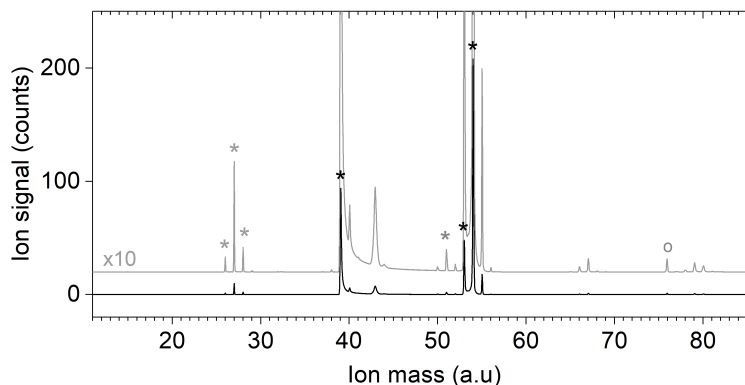


## Supplementary Information

### 1 Averaged Mass Spectrum of Butadiene

Fig. S1 shows the mass spectrum corresponding to the data shown in Fig. 3A of the manuscript, but averaged over all pump-probe delays (average of 28086 mass spectra). Small signals for rare isotopologues and molecular impurities are better visible in the 10-fold enlarged inset, as is the pronounced shoulder of the mass 39 u signal to higher masses.



**Fig. S1** Mass spectrum of butadiene. The grey trace shows the spectrum with 10-fold enlarged ordinate and a vertical offset. Signals marked with (\*) were assigned to butadiene (54 u) and its cationic fragments  $C_4H_5^+$  (53 u),  $C_4H_3^+$  (51 u),  $C_3H_3^+$  (39 u),  $C_2H_4^+$  (28 u),  $C_2H_3^+$  (27 u), and  $C_2H_2^+$  (26 u). Signals at mass 55 u and 40 u originated from corresponding  $^{13}C$  isotopologues. A signal at mass 76 u, marked with (o), stemmed from carbon disulfide. Other signals were due to hydrocarbon impurities in the butadiene sample.

The signal at mass 43 u was due to a spectrometer artifact, probably due to a malfunction of the pulsed ion acceleration in the mass spectrometer, caused by electrical discharging. We since changed electronic elements in the ion acceleration set-up and lowered the chamber pressure, which removed the artifact but did not otherwise affect the measurements. The rotational spectrum correlated with the artifact signal was identical to the dominant butadiene signal, consistent with the malfunction described above.

### 2 Comparison of Randomly Sampled and Continuously Sampled Pump-Probe Traces

Fig. S2 compares the randomly sampled butadiene ion signal as shown in Fig. 3B of the manuscript to a continuously sampled signal based on the measurement of 15'301 delay-dependent mass spectra (4000 laser shots per spectrum) with constant 1 ps delay step-size. In the continuously sampled data, periodic signal modulations due to the interference between coherently excited rotational states are readily apparent. In the randomly sampled data, the same signal oscillations are present but are obscured because unsampled data-points appear as zero signal. Upon Fourier transformation, both traces reveal the rotational Raman spectrum of the probed butadiene species, but the randomly sampled data shows additional random noise and, due to the longer sampled delay range, a much higher resolution. A more detailed discussion about random sampling in CRASY measurements can be found in Ref. 1. Further discussions of sampling strategies can be found in the NMR literature<sup>2,3</sup>.

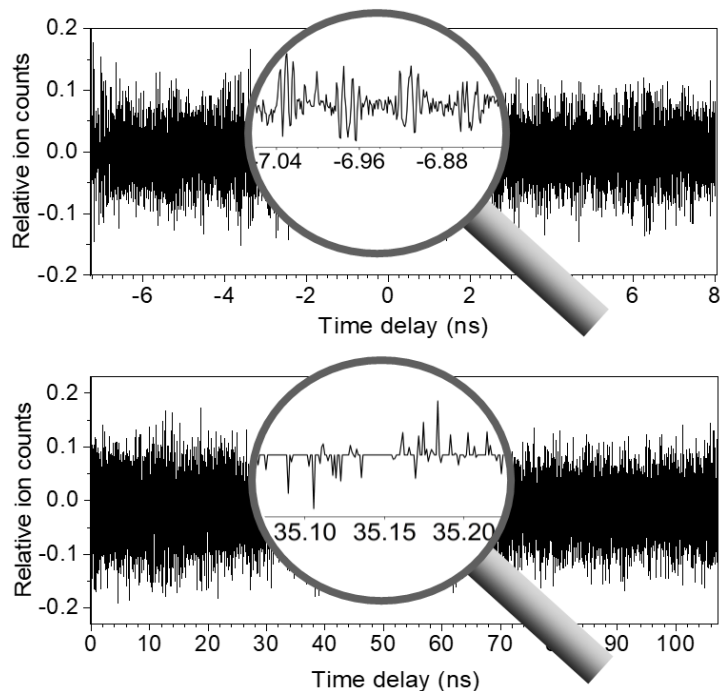
### 3 Line List for Main Butadiene Isotopologue and Fitting of Rotational Constants

Butadiene rotational constants were determined through a fit of measured line positions in the butadiene spectrum, using the PGOPHER program<sup>4</sup>. The trans-butadiene molecule is an asymmetric top rotor and belongs to the  $C_{2h}$  point group. The fit required a choice of how to map the molecular axes on the x,y,z coordinates of the symmetric top wave functions. This choice must be specified in the *Asymmetric Molecule* section of the PGOPHER fit constants. We chose the *I'* representation, mapping  $z \leftrightarrow a$ ,  $x \leftrightarrow b$ , and  $y \leftrightarrow c$  (see Fig. 1) and specified that the  $C_{2z}$  axis corresponds to the c principal rotational axis (mapped onto the y axis in the *I* representation).

Signal amplitudes are governed by the Boltzmann distribution for the molecular beam temperature and the Fermi spin statistics for the 6 spin-1/2 hydrogen atoms. The fit temperature was adjusted for the best match between fitted and measured spectral envelope ( $\approx 8$  K) and the spin statistics are 28 to 36 for even (labeled ee, oe) to odd (labeled eo, oo) states. Because we model a Raman spectrum, the rank of the *Spherical Transition Moment* was set to two.

Rotational lines were readily assigned based on a spectrum simulation using a set of literature constants. Table S1 lists the observed and fitted transition frequencies with the respective line amplitudes. To avoid spurious assignments, we only assigned lines with amplitudes near, or above  $5\sigma$ , with  $\sigma$  being the estimated noise level. To obtain a robust estimate for  $\sigma$ , we used the modified Z-score as proposed by Iglewicz and Hoaglin<sup>5</sup>. We found that the spectral noise in the power spectra was well-represented by an exponential distribution and we expect an  $e^{-n}$  probability that an observed line with  $n\cdot\sigma$  amplitude is noise ( $<1\%$  for a  $5\sigma$  line).

In the PGOPHER fit, the distortion constants  $\Delta_K$  and  $\delta_K$  did not converge towards meaningful values and had a negligible effect on the observed transition frequencies. We therefore fixed these values at the literature values given by Craig et al. (see Table 1). Our



**Fig. S2** Continuously sampled (top) versus randomly sampled (bottom) delay traces for butadiene cation (mass 54 u).

PGOPHER fit optimized 6 spectroscopic constants, namely  $A$ ,  $B$ ,  $C$ ,  $\Delta_J$ ,  $\Delta_{JK}$ ,  $\delta_J$ . Fitted frequencies and fit errors (observed - calculated line frequencies) for all assigned transitions are listed in Table S1.

To verify the robustness of the fitted rotational constants, we performed an extensive number of fits, holding different sets of distortion constants to a variety of literature values. Table ?? shows results for fitting the main isotopologue lines, using the distortion constants  $\Delta_K$  and  $\delta_K$  and  $\Delta_{JK}$  reported by Craig based on the analysis of the  $\nu_{11}$ ,  $\nu_{12}$ , and  $\nu_{13}$  bands<sup>6,7</sup>. We found the fit results to be fairly robust.

**Table S1** Assigned lines for the main butadiene isotopologue and PGOPHER fit results. The root-mean-square error of observed-calculated line positions is 1.01 MHz.

Observed (MHz)	Amplitude ( $\sigma$ )	Calculated (MHz)	Lower			Upper			Obs.-Calc. (MHz)
			J	$K_a$	$K_c$	J	$K_a$	$K_c$	
17731.95	5.2	17733.98	1	1	1	2	1	1	-2.03
25320.66	12.0	25320.97	0	0	0	2	0	2	-0.31
	12.0	25321.02	2	2	0	3	2	2	-0.36
33746.81	7.9	33745.16	3	2	1	4	2	3	1.65
41142.29	10.3	41141.76	1	1	1	3	1	3	0.53
42189.24	37.4	42189.47	1	0	1	3	0	3	-0.23
42329.82	8.8	42326.12	4	2	3	5	2	3	3.70
43270.28	4.7	43268.98	1	1	0	3	1	2	1.30
57592.63	12.8	57592.05	2	1	2	4	1	4	0.58
59039.76	50.2	59039.76	2	0	2	4	0	4	0.00
60569.69	42.3	60570.00	2	1	1	4	1	3	-0.31
74035.81	96.3	74036.01	3	1	3	5	1	5	-0.20
75864.80	183.4	75864.60	3	0	3	5	0	5	0.20
75966.13	8.9	75962.69	3	2	2	5	2	4	3.44
76071.22	5.6	76071.29	3	2	1	5	2	3	-0.07
77863.82	42.4	77864.38	3	1	2	5	1	4	-0.56
90471.89	67.4	90471.94	4	1	4	6	1	6	-0.05
92656.59	142.5	92656.85	4	0	4	6	0	6	-0.26
92832.28	12.5	92831.83	4	2	3	6	2	5	0.45
93030.53	9.3	93030.72	4	2	2	6	2	4	-0.19
95150.08	108.5	95150.10	4	1	3	6	1	5	-0.02

Table S1 (continued).

Observed (MHz)	Amplitude ( $\sigma$ )	Calculated (MHz)	Lower			Upper			Obs.-Calc. (MHz)
			J	K <sub>a</sub>	K <sub>c</sub>	J	K <sub>a</sub>	K <sub>c</sub>	
106898.27	104.7	106898.24	5	1	5	7	1	7	0.03
109409.15	226.6	109409.52	5	0	5	7	0	7	-0.37
109694.76	15.6	109694.10	5	2	4	7	2	6	0.66
109788.47	4.8	109787.51	5	3	2	7	3	4	0.96
	4.8	109791.01	5	3	3	7	3	5	-2.54
110022.73	25.0	110022.62	5	2	3	7	2	5	0.11
112424.66	85.2	112425.05	5	1	4	7	1	6	-0.39
123313.66	59.3	123313.39	6	1	6	8	1	8	0.27
126115.78	124.1	126115.96	6	0	6	8	0	8	-0.18
126547.20	25.6	126548.27	6	2	5	8	2	7	-1.07
127051.79	17.6	127052.34	6	2	4	8	2	6	-0.55
129687.10	148.6	129687.03	6	1	5	8	1	7	0.07
139715.58	87.5	139716.02	7	1	7	9	1	9	-0.44
142769.53	154.1	142769.97	7	0	7	9	0	9	-0.44
143392.98	12.1	143393.08	7	2	6	9	2	8	-0.10
144125.04	21.9	144124.79	7	2	5	9	2	7	0.25
146933.92	62.3	146933.69	7	1	6	9	1	8	0.23
156104.56	44.3	156104.87	8	1	8	10	1	10	-0.31
159365.95	57.5	159366.09	8	0	8	10	0	10	-0.14
160226.85	30.4	160227.31	8	2	7	10	2	9	-0.46
161245.9	12.6	161244.13	8	2	6	10	2	8	1.77
164162.44	79.0	164162.56	8	1	7	10	1	9	-0.12
172478.16	49.6	172478.83	9	1	9	11	1	11	-0.67
175899.39	59.1	175899.81	9	0	9	11	0	11	-0.42
177049.63	16.1	177049.75	9	2	8	11	2	10	-0.12
178413.94	9.5	178413.57	9	2	7	11	2	9	0.37
181370.68	43.7	181370.96	9	1	8	11	1	10	-0.28
188837.91	17.6	188836.95	10	1	10	12	1	12	0.97
192366.89	28.6	192367.84	10	0	10	12	0	12	-0.95
193859.72	7.1	193859.19	10	2	9	12	2	11	0.53
195633.32	9.8	195635.06	10	2	8	12	2	10	-1.74
198555.26	31.2	198556.07	10	1	9	12	1	11	-0.81
205179.24	17.3	205178.44	11	1	11	13	1	13	0.80
208767.58	35.0	208768.41	11	0	11	13	0	13	-0.83
212908.63	11.2	212909.08	11	2	9	13	2	11	-0.45
215716.85	26.0	215714.84	11	1	10	13	1	12	2.01
221502.34	9.7	221502.71	12	1	12	14	1	14	-0.37
225101.63	9.0	225101.40	12	0	12	14	0	14	0.23
232844.00	8.9	232843.99	12	1	11	14	1	13	0.01
241369.10	7.7	241368.49	13	0	13	15	0	15	0.61

**Table S2** PGOPHER fits for the main butadiene isotopologue for different fixed values of  $\Delta_K$ ,  $\delta_K$ , and  $\Delta_{JK}$ . All frequencies in MHz.

	Refs. 6, 7	Ref. 7	Fixed Parameters		
	( $\nu_{11} + \nu_{12}$ )	( $\nu_{13}$ )	$\Delta_K, \delta_K^a$	$\Delta_K, \delta_K^b$	$\Delta_K, \delta_K, \Delta_{JK}^a$
A	41682.658(21)	41682.454(30)	41685(11)	41683(10)	41689.9(91)
B	4433.5047(30)	4433.532(15)	4433.506(35)	4433.515(33)	4433.497(33)
C	4008.0423(60)	4008.0453(60)	4008.035(30)	4008.023(28)	4008.032(30)
$\Delta_K$	0.219388(90)	0.21846(12)	[0.219388]	[0.21846]	[0.219388]
$\Delta_{JK}$	-0.007324(15)	-0.007195(30)	-0.0049(30)	-0.0047(27)	[-0.007324]
$\Delta_J$	0.000876(12)	0.000872(12)	0.000891(44)	0.000880(41)	0.000889(43)
$\delta_J$	0.0001075(27)	0.0001145(36)	0.000133(57)	0.000158(51)	0.000127(57)
$\delta_K$	0.004017(60)	0.00444(96)	[0.004017]	[0.00444]	[0.004017]
$J_{\max}$	66	53	15	15	15
$K_{a,\max}$	21	17	3	3	3
Assigned lines	1571	2990	61	61	61
Fit error <sup>d</sup>	7.3	11.4	1.01	0.97	1.01

<sup>a</sup>Parameters fixed to  $\nu_{11} + \nu_{12}$  values from column 1; <sup>b</sup>Parameters fixed to  $\nu_{13}$  values from column 2; <sup>c</sup>Root-mean-square of the fit errors.

#### 4 Line List for the <sup>13</sup>C-Butadiene Isotopologues and Fitting of Rotational Constants

The symmetry of <sup>13</sup>C-butadiene is broken by the presence of a single heavy isotope and the symmetry point group is therefore reduced to  $C_1$ . We obtained a much lower signal-to-noise ratio in the heavy isotopologue mass channel, as reflected in the much lower signal amplitudes. We assigned lines by comparison of measured line positions to a simulation for the expected 1-<sup>13</sup>C and 2-<sup>13</sup>C isotopologues. We again restricted the assignment to line amplitudes near or above  $5\sigma$ . For the analysis of the 1-<sup>13</sup>C isotopologue, we held the  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_K$  distortion constants to the literature values from Craig et al. (see Table 1 in manuscript) to avoid arbitrary or non-physical results. The five rotational constants A, B, C,  $\Delta_J$ , and  $\delta_J$  were then fit with PGOPHER. In the case of the 2-<sup>13</sup>C isotopologue, no literature values for the rotational constants exist. We therefore held the distortion constants  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_K$  to rounded literature values corresponding to those in the <sup>12</sup>C and 1-<sup>13</sup>C isotopologues to avoid arbitrary or non-physical results. Again, the five rotational constants A, B, C,  $\Delta_J$ , and  $\delta_J$  were fit in PGOPHER. Table S3 lists all assigned band, band amplitudes and fit results for the <sup>13</sup>C isotopologues.

We again verified the robustness of the fitted rotational constants, by holding distortion constants to a variety of literature values. Table S4 shows results for fitting the heavy isotopologue lines, holding some or all distortion constants to values reported by Craig et al. For the 1-<sup>13</sup>C-butadiene isotopologue, we used the values reported in Ref. 8. For the 2-<sup>13</sup>C-butadiene isotopologue, literature values do not exist and we instead used rounded values from the main isotopologue. The distortion constants for the main and the 1-<sup>13</sup>C-butadiene isotopologue are very similar and we do not expect a large deviation for the 1-<sup>13</sup>C-butadiene isotopologue values.

**Table S3** Assigned lines for <sup>13</sup>C-butadiene isotopologues and PGOPHER fit results. The root-mean-square error of observed-calculated line positions is 0.59 MHz and 0.43 MHz for the 1-<sup>13</sup>C and 2-<sup>13</sup>C isotopologue, respectively.

Observed (MHz)	Amplitude ( $\sigma$ )	Calculated (MHz)	Lower			Upper			Obs.-Calc. (MHz)
			J	$K_a$	$K_c$	J	$K_a$	$K_c$	
<b>1-<sup>13</sup>C-butadiene</b>									
57431.08	8.1	57431.77	2	0	2	4	0	4	-0.69
73801.92	10.6	73801.69	3	0	3	5	0	5	0.23
75690.21	6.5	75689.68	3	1	2	5	1	4	0.53
90142.81	14.6	90142.35	4	0	4	6	0	6	0.46
104057.64	8.2	104057.00	5	1	5	7	1	7	0.64
106445.93	10.6	106447.41	5	0	5	7	0	7	-1.48
109289.44	7.1	109289.45	5	1	4	7	1	6	-0.01
120037.35	12.4	120037.13	6	1	6	8	1	8	0.22
122710.77	11.1	122710.77	6	0	6	8	0	8	0.00
136005.02	8.0	136005.49	7	1	7	9	1	9	-0.47
138927.29	13.2	138926.73	7	0	7	9	0	9	0.56
142843.51	11.0	142843.56	7	1	6	9	1	8	-0.05
<b>2-<sup>13</sup>C-butadiene</b>									
58825.66	13.1	58825.37	2	0	2	4	0	4	0.29
73748.31	4.5	73749.02	3	1	3	5	1	5	-0.71
92317.72	8.8	92316.88	4	0	4	6	0	6	0.84

Table S3 (continued)

Observed (MHz)	Amplitude ( $\sigma$ )	Calculated (MHz)	Lower			Upper			Obs.-Calc. (MHz)
			J	$K_a$	$K_c$	J	$K_a$	$K_c$	
94 830.21	12.9	94 830.31	4	1	3	6	1	5	-0.10
106 485.03	9.0	106 484.61	5	1	5	7	1	7	0.42
109 004.67	11.3	109 005.44	5	0	5	7	0	7	-0.77
112 045.90	9.3	112 046.14	5	1	4	7	1	6	-0.24
125 646.54	14.1	125 646.79	6	0	6	8	0	8	-0.25
129 248.70	6.5	129 248.50	6	1	5	8	1	7	0.20
139 176.85	5.0	139 176.99	7	1	7	9	1	9	-0.14
142 234.99	12.2	142 234.73	7	0	7	9	0	9	0.26

Table S4 PGOPHER fit of transitions for the  $^{13}\text{C}$ -butadiene isotopologues with a variety of fixed distortion constants. All frequencies in MHz.

	Ref. 8	Fixed Parameters			Fixed Parameters			
		$\Delta_K, \Delta_{JK}, \delta_J^a$	$\Delta_K, \Delta_{JK}, \delta_J, \delta_K^a$	$\Delta_K, \Delta_{JK}, \delta_J^b$	$\Delta_K, \Delta_{JK}, \delta_J, \delta_K^b$	$\Delta_K, \Delta_{JK}, \delta_J, \delta_J, \delta_K^b$		
A	41634.934(17)	41606(57)	41630(76)	41018(38)	41088(44)	41098(85)		
B	4307.0672(90)	4306.763(84)	4306.971(45)	4419.823(70)	4419.981(69)	4419.645(53)		
C	3904.0502(90)	3904.308(91)	3904.083(48)	3991.283(50)	3991.243(68)	3991.578(48)		
$\Delta_K$	0.2177(3)	[0.2177]	[0.2177]	[0.218]	[0.218]	[0.218]		
$\Delta_{JK}$	-0.006928(15)	[-0.006928]	[-0.006928]	[-0.007]	[-0.007]	[-0.007]		
$\Delta_J$	0.0008118(24)	0.00107(25)	0.00102(33)	0.00013(25)	[0.0009]	[0.0009]		
$\delta_J$	0.0000923(21)	0.00083(34)	[0.0000923]	0.00125(29)	1.80(32)e-3	[0.0001]		
$\delta_K$	0.0045(6)	[0.0045]	[0.0045]	[0.004]	[0.004]	[0.004]		
$J_{\max}$	67	9	9	9	9	9		
$K_{a,\max}$	23	1	1	1	1	1		
Assigned lines	2181	12	12	13	13	13		
Fit error <sup>c</sup>	9.6	0.59 <sup>e</sup>	0.84 <sup>e</sup>	0.43 <sup>e</sup>	0.64 <sup>e</sup>	1.23 <sup>e</sup>		

<sup>a</sup>Parameters fixed to values from column 1; <sup>b</sup>Parameters fixed to rounded main isotopologue values; see Tables 1, S2; <sup>c</sup>Root-mean-square of the fit errors.

## 5 Structural Analysis with the Kraitchman Method

Rotational parameters fit to the isotopologue lines are summarized in Table 1 of the manuscript (see also: Tables S2 and S4). We performed a structure analysis of the carbon atom positions using the Kraitchman method<sup>9</sup> and the  $B, C$  rotational constants. Calculations were performed with a Python script, implementing the planar asymmetric-top equations for singly-substituted species as given by Gordy&Cook<sup>10</sup> (equations 13.64 and 13.65). Results were identical to those obtained using the KRA program from the PROSPE program package<sup>11</sup>. Error propagation from inertial moments to principal axis parameters was directly adapted from the KRA program. Calculation results are summarized in List S1.

### List S1 Results of the Kraitchman analysis

C1 isotope displacement based on B,C (planar asymmetric top):  
a1: 1.8454 (0.0007); b1: 0.0702 (0.0299); r: 1.8468 (0.0299)  
Costain errors: (0.0011); (0.0367); (0.0368)

C2 isotope displacement based on B,C (planar asymmetric top):  
a2: 0.5980 (0.0017); b2: 0.4238 (0.0033); r: 0.7330 (0.0037)  
Costain errors: (0.0030); (0.0048); (0.0057)

Substitution bond lengths and angles were calculated with simple geometric considerations of the triangle formed by the molecular center-of-mass and the positions of carbon atoms C1 and C2:  $r_A = \sqrt{(a2)^2 + (b2)^2}$ ;  $r_B = \sqrt{(a2 - a1)^2 + (b2 - b1)^2}$ ;  $r_C = \sqrt{((a1)^2 + (b1)^2)}$ . The bond lengths are  $r_s(\text{C-C}) = 2 \cdot r_A$  and  $r_s(\text{C=C}) = r_B$ . The bond angle is  $\alpha(\text{C=C-C}) = \arccos((r_A^2 + r_B^2 - r_C^2)/(2 \cdot r_A \cdot r_B))$ . Please note that changes in the moments-of-inertia are quadratic in the atom positions and the relative sign of the C1 and C2 isotope displacements is therefore unknown. List S2 shows the results for all possible displacement signs. Our general knowledge about common bond lengths and angles ( $r(\text{C-C}) \approx 1.45 \text{ \AA}$  to  $1.55 \text{ \AA}$ ,  $r(\text{C=C}) \approx 1.35 \text{ \AA}$ ,  $\alpha(\text{C=C-C}) \approx 120$  degrees) allows us to immediately identify the physically meaningful choice (*e, o*) of displacement signs. For the case of butadiene, the choice of displacement signs is also obvious due to symmetry reasons (see Fig. 1).

Errors were estimated using the error propagation formula<sup>12</sup> and the partial derivatives for each evaluation step. The Costain errors contain an additional  $\delta r = K/|r|$  uncertainty with  $K = 0.0015 \text{ \AA}^2$  and should ideally account for the limited accuracy of the substitution coordinates  $r_s$  with respect to the equilibrium coordinates  $r_e$ .

**List S2** Calculated bond lengths and angles based on the Kraitchman isotope displacements. The C1 and C2 displacements along the  $a$ ,  $b$  principal molecular axes can be of equal ( $e$ ) or opposite sign ( $o$ ).

$a, b$	$r(\text{C-C})$	$r(\text{C=C})$	angle (C=C-C)
$e, e$	1.466(0.007)	1.297(0.011)	128.8(1.2)
$o, e$	1.466(0.007)	2.469(0.006)	27.1(1.3)
$e, o$	1.466(0.007)	1.342(0.014)	123.1(1.4)
$o, o$	1.466(0.007)	2.493(0.008)	23.9(1.8)

## 6 Comparison of Butadiene Structural Parameters

Table S5 shows structural parameters for butadiene determined from our data (see also Table 2 in the manuscript), compared to a wider set of literature and ab initio calculated values. Ab initio values were calculated using Gamess Firefly<sup>13</sup> and the Dunning's augmented correlation-consistent triple-zeta basis set<sup>14</sup> at  $C_{2h}$  symmetry. Note that the MP2 results are significantly different from the values given for the same basis set in the *Computational Chemistry Comparison and Benchmark DataBase*<sup>15</sup>, but are close to those given by Craig et al.<sup>6</sup>, who used the unaugmented cc-pVTZ basis set. Calculated equilibrium geometries and corresponding total energies are given in List S3. Keywords specifying non-default settings are given together with the calculation results. Bond distances and angles were calculated with vector operations using appropriate numpy functions. The principal moments of inertia and corresponding rotational constants were calculated from the atomic coordinates and atomic masses (NIST masses as encoded in pyteomics.py, version 4.1.2<sup>16</sup>) according to the formalism outlined by Kraitchman<sup>9</sup>.

**Table S5** Experimental, semi-experimental, and theoretical structure parameters of butadiene. For details, see text.

	OUR WORK						CRAIG ET AL. <sup>a</sup>				KVESETH <sup>b</sup>	CCCDB <sup>c</sup>		
	Experimental, $r_s$			Ab initio, $r_e$			Exp.	Ab initio., $r_e$		Semi-Exp.		Exp.	Ab initio, $r_e$	
	$r_s$	SE <sup>d</sup>	Costain <sup>e</sup>	MP2	B3Lyp5	X3Lyp	$r_s^e$	MP2	$r_e^f$	$r_0^g$	$r_0$	MP2	B3Lyp	
r(C-C)	1.466	(0.005)	(0.007)	1.453	1.454	1.453	1.451(4)	1.453	1.454(1)	1.458(3)	1.468	1.465	1.453	
r(C=C)	1.342	(0.011)	(0.014)	1.341	1.335	1.334	1.344(6)	1.340	1.338(1)	1.346(3)	1.348	1.340	1.334	
$\alpha(\text{C=C-C})$	123.1	(0.6)	(1.1)	123.5	124.4	124.3	123.6(6)	123.5	123.6(1)	123.4(1)	124.3	124.2	124.3	

<sup>a</sup>Craig2006<sup>6</sup>; <sup>b</sup>Kveseth1980<sup>17</sup>; <sup>c</sup>Computational Chemistry Comparison and Benchmark DataBase<sup>15</sup>; <sup>d</sup>Standard errors (SE) are propagated errors from the rotational constant uncertainties. <sup>e</sup>Values in brackets give the Costain uncertainties; <sup>f</sup>Uncertainties span the range obtained with four different quantum chemical models; <sup>g</sup>Statistical uncertainties in a global fit.

## List S3 Ab initio results.

RHF + MP2 EQUILIBRIUM GEOMETRY, acc-pVTZ basis  
Keywords: INTTYP=hondo, DIIS=.t., SOSCF=.f.

TOTAL ENERGY = -155.6442 Ha

COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
C0	6.0	-1.8418349418	-0.1194684317	0.0000000000
C1	6.0	1.8418927667	0.1194827255	0.0000000000
C2	6.0	-0.6062392988	0.4004783506	0.0000000000
C3	6.0	0.6061866146	-0.4004951133	0.0000000000
H4	1.0	-1.9974625774	-1.1904255783	0.0000000000
H5	1.0	1.9974591488	1.1904294306	0.0000000000
H6	1.0	-2.7152377510	0.5169345022	0.0000000000
H7	1.0	2.7152408812	-0.5169289344	0.0000000000
H8	1.0	-0.4854997604	1.4792826907	0.0000000000
H9	1.0	0.4854949182	-1.4792896418	0.0000000000

distance C0-C2: 1.341 Angstrom

distance C2-C3: 1.453 Angstrom

angle C0-C2-C3: 123.54 degrees

Rotational Constants along Principal Molecular Axes (GHz)

A: 42.052219

B: 4.455701

C: 4.028822

B3LYP5 EQUILIBRIUM GEOMETRY, acc-pVTZ basis

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TOTAL ENERGY = -155.9511 Ha

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COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
C0	6.0	-1.8416075840	-0.1185169061	0.0000000000
C1	6.0	1.8416075840	0.1185169061	0.0000000000
C2	6.0	-0.6095976212	0.3957017132	0.0000000000
C3	6.0	0.6095976212	-0.3957017132	0.0000000000
H4	1.0	-2.0079697634	-1.1892674212	0.0000000000
H5	1.0	2.0079697634	1.1892674212	0.0000000000
H6	1.0	-2.7192101015	0.5131553015	0.0000000000
H7	1.0	2.7192101015	-0.5131553015	0.0000000000
H8	1.0	-0.4838394070	1.4746426195	0.0000000000
H9	1.0	0.4838394070	-1.4746426195	0.0000000000

distance C0-C2: 1.335 Angstrom

distance C2-C3: 1.454 Angstrom

angle C0-C2-C3: 124.36 degrees

Rotational Constants along Principal Molecular Axes (GHz)

A: 42.612685  
 B: 4.440244  
 C: 4.021232

X3LYP5 EQUILIBRIUM GEOMETRY, acc-pVTZ basis

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TOTAL ENERGY = -155.9454 Ha

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COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
C0	6.0	-1.8397150494	-0.1178698488	0.0000000000
C1	6.0	1.8397150494	0.1178698488	0.0000000000
C2	6.0	-0.6088714468	0.3960410325	0.0000000000
C3	6.0	0.6088714468	-0.3960410325	0.0000000000
H4	1.0	-2.0038340438	-1.1883418184	0.0000000000
H5	1.0	2.0038340438	1.1883418184	0.0000000000
H6	1.0	-2.7175685905	0.5125953457	0.0000000000
H7	1.0	2.7175685905	-0.5125953457	0.0000000000
H8	1.0	-0.4821817171	1.4743057364	0.0000000000
H9	1.0	0.4821817171	-1.4743057364	0.0000000000

distance C0-C2: 1.334 Angstrom

distance C2-C3: 1.453 Angstrom

angle C0-C2-C3: 124.30 degrees

Rotational Constants along Principal Molecular Axes (GHz)

A: 42.630023  
 B: 4.449748  
 C: 4.029180

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