SUPPLEMENTARY INFORMATION

Structure of Benzene from Mass-Correlated Rotational Raman Spectroscopy

In Heo, Jong Chan Lee, Begüm Rukiye Özer, and Thomas Schultz

Contents

1 Data Analysis and Line Lists **1**
2 Fitted Rotational Constants **14**
3 Structure Analysis **16**
3.1 (Script for Benzene r_0 Structure Analysis . . . 16
3.1.1 (CODE SECTION (A1)) Imports, natural constants and conversion functions . . . 16
3.1.2 (CODE SECTION (A2)) Experimental and theoretical data for benzene . . . 16
3.1.3 (CODE SECTION (A3)) Explicit derivation of benzene inertial moments and analytical r_0 bond lengths . . . 16
3.1.4 (CODE SECTION (A4)) Principal moments of inertia calculation . . . 17
3.1.5 (CODE SECTION (A5)) Fitting of r_0 geometric parameters from MOI . . . 17
3.1.6 (CODE SECTION (A6)) Monte-Carlo analysis (error propagation) . . . 17
3.1.7 (CODE SECTION (A7)) Fitting and Monte Carlo simulations for synthetic data . . . 17
3.1.8 (CODE SECTION (A8)) Fitting with rovibrational correction terms . . . 18
3.2 Rotational Structure Analysis: Fitting of r_0, r_s, r_m Parameters . . . 18
3.2.1 (CODE SECTION (B1)) Imports, natural constants and conversion functions . . . 19
3.2.2 (CODE SECTION (B2)) Functions for geometry fitting . . . 19
3.2.3 (CODE SECTION (B3)) Graphical User Interface for fitting . . . 19
3.2.4 (CODE SECTION (4)) Isotopologue data for benzene and reference molecules . . . 20
3.2.5 Special Issues Encountered in Geometry Fitting . . . 20
3.2.6 Results for Benzene Geometry Analysis . . . 23
4 References **26**

1 Data Analysis and Line Lists

The tables list assigned lines for C_6H_6 (1), C_6D_6 (1), $^{13}C{-}C_5H_6$ (1), $^{13}C{-}C_5D_6$ (1), and $^{13}C_6H_6$ (1). The first four data-sets were obtained from a single CRASY measurement, using a mixed sample of C_6H_6 and C_6D_6, with heavy carbon isotopologues observed at natural abundance. The last data-set was obtained in a separate experiment, using a mixture of C_6H_6 and $^{13}C_6H_6$. In each case, the Fourier-transform of time-dependent ion signals in a selected parent ion mass channel gave a clean rotational-Raman spectrum of the corresponding neutral species.

Line positions were determined by a Gaussian fit to three points bracketing the center of the line in an adequately padded Fourier-transformed spectrum. Meaningful line amplitudes were estimated relative to the spectral noise, using the modified Z-score as proposed by Iglewitz and Hoaglin.[1] We give line amplitudes in units of $n-\sigma$, relative to the 1-σ noise level estimated for the respective spectrum. Experimental noise in the power spectra scaled proportional to e^{-n} with signal appearing as outliers in the noise histogram.

Lines were assigned programmatically by comparison of observed and simulated rotational Raman spectra. Spectrum simulations were performed in PGOPHER,[2], based on rotational constants from literature or from ab initio calculations (MP2aug-cc-pVTZ level of theory in Gaussian[3]. Each transition was assigned a fit weight based on the observed line strength Sline, the calculated and normalized transition strengths $S_{\text{transition}}$, and the number of observed transitions $N_{\text{transitions}}$ within a line: $weight = \sqrt{S_{\text{line}}} \cdot S_{\text{transition}} / \sqrt{N_{\text{transitions}}}$. The last term was included to account for the additional uncertainty associated with multiple unresolved transitions. Transitions with a fit weight below 10^{-5} or with a low transition strength were excluded from the line list and fit. For $^{13}C{-}C_5H_6$ and $^{13}C{-}C_5D_6$, the spin statics of even (ee, eo) to odd (oe, oo) states was set as 10:6 and 45:36, respectively. We chose the Watson III^r representation and A-reduction for simulating and fitting of spectra for both isotopologues. After automated line assignment, we reviewed all assigned lines and removed spurious assignments. Values for fitted line frequencies and the difference between observed and fitted frequencies in the line lists correspond to subsequent fits, as listed in section 2 .

Spectra for C_6H_6, C_6D_6, $13C{-}C_5H_6$ and $13C{-}C_5D_6$ were taken from the same CRASY data-set, based on a sparse delay scan of nearly 200 ns (see Ref. 4 for a description of sparse data acquisition), resulting in a median resolution near 4.5 MHz. Figs. 1–4 in the manuscript show experimental data from this measurement. Higher- or lower- resolution scans gave similar results, with the expected trade-off between SN contrast versus resolution. The spectra for C_6H_6 and C_6D_6 showed good signal-to-noise (SN) ratio, with the

largest line amplitudes approaching $1000-\sigma$. The spectra for $^{13}C-C_5H_6$ and $^{13}C-C_5D_6$ showed much lower SN ratio due to the low natural abundance of ^{13}C, with the largest line amplitudes well-below $100-\sigma$.

The spectrum for $^{13}C_6H_6$ was taken from a different data set, based on a continuous delay scan of some 20 ns, resulting in a lower median resolution of approx. 45 MHz. Data from this measurement is shown in Fig. S1. For this species, we failed to obtain spectra with better resolution or SN contrast. The spectrum for $^{13}C_6H_6$ showed saturation effects in the parent ion channel and we summed signal from the unsaturated high-mass shoulder of the parent with that of fragments in mass channels 42 u, 56 u and 68 u to obtain a decent signal-to-noise (S/N) ratio. In this case, we also used a Hamming windowed Fourier-transform to improve the signal contrast, increasing the line FWHM by a factor of 50%.

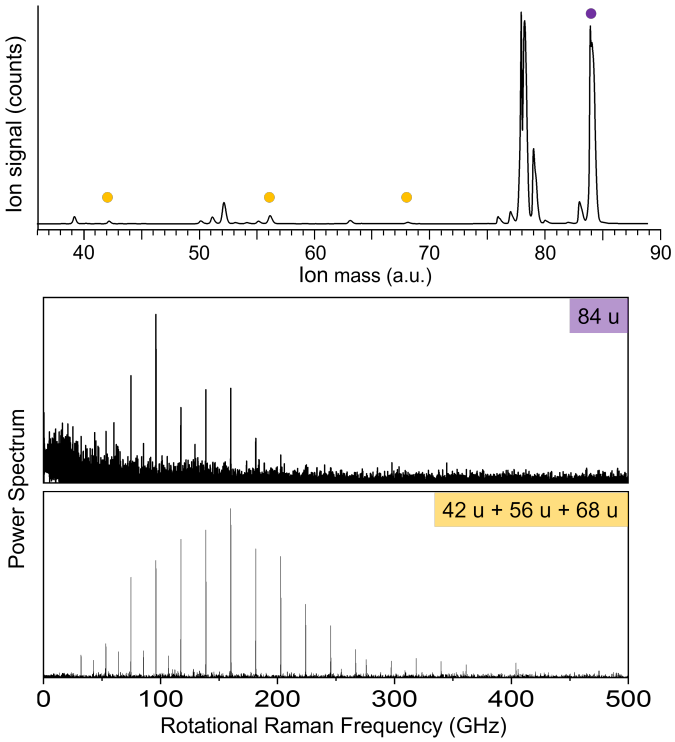

Fig. S1 CRASY data for a mixed sample of C_6H_6 and $^{13}C_6H_6$. (Top) Excerpt from the mass spectrum of the heterogeneous sample, showing the dominant parent and fragment ion signals. (Bottom) Rotational spectra correlated with ion signals at mass 84 u ($^{13}C_6H_6$, marked with blue dot in the mass spectrum) and the sum of ionic fragments at 42 u, 56 u, and 68 u ($^{13}C_3H_3$, $^{13}C_4H_4$, and $^{13}C_5H_3$, marked with yellow dots in mass spectrum).

Table S1 Line-list for C_6H_6 with 16 assigned lines, 142 transitions. Data represents signal for mass 78 u in measurement Nov26_17.36 with 20000 samples scanned over a delay of 199.976 ns and a nominal 1 ps step size (10% sampling).

Observed			Assignment					Calculated		
Frequency	Amplitude	FWHM	Branch	Upper		Lower		Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	K	J	K	(MHz)	(arb.u.)	(MHz)
22757.42264	35.64	4.73	R	2	1	1	1	22757.1188	0.33427	0.3039
34135.55214	307.56	4.51	R	3	1	2	1	34135.6243	0.22745	-0.0721
34135.55214	307.56	4.51	R	3	2	2	2	34135.6407	0.63923	-0.0885
34135.55214	307.56	4.51	S	2	0	0	0	34135.6835	0.34933	-0.1313
45514.19840	277.01	4.48	R	4	1	3	1	45514.0547	0.13268	0.1437
45514.19840	277.01	4.48	R	4	2	3	2	45514.0738	0.47728	0.1246
45514.19840	277.01	4.48	R	4	3	3	3	45514.1234	0.76133	0.0750
45514.19840	277.01	4.48	R	4	3	3	3	45514.1234	0.76133	0.0750
56892.57977	531.04	4.60	R	5	1	4	1	56892.3678	0.06635	0.2120
56892.57977	531.04	4.60	R	5	2	4	2	56892.3873	0.26103	0.1925
56892.57977	531.04	4.60	R	5	3	4	3	56892.4419	0.54385	0.1378
56892.57977	531.04	4.60	R	5	3	4	3	56892.4419	0.54385	0.1378
56892.57977	531.04	4.60	R	5	4	4	4	56892.5646	0.71460	0.0151
56892.57977	531.04	4.60	S	3	0	1	0	56892.7358	0.77953	-0.1561
56892.57977	531.04	4.60	S	3	1	1	1	56892.7431	0.54036	-0.1633
68270.88117	126.65	4.49	R	6	1	5	1	68270.5063	0.02844	0.3749
68270.88117	126.65	4.49	R	6	2	5	2	68270.5233	0.11692	0.3578
68270.88117	126.65	4.49	R	6	3	5	3	68270.5782	0.26976	0.3030
68270.88117	126.65	4.49	R	6	3	5	3	68270.5782	0.26976	0.3030
68270.88117	126.65	4.49	R	6	4	5	4	68270.7105	0.46677	0.1706
68270.88117	126.65	4.49	R	6	5	5	5	68270.9758	0.56983	-0.0947
79649.59179	716.59	4.55	R	7	1	6	1	79648.3946	0.01045	1.1972
79649.59179	716.59	4.55	R	7	2	6	2	79648.4056	0.04405	1.1862
79649.59179	716.59	4.55	R	7	3	6	3	79648.4549	0.10707	1.1369
79649.59179	716.59	4.55	R	7	3	6	3	79648.4549	0.10707	1.1369
79649.59179	716.59	4.55	R	7	4	6	4	79648.5887	0.20635	1.0031
79649.59179	716.59	4.55	R	7	5	6	5	79648.8717	0.33310	0.7200
79649.59179	716.59	4.55	R	7	6	6	6	79649.3873	0.39904	0.2045
79649.59179	716.59	4.55	R	7	6	6	6	79649.3873	0.39904	0.2045
79649.59179	716.59	4.55	S	4	0	2	0	79649.6702	1.00000	-0.0784
79649.59179	716.59	4.55	S	4	1	2	1	79649.6790	0.86648	-0.0872
79649.59179	716.59	4.55	S	4	2	2	2	79649.7145	0.48702	-0.1227
91026.66555	53.33	4.43	R	8	1	7	1	91025.9347	0.00329	0.7309
91026.66555	53.33	4.43	R	8	2	7	2	91025.9357	0.01409	0.7299
91026.66555	53.33	4.43	R	8	3	7	3	91025.9726	0.03533	0.6929
91026.66555	53.33	4.43	R	8	3	7	3	91025.9726	0.03533	0.6929
91026.66555	53.33	4.43	R	8	4	7	4	91026.0984	0.07203	0.5672
91026.66555	53.33	4.43	R	8	5	7	5	91026.3869	0.12990	0.2786
91026.66555	53.33	4.43	R	8	6	7	6	91026.9334	0.20625	-0.2679
91026.66555	53.33	4.43	R	8	6	7	6	91026.9334	0.20625	-0.2679
91026.66555	53.33	4.43	R	8	7	7	7	91027.8543	0.24971	-1.1887
102406.73712	577.57	4.32	R	9	1	8	1	102403.0027	0.00089	3.7344
102406.73712	577.57	4.32	R	9	2	8	2	102402.9890	0.00385	3.7481
102406.73712	577.57	4.32	R	9	3	8	3	102403.0058	0.00983	3.7313
102406.73712	577.57	4.32	R	9	3	8	3	102403.0058	0.00983	3.7313
102406.73712	577.57	4.32	R	9	4	8	4	102403.1127	0.02074	3.6245
102406.73712	577.57	4.32	R	9	5	8	5	102403.3928	0.03965	3.3444
102406.73712	577.57	4.32	R	9	6	8	6	102403.9532	0.07047	2.7839
102406.73712	577.57	4.32	R	9	6	8	6	102403.9532	0.07047	2.7839
102406.73712	577.57	4.32	R	9	7	8	7	102404.9248	0.11326	1.8123
102406.73712	577.57	4.32	R	9	8	8	8	102406.4623	0.14107	0.2749
102406.73712	577.57	4.32	S	5	0	3	0	102406.4135	0.92160	0.3236
102406.73712	577.57	4.32	S	5	1	3	1	102406.4225	0.86244	0.3147
102406.73712	577.57	4.32	S	5	2	3	2	102406.4611	0.67865	0.2760
102406.73712	577.57	4.32	S	5	3	3	3	102406.5653	0.36658	0.1718
102406.73712	577.57	4.32	S	5	3	3	3	102406.5653	0.36658	0.1718

Table S1 Line-list for C_6H_6 (continued).

Observed			Assignment					Calculated		
Frequency	Amplitude	FWHM	Branch	Upper		Lower		Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	K	J	K	(MHz)	(arb.u.)	(MHz)
113781.79087	21.00	6.31	R	10	1	9	1	113779.4452	0.00021	2.3457
113781.79087	21.00	6.31	R	10	2	9	2	113779.4115	0.00090	2.3794
113781.79087	21.00	6.31	R	10	3	9	3	113779.3995	0.00232	2.3914
113781.79087	21.00	6.31	R	10	3	9	3	113779.3995	0.00232	2.3914
113781.79087	21.00	6.31	R	10	4	9	4	113779.4752	0.00501	2.3157
113781.79087	21.00	6.31	R	10	5	9	5	113779.7311	0.00993	2.0598
113781.79087	21.00	6.31	R	10	6	9	6	113780.2862	0.01874	1.5047
113781.79087	21.00	6.31	R	10	6	9	6	113780.2862	0.01874	1.5047
113781.79087	21.00	6.31	R	10	7	9	7	113781.2859	0.03375	0.5050
113781.79087	21.00	6.31	R	10	8	9	8	113782.9020	0.05586	-1.1112
113781.79087	21.00	6.31	R	10	9	9	9	113785.3328	0.07242	-3.5420
113781.79087	21.00	6.31	R	10	9	9	9	113785.3328	0.07242	-3.5420
125162.85058	843.07	4.46	R	11	6	10	6	125155.7388	0.00407	7.1118
125162.85058	843.07	4.46	R	11	6	10	6	125155.7388	0.00407	7.1118
125162.85058	843.07	4.46	R	11	7	10	7	125156.7414	0.00780	6.1092
125162.85058	843.07	4.46	R	11	8	10	8	125158.4070	0.01447	4.4435
125162.85058	843.07	4.46	R	11	9	10	9	125160.9540	0.02495	1.8966
125162.85058	843.07	4.46	R	11	9	10	9	125160.9540	0.02495	1.8966
125162.85058	843.07	4.46	R	11	10	10	10	125164.6292	0.03392	-1.7787
125162.85058	843.07	4.46	S	6	0	4	0	125162.8667	0.65883	-0.0161
125162.85058	843.07	4.46	S	6	1	4	1	125162.8740	0.63937	-0.0234
125162.85058	843.07	4.46	S	6	2	4	2	125162.9106	0.57499	-0.0601
125162.85058	843.07	4.46	S	6	3	4	3	125163.0201	0.44924	-0.1695
125162.85058	843.07	4.46	S	6	3	4	3	125163.0201	0.44924	-0.1695
125162.85058	843.07	4.46	S	6	4	4	4	125163.2752	0.24595	-0.4246
147918.69980	529.59	4.51	S	7	0	5	0	147918.8972	0.37874	-0.1974
147918.69980	529.59	4.51	S	7	1	5	1	147918.9008	0.37505	-0.2010
147918.69980	529.59	4.51	S	7	2	5	2	147918.9290	0.36138	-0.2292
147918.69980	529.59	4.51	S	7	3	5	3	147919.0331	0.32940	-0.3333
147918.69980	529.59	4.51	S	7	3	5	3	147919.0331	0.32940	-0.3333
147918.69980	529.59	4.51	S	7	4	5	4	147919.2992	0.26450	-0.5994
147918.69980	529.59	4.51	S	7	5	5	5	147919.8476	0.15030	-1.1478
170674.43323	548.59	4.73	S	8	0	6	0	170674.3318	0.17859	0.1014
170674.43323	548.59	4.73	S	8	1	6	1	170674.3292	0.17906	0.1040
170674.43323	548.59	4.73	S	8	2	6	2	170674.3413	0.17972	0.0919
170674.43323	548.59	4.73	S	8	3	6	3	170674.4276	0.17798	0.0057
170674.43323	548.59	4.73	S	8	3	6	3	170674.4276	0.17798	0.0057
170674.43323	548.59	4.73	S	8	4	6	4	170674.6871	0.16838	-0.2538
170674.43323	548.59	4.73	S	8	5	6	5	170675.2587	0.14134	-0.8254
170674.43323	548.59	4.73	S	8	6	6	6	170676.3207	0.08442	-1.8875
170674.43323	548.59	4.73	S	8	6	6	6	170676.3207	0.08442	-1.8875
193429.47311	335.12	4.85	S	9	0	7	0	193428.9491	0.06991	0.5240
193429.47311	335.12	4.85	S	9	1	7	1	193428.9374	0.07068	0.5357
193429.47311	335.12	4.85	S	9	2	7	2	193428.9247	0.07283	0.5484
193429.47311	335.12	4.85	S	9	3	7	3	193428.9785	0.07587	0.4946
193429.47311	335.12	4.85	S	9	3	7	3	193428.9785	0.07587	0.4946
193429.47311	335.12	4.85	S	9	4	7	4	193429.2110	0.07854	0.2621
193429.47311	335.12	4.85	S	9	5	7	5	193429.7797	0.07810	-0.3066
193429.47311	335.12	4.85	S	9	6	7	6	193430.8866	0.06920	-1.4135
193429.47311	335.12	4.85	S	9	6	7	6	193430.8866	0.06920	-1.4135
193429.47311	335.12	4.85	S	9	7	7	7	193432.7791	0.04377	-3.3060

Table S1 Line-list for C_6H_6 (continued).

Observed			Assignment					Calculated		
Frequency	Amplitude	FWHM	Branch	Upper		Lower		Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	K	J	K	(MHz)	(arb.u.)	(MHz)
216184.29201	211.35	4.71	S	10	0	8	0	216182.4720	0.02290	1.8200
216184.29201	211.35	4.71	S	10	1	8	1	216182.4479	0.02328	1.8441
216184.29201	211.35	4.71	S	10	2	8	2	216182.4005	0.02443	1.8915
216184.29201	211.35	4.71	S	10	3	8	3	216182.4053	0.02631	1.8867
216184.29201	211.35	4.71	S	10	3	8	3	216182.4053	0.02631	1.8867
216184.29201	211.35	4.71	S	10	4	8	4	216182.5878	0.02881	1.7042
216184.29201	211.35	4.71	S	10	5	8	5	216183.1239	0.03148	1.1682
216184.29201	211.35	4.71	S	10	6	8	6	216184.2394	0.03316	0.0526
216184.29201	211.35	4.71	S	10	6	8	6	216184.2394	0.03316	0.0526
216184.29201	211.35	4.71	S	10	7	8	7	216186.2107	0.03120	-1.9187
216184.29201	211.35	4.71	S	10	8	8	8	216189.3643	0.02100	-5.0723
238938.21912	64.08	4.86	S	11	0	9	0	238934.5605	0.00631	3.6586
238938.21912	64.08	4.86	S	11	1	9	1	238934.5202	0.00644	3.6989
238938.21912	64.08	4.86	S	11	2	9	2	238934.4271	0.00685	3.7920
238938.21912	64.08	4.86	S	11	3	9	3	238934.3645	0.00755	3.8546
238938.21912	64.08	4.86	S	11	3	9	3	238934.3645	0.00755	3.8546
238938.21912	64.08	4.86	S	11	4	9	4	238934.4712	0.00858	3.7479
238938.21912	64.08	4.86	S	11	5	9	5	238934.9414	0.00995	3.2777
238938.21912	64.08	4.86	S	11	6	9	6	238936.0250	0.01155	2.1941
238938.21912	64.08	4.86	S	11	6	9	6	238936.0250	0.01155	2.1941
238938.21912	64.08	4.86	S	11	7	9	7	238938.0273	0.01295	0.1919
238938.21912	64.08	4.86	S	11	8	9	8	238941.3091	0.01299	-3.0900
261691.60483	33.08	5.39	S	12	0	10	0	261684.8039	0.00147	6.8009
261691.60483	33.08	5.39	S	12	1	10	1	261684.7435	0.00150	6.8614
261691.60483	33.08	5.39	S	12	2	10	2	261684.5924	0.00161	7.0124
261691.60483	33.08	5.39	S	12	3	10	3	261684.4421	0.00181	7.1628
261691.60483	33.08	5.39	S	12	3	10	3	261684.4421	0.00181	7.1628
261691.60483	33.08	5.39	S	12	4	10	4	261684.4443	0.00211	7.1605
261691.60483	33.08	5.39	S	12	5	10	5	261684.8121	0.00255	6.7927
261691.60483	33.08	5.39	S	12	6	10	6	261685.8189	0.00315	5.7859
261691.60483	33.08	5.39	S	12	6	10	6	261685.8189	0.00315	5.7859
261691.60483	33.08	5.39	S	12	7	10	7	261687.7992	0.00390	3.8057
261691.60483	33.08	5.39	S	12	8	10	8	261691.1481	0.00466	0.4567
261691.60483	33.08	5.39	S	12	9	10	9	261696.3218	0.00500	-4.7169
261691.60483	33.08	5.39	S	12	9	10	9	261696.3218	0.00500	-4.7169

Table S2 Line-list for C_6D_6 with 18 assigned lines (170 transitions). Data represents signal for mass 84 u in measurement Nov26_17.36 with 20000 samples scanned over a delay of 199.976 ns and a nominal 1 ps step size (10% sampling).

Observed			Assignment					Calculated		
Frequency	Amplitude	FWHM	Branch	Upper		Lower		Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	K	J	K	(MHz)	(arb.u.)	(MHz)
18829.73549	28.82	4.26	R	2	1	1	1	18829.2530	0.29351	0.4824
28244.06663	213.73	4.61	R	3	1	2	1	28243.8392	0.21328	0.2274
28244.06663	213.73	4.61	R	3	2	2	2	28243.8562	0.58742	0.2104
28244.06663	213.73	4.61	S	2	0	0	0	28243.8819	0.30419	0.1847
37658.56653	138.43	4.34	R	4	1	3	1	37658.3742	0.13641	0.1923
37658.56653	138.43	4.34	R	4	2	3	2	37658.3952	0.48088	0.1714
37658.56653	138.43	4.34	R	4	3	3	3	37658.4371	0.74168	0.1294
37658.56653	138.43	4.34	R	4	3	3	3	37658.4371	0.74168	0.1294
47073.07547	346.59	4.51	R	5	1	4	1	47072.8364	0.07678	0.2391
47073.07547	346.59	4.51	R	5	2	4	2	47072.8597	0.29605	0.2157
47073.07547	346.59	4.51	R	5	3	4	3	47072.9075	0.59638	0.1679
47073.07547	346.59	4.51	R	5	3	4	3	47072.9075	0.59638	0.1679
47073.07547	346.59	4.51	S	3	0	1	0	47073.0835	0.71274	-0.0080
47073.07547	346.59	4.51	R	5	4	4	4	47072.9930	0.74754	0.0824
47073.07547	346.59	4.51	S	3	1	1	1	47073.0923	0.49075	-0.0168
56487.73818	108.75	4.32	R	6	1	5	1	56487.1999	0.03803	0.5383
56487.73818	108.75	4.32	R	6	2	5	2	56487.2239	0.15324	0.5143
56487.73818	108.75	4.32	R	6	3	5	3	56487.2744	0.34185	0.4638
56487.73818	108.75	4.32	R	6	3	5	3	56487.2744	0.34185	0.4638
56487.73818	108.75	4.32	R	6	4	5	4	56487.3675	0.56428	0.3707
56487.73818	108.75	4.32	R	6	5	5	5	56487.5253	0.64837	0.2129
65902.07352	691.32	4.63	R	7	1	6	1	65901.4343	0.01658	0.6392
65902.07352	691.32	4.63	R	7	2	6	2	65901.4566	0.06850	0.6169
65902.07352	691.32	4.63	R	7	3	6	3	65901.5061	0.16100	0.5674
65902.07352	691.32	4.63	R	7	3	6	3	65901.5061	0.16100	0.5674
65902.07352	691.32	4.63	R	7	4	6	4	65901.6015	0.29598	0.4720
65902.07352	691.32	4.63	R	7	5	6	5	65901.7687	0.44970	0.3048
65902.07352	691.32	4.63	S	4	0	2	0	65902.2020	0.98386	-0.1285
65902.07352	691.32	4.63	S	4	1	2	1	65902.2135	0.84677	-0.1399
65902.07352	691.32	4.63	S	4	2	2	2	65902.2514	0.46643	-0.1779
65902.07352	691.32	4.63	R	7	6	6	6	65902.0412	0.50025	0.0323
65902.07352	691.32	4.63	R	7	6	6	6	65902.0412	0.50025	0.0323
75315.84124	78.88	4.52	R	8	1	7	1	75315.5029	0.00636	0.3383
75315.84124	78.88	4.52	R	8	2	7	2	75315.5209	0.02670	0.3203
75315.84124	78.88	4.52	R	8	3	7	3	75315.5651	0.06471	0.2762
75315.84124	78.88	4.52	R	8	3	7	3	75315.5651	0.06471	0.2762
75315.84124	78.88	4.52	R	8	4	7	4	75315.6567	0.12585	0.1846
75315.84124	78.88	4.52	R	8	5	7	5	75315.8254	0.21362	0.0159
75315.84124	78.88	4.52	R	8	6	7	6	75316.1095	0.31497	-0.2682
75315.84124	78.88	4.52	R	8	6	7	6	75316.1095	0.31497	-0.2682
75315.84124	78.88	4.52	R	8	7	7	7	75316.5556	0.34938	-0.7144
84731.25191	540.98	4.58	R	9	1	8	1	84729.3621	0.00215	1.8898
84731.25191	540.98	4.58	R	9	2	8	2	84729.3729	0.00911	1.8790
84731.25191	540.98	4.58	R	9	3	8	3	84729.4068	0.02253	1.8452
84731.25191	540.98	4.58	R	9	3	8	3	84729.4068	0.02253	1.8452
84731.25191	540.98	4.58	R	9	4	8	4	84729.4876	0.04532	1.7643
84731.25191	540.98	4.58	R	9	5	8	5	84729.6489	0.08156	1.6030
84731.25191	540.98	4.58	R	9	6	8	6	84729.9336	0.13460	1.3183
84731.25191	540.98	4.58	R	9	6	8	6	84729.9336	0.13460	1.3183
84731.25191	540.98	4.58	R	9	7	8	7	84730.3944	0.19819	0.8575
84731.25191	540.98	4.58	S	5	0	3	0	84731.1974	1.00000	0.0545
84731.25191	540.98	4.58	S	5	1	3	1	84731.2106	0.92952	0.0413
84731.25191	540.98	4.58	S	5	2	3	2	84731.2549	0.71681	-0.0030
84731.25191	540.98	4.58	S	5	3	3	3	84731.3447	0.37437	-0.0928
84731.25191	540.98	4.58	S	5	3	3	3	84731.3447	0.37437	-0.0928
84731.25191	540.98	4.58	R	9	8	8	8	84731.0932	0.22315	0.1587

Table S2 Line-list for C_6D_6 (continued).

Observed			Assignment					Calculated		
Frequency	Amplitude	FWHM	Branch	Upper		Lower		Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	K	J	K	(MHz)	(arb.u.)	(MHz)
94144.06648	35.06	4.37	R	10	1	9	1	94142.9605	0.00064	1.1059
94144.06648	35.06	4.37	R	10	2	9	2	94142.9607	0.00273	1.1058
94144.06648	35.06	4.37	R	10	3	9	3	94142.9786	0.00684	1.0879
94144.06648	35.06	4.37	R	10	3	9	3	94142.9786	0.00684	1.0879
94144.06648	35.06	4.37	R	10	4	9	4	94143.0409	0.01406	1.0256
94144.06648	35.06	4.37	R	10	5	9	5	94143.1847	0.02623	0.8818
94144.06648	35.06	4.37	R	10	6	9	6	94143.4578	0.04597	0.6087
94144.06648	35.06	4.37	R	10	6	9	6	94143.4578	0.04597	0.6087
94144.06648	35.06	4.37	R	10	7	9	7	94143.9185	0.07585	0.1479
94144.06648	35.06	4.37	R	10	8	9	8	94144.6360	0.11347	-0.5696
94144.06648	35.06	4.37	R	10	9	9	9	94145.6899	0.13119	-1.6234
94144.06648	35.06	4.37	R	10	9	9	9	94145.6899	0.13119	-1.6234
103560.12618	772.22	4.51	R	11	1	10	1	103556.2376	0.00017	3.8885
103560.12618	772.22	4.51	R	11	2	10	2	103556.2234	0.00072	3.9027
103560.12618	772.22	4.51	R	11	3	10	3	103556.2192	0.00182	3.9069
103560.12618	772.22	4.51	R	11	3	10	3	103556.2192	0.00182	3.9069
103560.12618	772.22	4.51	R	11	4	10	4	103556.2543	0.00379	3.8719
103560.12618	772.22	4.51	R	11	5	10	5	103556.3694	0.00724	3.7568
103560.12618	772.22	4.51	R	11	6	10	6	103556.6171	0.01317	3.5091
103560.12618	772.22	4.51	R	11	6	10	6	103556.6171	0.01317	3.5091
103560.12618	772.22	4.51	R	11	7	10	7	103557.0618	0.02310	3.0644
103560.12618	772.22	4.51	R	11	8	10	8	103557.7792	0.03876	2.3469
103560.12618	772.22	4.51	S	6	0	4	0	103560.0225	0.80817	0.1037
103560.12618	772.22	4.51	S	6	1	4	1	103560.0363	0.77903	0.0899
103560.12618	772.22	4.51	R	11	9	10	9	103558.8571	0.05958	1.2690
103560.12618	772.22	4.51	R	11	9	10	9	103558.8571	0.05958	1.2690
103560.12618	772.22	4.51	S	6	2	4	2	103560.0836	0.68659	0.0426
103560.12618	772.22	4.51	S	6	3	4	3	103560.1819	0.51867	-0.0558
103560.12618	772.22	4.51	S	6	3	4	3	103560.1819	0.51867	-0.0558
103560.12618	772.22	4.51	S	6	4	4	4	103560.3605	0.27089	-0.2343
103560.12618	772.22	4.51	R	11	10	10	10	103560.3948	0.07130	-0.2686
112970.85966	9.20	5.37	R	12	1	11	1	112969.1231	0.00004	1.7366
112970.85966	9.20	5.37	R	12	2	11	2	112969.0904	0.00017	1.7692
112970.85966	9.20	5.37	R	12	3	11	3	112969.0573	0.00042	1.8024
112970.85966	9.20	5.37	R	12	3	11	3	112969.0573	0.00042	1.8024
112970.85966	9.20	5.37	R	12	4	11	4	112969.0554	0.00089	1.8042
112970.85966	9.20	5.37	R	12	5	11	5	112969.1296	0.00173	1.7301
112970.85966	9.20	5.37	R	12	6	11	6	112969.3369	0.00323	1.5227
112970.85966	9.20	5.37	R	12	6	11	6	112969.3369	0.00323	1.5227
112970.85966	9.20	5.37	R	12	7	11	7	112969.7477	0.00589	1.1120
112970.85966	9.20	5.37	R	12	8	11	8	112970.4446	0.01050	0.4150
112970.85966	9.20	5.37	R	12	9	11	9	112971.5233	0.01812	-0.6637
112970.85966	9.20	5.37	R	12	9	11	9	112971.5233	0.01812	-0.6637
112970.85966	9.20	5.37	R	12	10	11	10	112973.0921	0.02885	-2.2325
112970.85966	9.20	5.37	R	12	11	11	11	112975.2720	0.03593	-4.4124
122388.60967	576.37	4.62	S	7	0	5	0	122388.6211	0.53848	-0.0115
122388.60967	576.37	4.62	S	7	1	5	1	122388.6342	0.52966	-0.0246
122388.60967	576.37	4.62	S	7	2	5	2	122388.6805	0.50014	-0.0708
122388.60967	576.37	4.62	S	7	3	5	3	122388.7805	0.44080	-0.1709
122388.60967	576.37	4.62	S	7	3	5	3	122388.7805	0.44080	-0.1709
122388.60967	576.37	4.62	S	7	4	5	4	122388.9689	0.33765	-0.3593
122388.60967	576.37	4.62	S	7	5	5	5	122389.2940	0.18058	-0.6843
141216.94505	643.24	4.66	S	8	0	6	0	141216.9264	0.30178	0.0186
141216.94505	643.24	4.66	S	8	1	6	1	141216.9372	0.30054	0.0078
141216.94505	643.24	4.66	S	8	2	6	2	141216.9775	0.29562	-0.0325
141216.94505	643.24	4.66	S	8	3	6	3	141217.0712	0.28306	-0.1262

Table S2 Line-list for C_6D_6 (continued).

Observed			Assignment					Calculated		
Frequency	Amplitude	FWHM	Branch	Upper		Lower		Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	K	J	K	(MHz)	(arb.u.)	(MHz)
141216.94505	643.24	4.66	S	8	3	6	3	141217.0712	0.28306	-0.1262
141216.94505	643.24	4.66	S	8	4	6	4	141217.2582	0.25546	-0.3131
141216.94505	643.24	4.66	S	8	5	6	5	141217.5941	0.20183	-0.6490
141216.94505	643.24	4.66	S	8	6	6	6	141218.1507	0.11194	-1.2056
141216.94505	643.24	4.66	S	8	6	6	6	141218.1507	0.11194	-1.2056
160044.82381	364.92	4.51	S	9	0	7	0	160044.8585	0.14400	-0.0346
160044.82381	364.92	4.51	S	9	1	7	1	160044.8650	0.14459	-0.0412
160044.82381	364.92	4.51	S	9	2	7	2	160044.8938	0.14602	-0.0700
160044.82381	364.92	4.51	S	9	3	7	3	160044.9718	0.14707	-0.1480
160044.82381	364.92	4.51	S	9	3	7	3	160044.9718	0.14707	-0.1480
160044.82381	364.92	4.51	S	9	4	7	4	160045.1443	0.14525	-0.3205
160044.82381	364.92	4.51	S	9	5	7	5	160045.4743	0.13594	-0.6505
160044.82381	364.92	4.51	S	9	6	7	6	160046.0431	0.11185	-1.2193
160044.82381	364.92	4.51	S	9	6	7	6	160046.0431	0.11185	-1.2193
160044.82381	364.92	4.51	S	9	7	7	7	160046.9500	0.06482	-2.1262
178872.50709	281.38	4.46	S	10	0	8	0	178872.3224	0.05898	0.1847
178872.50709	281.38	4.46	S	10	1	8	1	178872.3227	0.05956	0.1844
178872.50709	281.38	4.46	S	10	2	8	2	178872.3336	0.06124	0.1735
178872.50709	281.38	4.46	S	10	3	8	3	178872.3854	0.06378	0.1217
178872.50709	281.38	4.46	S	10	3	8	3	178872.3854	0.06378	0.1217
178872.50709	281.38	4.46	S	10	4	8	4	178872.5285	0.06662	-0.0214
178872.50709	281.38	4.46	S	10	5	8	5	178872.8336	0.06852	-0.3265
178872.50709	281.38	4.46	S	10	6	8	6	178873.3914	0.06701	-0.8843
178872.50709	281.38	4.46	S	10	6	8	6	178873.3914	0.06701	-0.8843
178872.50709	281.38	4.46	S	10	7	8	7	178874.3129	0.05777	-1.8058
197700.18225	172.83	4.43	S	11	0	9	0	197699.2066	0.02084	0.9757
197700.18225	172.83	4.43	S	11	1	9	1	197699.1982	0.02114	0.9841
197700.18225	172.83	4.43	S	11	2	9	2	197699.1841	0.02202	0.9981
197700.18225	172.83	4.43	S	11	3	9	3	197699.1979	0.02348	0.9844
197700.18225	172.83	4.43	S	11	3	9	3	197699.1979	0.02348	0.9844
197700.18225	172.83	4.43	S	11	4	9	4	197699.2952	0.02546	0.8871
197700.18225	172.83	4.43	S	11	5	9	5	197699.5540	0.02779	0.6282
197700.18225	172.83	4.43	S	11	6	9	6	197700.0749	0.02995	0.1074
216527.01260	89.92	4.78	S	12	0	10	0	216525.3804	0.00638	1.6322
216527.01260	89.92	4.78	S	12	1	10	1	216525.3607	0.00649	1.6519
216527.01260	89.92	4.78	S	12	2	10	2	216525.3139	0.00683	1.6987
216527.01260	89.92	4.78	S	12	3	10	3	216525.2765	0.00741	1.7361
216527.01260	89.92	4.78	S	12	3	10	3	216525.2765	0.00741	1.7361
216527.01260	89.92	4.78	S	12	4	10	4	216525.3097	0.00825	1.7029
216527.01260	89.92	4.78	S	12	5	10	5	216525.4989	0.00938	1.5137
216527.01260	89.92	4.78	S	12	6	10	6	216525.9541	0.01075	1.0585
216527.01260	89.92	4.78	S	12	6	10	6	216525.9541	0.01075	1.0585
216527.01260	89.92	4.78	S	12	7	10	7	216526.8095	0.01218	0.2031
216527.01260	89.92	4.78	S	12	8	10	8	216528.2239	0.01318	-1.2113
235354.23085	38.57	4.94	S	13	0	11	0	235350.6924	0.00170	3.5385
235354.23085	38.57	4.94	S	13	1	11	1	235350.6586	0.00173	3.5723
235354.23085	38.57	4.94	S	13	2	11	2	235350.5704	0.00183	3.6605
235354.23085	38.57	4.94	S	13	3	11	3	235350.4676	0.00202	3.7632
235354.23085	38.57	4.94	S	13	3	11	3	235350.4676	0.00202	3.7632
235354.23085	38.57	4.94	S	13	4	11	4	235350.4167	0.00229	3.8141
235354.23085	38.57	4.94	S	13	5	11	5	235350.5105	0.00268	3.7203
235354.23085	38.57	4.94	S	13	6	11	6	235350.8685	0.00320	3.3623
235354.23085	38.57	4.94	S	13	6	11	6	235350.8685	0.00320	3.3623
235354.23085	38.57	4.94	S	13	7	11	7	235351.6368	0.00387	2.5941
235354.23085	38.57	4.94	S	13	8	11	8	235352.9877	0.00462	1.2431

Table S3 Line-list for $^{13}C_6H_6$ with 16 assigned lines (169 transitions). Data represents sum of signals for mass 84.5-85 u, 68 u, 56 u, and 42 u in measurement Aug11_12.27 with 20152 samples scanned over a delay of 20152 ns in 1 ps steps (100% sampling). Delay-trace was treated with a Hamming window before Fourier transformation.

Observed			Assignment					Calculated		
Frequency	Amplitude	FWHM	Branch	Upper		Lower		Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	K	J	K	(MHz)	(arb.u.)	(MHz)
32034.41500	10.36	60.89	R	3	1	2	1	32027.2363	0.19603	7.1787
32034.41500	10.36	60.89	S	2	0	0	0	32027.2722	0.26810	7.1428
32034.41500	10.36	60.89	R	3	2	2	2	32027.3096	0.53376	7.1054
42690.68467	11.47	67.68	R	4	1	3	1	42702.8881	0.13210	-12.2034
42690.68467	11.47	67.68	R	4	2	3	2	42702.9857	0.46039	-12.3011
42690.68467	11.47	67.68	R	4	3	3	3	42703.1485	0.69668	-12.4638
42690.68467	11.47	67.68	R	4	3	3	3	42703.1485	0.69668	-12.4638
53373.60890	29.54	59.02	R	5	1	4	1	53378.4595	0.07952	-4.8506
53373.60890	29.54	59.02	R	5	2	4	2	53378.5816	0.30313	-4.9727
53373.60890	29.54	59.02	S	3	0	1	0	53378.7200	0.64605	-5.1111
53373.60890	29.54	59.02	S	3	1	1	1	53378.7607	0.44313	-5.1518
53373.60890	29.54	59.02	R	5	3	4	3	53378.7850	0.59913	-5.1761
53373.60890	29.54	59.02	R	5	3	4	3	53378.7850	0.59913	-5.1761
53373.60890	29.54	59.02	R	5	4	4	4	53379.0698	0.73123	-5.4609
64049.46293	27.80	66.15	R	6	1	5	1	64053.9306	0.04276	-4.4676
64049.46293	27.80	66.15	R	6	2	5	2	64054.0770	0.17034	-4.6141
64049.46293	27.80	66.15	R	6	3	5	3	64054.3211	0.37283	-4.8582
64049.46293	27.80	66.15	R	6	3	5	3	64054.3211	0.37283	-4.8582
64049.46293	27.80	66.15	R	6	4	5	4	64054.6629	0.59922	-5.1999
64049.46293	27.80	66.15	R	6	5	5	5	64055.1022	0.66531	-5.6393
74737.44473	65.07	57.99	R	7	1	6	1	74729.2811	0.02054	8.1636
74737.44473	65.07	57.99	R	7	2	6	2	74729.4520	0.08391	7.9927
74737.44473	65.07	57.99	R	7	3	6	3	74729.7368	0.19349	7.7079
74737.44473	65.07	57.99	R	7	3	6	3	74729.7368	0.19349	7.7079
74737.44473	65.07	57.99	S	4	0	2	0	74730.0675	0.93012	7.3773
74737.44473	65.07	57.99	R	7	4	6	4	74730.1355	0.34635	7.3093
74737.44473	65.07	57.99	S	4	1	2	1	74730.1244	0.79748	7.3203
74737.44473	65.07	57.99	S	4	2	2	2	74730.2953	0.43428	7.1494
74737.44473	65.07	57.99	R	7	5	6	5	74730.6481	0.50849	6.7967
74737.44473	65.07	57.99	R	7	6	6	6	74731.2746	0.54244	6.1702
74737.44473	65.07	57.99	R	7	6	6	6	74731.2746	0.54244	6.1702
85415.33300	18.69	64.19	R	8	1	7	1	85404.4912	0.00882	10.8418
85415.33300	18.69	64.19	R	8	2	7	2	85404.6865	0.03658	10.6465
85415.33300	18.69	64.19	R	8	3	7	3	85405.0119	0.08699	10.3211
85415.33300	18.69	64.19	R	8	3	7	3	85405.0119	0.08699	10.3211
85415.33300	18.69	64.19	R	8	4	7	4	85405.4676	0.16473	9.8654
85415.33300	18.69	64.19	R	8	5	7	5	85406.0534	0.27018	9.2796
85415.33300	18.69	64.19	R	8	6	7	6	85406.7694	0.38202	8.5636
85415.33300	18.69	64.19	R	8	6	7	6	85406.7694	0.38202	8.5636
85415.33300	18.69	64.19	R	8	7	7	7	85407.6156	0.40329	7.7174
96078.61419	77.07	56.24	R	9	1	8	1	96079.5406	0.00338	-0.9264
96078.61419	77.07	56.24	R	9	2	8	2	96079.7603	0.01417	-1.1461
96078.61419	77.07	56.24	R	9	3	8	3	96080.1264	0.03438	-1.5122
96078.61419	77.07	56.24	R	9	3	8	3	96080.1264	0.03438	-1.5122
96078.61419	77.07	56.24	R	9	4	8	4	96080.6390	0.06735	-2.0248
96078.61419	77.07	56.24	R	9	5	8	5	96081.2981	0.11713	-2.6839
96078.61419	77.07	56.24	S	5	0	3	0	96081.2744	1.00000	-2.6602
96078.61419	77.07	56.24	S	5	1	3	1	96081.3476	0.92599	-2.7334
96078.61419	77.07	56.24	S	5	2	3	2	96081.5673	0.70597	-2.9531
96078.61419	77.07	56.24	S	5	3	3	3	96081.9334	0.36176	-3.3192
96078.61419	77.07	56.24	S	5	3	3	3	96081.9334	0.36176	-3.3192
96078.61419	77.07	56.24	R	9	6	8	6	96082.1036	0.18536	-3.4894
96078.61419	77.07	56.24	R	9	6	8	6	96082.1036	0.18536	-3.4894
96078.61419	77.07	56.24	R	9	7	8	7	96083.0555	0.25974	-4.4413
96078.61419	77.07	56.24	R	9	8	8	8	96084.1540	0.27621	-5.5398

Table S3 Line-list for $^{13}C_6H_6$ (continued).

Observed			Assignment					Calculated		
Frequency	Amplitude	FWHM	Branch	Upper		Lower		Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	K	J	K	(MHz)	(arb.u.)	(MHz)
106750.08810	8.59	67.73	R	10	1	9	1	106754.4093	0.00116	-4.3212
106750.08810	8.59	67.73	R	10	2	9	2	106754.6534	0.00489	-4.5653
106750.08810	8.59	67.73	R	10	3	9	3	106755.0602	0.01203	-4.9721
106750.08810	8.59	67.73	R	10	3	9	3	106755.0602	0.01203	-4.9721
106750.08810	8.59	67.73	R	10	4	9	4	106755.6298	0.02409	-5.5417
106750.08810	8.59	67.73	R	10	5	9	5	106756.3620	0.04341	-6.2739
106750.08810	8.59	67.73	R	10	6	9	6	106757.2571	0.07295	-7.1690
106750.08810	8.59	67.73	R	10	6	9	6	106757.2571	0.07295	-7.1690
106750.08810	8.59	67.73	R	10	7	9	7	106758.3148	0.11456	-8.2267
106750.08810	8.59	67.73	R	10	8	9	8	106759.5353	0.16187	-9.4472
106750.08810	8.59	67.73	R	10	9	9	9	106760.9185	0.17541	-10.8304
106750.08810	8.59	67.73	R	10	9	9	9	106760.9185	0.17541	-10.8304
117433.62437	46.53	54.39	R	11	1	10	1	117429.0772	0.00035	4.5472
117433.62437	46.53	54.39	R	11	2	10	2	117429.3457	0.00150	4.2786
117433.62437	46.53	54.39	R	11	3	10	3	117429.7932	0.00374	3.8311
117433.62437	46.53	54.39	R	11	3	10	3	117429.7932	0.00374	3.8311
117433.62437	46.53	54.39	R	11	4	10	4	117430.4197	0.00760	3.2046
117433.62437	46.53	54.39	R	11	5	10	5	117431.2252	0.01402	2.3991
117433.62437	46.53	54.39	R	11	6	10	6	117432.2098	0.02445	1.4146
117433.62437	46.53	54.39	R	11	6	10	6	117432.2098	0.02445	1.4146
117433.62437	46.53	54.39	S	6	0	4	0	117432.3006	0.86704	1.3238
117433.62437	46.53	54.39	S	6	1	4	1	117432.3901	0.83260	1.2343
117433.62437	46.53	54.39	S	6	2	4	2	117432.6586	0.72546	0.9658
117433.62437	46.53	54.39	S	6	3	4	3	117433.1061	0.53769	0.5183
117433.62437	46.53	54.39	S	6	3	4	3	117433.1061	0.53769	0.5183
117433.62437	46.53	54.39	R	11	7	10	7	117433.3733	0.04082	0.2511
117433.62437	46.53	54.39	S	6	4	4	4	117433.7326	0.27344	-0.1082
117433.62437	46.53	54.39	R	11	8	10	8	117434.7158	0.06468	-1.0914
117433.62437	46.53	54.39	R	11	9	10	9	117436.2373	0.09320	-2.6129
117433.62437	46.53	54.39	R	11	9	10	9	117436.2373	0.09320	-2.6129
117433.62437	46.53	54.39	R	11	10	10	10	117437.9378	0.10374	-4.3135
138785.77175	40.61	55.22	S	7	0	5	0	138783.1059	0.62865	2.6658
138785.77175	40.61	55.22	S	7	1	5	1	138783.2117	0.61600	2.5600
138785.77175	40.61	55.22	S	7	2	5	2	138783.5290	0.57506	2.2427
138785.77175	40.61	55.22	S	7	3	5	3	138784.0579	0.49726	1.7138
138785.77175	40.61	55.22	S	7	3	5	3	138784.0579	0.49726	1.7138
138785.77175	40.61	55.22	S	7	4	5	4	138784.7983	0.37088	0.9734
138785.77175	40.61	55.22	S	7	5	5	5	138785.7503	0.19167	0.0215
160131.85619	56.99	57.73	S	8	0	6	0	160133.6503	0.38889	-1.7941
160131.85619	56.99	57.73	S	8	1	6	1	160133.7723	0.38583	-1.9161
160131.85619	56.99	57.73	S	8	2	6	2	160134.1385	0.37520	-2.2823
160131.85619	56.99	57.73	S	8	3	6	3	160134.7487	0.35247	-2.8925
160131.85619	56.99	57.73	S	8	3	6	3	160134.7487	0.35247	-2.8925
160131.85619	56.99	57.73	S	8	4	6	4	160135.6030	0.30973	-3.7468
160131.85619	56.99	57.73	S	8	5	6	5	160136.7015	0.23646	-4.8453
160131.85619	56.99	57.73	S	8	6	6	6	160138.0440	0.12577	-6.1878
160131.85619	56.99	57.73	S	8	6	6	6	160138.0440	0.12577	-6.1878
181483.79451	28.06	54.97	S	9	0	7	0	181483.8934	0.20780	-0.0989
181483.79451	28.06	54.97	S	9	1	7	1	181484.0318	0.20786	-0.2373
181483.79451	28.06	54.97	S	9	2	7	2	181484.4467	0.20752	-0.6522
181483.79451	28.06	54.97	S	9	3	7	3	181485.1383	0.20508	-1.3438
181483.79451	28.06	54.97	S	9	3	7	3	181485.1383	0.20508	-1.3438
181483.79451	28.06	54.97	S	9	4	7	4	181486.1066	0.19720	-2.3121
181483.79451	28.06	54.97	S	9	5	7	5	181487.3514	0.17834	-3.5569
181483.79451	28.06	54.97	S	9	6	7	6	181488.8730	0.14072	-5.0784
181483.79451	28.06	54.97	S	9	6	7	6	181488.8730	0.14072	-5.0784
181483.79451	28.06	54.97	S	9	7	7	7	181490.6711	0.07761	-6.8766

Table S3 Line-list for $^{13}C_6H_6$ (continued).

Observed			Assignment					Calculated		
Frequency	Amplitude	FWHM	Branch	Upper		Lower		Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	K	J	K	(MHz)	(arb.u.)	(MHz)
202838.49160	27.06	54.99	S	10	0	8	0	202833.7953	0.09668	4.6963
202838.49160	27.06	54.99	S	10	1	8	1	202833.9499	0.09726	4.5417
202838.49160	27.06	54.99	S	10	2	8	2	202834.4137	0.09887	4.0779
202838.49160	27.06	54.99	S	10	3	8	3	202835.1866	0.10104	3.3050
202838.49160	27.06	54.99	S	10	3	8	3	202835.1866	0.10104	3.3050
202838.49160	27.06	54.99	S	10	4	8	4	202836.2688	0.10276	2.2228
202838.49160	27.06	54.99	S	10	5	8	5	202837.6601	0.10212	0.8315
202838.49160	27.06	54.99	S	10	6	8	6	202839.3606	0.09577	-0.8690
202838.49160	27.06	54.99	S	10	6	8	6	202839.3606	0.09577	-0.8690
202838.49160	27.06	54.99	S	10	7	8	7	202841.3703	0.07857	-2.8787
202838.49160	27.06	54.99	S	10	8	8	8	202843.6892	0.04516	-5.1976
224185.43330	19.93	61.55	S	11	0	9	0	224183.3156	0.03939	2.1177
224185.43330	19.93	61.55	S	11	1	9	1	224183.4865	0.03979	1.9468
224185.43330	19.93	61.55	S	11	2	9	2	224183.9991	0.04097	1.4342
224185.43330	19.93	61.55	S	11	3	9	3	224184.8534	0.04286	0.5799
224185.43330	19.93	61.55	S	11	3	9	3	224184.8534	0.04286	0.5799
224185.43330	19.93	61.55	S	11	4	9	4	224186.0495	0.04527	-0.6162
224185.43330	19.93	61.55	S	11	5	9	5	224187.5873	0.04774	-2.1540
224185.43330	19.93	61.55	S	11	6	9	6	224189.4668	0.04933	-4.0335
224185.43330	19.93	61.55	S	11	6	9	6	224189.4668	0.04933	-4.0335
224185.43330	19.93	61.55	S	11	7	9	7	224191.6881	0.04821	-6.2548
224185.43330	19.93	61.55	S	11	8	9	8	224194.2510	0.04129	-8.8177
224185.43330	19.93	61.55	S	11	9	9	9	224197.1558	0.02481	-11.7225
224185.43330	19.93	61.55	S	11	9	9	9	224197.1558	0.02481	-11.7225
245523.97993	9.40	62.63	S	12	0	10	0	245532.4144	0.01411	-8.4344
245523.97993	9.40	62.63	S	12	1	10	1	245532.6015	0.01429	-8.6216
245523.97993	9.40	62.63	S	12	2	10	2	245533.1629	0.01486	-9.1830
245523.97993	9.40	62.63	S	12	3	10	3	245534.0986	0.01581	-10.1187
245523.97993	9.40	62.63	S	12	3	10	3	245534.0986	0.01581	-10.1187
245523.97993	9.40	62.63	S	12	4	10	4	245535.4086	0.01716	-11.4287
245523.97993	9.40	62.63	S	12	5	10	5	245537.0928	0.01884	-13.1129
245523.97993	9.40	62.63	S	12	6	10	6	245539.1514	0.02070	-15.1714
245523.97993	9.40	62.63	S	12	6	10	6	245539.1514	0.02070	-15.1714
245523.97993	9.40	62.63	S	12	7	10	7	245541.5842	0.02233	-17.6042
245523.97993	9.40	62.63	S	12	8	10	8	245544.3912	0.02282	-20.4113
245523.97993	9.40	62.63	S	12	9	10	9	245547.5726	0.02046	-23.5927
245523.97993	9.40	62.63	S	12	9	10	9	245547.5726	0.02046	-23.5927
245523.97993	9.40	62.63	S	12	10	10	10	245551.1282	0.01288	-27.1483
266821.70541	5.76	140.70	S	13	0	11	0	266881.0513	0.00445	-59.3459
266821.70541	5.76	140.70	S	13	1	11	1	266881.2547	0.00452	-59.5493
266821.70541	5.76	140.70	S	13	2	11	2	266881.8649	0.00474	-60.1595
266821.70541	5.76	140.70	S	13	3	11	3	266882.8820	0.00511	-61.1766
266821.70541	5.76	140.70	S	13	3	11	3	266882.8820	0.00511	-61.1766
266821.70541	5.76	140.70	S	13	4	11	4	266884.3059	0.00565	-62.6005
266821.70541	5.76	140.70	S	13	5	11	5	266886.1366	0.00639	-64.4312
266821.70541	5.76	140.70	S	13	6	11	6	266888.3741	0.00732	-66.6687
266821.70541	5.76	140.70	S	13	6	11	6	266888.3741	0.00732	-66.6687
266821.70541	5.76	140.70	S	13	7	11	7	266891.0185	0.00841	-69.3130
266821.70541	5.76	140.70	S	13	8	11	8	266894.0696	0.00950	-72.3642
266821.70541	5.76	140.70	S	13	9	11	9	266897.5276	0.01017	-75.8222
266821.70541	5.76	140.70	S	13	9	11	9	266897.5276	0.01017	-75.8222
266821.70541	5.76	140.70	S	13	10	11	10	266901.3924	0.00957	-79.6870
266821.70541	5.76	140.70	S	13	11	11	11	266905.6641	0.00632	-83.9587

Table S4 Line-list for $^{13}C-C_5H_6$ with 35 assigned lines (37 transitions). Data represents signal for mass 79 u in measurement Nov26_17.36 with 20000 samples scanned over a delay of 199.976 ns and a nominal 1 ps step size (10% sampling).

Observed			Assignment							Calculated		
Frequency	Amplitude	FWHM	Branch	Upper			Lower			Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	Ka	Kc	J	Ka	Kc	(MHz)	(arb.u.)	(MHz)
22757.78691	31.81	4.14	R	2	2	1	1	0	1	22757.8449	-0.0579	0.28473
33777.79149	76.02	4.43	R	3	2	2	2	0	2	33777.7636	0.0279	0.69873
33777.79149	76.02	4.43	S	2	2	0	0	0	0	33777.7169	0.0746	0.32940
34320.37220	12.14	4.27	R	3	3	1	2	1	1	34320.5447	-0.1725	0.02765
44977.25614	11.59	6.71	R	4	2	2	3	2	2	44975.1386	2.1176	0.17811
45023.90867	33.59	4.79	R	4	1	3	3	1	3	45023.5326	0.3761	0.21938
45023.90867	33.59	4.79	R	4	2	3	3	0	3	45024.1860	-0.2773	0.60944
45054.56481	6.27	3.58	R	4	3	2	3	1	2	45054.3529	0.2119	0.06474
55989.40302	30.75	3.98	S	3	2	1	1	0	1	55989.4787	-0.0757	0.56201
56281.76313	9.08	4.52	R	5	1	4	4	1	4	56281.1448	0.6183	0.10690
56281.76313	9.08	4.52	R	5	2	4	4	0	4	56281.1588	0.6044	0.29695
56308.59416	8.63	4.65	S	3	3	0	1	1	0	56309.2003	-0.6061	0.39743
56595.36145	13.03	4.04	S	3	3	1	1	1	1	56594.3916	0.9699	0.20321
78392.08040	10.64	5.36	S	4	3	1	2	1	1	78392.0004	0.0800	0.28944
78752.92995	15.38	4.15	S	4	2	2	2	0	2	78752.9022	0.0278	0.29918
78860.14240	38.24	4.74	S	4	4	0	2	2	0	78860.0075	0.1349	1.00000
79238.21750	28.45	4.28	S	4	4	1	2	2	1	79238.4156	-0.1981	0.79591
100801.21277	39.75	4.34	S	5	4	1	3	2	1	100801.6014	-0.3887	0.36267
101216.47268	18.84	4.47	S	5	3	2	3	1	2	101214.3328	2.1398	0.09427
101332.65259	18.19	4.57	S	5	4	2	3	2	2	101332.0935	0.5591	0.26288
101436.49258	21.99	4.76	S	5	5	0	3	3	0	101437.2060	-0.7134	0.13721
101888.67974	8.99	4.79	S	5	5	1	3	3	1	101888.3727	0.3070	0.12676
123220.67435	8.51	5.44	S	6	5	1	4	3	1	123220.8080	-0.1336	0.02664
123652.49813	16.68	5.40	S	6	4	2	4	2	2	123648.3740	4.1241	0.06902
124045.78362	32.63	4.52	S	6	6	0	4	4	0	124046.5884	-0.8048	0.07100
124546.60906	19.49	4.47	S	6	6	1	4	4	1	124545.4939	1.1152	0.07013
145653.01580	22.48	4.65	S	7	6	1	5	4	1	145652.5246	0.4912	0.00768
146288.46797	8.52	4.34	S	7	4	3	5	2	3	146287.0118	1.4562	0.00902
146398.31284	15.60	4.99	S	7	6	2	5	4	2	146396.9314	1.3815	0.00814
146688.96865	13.19	3.92	S	7	7	0	5	5	0	146691.6820	-2.7133	0.00249
147212.32055	12.40	4.45	S	7	7	1	5	5	1	147210.6887	1.6319	0.00254
168102.43094	10.56	3.96	S	8	7	1	6	5	1	168100.1037	2.3272	0.00015
168800.14639	7.80	4.13	S	8	6	3	6	4	3	168796.4611	3.6853	0.00063
168942.97367	9.68	4.67	S	8	7	2	6	5	2	168940.2603	2.7133	0.00017
169370.20105	16.26	4.22	S	8	8	0	6	6	0	169372.7975	-2.5964	0.00037
169887.54061	12.24	3.62	S	8	8	1	6	6	1	169884.5076	3.0330	0.00038

Table S5 Line-list for $^{13}C-C_5D_6$ with 28 assigned lines (35 transitions). Data represents signal for mass 85 u in measurement Nov26_17.36 with 20000 samples scanned over a delay of 199.976 ns and a nominal 1 ps step size (10% sampling).

Observed			Assignment							Calculated		
Frequency	Amplitude	FWHM	Branch	Upper			Lower			Frequency	Strength	Obs.-Calc.
(MHz)	(σ)	(MHz)		J	Ka	Kc	J	Ka	Kc	(MHz)	(arb.u.)	(MHz)
18829.39366	17.86	4.45	R	2	2	1	1	0	1	18830.1463	0.10786	-0.7527
27984.41207	10.70	4.62	R	3	1	2	2	1	2	27983.9889	0.14237	0.4231
27997.83440	21.50	4.51	S	2	2	0	0	0	0	27997.3946	0.11535	0.4398
27997.83440	21.50	4.51	R	3	2	2	2	0	2	27997.3716	0.39655	0.4628
37322.18843	19.89	4.51	R	4	1	3	3	1	3	37322.2042	0.20823	-0.0158
37322.18843	19.89	4.51	R	4	2	3	3	0	3	37322.5031	0.57845	-0.3147
46453.26444	6.84	4.64	S	3	2	1	1	0	1	46451.5917	0.28053	1.6727
46654.92759	8.15	5.06	R	5	2	3	4	2	3	46650.0644	0.31281	4.8632
46654.92759	8.15	5.06	R	5	3	3	4	1	3	46651.3713	0.11263	3.5563
46654.92759	8.15	5.06	R	5	1	4	4	1	4	46653.5149	0.18992	1.4127
46654.92759	8.15	5.06	R	5	2	4	4	0	4	46653.5200	0.52754	1.4075
46669.90570	10.00	5.07	S	3	3	0	1	1	0	46669.6977	0.21150	0.2080
46869.51085	10.71	5.49	S	3	3	1	1	1	1	46868.3172	0.10194	1.1936
65036.42685	8.07	4.93	S	4	3	1	2	1	1	65036.1233	0.27017	0.3036
65293.00117	8.27	8.98	S	4	2	2	2	0	2	65292.5049	0.23439	0.4963
65293.00117	8.27	8.98	R	7	4	3	6	4	3	65297.1975	0.01413	-4.1963
65354.49523	9.40	6.32	S	4	4	0	2	2	0	65352.9914	1.00000	1.5039
65619.00839	6.92	4.66	S	4	4	1	2	2	1	65619.3270	0.75210	-0.3186
83624.30736	16.08	4.69	S	5	4	1	3	2	1	83624.7087	0.78382	-0.4013
83924.98850	7.38	3.92	S	5	3	2	3	1	2	83925.4192	0.17178	-0.4307
83990.68731	10.05	4.44	S	5	4	2	3	2	2	83991.8076	0.47882	-1.1203
84050.33239	8.06	5.28	S	5	5	0	3	3	0	84051.4208	0.31983	-1.0884
84373.02305	7.44	6.16	S	5	5	1	3	3	1	84373.8657	0.28011	-0.8427
102219.83871	7.54	4.38	S	6	5	1	4	3	1	102218.7354	0.16568	1.1033
102663.42060	6.33	5.04	S	6	5	2	4	3	2	102663.1561	0.13146	0.2645
102767.75366	11.09	4.60	S	6	6	0	4	4	0	102768.6372	0.48027	-0.8836
103132.25466	11.99	4.00	S	6	6	1	4	4	1	103132.7263	0.45146	-0.4717
120820.23745	8.00	4.83	S	7	6	1	5	4	1	120819.7646	0.17142	0.4728
121143.13813	7.22	5.85	S	7	5	2	5	3	2	121141.9925	0.05563	1.1456
121338.24172	20.50	4.70	S	7	6	2	5	4	2	121338.3932	0.15514	-0.1515
139937.65681	6.29	4.04	S	8	6	3	6	4	3	139935.2985	0.04033	2.3583
139945.36246	7.59	4.84	S	8	4	4	6	2	4	139947.1482	0.03523	-1.7857
139945.36246	7.59	4.84	S	8	5	4	6	3	4	139947.3812	0.01268	-2.0187
158704.24819	12.37	4.50	S	9	8	2	7	6	2	158703.2624	0.00756	0.9858
159051.60375	6.77	4.43	S	9	9	0	7	7	0	159053.0125	0.00247	-1.4088

2 Fitted Rotational Constants

Rotational constants were fitted in PGOPHER[2], based on the line assignment described in section 1. Three observed isotopologues, C_6H_6, C_6D_6 and $^{13}C_6H_6$, are planar oblate top molecules with D_{6h} symmetry. Due to symmetry, we expect the relation $A = B = 2C$ between the rotational constants and $2D_J + 3D_{JK} + 4D_K = 0$ for the distortion constants. Small deviations for the c-axis constant can be expected due to the inertial defect but due to our excitation and probing scheme, our data contained little or no spectroscopic information to define the C, Δ_K, and δ_K constants. We therefore fixed $C \approx B/2$ and the distortion constants to ab initio values, as indicated in the tables. Ab initio calculations were performed in Gaussian[3] at the MP2/aug-cc-pVTZ level of theory. Two observed isotopologues, $^{13}C{-}C_5H_6$and $^{13}C{-}C_5D_6$, are planar asymmetric top molecules. In this case, independent A, B, and C constants could be fitted, but the latter remained badly determined due to our excitation scheme. Again, distortion constants were fixed to ab initio values if they remained badly determined in the fit.

The frequency calibration in our spectra was tested by fitting rotational constants for residual carbon disulfide signals. Fitted values agreed with literature values[4] with an error of $\Delta\nu/\nu$ = 1.2e-6 (500 ns scan, Nov30_10.57), 2.2e-6 (200 ns scan Nov26_17.36). For the D_{6h} symmetric isotopologues C_6H_6 (mass 78 u), C_6D_6, and $^{13}C_6H_6$, K-splitting was unresolved and assigned lines include multiple transitions with different K quantum numbers (see Ref. 5). The resulting uncertainty in fitted distortion constants increased the range of fitted rotational constants B significantly and B values obtained from data measured under different experimental conditions differed by up to $\Delta\nu/\nu \leq 10^{-5}$ (range of fitted B constants for benzene (5689.25 – 5689.31) MHz). The difference was reduced by a factor 4 when higher J transitions and mixed Q,R-branch transitions were excluded from the fit. It should be noted that we certainly underestimate distortion constants because unresolved transitions are assigned to the same observed line frequency. This issue can only be resolved with experimental data of significantly higher resolution, which is currently not available.

For the higher-resolution data, higher-order distortion constants H_J, H_{JK} and H_{KJ} removed systematic deviations in the fit residuals and were included, even though the resulting distortion constants remained badly determined. The inclusion of higher-order distortion constants had little effect on the fitted rotational constants but affected the lower-order distortion constants. Table S6 compares fitted rotational constants for C_6H_6 to a number of literature values. As opposed to our own earlier results[5], but in line with literature constants from other groups, the data presented here was measured with lower resolution, insufficient to observe K-splitting.

Table S6 C_6H_6 Fitted ground state rotational constants and centrifugal distortion constants (in MHz) and corresponding literature values for. Numbers in round brackets give the 1-σ standard deviation in the corresponding last digits. Square brackets indicate that the parameter was fixed.

	This work	Junttila[6]	Okruss[7]	Matylitsky[8]		ab initio
				gas	supersonic	M2/acc-pVTZ
B	5689.2855(54)	5689.2781(10)	5689.220(26)	5688.95(55)	5689.25(11)	5706.25568
D_J	$0.79(19)\times10^{-3}$	$1.242(10)\times10^{-3}$	$0.96(07)\times10^{-3}$	$1.1(2)\times10^{-3}$		1.230938×10^{-3}
D_{JK}	$-0.78(51)\times10^{-3}$	$-2.059(22)\times10^{-3}$	$1.96(21)\times10^{-3}$	$-1.4(4)\times10^{-3}$		-2.066763×10^{-3}
D_K	[a] $[0.935\times10^{-3}]$					0.934603×10^{-3}
H_J	$-5.1(20)\times10^{-6}$					
H_{JK}	$-8.1(91)\times10^{-6}$					
H_{KJ}	$55(17)\times10^{-6}$					

[a] fixed to MP2/aug-cc-pVTZ value.

Fitted rotational constants and literature values for D_6-benzene-d (C_6D_6) are shown in Table S7.

Fitted rotational constants for $^{13}C_6H_6$ and comparison values from an MP2/aug-cc-pVTZ calculation are shown in Table S8. The data for $^{13}C_6H_6$ came from a lower resolution scan (20 ns scan range). Therefore, we omitted higher-order distortion constants from the fit.

In data for the mixed C_6H_6 and C_6D_6 sample, we observed two naturally occurring ^{13}C isotopologues at mass 79 u and 85 u. Fitted rotational constants and corresponding ab initio values for these isotopologues, based on the line assignments in Tables 1 and 1, are given in Tables S9 and S10.

Table S7 C_6D_6 fitted ground state rotational constants and centrifugal distortion constants (in MHz) and corresponding literature. Numbers in round brackets give the 1-σ standard deviation in the corresponding last digits. Square brackets indicate that the parameter was fixed.

	This work	Pliva[9]	Doi[10]	Jarzeba[11]		ab initio
				gas	supersonic	MP2/acc-pVTZ
B	4707.3175(34)	4707.312(52)	4707.125(6)	4706.4(3)	4707.233(84)	4719.490363
D_J	$0.64(10)\times10^{-3}$	$0.749(34)\times10^{-3}$	$0.719(9)\times10^{-3}$	$0.41(4)\times10^{-3}$	$[0.749\times10^{-3}]$	0.72077×10^{-3}
D_{JK}	$-0.93(27)\times10^{-3}$	$-0.417(112)\times10^{-3}$	$-1.151(9)\times10^{-3}$	$-0.22(30)\times10^{-3}$	$[-1.251\times10^{-3}]$	-1.19494×10^{-3}
D_K	[a] $[0.536\times10^{-3}]$					0.535822×10^{-3}
H_J	$-1.38(92)\times10^{-6}$					
H_{JK}	$-5.2(41)\times10^{-6}$					
H_{KJ}	$0.221(74)\times10^{-6}$					

[a] fixed to MP2/aug-cc-pVTZ value.

Table S8 $^{13}C_6H_6$ fitted ground state rotational constants and centrifugal distortion constants (in MHz) and corresponding literature and ab initio values. Numbers in round brackets give the 1-σ standard deviation in the corresponding last digits. Square brackets indicate that the parameter was fixed.

	This work	Pliva[9,12]	MP2/acc-pVTZ
B	5337.884(51)	5337.9156(60)	5352.430482
D_J	$0.84(74)\times10^{-3}$	$1.107(08)\times10^{-3}$	0.001100965
D_{JK}	$-4.1(23)\times10^{-3}$	$-1.843(29)\times10^{-3}$	0.001850891
D_K	[a] $[0.838\times10^{-3}]$	$[0.827\times10^{-3}]$	0.000837686

[a] Fixed to MP2/aug-cc-pVTZ value. [b] Pliva et al. gave different standard errors for B in refs. 12 and 9. Here we give the larger error from the latter reference.

Table S9 $^{13}C-C_5H_6$ fitted ground state rotational constants and centrifugal distortion constants (in MHz) and corresponding literature and ab initio values. Numbers in round brackets give the 1-σ standard deviation in the corresponding last digits. Square brackets indicate that the parameter was fixed to a corresponding ab initio value.

	This work	MP2/acc-pVTZ
A	5689.474(18)	5706.247944
B	5568.473(23)	5584.755062
C	2868.6(73)	2822.423931
Δ_J	$2.77(53)\times10^{-3}$	0.001205801
Δ_{JK}	$-10.3(29)\times10^{-3}$	0.002011344
Δ_K	[a] $[0.902\times10^{-3}]$	0.000902457
δ_J	[a] $[16.906\times10^{-6}]$	0.000016906
δ_K	[a] $[276.963\times10^{-6}]$	0.000276963

[a] fixed to MP2/aug-cc-pVTZ value.

Table S10 $^{13}C-C_5D_6$ fitted ground state rotational constants and centrifugal distortion constants (in MHz) and corresponding ab initio values. Numbers in round brackets give the 1-σ standard deviation in the corresponding last digits. Square brackets indicate that the parameter was fixed to a corresponding ab initio value.

	This work	MP2/acc-pVTZ
A	4707.541(36)	4719.482348
B	4624.188(31)	4635.996096
C	2332(16)	2338.683358
Δ_J	[a] $[0.709\times10^{-3}]$	0.000709026
Δ_{JK}	[a] $[-1.169\times10^{-3}]$	-0.001169092
Δ_K	[a] $[0.521\times10^{-3}]$	0.000520773
δ_J	[a] $[8.121\times10^{-6}]$	0.000008121
δ_K	[a] $[0.164\times10^{-3}]$	0.000164263

[a] fixed to MP2/aug-cc-pVTZ value.

3 Structure Analysis

The structure analysis for benzene was performed using Phyton scripts, based on our own and literature rotational constants. The scripts are thoroughly commented and develop the relevant code for fitting molecular structure based on isotopologue rotational constants and for a Monte-Carlo propagation of experimental uncertainties. The code was written with minimal dependencies and should be easily executable in any Python IDE. The code is presented in two files, which are described in more detail below:

(A) Benzene_r0_Structure_Fit.py
(Walk-through for benzene r_0 geometry fitting and associated calculations.)

(B) FitMOI.py
(Generalized fit program for r_0, r_S, r_m geometry analysis.)

File (A) contains presents a step-by-step guide for the fitting of benzene r_0 geometries with 2, 3, or 4 geometry parameters and can be executed in any suitable Python interactive shell, such as iPython or Jupyter. File (B) contains Python code to fit r_0, r_s (Nössberger-type fit of Kraitchman substitution structures), and r_m (Watson's mass-weighted fits) structures with a simple graphical user interface. The code is implemented to allow facile fitting of other molecular structures.

3.1 (Script for Benzene r_0 Structure Analysis

The following is a brief description of the Python script for the analysis of the benzene r_0 structure (File (A)). A more detailed documentation can be found in the code comments. The r_0 structure denotes the 'effective' molecular geometry based on measured inertial moments ($\propto$ inverse of the rotational constants). A description of the relevant physical concepts and mathematical equations can be found in Chapter 13 of the book Microwave Molecular Spectra by Gordy and Cook[13].

3.1.1 (CODE SECTION (A1)) Imports, natural constants and conversion functions

The code requires importing functions and constant definitions from numpy (mathematical functions), scipy (scientific functions and natural constants), tqdm (display of a progress bar), and matplotlib (plotting of data). This section also defines relevant atomic masses and convenience functions for converting between physical units.

3.1.2 (CODE SECTION (A2)) Experimental and theoretical data for benzene

This section gives a calculated ab initio geometry for benzene, based on a RI-MP2 / aug-cc-pVTZ geometry optimization performed in Orca and tabulates rotational constants measured by us and from the literature. We defined several sub-sets of data for the subsequent geometry analysis, e.g., a 'complete' data-set encompassing all experimental values, a data-set based purely on our measurement results, a data-set of deuterated isotopologues that allowed us to reproduce results from Kunishige et al.[14], and a 'masked' data-set, where we removed outliers from the literature data. The ab initio geometry was used to test our code in sections 3.1.3 and 3.1.4 against theoretical values.

3.1.3 (CODE SECTION (A3)) Explicit derivation of benzene inertial moments and analytical r_0 bond lengths

This section derives analytical functions for the benzene moment of inertia as function of r(C) (distance of carbon atom from the molecular center, equivalent to the bond length r(CC) in symmetric isotopologues), and bond lengths r(CH), r(CD), and $r(^{13}\mathrm{C})$ geometry parameters. The results are used for a direct calculation of the benzene r_0 structure based on the assumption of $r_H = r_D$ and are also used to check the numerical accuracy of the general molecular moment-of-inertia (MOI) functions defined in section (A4). The calculation of r_0 bond lengths based on literature values from Doi et al.[10] reproduce the exact values given in their paper. A calculation based on our own C_6H_6 and C_6D_6 data gave r(C) = 1.3971(0)[11] Åand r(CH) = 1.0804(0)[12] Å*, in excellent agreement with the r_0 literature values from Doi and others (see Table 4 of the main manuscript). A corresponding calculation based on the isotopologue pair C_6H_6 and $^{13}C_6H_6$ gave quite different bond lengths $r_{0,CH}$ = 1.1058(1)[12] Å and $r_{0,CC}$ = 1.3938(0)[11] ÅThe former is based on the approximation $r_{0,CH} = r_{0,CD}$, whereas the latter assumes $r_{0,^{12}C} = r_{0,^{13}C}$. The vibrational amplitude and mass difference is larger for H_D

* We give the propagated experimental uncertainty in round parentheses and Costain uncertainties[13,15] in square brackets.

as compared to ^{12}C,^{13}C and we should expect the latter to be a better approximation for the actual bond lengths, even if the value is in contradiction to literature values.

3.1.4 (CODE SECTION (A4)) Principal moments of inertia calculation

For a fit of structural r_0 parameters to experimental MOI, we need to relate the structure parameters to calculated MOI_{calc}. We can then minimize (MOI_{exp} - MOI_{calc}) to find r_0 parameters that are in best agreement with experimental data. Function PMI calculates principal MOI based on the masses and Cartesian coordinates of the atoms in a molecule. Functions bzMOI convert a minimal set of benzene internal coordinates to the corresponding Cartesian coordinates. Three distinct functions for internal to Cartesian coordinate mapping are based on the following minimal set of internal coordinates: (i) r(C) ($\equiv r(^{13}\mathrm{C})$, r(CH) ($\equiv r$(CD)), (ii) r(C) ($\equiv r(^{13}\mathrm{C})$, r(CH), r(CD), (iii) r(C), r(CH), r(CD), $r(^{13}\mathrm{C})$. The last function requires an additional parameter f_{HC} to specify how much a ^{12}C,^{13}C atom displacement leads to a corresponding displacement of the attached H,D atom.

3.1.5 (CODE SECTION (A5)) Fitting of r_0 geometric parameters from MOI

Fitting r_0 geometry parameters to experimental MIM, as opposed to using analytical equations as given in section (A3), has three advantages: (i) We are no longer limited to isotopologue pairs, but we can use arbitrary amounts of data, (ii) We obtain fit uncertainties and deviations, which help to diagnose the quality of data and fit, (iii) The fit can be easily adjusted to account for different fit assumptions.

Fits were performed using the Levenberg-Marquardt nonlinear fit method as implemented in the library scipy.leastsq, which in turn is based on the lmdif and lmder algorithms in MINPACK. The fits minimized squared residuals between calculated principal inertial moments, as defined in Section 3.1.4, and experimental values, as listed in Section A2. Parameter uncertainties were estimated from residuals and parameter covariances, following the algorithm implemented in the scipy.optimize.curve_fit package. Costain uncertainties were calculated for bond lengths as discussed by Demaison and Rudolph.[16] Fit results that correspond to tabulated values in the manuscript, Table 4, cols. 1–6, are marked with comments "Tabulated value". Other values in Table 4 (cols. 7–11) were obtained using the graphical user interface as described in section 3.2.

The fit of r(C) ($\equiv r(^{13}\mathrm{C})$, r(CH) ($\equiv r$(CD)) parameters gave bond lengths in agreement with values in section (A3). The fit of distinct r(CH) and r(CD) bond lengths gave excessive parameter uncertainties if only data for deuterated benzene was fitted. We could therefore reproduce the analysis by Kunishige et al.[14] but not confirm that the results are meaningful. When data for $r(^{13}\mathrm{C})$ isotopologues was included, the fit gave a significantly reduced bond length r(C) = 1.3937(3)[11] Å and elongated bond lengths r(CH) = 1.1066(20)[24] Å; r(CD) = 1.0952(11)[18] Å. The fit of distinct r(C), r(CH), r(CD), and $r(^{13}\mathrm{C})$ parameters always resulted in large parameter uncertainties, especially for small values of f_{HC}. Reasonable agreement with literature values was only obtained for values $f_{HC} \geq 0.9$.

3.1.6 (CODE SECTION (A6)) Monte-Carlo analysis (error propagation)

A Monte Carlo analysis was used to determine how measurement uncertainties affect the fitted geometry parameters and to explore the correlation between fitted parameters. This analysis corresponds to a robust error propagation of experimental uncertainties. The implementation of the Monte Carlo analysis followed an approach outlined by Will Clarkson[17]. Propagated uncertainties should be similar to the fit uncertainties if the experimental uncertainties represent the dominant source of error. The fit uncertainties may be significantly larger that the propagated errors if there are significant model errors, originating either from the fit assumptions (i.e., the approximate physical model implemented in the fit) or if experimental values contain systematic errors that are larger than the stated experimental uncertainties. We found that fit uncertainties were significantly higher than the propagated 1-sigma experimental uncertainties. This indicates that model errors or systematic errors dominate the fit uncertainties. The result is not surprising, considering the high resolution of the experimental data. We also observed a strong linear correlation between fitted bond lengths in most fits and this correlation offers an obvious explanation for the sometimes large fit uncertainties.

3.1.7 (CODE SECTION (A7)) Fitting and Monte Carlo simulations for synthetic data

To illustrate the limitation for retrieving a number of structural parameters exceeding the number of 'unique' isotopologues, we fitted synthetic data. As expected (and in line with our results for experimental data), data for C,H,D isotopologues allowed to fit two geometry parameters with high fidelity but gave excessive uncertainties when three geometry parameters were fitted. This is easily rationalized: within C_6 symmetry, any deuterated benzene isotopologue contributes the same 'type' of information. Symmetric isotopologues only contribute to linearly-dependent MOI equations, that do not allow to fit an additional parameter. Asymmetric isotopologues only

weakly break this linear dependence. Adding data for many deuterated isotopologues therefore does not allow to fit the third structural parameter with any reasonable confidence. We observed the same issue in 4-parameter fits, where $f_{HC} > 0$ is required to break the linear dependence of fit parameters.

3.1.8 (CODE SECTION (A8)) Fitting with rovibrational correction terms

Isotope-specific bond lengths arise due to rovibrational coupling. The r_0 parameters fitted in section (A5), however, correspond to rigid rotor bond lengths and do not account for our physical understanding of rovibrational coupling. Watson derived rovibrational correction terms[18] that approximate the expected mass-weighted rovibrational coupling effects in isotopologues. This section illustrates how to implement Watson's second order $r_\mathrm{m}^{(2)}$ mass-weighted rovibrational corrections to give an example for the corresponding fit algorithms. Note that the $r_\mathrm{m}^{(2)}$ model represents the most complex case and other models are readily obtained by removing parameters and code. A general (molecule-independent) implementation of all relevant fit types with a simple graphical user interface is provided in a separate file and is described in section 3.2, below.

3.2 Rotational Structure Analysis: Fitting of r_0, r_s, r_m Parameters

The Python code presented in File (B) implements streamlined code and a simple graphical user interface for fitting molecular structures based on measured rotational constants. On a functional level, the code is similar to that described in section 3.1, but differs in the handling of fit data and fit parameters. The code can be executed from the command line ('python FitMOI.py') or within an interactive command shell, such as iPython. Refer to the code file for a detailed documentation. The code file includes a data-set for benzene rotational constants, as well as data for H_2O, HCN, O_3 and HNCO. Fit results given in our manuscript or by Watson[18] can be reproduced by selecting the corresponding data-set and fit methods.

Fit methods for fitting r_0, r_s, and r_m geometry parameters were implemented, axis rotation between isotopologues is accounted for, and a Laurie-type correction can be used to describe large H,D,T isotope effects. The code was tested against reference values for H_2O, HCN, O_3, OCS, and HNCO given by Watson[18] and on the website for the STRFIT program[19,20]. We obtained numerically identical results whenever we could identify the precise fitted data sets, except for STRFIT examples where Laurie correction and axis rotation coincided. In the latter case, we reproduced numerically exact values from Watson[18], but found small differences to STRFIT results. This seems to be due to an approximate mapping of Laurie corrections onto the principle moment axes in the STRFIT code.

As opposed to the STRFIT program, our code requires an explicit function to convert internal to Cartesian coordinates. This allows facile and transparent handling of symmetry cases, i.e., planar oblate top or planar symmetry for benzene isotopologues, but requires some coding knowledge to create a custom conversion function for each molecule. Fit residuals can be plotted to allow the easy identification of outliers in the fitted data. A Monte-Carlo simulation was implemented to propagate experimental uncertainties onto parameter uncertainties and to test for artifacts from coordinate system rotation when rovibrational correction terms are applied. Such artifacts occur when the principal rotation axes in different isotopologues are significantly tilted and, as a result, rovibrational corrections terms $r_\mathrm{m}^{(1)}$ and $r_\mathrm{m}^{(2)}$ are not applied along identical axes within the molecular frame.

All structure fits minimize the residuals between measured and calculated MOI ($I_{\mathrm{exp,g}} - I_{\mathrm{calc,g}}$, for axes $\mathrm{g} = \mathrm{a,b,c}$). Different rovibrationally corrected fits[18] differ in the definition of the molecular inertial moment I_calc:

- Effective bond lengths r_0 (rigid-rotor inertial moment): $I_{\mathrm{r_0,g}} = \sum (m \cdot r_{0,\mathrm{g}}^2)$ (1)
- Substitution bond lengths r_s (constant correction factors c_g): $I_{\mathrm{s,g}} = I_{\mathrm{r_0,g}} + c_\mathrm{g}$ (2)
- 1st order mass-corrected bond lengths $r_\mathrm{m}^{(1)}$: $I_{\mathrm{m^{(1)},g}} = I_{\mathrm{r,g}} + c_\mathrm{g} \cdot \sqrt{I_{\mathrm{m^{(1)},g}}}$ (3)
- 2nd order mass-corrected bond lengths $r_\mathrm{m}^{(2)}$: $I_{\mathrm{m^{(2)},g}} = I_{\mathrm{m^{(1)},g}} + d_\mathrm{g} \cdot (\prod m / \sum m)^{1/(2N-2)}$ (4)

Sums and products are calculated over atomic masses m_i and distances from the molecular center-of-mass r_i. N represents the number of atoms in the molecule.

Fitting of r_0 parameters (eq. 1) was described in section (A). The r_s parameters obtained though eq. 2 correspond to the substitution bond lengths obtained from a Kraitchman analysis. The latter is based on solving equations $I_{\mathrm{exp,g}} - I_{\mathrm{exp,g}}^{\mathrm{reference}} = I_{\mathrm{r_s,g}} - I_{\mathrm{r_s,g}}^{\mathrm{reference}}$ for isotopologue pairs. This approach inherently removes removes rovibrational correction terms on both sides of the equation under the assumption that they can be described by isotope-independent constants c_g. The Kraitchman analysis requires the choice of a 'reference'

isotopologue against which the inertial moment differences are calculated and this choice affects the fit results. The dependence on a reference isotopologue can be removed by fitting substitution bond lengths r_s together with explicit correction constants c_g (eq. 2) and gives balanced results with equal weight for all isotopologues.

The $r_m^{(1)}$ and $r_m^{(2)}$ parameters (eqs. 3, 4) represent an approximation to equilibrium bond lengths. The first-order rovibrational correction terms $c_g \cdot \sqrt{I_{m^{(1)},g}}$ describe, approximately, the expected mass-dependence for harmonic vibration. The amplitude of harmonic vibrational motion is proportional to $1/\sqrt{m}$. Because the motion is symmetric around the equilibrium atom position r_e and the inertial moment is proportional to r^2, this leads to an apparent atomic displacement $\Delta r \propto r_e/\sqrt{m}$. We can therefore describe $I_0 = \sum(m \cdot r_0^2) = \sum(m \cdot (r_e + \Delta r)^2) = \sum(m \cdot r_e^2) + \sum(m \cdot 2 \cdot r_e \cdot \Delta r) + \sum(m \cdot \Delta r^2)$. For small values for Δr, we ignore the last term. By substituting $2 \cdot \Delta r = c \cdot r_e/\sqrt{m}$, with parameter c to be determined by fitting experimental data, we find: $I_0 = I_e + c \cdot \sqrt{I_e}$, i.e., Watson's first-order rovibrational correction term. The mass-dependence of second-order correction terms were derived by Watson based on a consideration of Wilson's G-Matrix.[18]

3.2.1 (CODE SECTION (B1)) Imports, natural constants and conversion functions

To keep the code compact, I defined natural constants manually and minimized the number of dependencies. Numerical values for atomic masses were taken from NIST[21] and natural constants were taken from scipy.constants (CODATA2018 values).

3.2.2 (CODE SECTION (B2)) Functions for geometry fitting

Fitting is based on the Levenberg-Marquardt nonlinear fit method as implemented in the library scipy.leastsq. Fits minimize residuals $(I_{exp} - I_{calc}) \cdot weight$ for a set of rotational inertial moments I_{exp}. Three steps are required to calculate I_{calc} from a set of internal coordinates r: (1) A molecule-specific function *int2cart* is required to map a minimal set of internal coordinates to Cartesian atomic coordinates, accounting for molecular symmetry. Mapping functions for benzene, H_2O, HCN, O_3, OCS, and HNCO are given in the code. (2) The rigid-rotor principal moment of inertia I_0 are calculated based on Cartesian coordinates and masses for all atoms. The principal moments are eigenvalues of the inertial moment tensor. (3) The desired rovibrational correction terms are added to I_0 to obtain I_{calc}, depending on the desired rovibrational correction model. Step (3) is performed in the functions that calculate fit residuals.

Residual functions ending with 'r' implement an additional step to ensure that first-order correction terms are applied along invariant intramolecular axes. This can be relevant when the orientation of principal axes is significantly different between isotopologues. Instead of adding correction terms within the principal axis system, corrections are applied to the inertial moment tensor in the reference coordinate system before principal moments are calculated. Depending on molecular symmetry, this may require additional correction parameters for off-diagonal elements of the inertial moments tensor. We implemented additional options to control the orientation of the reference coordinate system to test for rotation artifacts. A discussion of this issue is given below in section **??**. Note that only z-axis rotations of the reference coordinate system were tested, because we considered planar molecules with a reduced set of off-diagonal parameters.

3.2.3 (CODE SECTION (B3)) Graphical User Interface for fitting

The graphical user interface, as depicted in Fig. S2, contains a text field for entering rotational data and multiple options to control the fit type and fit parameters. The data format for rotational data must follow the template examples with [a,b,c]-axis rotational constants listed in MHz, cm^{-1}, or as inertial moments in amu·Å^2 units and can be saved to, or loaded from a file. Isotopologue composition must be specified with a string, using single-letter codes for each atom, with atoms ordered as required by the Internal→Cartesian coordinate transformation function. Corresponding isotope masses should be specified at the bottom of the list. Experimental uncertainties can be specified, if available, to adjust the weight of corresponding data points in the fit procedure. A selection listbox allows to choose a weight function for the fitted data; If experimental uncertainties are available, the weight function suggested by Eijck[22] offers a sensible compromise, avoiding excessive weights for high-resolution data. An integer list specifies whether data for a particular rotational axis should be fitted and setting corresponding values to zero allows to mask out questionable experimental values without removing the data from the list.

Available functions for internal to Cartesian (*int2cart*) coordinate transformation are collected in a selection listbox. New functions can be defined in the code file and added to the list. The correct number of internal parameters, with a reasonable set of start values for the fit, must then be specified in the *Internal Coordinates* field. Additional selections area available to specify the molecular symmetry and control the number of rovibrational fit parameters.

Beyond a simple fit of data with the chosen model, a Monte-Carlo analysis of the data can be performed to propagate experimental

uncertainties. The latter performs a specified number of fits while varying the rotational constants within the 1-sigma experimental uncertainties. The Monte-Carlo analysis can also be used to check for artifacts arising from reference frame rotation in $r_s^{(r)}$, $r_m^{(1r)}$, and $r_m^{(2r)}$ fits (currently only implemented for the z-axis), by entering a range of coordinate-system rotation angles, e.g., "z:1..90". Alternatively, a discrete (constant) coordinate-system rotation angle can be entered (implemented for all three axes, x,y,z).

3.2.4 (CODE SECTION (4)) Isotopologue data for benzene and reference molecules

This section lists rotational data for the molecules C_6H_6, H_2O, HCN, O_3, OCS, and HNCO. These data-sets allow to reproduce our own fit results, as well as literature results from Watson[18] and Kisiel[19]. Follow the instructions in the code file to load the data-sets into the user-interface. Remember to choose the appropriate internal-to-Cartesian conversion function and geometry parameter set for your molecule.

3.2.5 Special Issues Encountered in Geometry Fitting

Here I want to comment on selected fit results and show relevant plots to illustrate issues encountered in the structure fitting described in sections 3.1 and 3.2. As mentioned in section 3.2.2, a major issue encountered in $r_m^{(1r)}$, and $r_m^{(2r)}$ fits was that the fit results depended on the mapping of rovibrational corrections onto the molecular axis. The corrections describe the sum of all rovibrational effects and there is no inherently 'correct' axis system for these corrections. In the literature, the reference coordinate system was typically chosen to coincide with the principal axes of the main isotopologue. We found this to be a problematic choice if many isotopologues share the same principal axes: in this case, corrections associated with off-diagonal elements of the inertial moment tensor are undetermined for the reference species and all other isotopologues that share the same principal axes. The off-diagonal elements are then purely determined by a smaller sub-set of isotopologues with rotated principal axes, distorting the fit.

In the case of $r_m^{(2r)}$ fits, second-order corrections are only applied along reference principal axes, whereas first-order corrections are also applied to off-diagonal elements of the inertial moment tensor, leading to further complications. An illustrative example of this problem is found in the analysis of the H_2O structure, where $r_m^{(2rL)}$ fits gave unexpected negative values of δ_H = -0.0111(53) amu$^{1/2}$Å for the Laurie correction[18,19]. After collecting relevant rotational constants from the literature[23–28], we reproduced the $r_m^{(2rL)}$ fit results given by Watson[18†]. Results are summarized in list 3.2.5.

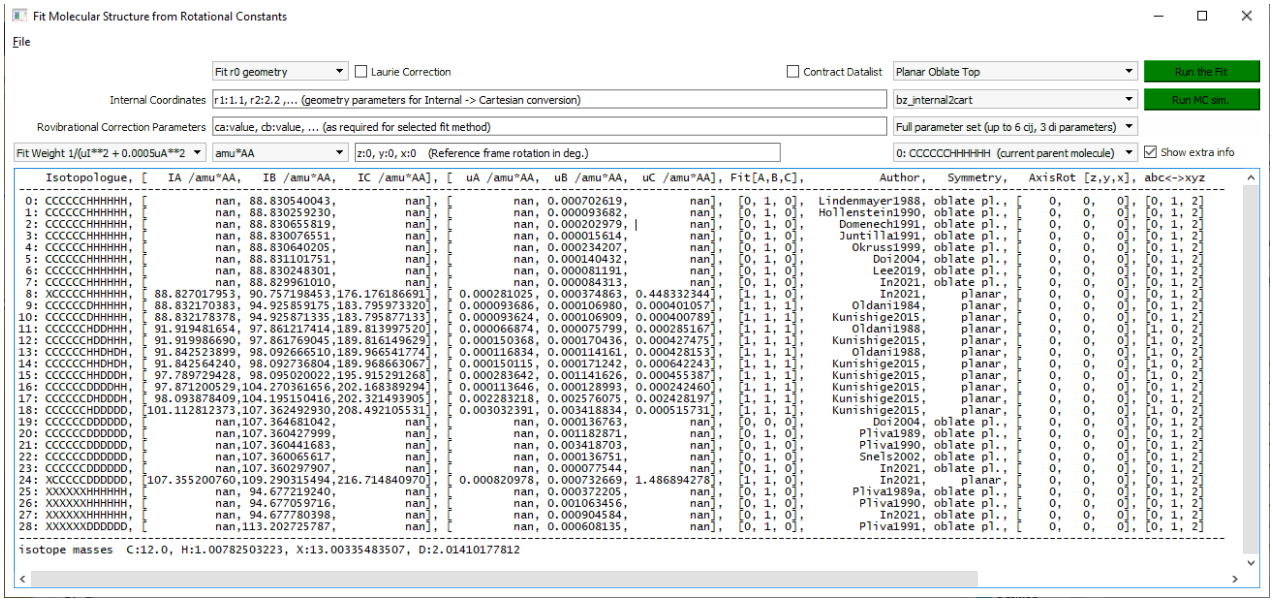

Fig. S2 Graphical user interface for Rotational Structure Analysis.

† We had to omit the duplicate value for D^{18}OD from Bellet from our fit data to obtain a numerical agrement with Watson's values. Very small deviations between our values and those of Watson are due to our use of updated values for natural constants and isotope masses, as specified in section (B1).

List S1 Fitted $r_m^{(2rL)}$ geometry parameters for water. For details, see text.

```
Fit Function: Residuals_rmIIrL, h2o_internal2cart_sym
Fitted parameters (1-sigma uncertainties) [Costain uncertainties]:
-------------------------
  rOH =    0.95821(9.1e-05)
 aHOH =  104.34227(4.7e-02)
   ca =    0.02167(1.4e-02)
   cb =    0.08639(1.0e-02)
   cc =    0.04431(7.8e-03)
  cab =    0.01510(1.1e-02)
   da =   -0.01613(4.9e-03)
   db =   -0.05955(4.4e-03)
   dc =    0.02848(1.1e-02)
   dH =   -0.01114(5.3e-03)
-------------------------------------------------------------------------------
      Chi-squared =  0.000001        [Sum(Iobs-Icalc)**2]
 Deviation of fit =  0.000996 uA^2   [Sqrt(scaledChiSqr/Ndegf),  Ndegf= 26]
-------------------------------------------------------------------------------
```

When we choose HOD as reference molecule for $r_m^{(2r)}$ rovibrational corrections, with a 12.4° rotated principal axes system as compared to H_2O, the Laurie correction became $\delta_H = 0.0477(48)$ amu$^{1/2}$Å. This value is significantly larger than the generally expected value of 0.010 amu$^{1/2}$Å. We found that negative Laurie corrections only occur for near-zero angles between the reference and the main isotopologue principal axis system. Fig. S3 shows the correlation of fit parameters, obtained from a $r_m^{(1rL)}$ and a $r_m^{(2rL)}$ Monte-Carlo analysis, with the reference coordinate system rotated within a 90° angle, within the molecular plane. We should not be surprised that Laurie-corrections are badly determined for this small molecule: the fit model uses 8 parameters to correct rovibrational effects that arise from only 3 vibrational degrees-of-freedom‡. The $r_m^{(1r)}$ fit has fewer parameters and gave a more stable result with an angle-averaged Laurie correction of $\delta_H = 0.013(4)$ amu$^{1/2}$Å.

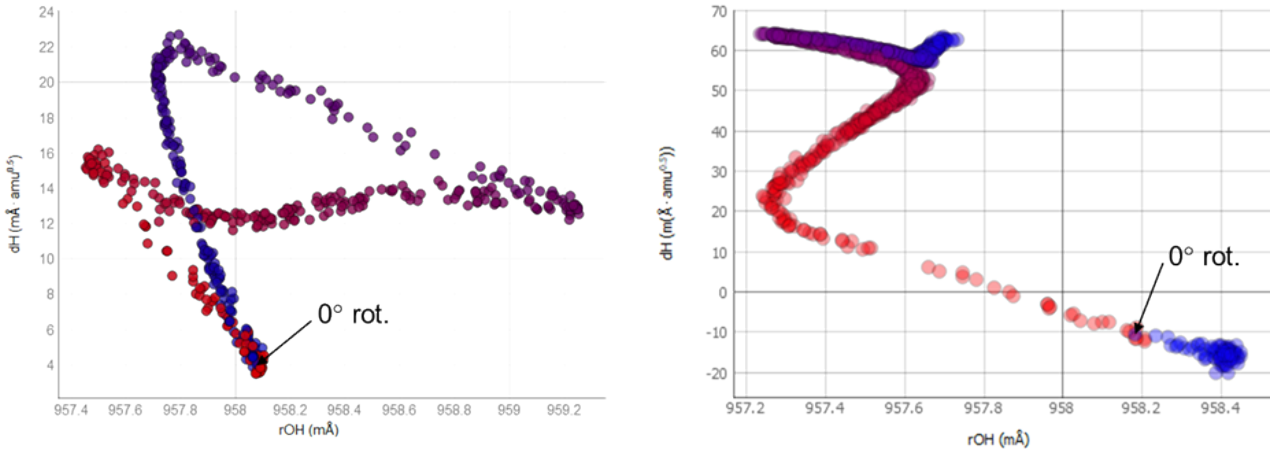

Fig. S3 Correlations between r(OH) bond length, Laurie correction δ_H, and reference coordinate system rotation in the H_2O molecular plane between 0° (blue) and 90° (red). (Left) Correlation for $r_m^{(1rL)}$ analysis. (Right) Correlation for $r_m^{(2rL)}$ analysis.

Benzene is a planar oblate top and, to first order, rovibrational corrections should be identical along the a and b axis. Accordingly, we found a very high linear correlation between rovibrational correction parameters in $r_m^{(2rL)}$ fits. Accounting for symmetry, we can equate the correction parameters for a- and b-axis to reduce parameter correlation, obtain a more robust fit, and to remove artifacts from the reference coordinate system orientation. Resulting 1st-order (c-terms) and 2nd-order (d-terms) rovibrational parameters are uncorrelated (Fig. S4, left), but the Laurie correction parameter and C−C, C−H bond lengths are still strongly correlated (Fig. S4, right). This correlation is reflected in the large parameter uncertainties for the Laurie parameter and C−C, C−H bond lengths in the $r_m^{(2rL)}$ analysis.

‡ Because the molecule is planar, we use 4 parameters to describe c_{aa}, c_{bb}, c_{cc}, and c_{ab} first-order and three parameters d_a, d_b, d_c to describe second-order corrections.

3.2.6 Results for Benzene Geometry Analysis

Results for r_0 structure analyses are fully characterized by the effective r_0 bond lengths as tabulated in the manuscript, Table 4, Cols. 1-6. The calculation of these values is fully documented in the Python code described in section 3.1. These values can also be reproduced to full accuracy using the graphical user interface (GUI, section 3.2). Results presented in manuscript Table 4, Cols. 7-11 require the fitting of additional rovibrational correction factors. Below, we list all fitted parameter values for the latter structure analyses.

List S2 Fitted $r_m^{(1)}$ geometry parameters for benzene (manuscript Table 4, Cols. 7,7').

```
Fit Function: Residuals_r0L, bz_internal2cart
Fitted parameters (1-sigma uncertainties) [Costain uncertainties]:
 ------------------------------------
   rC =   1.39294(9.70e-04) [0.00145]
   rH =   2.45723(4.70e-03) [0.00474]
   dH =   0.04847(1.11e-02) [nan]
 ------------------------------------
  r12 =   1.06429(0.00480) [0.00495]
 r0(H) =  1.11307(0.01215)
 r0(D) =  1.09901(0.00928)

-------------------------------------------------------------------------------
     Chi-squared =  0.005501       [Sum(Iobs-Icalc)**2]
 Deviation of fit =  0.074170 uA^2 [Sqrt(scaledChiSqr/Ndegf),  Ndegf= 47]
-------------------------------------------------------------------------------

Parameter Correlation Coefficients
          rC      rH      dH
 rC    1.000
 rH    0.994   1.000
 dH   -0.998  -0.998   1.000
```

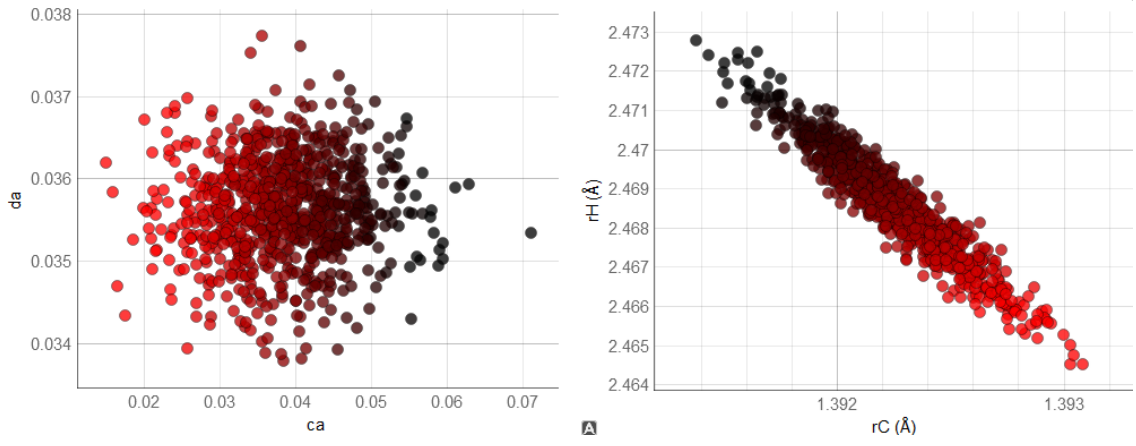

Fig. S4 Parameter correlation in a $r_m^{(2rL)}$ obtained from a Monte-Carlo analysis for benzene. Data points are color coded according to the Laurie parameter value in the range from 0.004 amu$^{1/2}$Å (red) to 22 amu$^{1/2}$Å (black). (Left) Correlation between c_a (abscissa), d_a (ordinate). The plot reveals a strong linear correlation between δ_H and c_a, but not between c_a and d_a. (Right) Correlation between r(C) ($\equiv r$(CC)) and r(H) ($\equiv r$(C) + r(CH)).

List S3 Fitted $r_m^{(1)}$ geometry parameters for benzene (manuscript Table 4, Col. 8).

```
Fit Function: Residuals_rmI, bz_internal2cart
Fitted parameters (1-sigma uncertainties) [Costain uncertainties]:
      ---------------------------------
        rC =   1.39120(3.81e-04) [0.00114]
        rH =   2.47285(2.97e-04) [0.00068]
        ca =   0.07095(4.55e-03) [nan]
        cc =   0.10268(6.42e-03) [nan]
       ----------------------------------
       r12 =   1.08165(0.00048) [0.00133]

-------------------------------------------------------------------------------
      Chi-squared =  0.000328       [Sum(Iobs-Icalc)**2]
  Deviation of fit =  0.018101 uA^2 [Sqrt(scaledChiSqr/Ndegf),  Ndegf= 46]
-------------------------------------------------------------------------------

Parameter Correlation Coefficients
           rC      rH      ca      cc
      rC   1.000
      rH   0.973   1.000
      ca  -1.000  -0.979   1.000
      cc  -0.999  -0.980   1.000   1.000
```

List S1 Fitted $r_m^{(1L)}$ geometry parameters for benzene (manuscript Table 4, Col. 9).

```
Fit Function: Residuals_rmIL, bz_internal2cart
Fitted parameters (1-sigma uncertainties) [Costain uncertainties]:
      ---------------------------------
        rC =   1.39388(2.77e-03) [0.00297]
        rH =   2.45983(1.33e-02) [0.01333]
        ca =  -0.00421(7.74e-02) [nan]
        cc =  -0.00358(1.09e-01) [nan]
        dH =   0.04205(4.32e-02) [nan]
       ----------------------------------
       r12 =   1.06595(0.01360) [0.01366]
    r0(H) =   1.10826(0.04554)
    r0(D) =   1.09606(0.03379)

-------------------------------------------------------------------------------
      Chi-squared =  0.000315       [Sum(Iobs-Icalc)**2]
  Deviation of fit =  0.017749 uA^2 [Sqrt(scaledChiSqr/Ndegf),  Ndegf= 45]
-------------------------------------------------------------------------------

Parameter Correlation Coefficients
           rC      rH      ca      cc      dH
      rC   1.000
      rH  -0.987   1.000
      ca  -0.997   0.997   1.000
      cc  -0.997   0.997   1.000   1.000
      dH   0.991  -1.000  -0.998  -0.998   1.000
```

List S1 Fitted $r_m^{(2)}$ geometry parameters for benzene (manuscript Table 4, Col. 10).

```
Fit Function: Residuals_rmII, bz_internal2cart
Fitted parameters (1-sigma uncertainties) [Costain uncertainties]:
      ---------------------------------
        rC =   1.39133(2.03e-04) [0.00110]
        rH =   2.47275(1.63e-04) [0.00063]
        ca =   0.06342(2.57e-03) [nan]
        cc =   0.10887(3.95e-03) [nan]
        da =   0.03631(4.57e-03) [nan]
        dc =  -0.06085(1.65e-02) [nan]
       ---------------------------------
       r12 =   1.08142(0.00026) [0.00126]

-------------------------------------------------------------------------------
      Chi-squared =  0.000153       [Sum(Iobs-Icalc)**2]
  Deviation of fit =  0.012357 uA^2 [Sqrt(scaledChiSqr/Ndegf),  Ndegf= 44]
-------------------------------------------------------------------------------

Parameter Correlation Coefficients
           rC      rH      ca      cc      da      dc
      rC  1.000
      rH  0.936   1.000
      ca -0.959  -0.835   1.000
      cc -0.863  -0.720   0.871   1.000
      da  0.049  -0.203  -0.330  -0.219   1.000
      dc -0.008  -0.203  -0.092  -0.498   0.393   1.000
```

List S1 Fitted $r_m^{(2L)}$ geometry parameters for benzene (manuscript Table 4, Col. 11).

```
Fit Function: Residuals_rmIIL, bz_internal2cart
Fitted parameters (1-sigma uncertainties) [Costain uncertainties]:
      ---------------------------------
        rC =   1.39209(1.53e-03) [0.00187]
        rH =   2.46902(7.41e-03) [0.00743]
        ca =   0.04210(4.25e-02) [nan]
        cc =   0.07868(6.02e-02) [nan]
        da =   0.03585(4.70e-03) [nan]
        dc =  -0.06154(1.67e-02) [nan]
        dH =   0.01200(2.39e-02) [nan]
       ---------------------------------
       r12 =   1.07693(0.00756) [0.00766]
     r0(H) =   1.08901(0.02518)
     r0(D) =   1.08553(0.01869)

-------------------------------------------------------------------------------
      Chi-squared =  0.000151       [Sum(Iobs-Icalc)**2]
  Deviation of fit =  0.012278 uA^2 [Sqrt(scaledChiSqr/Ndegf),  Ndegf= 43]
-------------------------------------------------------------------------------

Parameter Correlation Coefficients
           rC      rH      ca      cc      da      dc      dH
      rC  1.000
      rH -0.988   1.000
      ca -0.997   0.997   1.000
      cc -0.996   0.997   0.999   1.000
      da -0.190   0.194   0.178   0.184   1.000
      dc -0.080   0.075   0.074   0.046   0.400   1.000
      dH  0.991  -1.000  -0.998  -0.998  -0.198  -0.079   1.000
```

4 References

1 B. Iglewicz and D. Hoaglin, in *The ASQC Basic References in Quality Control: Statistical Techniques*, ed. E. Mykytka, American Society for Quality Control, 1993, vol. 16 of The ASQC Basic References in Quality Control: Statistical Techniques.

2 C. M. Western and B. E. Billinghurst, *Phys. Chem. Chem. Phys.*, 2017, **19**, 10222–10226.

3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 Revision A.1*, Gaussian Inc. Wallingford CT 2009.

4 C. Schröter, J. C. Lee and T. Schultz, *Proceedings of the National Academy of Sciences*, 2018, **115**, 5072–5076.

5 J. C. Lee, D. E. Lee and T. Schultz, *Phys. Chem. Chem. Phys.*, 2019, **21**, 2857–2860.

6 M. Junttila, J. Domenech, G. T. Fraser and A. Pine, *Journal of Molecular Spectroscopy*, 1991, **147**, 513–520.

7 M. Okruss, R. Müller and A. Hese, *Journal of Molecular Spectroscopy*, 1999, **193**, 293–305.

8 V. Matylitsky, W. Jarzeba, C. Riehn and B. Brutschy, *Journal of Raman Spectroscopy*, 2002, **33**, 877–883.

9 J. Pliva, J. Johns and L. Goodman, *Journal of Molecular Spectroscopy*, 1990, **140**, 214–225.

10 A. Doi, S. Kasahara, H. Katô and M. Baba, *The Journal of Chemical Physics*, 2004, **120**, 6439–6448.

11 W. Jarzęba, V. Matylitsky, C. Riehn and B. Brutschy, *Chemical physics letters*, 2003, **368**, 680–689.

12 J. Pliva, J. Johns and L. Goodman, *Journal of Molecular Spectroscopy*, 1989, **134**, 227–233.

13 W. Gordy and R. Cook, in *Microwave Molecular Spectra*, John Wiley & Sons, New York, 1984, ch. XIII.

14 S. Kunishige, T. Katori, M. Baba, M. Nakajima and Y. Endo, *The Journal of Chemical Physics*, 2015, **143**, 244302.

15 C. C. Costain, *The Journal of Chemical Physics*, 1958, **29**, 864–874.

16 J. Demaison and H. Rudolph, *Journal of Molecular Spectroscopy*, 2002, **215**, 78–84.

17 W. Clarkson, *HOWTO estimate parameter-errors using Monte Carlo - an example with python*, `http://www-personal.umd.umich.edu/~wiclarks/AstroLab/HOWTOs/NotebookStuff/MonteCarloHOWTO.html`, Accessed: 2021-10-30.

18 J. K. Watson, A. Roytburg and W. Ulrich, *Journal of Molecular Spectroscopy*, 1999, **196**, 102–119.

19 Z. Kisiel, *STRFIT - GENERAL STRUCTURE FITTING PROGRAM*, `http://www.ifpan.edu.pl/~kisiel/struct/struct.htm`, Accessed: 2021-10-30.

20 Z. Kisiel, *Journal of Molecular Spectroscopy*, 2003, **218**, 58–67.

21 J. Coursey, D. Schwab, J. Tsai and R. Dragoset, in *NIST Physical Measurement Laboratory*, National Institute of Science and Technology [Online] February 16, 2001. https://www.nist.gov/pml/atomic-weights-and-isotopic-compositions-relative-atomic-masses (accessed July 20, 2021), 2021.

22 B. van Eijck, *Journal of Molecular Spectroscopy*, 1982, **91**, 348–362.

23 J. Bellet, W. J. Lafferty and G. Steenbeckeliers, *Journal of Molecular Spectroscopy*, 1973, **47**, 388–402.

24 F. C. De Lucia, P. Helminger, W. Gordy, H. W. Morgan and P. A. Staats, *Physical Review A*, 1973, **8**, 2785–2791.

25 P. Helminger, F. C. De Lucia, W. Gordy, P. A. Staats and H. W. Morgan, *Physical Review A*, 1974, **10**, 1072–1081.

26 E. Kyrö, *Journal of Molecular Spectroscopy*, 1981, **88**, 167–174.

27 R. Toth, *Journal of Molecular Spectroscopy*, 1993, **162**, 41–54.

28 R. Toth, *Journal of Molecular Spectroscopy*, 1993, **162**, 20–40.