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

Electronic supplementary information for: Rotationally Resolved Electronic Spectroscopy of Rotamers of 1,3-Dimethoxybenzene

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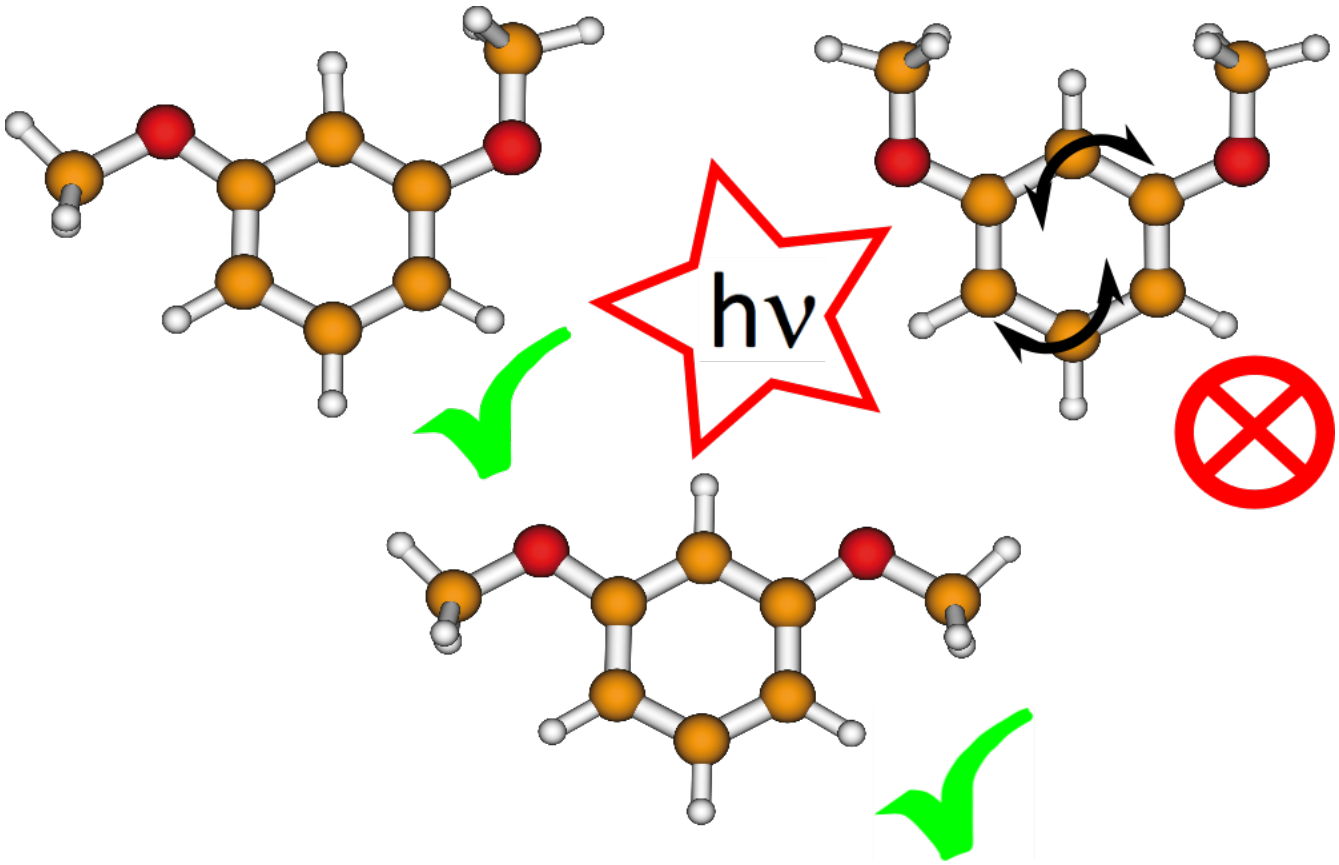

FIG. 1. Graphical Abstract: Only two of three different rotamers of 1,3-dimethoxybenzene can be observed in molecular beam experiments. The missing rotamer adopts a non-planar ring structure upon electronic excitation and is absent due to small Franck-Condon factors. The different behavior of the three rotamers is a consequence of different electron densities in the aromatic ring, which partly lift the aromaticity.

ELECTRONIC SUPPORTING MATERIAL

The online supporting material contains the one figure with the rotationally resolved electronic spectrum of the C-band of 1,3-dimethoxybenzene (Figure S1), modified versions of Figures 5 and 6 of the main paper with added residues of the fit, and tables with the Cartesian coordinates of the CC2/cc-pVTZ optimized structures of the (180, 180), (0, 180), and (180, 0) rotamers in their S_0 and S_1 states, respectively (Tables S1 to S6). Furthermore, the dihedral angles of the three rotamers are compared in Table S7.

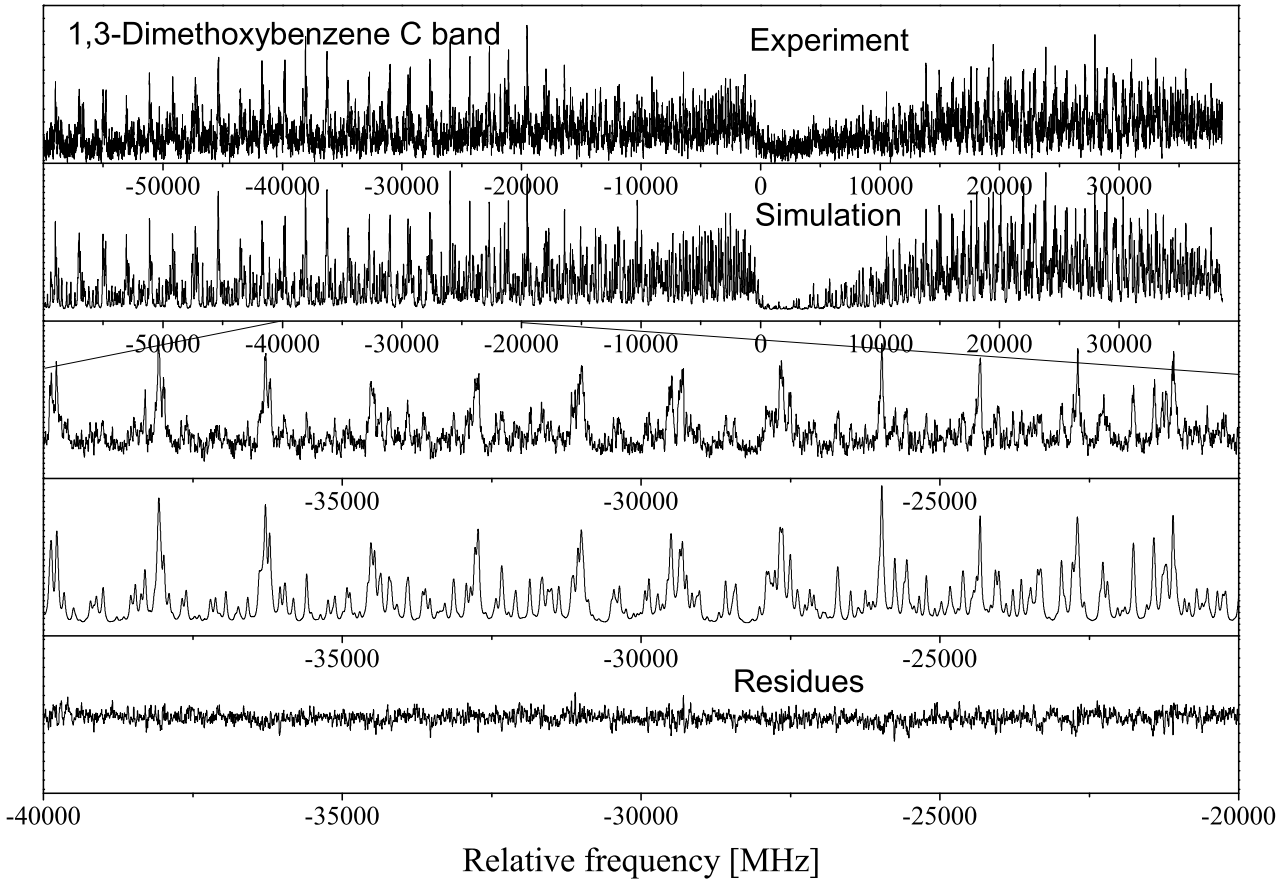

FIG. S1. Rotationally resolved spectrum of the electronic origin of the C band of 1,3-dimethoxybenzene, along with a simulation using the best CMA-ES fit parameters, given in Table 2 of the main publication.

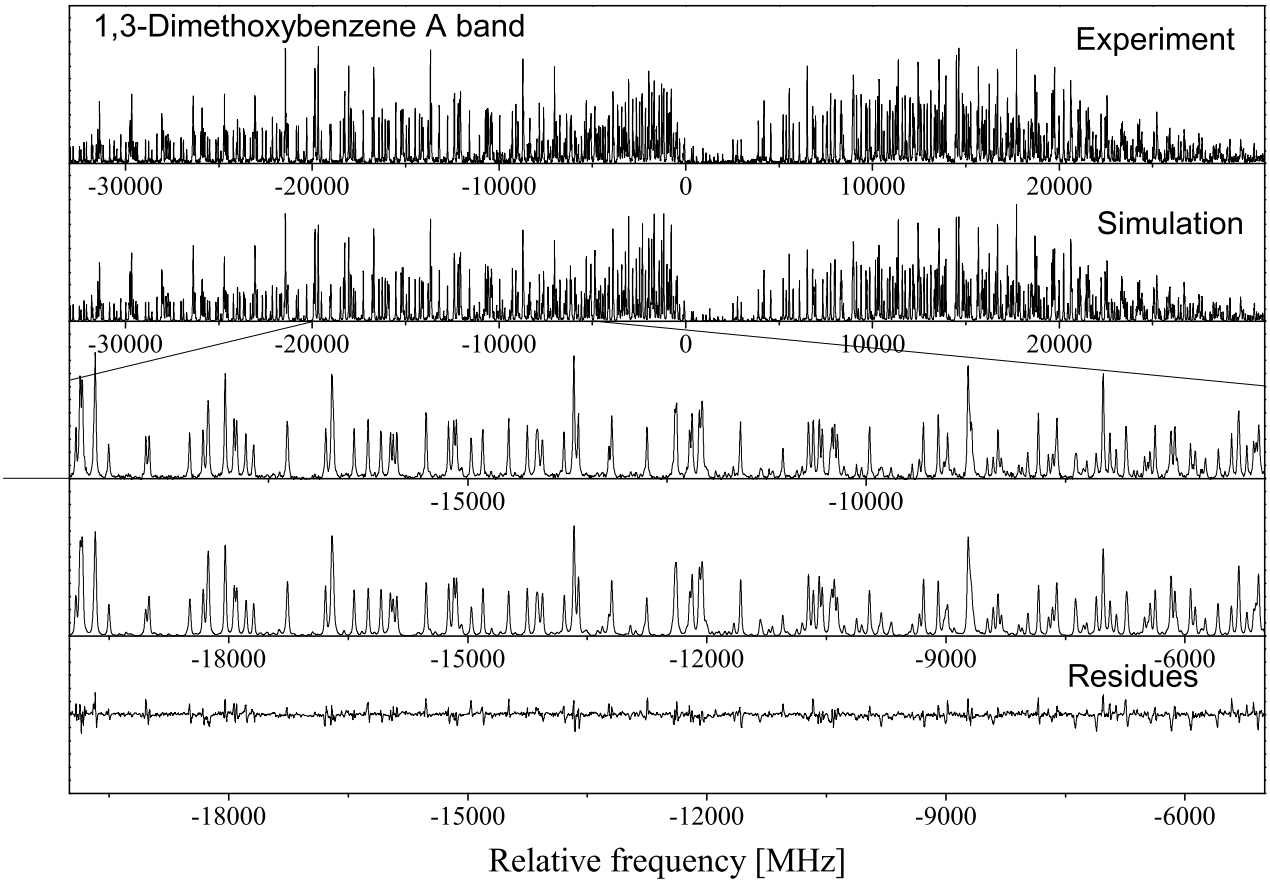

FIG. S2. Modified version of Figure 5 of the main paper, along with the residues of the fit. Rotationally resolved spectrum of the electronic origin of the A band of 1,3-dimethoxybenzene, along with a simulation using the best CMA-ES fit parameters, given in Table 2 of the main publication.

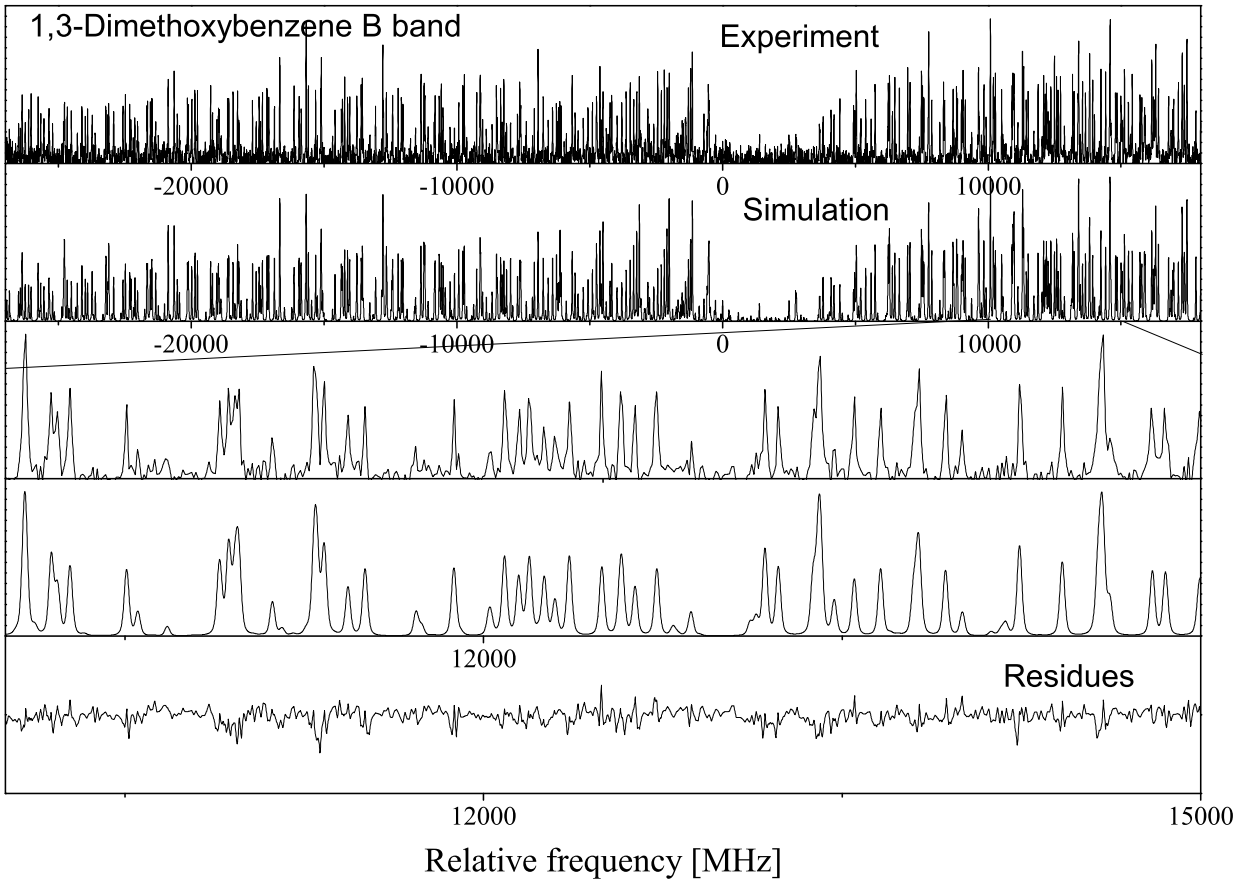

FIG. S3. Modified version of Figure 6 of the main paper, along with the residues of the fit. Rotationally resolved spectrum of the electronic origin of the *B* band of 1,3-dimethoxybenzene, along with a simulation using the best CMA-ES fit parameters, given in Table 2 of the main publication.

TABLE S1. CC2/cc-pVTZ calculated optimized S_0 cartesian coordinates of the (180, 180) rotamer 1,3-dimethoxybenzene (in bohr).

c	2.20820052	-0.00196223	-1.11432118
c	0.01128903	0.00059650	0.36998304
c	0.15869541	0.00139076	3.00129312
c	2.55392723	-0.00053052	4.13041856
c	4.74699941	-0.00305763	2.70082224
c	4.56482537	-0.00383312	0.05525691
o	-2.19340290	0.00220815	-0.97459382
c	-4.45317050	0.00459887	0.47803233
o	6.80769360	-0.00631611	-1.21756510
h	1.98347890	-0.00218489	-3.14130539
h	-1.51256164	0.00344158	4.16788246
h	2.68831484	-0.00005498	6.17087590
c	6.64133331	-0.00695732	-3.89897704
h	6.59715833	-0.00437499	3.56501998
h	-5.99055028	0.00540001	-0.87913151
h	-4.57743571	-1.67812605	1.66467168
h	-4.57465527	1.68835507	1.663494277
h	8.57567008	-0.00873511	-4.579508013
h	5.66357999	-1.68947649	-4.58359368
h	5.66631622	1.67676605	-4.58454606

TABLE S2. CC2/cc-pVTZ calculated optimized S_0 cartesian coordinates of the (180, 0) rotamer 1,3-dimethoxybenzene (in bohr).

c	2.64031916	0.00089978	-1.12085448
c	0.36690703	0.00187427	0.21041212
c	0.37439989	0.00244476	2.84492847
c	2.66346284	0.00208508	4.17677518
c	4.91527321	0.00108816	2.80923839
c	4.95001041	0.00050171	0.17492832
o	-1.95545274	0.00341887	3.95567917
c	-1.98134028	0.00388183	6.64164168
o	2.41422554	0.00024840	-3.69202582
h	-1.40678759	0.00219042	-0.80289667
h	2.71698084	0.00265829	6.21432397
h	6.69104537	0.00082995	3.82390507
h	6.73248236	-0.00027412	-0.81363773
h	-3.96000823	0.00454144	7.18044126
h	-1.06003974	-1.67970828	7.39785754
h	-1.05907338	1.68719461	7.39729645
c	4.71498608	-0.00073046	-5.07821517
h	4.17439276	-0.00113500	-7.05639993
h	5.83472360	1.68254174	-4.66845409
h	5.83385514	-1.68435552	-4.66753230

TABLE S3. CC2/cc-pVTZ calculated optimized S_0 cartesian coordinates of the (0, 180) rotamer 1,3-dimethoxybenzene (in bohr).

c	2.19021604	-0.00001405	-1.19930000
c	-0.05921458	-0.00034247	0.19786066
c	0.07374323	-0.00011837	2.84258796
c	2.40604415	0.00000421	4.07672490
c	4.61179385	0.00001592	2.64387875
c	4.53311243	0.00000436	0.01474538
o	-2.00686823	0.00028887	4.37287822
c	-4.39367424	0.00011179	3.14586764
o	2.26285887	0.00012765	-3.78107630
h	2.44501046	0.00019994	6.11826130
h	6.42306034	0.00000046	3.59237749
h	6.23325589	-0.00014366	-1.11612212
h	-1.86192050	-0.00104862	-0.74608010
c	-0.10525292	0.00021882	-5.04379786
h	-5.79290039	0.00034028	4.64514778
h	-4.63562879	1.68439509	1.97820545
h	-4.63559982	-1.68452649	1.97870332
h	0.33002230	0.00048761	-7.04787759
h	-1.20250338	-1.68432700	-4.57793826
h	-1.20258812	1.68459211	-4.57751006

TABLE S4. CC2/cc-pVTZ calculated optimized S_1 cartesian coordinates of the (180, 180) rotamer 1,3-dimethoxybenzene (in bohr).

c	2.17208582	-0.00235493	-1.25040988
c	-0.00216500	0.00037515	0.33592625
c	0.15176911	0.00130885	3.02902142
c	2.55279608	-0.00061952	4.26229640
c	4.76343575	-0.00312148	2.69336637
c	4.55531760	-0.00394462	0.02614732
o	-2.23112087	0.00205487	-0.94019774
c	-4.50212129	0.00484336	0.51477679
o	6.80872991	-0.00620654	-1.21596842
h	1.94172559	-0.00350330	-3.27078087
h	-1.55399135	0.00352468	4.14746771
h	2.69271171	0.00004278	6.29424791
c	6.70297172	-0.00675969	-3.91283189
h	6.64269937	-0.00435881	3.49522693
h	-6.02995857	0.00579617	-0.85198499
h	-4.61847944	-1.68087101	1.69390661
h	-4.61518019	1.69171589	1.69257094
h	8.65430158	-0.00830255	-4.54169037
h	5.73889609	-1.69110101	-4.60305598
h	5.74128232	1.67862926	-4.60382582

TABLE S5. CC2/cc-pVTZ calculated optimized S_1 cartesian coordinates of the (180, 0) rotamer 1,3-dimethoxybenzene (in bohr).

c	2.62838065	0.00093485	-1.13907145
c	0.26919017	0.00197621	0.15479900
c	0.35293341	0.00250077	2.84420287
c	2.67712071	0.00208551	4.20773738
c	5.03185532	0.00116064	2.87548764
c	4.98343294	0.00053646	0.17043459
o	-1.95032777	0.00340072	3.98189840
c	-2.00041808	0.00386621	6.67741242
o	2.43852395	0.00032560	-3.70097291
h	-1.49943777	0.00226413	-0.85549183
h	2.67956700	0.00246482	6.24706412
h	6.80130586	0.00094738	3.88629606
h	6.74136352	-0.00022937	-0.86327053
h	-3.98497232	0.00454490	7.19125821
h	-1.08367947	-1.68240699	7.42747010
h	-1.08267303	1.68984135	7.42690849
c	4.73501625	-0.00079272	-5.11321221
h	4.16966543	-0.00122503	-7.08371286
h	5.84726202	1.68512547	-4.70442893
h	5.84625350	-1.68712500	-4.70339713

TABLE S6. CC2/cc-pVTZ calculated optimized S_1 cartesian coordinates of the (0, 180) rotamer 1,3-dimethoxybenzene (in bohr).

c	2.41674795	0.10180528	-1.14182430
c	-0.24927471	-0.02400580	-1.59447058
c	-1.71401179	-0.09387413	0.68106410
c	-0.65341084	-0.11917591	3.14035866
c	2.01660166	-0.23576342	3.51736697
c	3.52062125	0.07838551	1.29837347
o	-4.28730389	-0.03260409	0.66278141
c	-5.48185557	0.10690265	-1.75655131
o	4.12469718	0.36606914	-3.04943372
h	-1.95473150	0.00672643	4.71324175
h	2.83805131	-0.22318557	5.38019356
h	5.54346598	0.36146470	1.40430108
h	-0.99706295	-0.71849157	-3.36363207
c	3.13105682	0.51586745	-5.55739271
h	-7.47305481	0.40904434	-1.37239600
h	-4.71340333	1.67185923	-2.85186166
h	-5.23515424	-1.65731934	-2.79187411
h	4.72617794	0.98823308	-6.75580938
h	2.34175506	-1.29724041	-6.13607869
h	1.68404825	1.97591978	-5.67451458

TABLE S7. Dihedral angles of the different rotamers of 1,3-dimethoxybenzene according to the optimized CC2/cc-pVTZ structures. The atomic labeling is given in the full text article. All angles are given in degree.

	$(180, 180)$ / $(0, 0)$		$(180, 0)$		$(0, 180)$	
	S_0	S_1	S_0	S_1	S_0	S_1
C1C2C3C4	0.0	0.0	0.0	0.0	0.0	1.9
C2C3C4C5	0.0	0.0	0.0	0.0	0.0	4.0
C3C4C5C6	0.0	0.0	0.0	0.0	0.0	-9.5
C4C5C6C7	0.0	0.0	0.0	0.0	0.0	9.5
C5C6C1C2	0.0	0.0	0.0	0.0	0.0	-4.0
C6C1C2C3	0.0	0.0	0.0	0.0	0.0	-1.9
H2C2C3C4	180.0	180.0	180.0	180.0	180.0	155.9
H4C4C5C6	180.0	180.0	180.0	180.0	180.0	168.8
H5C5C6C1	180.0	180.0	180.0	180.0	180.0	178.9
H6C6C1C2	180.0	180.0	180.0	180.0	180.0	174.4