.446	1422.090	1398.415	0.774
46(2)	1269.335	1259.071	2.077	1262.520	1283.680	1.841
47(2)	1212.745	1207.329	0.284	1216.862	1222.860	1.326
48(2)	879.443	878.005	0.066	870.708	900.550	0.084
49(2)	766.152	858.015	18.732	757.802	984.934	18.587
50(2)	637.740	729.689	7.808	653.249	833.138	10.152
51(2)	499.482	559.513	0.030	470.400	609.099	1.833
52(2)	437.720	466.392	0.014	466.617	494.688	3.629
53(2)	293.505	314.779	0.013	293.752	319.155	0.035
54(2)	115.556	167.938	0.211	158.370	168.823	0.135

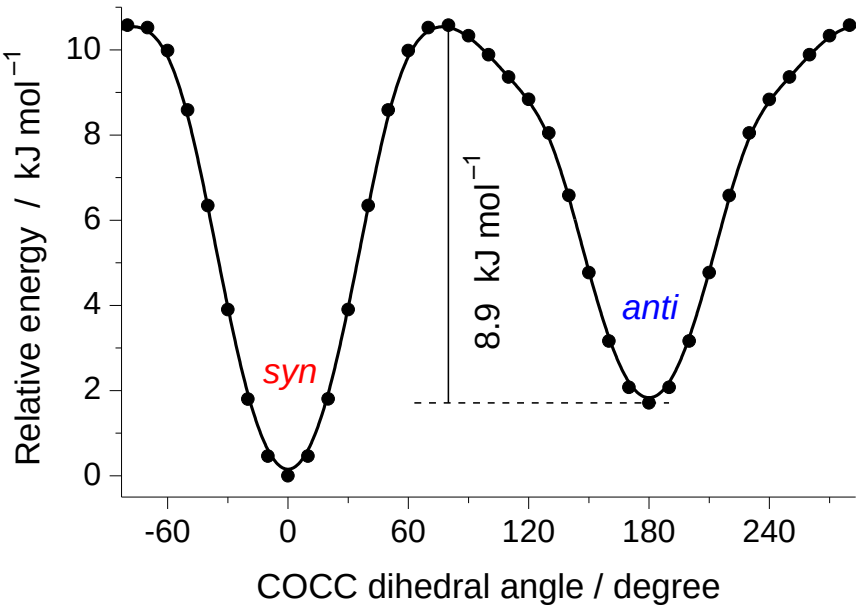

Figure S1. Relaxed potential energy scan calculated at the B3LYP/6-311++G(d,p) level showing the variation of the electronic energy as function of the torsion of the OCH_3 group. At each point all coordinates but the varying dihedral were optimized.

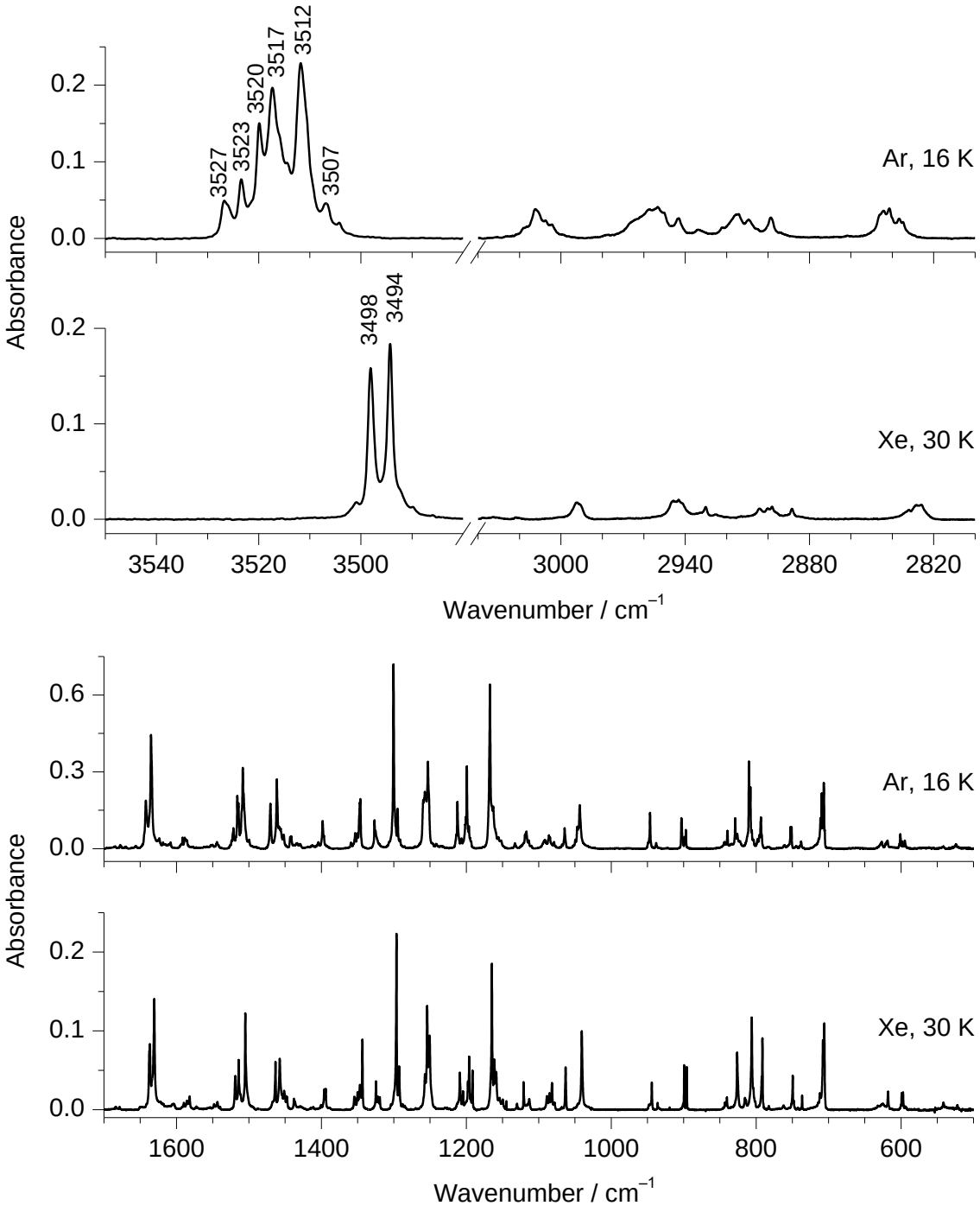

Figure S2. Mid-IR spectra of 6MOI isolated in argon and xenon matrixes, recorded immediately after deposition. The 3500-2800 cm^{-1} (top) and 1700-500 cm^{-1} (bottom) regions are shown.

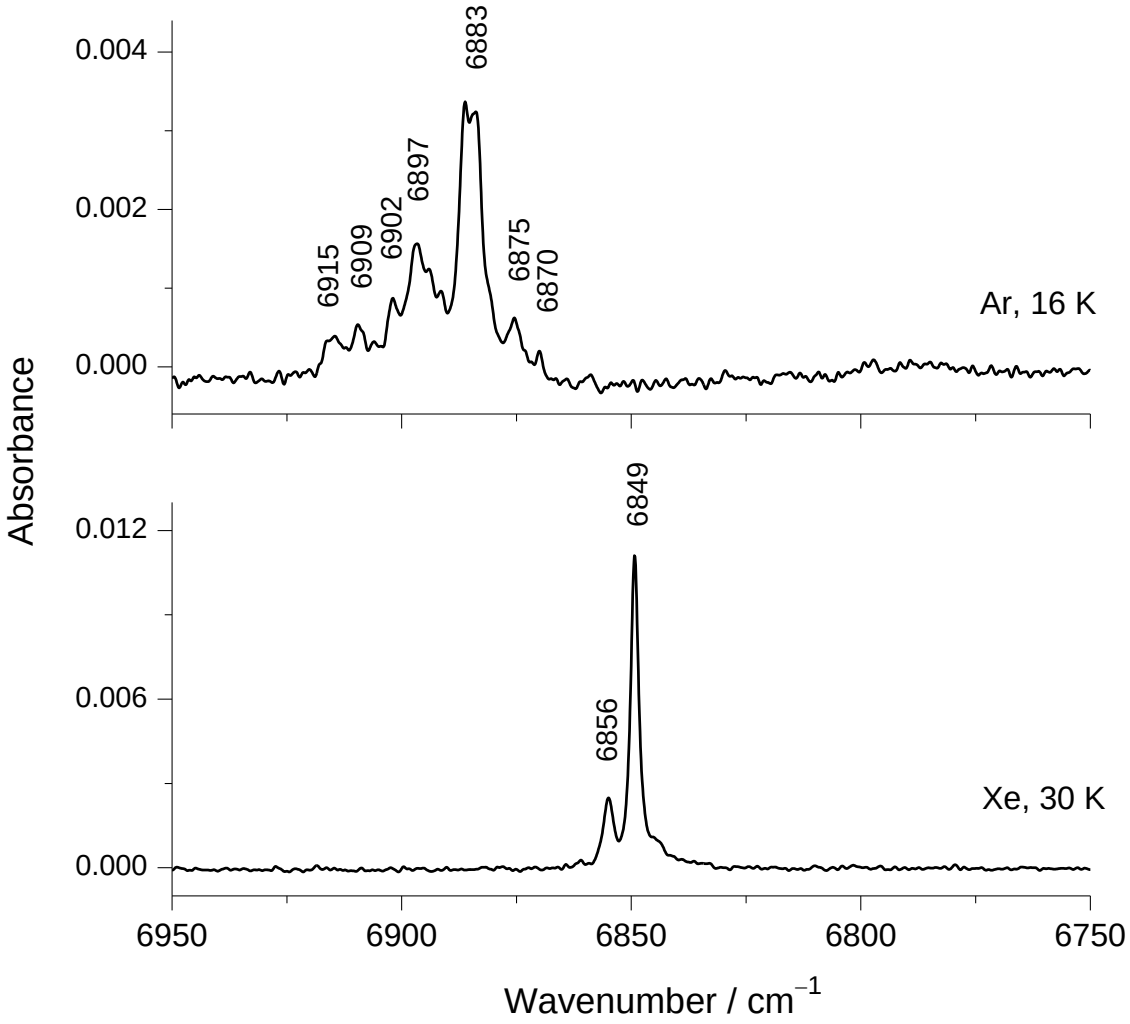

Figure S3. Fragments of the NIR spectra showing the overtone bands of 6MOI isolated in argon (top) and xenon (bottom) matrixes.

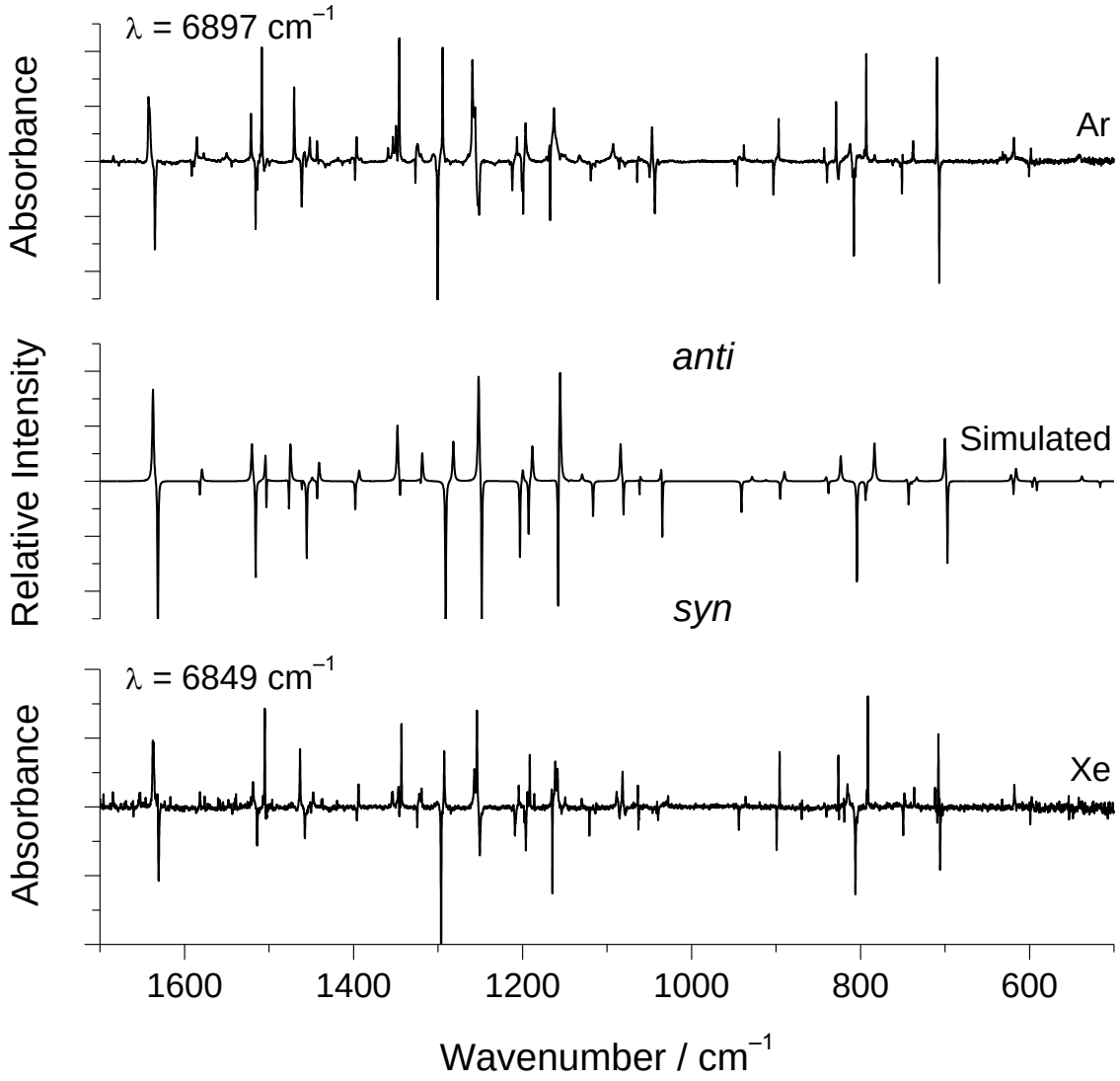

Figure S4. Top and bottom frames: mid-IR difference spectra in the fingerprint region obtained by the subtraction of the spectrum recorded after NIR irradiation at λ = 6897 cm^{-1} (Ar) or λ = 6849 cm^{-1} (Xe) from that recorded before any irradiation at these wavenumbers. Positive bands are those growing during the irradiation. Middle frame: Simulated difference spectrum (*anti* minus *syn*) obtained by using Lorentzian functions (FWHM = 1 cm^{-1}) centered at the B3LYP/6-311++G(d,p) calculated harmonic vibrational frequencies scaled by a factor of 0.98.

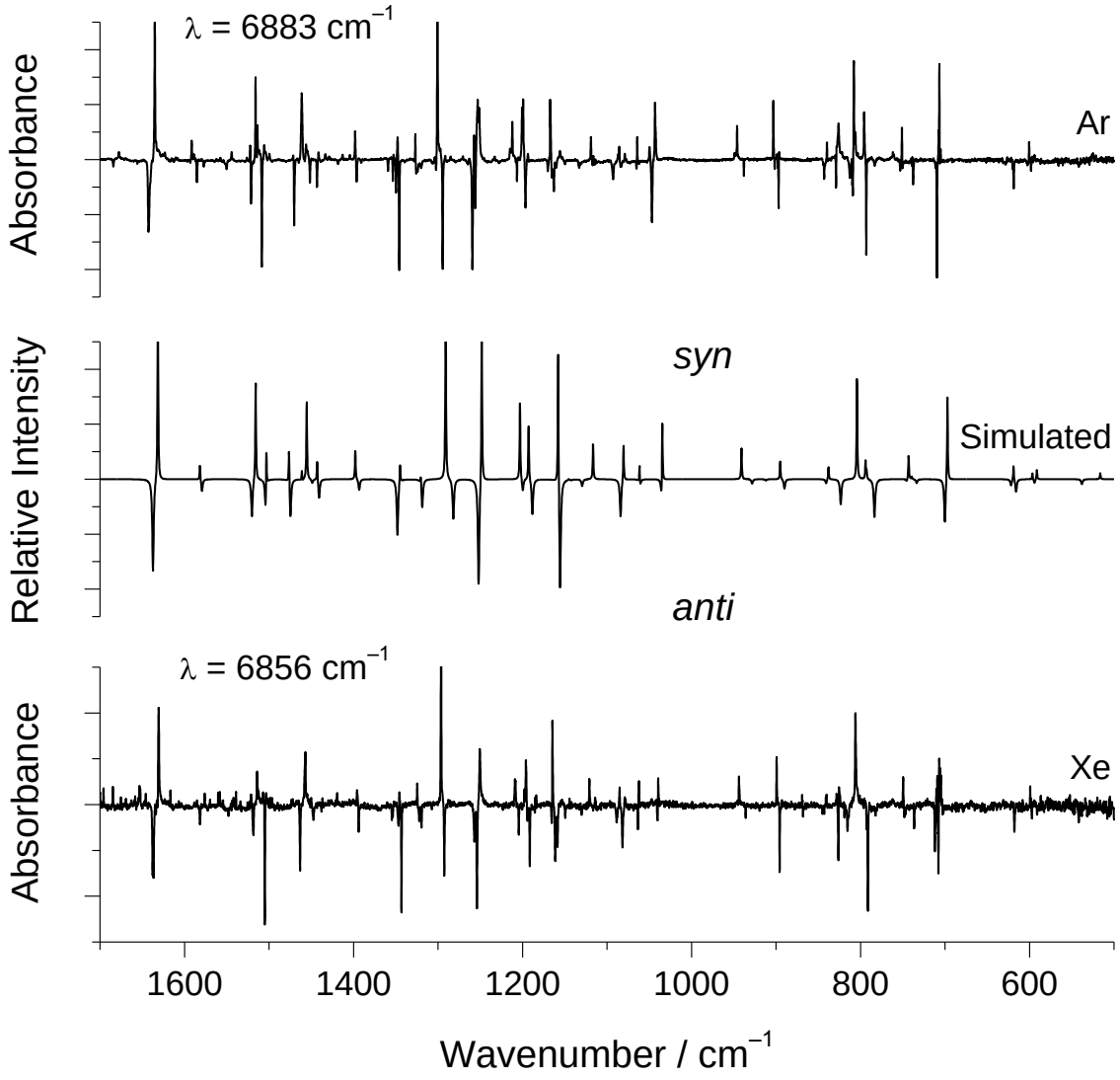

Figure S5. Top and bottom frames: mid-IR difference spectra in the fingerprint region obtained by the subtraction of the spectrum recorded after NIR irradiation at λ = 6883 cm^{-1} (Ar) or λ = 6856 cm^{-1} (Xe) from that recorded before any irradiation at these wavenumbers. Positive bands are those growing during the irradiation. Middle frame: Simulated difference spectrum (*syn* minus *anti*) obtained by using Lorentzian functions (FWHM = 1 cm^{-1}) centered at the B3LYP/6-311++G(d,p) calculated harmonic vibrational frequencies scaled by a factor of 0.98.