Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 577–581

The predicted value of potential barrier to internal rotation of benzaldehyde: is there a conflict between the theory and the experiment or not?

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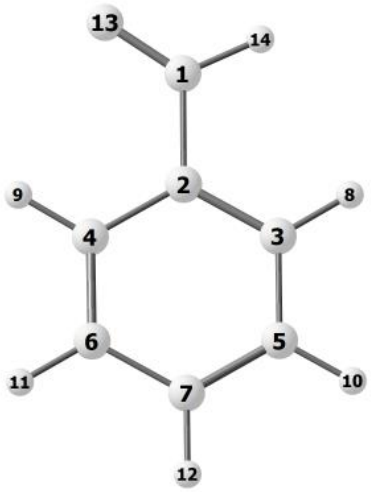

Figure S1 **N**umbering of atoms of benzaldehyde molecule.

Table S1 Cartesian coordinates of optimized (at the MP2/6-311G** level of theory) benzaldehyde molecule.

No	X	Y	Z	Name	A.m. amu
1	1.944778	–0.530271	0.000000	C	12
2	0.488055	–0.236668	0.000000	C	12
3	–0.431277	–1.294236	0.000000	C	12
4	0.037742	1.092330	0.000000	C	12
5	–1.803038	–1.025868	0.000000	C	12
6	–1.331608	1.356214	0.000000	C	12
7	–2.252921	0.299056	0.000000	C	12
8	–0.070237	–2.320750	0.000000	H	1
9	0.772219	1.892441	0.000000	H	1
10	–2.518632	–1.843026	0.000000	H	1
11	–1.686792	2.382864	0.000000	H	1
12	–3.318876	0.508956	0.000000	H	1
13	2.816469	0.317852	0.000000	O	16
14	2.198395	–1.612302	0.000000	H	1

Table S2 Comparison of MP2/6-311G** optimized geometry parameter of benzaldehyde with determined from electron diffraction (bond lengths/Å , bond angles/º).

Parameter	MP2/6-311G**	Экспер.[30]	Parameter	MP2/6-311G**	Экспер.[30]
C1–C2	1.486	1.479 ± 0.007	C6C7	1.402	1.397 ± 0.046
C2–C3	1.401	1.400 ± 0.003	C1–H14	1.111	1.12 ± 0.03
C=O	1.216	1.212 ± 0.003	C1–O13	1.216	1.210
C1–H	1.111	1.12 ± 0.03	O–C–H	121.023	121.2 ± 1.5
C–H	1.089	1.095 ± 0.005			

Table S3 The introduced internal coordinates for benzaldehyde molecule:

[Coordinates] Type=Internal (1 – stretching, 2 – bond angle, 3 – out-of-plane deformation, 6 – torsion)

No.	Name	Type	Atoms
1	Q1	1	2 4 // =1.397484
2	Q2	1	4 6 // =1.388890
3	Q3	1	6 7 // =1.396941
4	Q4	1	5 7 // =1.393636
5	Q5	1	3 5 // =1.392016
6	Q6	1	2 3 // =1.395849
7	QQ1	1	1 2 // =1.478147
8	qq2	1	4 9 // =1.081432
9	qq3	1	6 11 // =1.081259
10	qq4	1	7 12 // =1.081479
11	qq5	1	5 10 // =1.081112
12	qq6	1	3 8 // =1.083269
13	G1	2	2 3 4 // =120.298038
14	G2	2	4 6 2 // =119.612802
15	G3	2	6 4 7 // =120.123220
16	G4	2	7 6 5 // =120.261879
17	G5	2	5 3 7 // =119.731895
18	G6	2	3 5 2 // =119.972175
19	a1c	2	2 3 1 // =119.278788
20	b1c	2	2 1 4 // =120.423178
21	A2	2	4 2 9 // =118.705361
22	B2	2	4 9 6 // =121.681841
23	A3	2	6 4 11 // =120.035919
24	B3	2	6 11 7 // =119.840865
25	A4	2	7 6 12 // =119.879384
26	B4	2	7 12 5 // =119.858742
27	A5	2	5 7 10 // =120.062119
28	B5	2	5 10 3 // =120.205990
29	A6	2	3 5 8 // =120.535577
30	B6	2	3 8 2 // =119.492252
31	XX	3	1 2 3 4 //
32	X2	3	9 4 2 6 //
33	X3	3	11 6 4 7 //
34	X4	3	12 7 6 5 //
35	X5	3	10 5 7 3 //

36	X6	3	8 3 5 2 //
37	T1	6	3 1 0 9 6 0 2 4 //
38	T2	6	2 9 0 11 7 0 4 6 //
39	T3	6	4 11 0 12 5 0 6 7 //
40	T4	6	6 12 0 10 3 0 7 5 //
41	T5	6	7 10 0 2 8 0 5 3 //
42	T6	6	5 8 0 1 4 0 3 2 //
43	aHCO	2	1 14 13 // =120.793768
44	qCH	1	1 14 // =1.105916
45	qCO	1	1 13 // =1.216414
46	Tors	6	3 4 0 13 14 0 2 1 //
47	aHCC	2	1 14 2 // =114.611201
48	aOCC	2	1 13 2 // =124.595035
49	XH	3	14 1 2 13

Table S4 Matrix G of kinetic energy of benzaldehyde (optimized MP2/6-311G** structure, internal coordinates).

Q1	0.2829										
Q2	–0.0699	0.2829									
Q3	0.0000	–0.0711	0.2829								
Q4	0.0000	0.0000	–0.0711	0.2829							
Q5	0.0000	0.0000	0.0000	-0.0703	0.2829						
Q6	–0.0713	0.0000	0.0000	0.0000	–0.0706	0.2829					
QQ1	–0.0710	0.0000	0.0000	0.0000	0.0000	–0.0699	0.2829				
qq2	–0.0680	–0.0742	0.0000	0.0000	0.0000	0.0000	0.0000	1.8255			
qq3	0.0000	–0.0707	–0.0704	0.0000	0.0000	0.0000	0.0000	0.0000	1.8255		
qq4	0.0000	0.0000	–0.0706	-0.0705	0.0000	0.0000	0.0000	0.0000	0.0000	1.8255	
qq5	0.0000	0.0000	0.0000	–0.0708	–0.0710	0.0000	0.0000	0.0000	0.0000	0.0000	1.8255
qq6	0.0000	0.0000	0.0000	0.0000	–0.0717	-0.0699	0.0000	0.0000	0.0000	0.0000	0.0000
G1	–0.0872	0.0876	0.0000	0.0000	0.0875	–0.0870	0.1749	–0.0884	0.0000	0.0000	0.0000
G2	–0.0882	–0.0876	0.0877	0.0000	0.0000	0.0870	-0.0872	0.1747	–0.0878	0.0000	0.0000
G3	0.0882	–0.0872	–0.0877	0.0872	0.0000	0.0000	0.0000	–0.0863	0.1753	–0.0874	0.0000
G4	0.0000	0.0872	–0.0874	–0.0872	0.0877	0.0000	0.0000	0.0000	-0.0875	0.1750	-0.0875
G5	0.0000	0.0000	0.0874	–0.0878	–0.0877	0.0877	0.0000	0.0000	0.0000	-0.0876	0.1750
G6	0.0872	0.0000	0.0000	0.0878	–0.0875	-0.0877	–0.0878	0.0000	0.0000	0.0000	-0.0875
a1c	0.1695	0.0000	0.0000	0.0000	–0.0875	-0.0828	-0.0878	0.0000	0.0000	0.0000	0.0000
b1c	–0.0823	–0.0876	0.0000	0.0000	0.0000	0.1698	–0.0872	0.0884	0.0000	0.0000	0.0000
A2	–0.1142	0.1985	0.0000	0.0000	0.0000	-0.0870	0.0872	–0.0884	0.0000	0.0000	0.0000
B2	0.2024	–0.1109	–0.0877	0.0000	0.0000	0.0000	0.0000	–0.0863	0.0878	0.0000	0.0000
A3	–0.0882	–0.1128	0.2006	0.0000	0.0000	0.0000	0.0000	0.0863	–0.0878	0.0000	0.0000
B3	0.0000	0.2000	-0.1129	-0.0872	0.0000	0.0000	0.0000	0.0000	–0.0875	0.0874	0.0000
A4	0.0000	–0.0872	–0.1128	0.2001	0.0000	0.0000	0.0000	0.0000	0.0875	–0.0874	0.0000
B4	0.0000	0.0000	0.2002	-0.1129	–0.0877	0.0000	0.0000	0.0000	0.0000	–0.0876	0.0875
A5	0.0000	0.0000	–0.0874	-0.1127	0.2003	0.0000	0.0000	0.0000	0.0000	0.0876	-0.0875
B5	0.0000	0.0000	0.0000	0.2005	-0.1126	–0.0877	0.0000	0.0000	0.0000	0.0000	-0.0875
A6	0.0000	0.0000	0.0000	-0.0878	–0.1121	0.2007	0.0000	0.0000	0.0000	0.0000	0.0875
B6	–0.0872	0.0000	0.0000	0.0000	0.1995	–0.1130	0.0878	0.0000	0.0000	0.0000	0.0000
XX	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.2117	0.0000	0.0000	0.0000	0.0000
qCH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0588	0.0000	0.0000	0.0000	0.0000
qCO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0799	0.0000	0.0000	0.0000	0.0000
Tors	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
aHCC	–0.0823	0.0000	0.0000	0.0000	0.0000	0.0828	–0.1157	0.0000	0.0000	0.0000	0.0000
aOCC	0.0823	0.0000	0.0000	0.0000	0.0000	-0.0828	–0.0960	0.0000	0.0000	0.0000	0.0000
XH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	Q1	Q2	Q3	Q4	Q5	Q6	QQ1	qq2	qq3	qq4	qq5

qq6	1.8255										
G1	–0.0877	0.3603									
G2	0.0000	–0.2157	0.3606								
G3	0.0000	0.0357	–0.2175	0.3620							
G4	0.0000	0.0000	0.0363	–0.2164	0.3608						
G5	-0.0872	0.0360	0.0000	0.0362	–0.2167	0.3612					
G6	0.1750	–0.2164	0.0363	0.0000	0.0360	–0.2168	0.3609				
a1c	0.0877	–0.1799	0.0022	0.0000	0.0000	–0.0360	0.2136	0.3393			
b1c	0.0000	–0.1804	0.2134	–0.0357	0.0000	0.0000	0.0027	-0.1594	0.3398		
A2	0.0000	0.2245	–0.1750	–0.0133	0.0000	0.0000	–0.0363	-0.0022	–0.2223	1.7804	
B2	0.0000	–0.0089	–0.1856	0.2308	–0.0363	0.0000	0.0000	0.0000	0.0089	–1.6054	1.7909
A3	0.0000	–0.0357	0.2279	-0.1823	–0.0099	0.0000	0.0000	0.0000	0.0357	0.0133	–0.2411
B3	0.0000	0.0000	–0.0103	–0.1797	0.2263	–0.0362	0.0000	0.0000	0.0000	0.0000	0.0103
A4	0.0000	0.0000	–0.0363	0.2265	-0.1800	–0.0101	0.0000	0.0000	0.0000	0.0000	0.0363
B4	0.0000	0.0000	0.0000	–0.0101	–0.1808	0.2268	-0.0360	0.0000	0.0000	0.0000	0.0000
A5	0.0000	0.0000	0.0000	–0.0362	0.2273	-0.1803	-0.0108	0.0000	0.0000	0.0000	0.0000
B5	0.0872	–0.0360	0.0000	0.0000	–0.0106	–0.1809	0.2276	0.0360	0.0000	0.0000	0.0000
A6	-0.0872	–0.0098	0.0000	0.0000	–0.0360	0.2279	–0.1821	0.0098	0.0000	0.0000	0.0000
B6	-0.0877	0.2262	–0.0363	0.0000	0.0000	–0.0111	–0.1788	–0.2235	–0.0027	0.0363	0.0000
XX	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
T6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
aHCO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0086	0.0086	0.0000	0.0000
qCH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0865	-0.0865	0.0000	0.0000
qCO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0785	0.0785	0.0000	0.0000
Tors	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
aHCC	0.0000	–0.0005	0.0340	0.0000	0.0000	0.0000	–0.0336	–0.1973	0.1978	–0.0340	0.0000
aOCC	0.0000	0.0005	–0.0340	0.0000	0.0000	0.0000	0.0336	0.2059	–0.2063	0.0340	0.0000
XH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	qq6	G1	G2	G3	G4	G5	G6	a1c	b1c	A2	B2
A3	1.7856										
B3	–1.6033	1.7831									
A4	0.0099	–0.2364	1.7831								
B4	0.0000	0.0101	–1.6031	1.7838							
A5	0.0000	0.0362	0.0101	–0.2374	1.7849						
B5	0.0000	0.0000	0.0000	0.0106	–1.6047	1.7856–-					
A6	0.0000	0.0000	0.0000	0.0360	0.0108	0.2387	1.7807				
B6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0111	–1.5986	1.7775			
XX	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.8360		
X2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.4455	2.3463	
X3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0730	–0.4792	2.3563
X4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0732	–0.4758
X5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0722	0.0000	0.0720
X6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.4486	0.0701	0.0000
T1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0040	-0.8030	–0.1268
T2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.1072	0.8603	–0.8418
T3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0421	0.1260	0.8289
T4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0417	–0.0422	0.1254
T5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.1096	0.0406	–0.0416
T6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0042	–0.1400	0.0420
aHCO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
qCH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
qCO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Tors	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0327	0.1445	–0.0419
aHCC	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0336	0.0000	0.0000	0.0000
aOCC	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0336	0.0000	0.0000	0.0000
XH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.4465	0.0690	0.0000
	A3	B3	A4	B4	A5	B5	A6	B6	XX	X2	X3
X4	2.3541										
X5	–0.4748	2.3503									
X6	0.0727	–0.4752	2.3451								
T1	0.0417	–0.0417	0.1404	0.5354							
T2	–0.1236	0.0416	–0.0412	–0.4743	1.0214						
T3	–0.8302	–0.1258	0.0420	–0.0126	–0.4618	1.0012					
T4	0.8324	–0.8341	–0.1248	–0.0482	-0.0147	–0.4632	1.0028				
T5	0.1241	0.8390	–0.8390	–0.0056	–0.0479	–0.0140	–0.4644	1.0081			
T6	–0.0418	0.1261	0.8085	–0.0091	–0.0066	–0.0483	–0.0132	–0.4709	0.5417		
aHCO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	**1.7532**	
qCH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.0997	1.8255
qCO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.1091	–0.0729

Tors	0.0000	0.0414	–0.1280	–0.0343	0.0038	0.0242	0.0239	0.0122	–0.0261	0.0000	0.0000
aHCC	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	**–1.5234**	–0.0865
aOCC	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	–0.2299	0.1862
XH	0.0000	0.0000	0.0702	-0.1345	-0.0405	0.0000	0.0000	0.0407	0.1338	0.0000	0.0000
	X4	X5	X6	T1	T2	T3	T4	T5	T6	aHCO	qCH
qCO	0.2475										
Tors	0.0000	**0.4883**									
aHCC	0.1876	0.0000	**1.6774**								
2.aOCC	–0.0785	0.0000	–0.1540	0.3839							
XH	0.0000	**–0.6641**	0.0000	0.0000	**2.4070**						
	qCO	Tors	aHCC	aOCC	XH						

Table S5 Benzaldehyde and benzoyl fluoride: mean square amplitudes for bond stretchings (bond lengths/Å, bond angles/º), calculated with corresponding MP2/6-311G** force constant matrices.

C6H5–CHO			C6H5–CFO		
Internal coordinate	Mean square amplitudes		Internal coordinate	Mean square amplitudes	
	T=0 K	T=293 K		T=0 K	T=293 K
Q1	0.0446 Å	0.0448 Å	Q1	0.0445Å	0.0447 Å
Q2	0.0442 Å	0.0444 Å	Q2	0.0442Å	0.0444 Å
Q3	0.0447 Å	0.0448 Å	Q3	0.0446Å	0.0447 Å
Q4	0.0445 Å	0.0447 Å	Q4	0.0445Å	0.0446 Å
Q5	0.0444 Å	0.0445 Å	Q5	0.0443Å	0.0445 Å
Q6	0.0444 Å	0.0446 Å	Q6	0.0444Å	0.0446 Å
QQ1	0.0478 Å	0.0485 Å	QQ1	0.0468Å	0.0476 Å
qq2	0.0750 Å	0.0750 Å	qq2	0.0749Å	0.0749 Å
qq3	0.0751 Å	0.0751 Å	qq3	0.0750Å	0.0750 Å
qq4	0.0751 Å	0.0751 Å	qq4	0.0751Å	0.0751 Å
qq5	0.0751 Å	0.0751 Å	qq5	0.0750Å	0.0750 Å
qq6	0.0753 Å	0.0753 Å	qq6	0.0747Å	0.0747 Å
G1	3.3671º	3.4880º	G1	3.3461	3.4680º
G2	3.4211º	3.5239º	G2	3.4118	3.5121º
G3	3.4507º	3.5370º	G3	3.4502	3.5364º
G4	3.4380º	3.5245º	G4	3.4355	3.5218º
G5	3.4486º	3.5362º	G5	3.4500	3.5352º
G6	3.4211º	3.5234º	G6	3.4078	3.5096º
a1c	3.4702º	3.9788º	a1c	3.3814	3.7671º
b1c	3.4720º	3.9918º	b1c	3.3663	3.7656º
A2	6.6828º	6.7163º	A2	6.6540	6.6840º
B2	6.7101º	6.7435º	B2	6.6766	6.7076º
A3	6.6527º	6.6796º	A3	6.6513	6.6782º
B3	6.6531º	6.6810º	B3	6.6542	6.6819º
A4	6.6451º	6.6723º	A4	6.6445	6.6715º
B4	6.6458º	6.6730º	B4	6.6452	6.6723º
A5	6.6562º	6.6839º	A5	6.6523	6.6799º
B5	6.6565º	6.6838º	B5	6.6474	6.6739º
A6	6.6437º	6.6742º	A6	6.6545	6.6835º
B6	6.6399º	6.6710º	B6	6.6479	6.6759º
XX	7.8535º	9.3387º	XX	7.6791	9.1685º
X2	0.1634º	10.7377º	X2	0.0874	10.6022º
X3	0.2541º	10.8526º	X3	0.1684	10.7103º
X4	0.3220º	10.9129º	X4	0.2221	10.7539º
X5	0.3034º	10.9095º	X5	0.2045	10.7498º
X6	0.3223º	10.9242º	X6	0.1758	10.6998º
T1	5.1821º	5.9855º	T1	5.1654	5.9757º
T2	6.4320º	6.7459º	T2	6.4316	6.7559º

T3	6.4496º	6.7706º	T3	6.4401	6.7637º
T4	6.4355º	6.7460º	T4	6.4333	6.7557º
T5	6.4624º	6.7696º	T5	6.4361	6.7474º
T6	5.2337º	6.0911º	T6	5.2177	6.1043º
aHCO	6.3163º	6.3336º	aFCO	3.7062	3.8270º
qCH	0.0785 Å	0.0785 Å	qCF	0.0460	0.0465 Å
qCO	0.0375 Å	0.0376 Å	qCO	0.0364	0.0364 Å
Tors	7.5441º	12.0249º	Tors	5.6634	14.0569º
aHCC	6.2923º	6.3843º	aFCC	3.3395	3.6243º
aOCC	3.7872º	4.0383º	aOCC	3.8161	4.0679º
XH	8.8542º	8.9978º	XF	6.9605	7.3086º

Table S6 Calculated and experimental energies (cm^{-1}) of torsion and out-of-plane CHO deformation transitions of benzaldehyde molecule in the ground S_0 state.

Transition	Calculation[a]							Experiment		
	MP2[22]		CASSCF[22]		CASPT2[22]		MP2 anharm.[23]	d[15]	e	c[23]
	1D	2D	1D	2D	1D	2D				
Torsion										
1←0	137	112	124	110	132	112	109.13	110.85	110.85	109.41
2←1	136	112	122	110	130	112	108.42	108.51	110.55	107.58
3←2	135	112	121	108	130	112	107.7	106.52	110.28	105.61
4←3	133	112	119	108	128	112	106.99	104.17	110.05	-
CHO deformation										
1←0	**142**	**208**	**177**	**220**	**161**	**220**	**226.34**	**223.8**	**223.8**	-

[a] Harmonic frequencies of torsion and deformation vibrations, calculated by MP2/6-311G** and CASSCF/def2-TZVPP methods (*b*), are equal to 113 and 228 cm^{-1}, respectively.

In addition, the corresponding harmonic frequencies, calculated by MP2/cc-pVTZ method, are 113.05 and 232.90 cm^{-1}.

[e] Torsion wavenumbers from the Ref. 15 reassigned in Ref. 23.