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Lowest bending mode of ^{13}C -substituted C_3 and an experimentally derived structure

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The ν_2 lowest bending mode of linear C_3 and of all its ^{13}C -substituted isotopologues was recorded using a terahertz-supersonic jet spectrometer in combination with a laser ablation source. Sixty-five ro-vibrational transitions between 1.8 and 1.9 THz have been assigned to linear $^{12}\text{C}^{12}\text{C}^{12}\text{C}$, $^{12}\text{C}^{12}\text{C}^{13}\text{C}$, $^{12}\text{C}^{13}\text{C}^{12}\text{C}$, $^{13}\text{C}^{13}\text{C}^{12}\text{C}$, $^{13}\text{C}^{12}\text{C}^{13}\text{C}$, and $^{13}\text{C}^{13}\text{C}^{13}\text{C}$. For each isotopologue, molecular parameters were obtained and the C–C-bond length was derived experimentally. All results are in excellent agreement with recent *ab initio* calculations [B. Schröder and P. Sebald, *J. Chem. Phys.* **144**, 044307 (2016)]. The new measurements explain why the interstellar search for singly substituted $^{12}\text{C}^{12}\text{C}^{13}\text{C}$ has failed so far. A spectral line list with recommended transition frequencies based on global data fits is given to foster future interstellar detections. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4971854>]

I. INTRODUCTION

Linear C_3 is formed from carbonaceous materials in high temperature processes and in carbon rich plasmas.¹ Tricarbon has been found in flames, electrical discharges, and in laser ablation processes, as well as in astrophysical environments, such as cometary tails,² envelopes of aging carbon-stars,³ the diffuse interstellar medium,⁴ and towards star forming regions.^{5–9} First recognized by the turn of the twentieth century as unknown cometary emission features near 4050 Å, the unambiguous assignment to linear C_3 lasted another five decades until Douglas¹⁰ in 1951 and Gausset *et al.*¹¹ in 1965 performed spectroscopic laboratory investigations on a methane-discharge and flash photolysis of diazomethane. These laboratory spectra revealed the non-rigid nature of the C_3 radical which possesses a large amplitude ν_2 bending motion at an unusually low vibrational frequency of roughly 63 cm^{-1} . Because of its relevance to astrophysics and its unusual molecular properties, C_3 has been studied extensively over the last couple of decades, both by experiment and theory. To begin with, high resolution ro-vibrational spectra of the ν_3 asymmetric stretching mode and associated ν_2 hot bands were reported by Matsumura *et al.*¹² and Kawaguchi *et al.*¹³ which confirmed the large amplitude motion of the low bending mode. Schmuttenmaer *et al.*¹⁴ used a fixed frequency far infrared laser mixed with tunable microwave radiation to measure seven ro-vibrational absorption lines of the ν_2 bending mode of C_3 between 58 and 69.5 cm^{-1} , data which have later on been

extended by Gendriesch *et al.*^{15,16} in 2003. For review articles on C_3 and other small carbon clusters, see Van Orden and Saykally¹⁷ and Weltner and Van Zee.¹⁸ Recently rotationally resolved infrared hot band spectra at 3 μm have been published by Krieg *et al.*¹⁹ using an optical parametric oscillator (OPO) to provide high power tunable IR-radiation. Moazzen-Ahmadi and McKellar²⁰ performed infrared measurements using ^{13}C -enriched precursors and derived molecular parameters for the isotopologues $^{12}\text{C}^{12}\text{C}^{13}\text{C}$ and $^{13}\text{C}^{13}\text{C}^{13}\text{C}$. Later, Krieg *et al.*¹⁹ measured the first spectra of $^{12}\text{C}^{13}\text{C}^{12}\text{C}$ at 3 μm . Optical spectra of ^{13}C -isotopologues were reported by Haddad *et al.*,²¹ although with less frequency accuracy compared to the infrared studies. So far there have been no spectra published of the ^{13}C -substituted C_3 at the ν_2 lowest bending mode except Krieg *et al.*¹⁹ who reported a weak absorption band, centered at 60.747 cm^{-1} which was incorrectly assigned to singly substituted $^{12}\text{C}^{12}\text{C}^{13}\text{C}$. Our present data give evidence that the 60.747 cm^{-1} absorption belongs to the ν_2 band of $^{13}\text{C}^{13}\text{C}^{12}\text{C}$. Based on the faulty assignment, our search for interstellar $^{12}\text{C}^{12}\text{C}^{13}\text{C}$ using the Herschel space telescope failed, which finally led to the present systematic study on the low bending mode of C_3 and its ^{13}C -isotopologues.

This new study makes use of a substantially improved supersonic jet spectrometer and high quality samples of well defined isotopic mixing ratios. In the course of our present study, high level *ab initio* data became available by Schröder and Sebald²² which were communicated to us prior to publication and which helped assign our laboratory data to the six isotopologues of C_3 . From a least squares fit analysis, we derived molecular parameters for each of the six isotopologues including all rotationally resolved experimental data available from the literature. Finally we derived an

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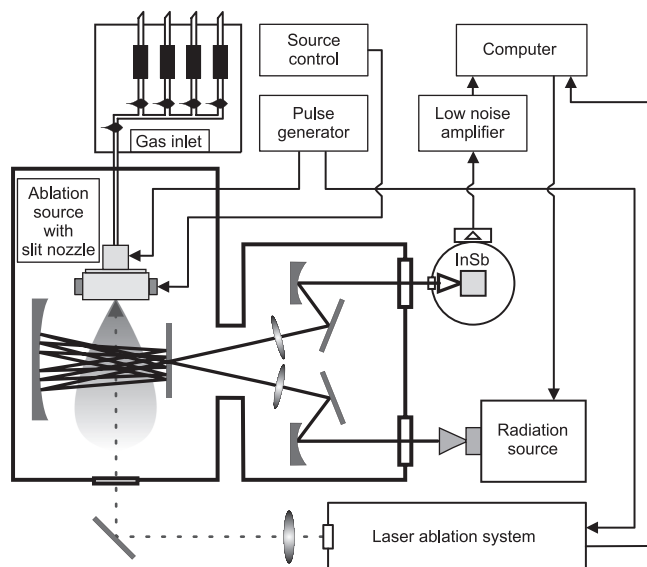


FIG. 1. Experimental setup of the supersonic jet spectrometer. The absorption signal detected by a hot electron bolometer is enhanced by multi-passing the THz beam through the supersonic jet.

equilibrium C–C bond distance from experimental data and compared results with *ab initio* values by Schröder and Sebald.²² We give recommended frequency positions of all six isotopologues for rotational quantum numbers up to $J = 12$ emphasizing their possible future detection in astrophysical environments.

II. EXPERIMENT

C_3 was produced by the laser ablation of a sintered carbon target using the fourth harmonic of a Q-switched Nd:YAG laser at a 30 Hz repetition rate. The sample rod rotated and translated simultaneously to constantly provide a pristine carbon surface during the measurements. The ablated carbon was seeded in a

TABLE I. Isotopic mole fractions and sample densities of the sintered carbon rods.

Sample	x_{12C}	x_{13C}	ρ (g/cm ³)
A	1	0	0.94
B	2/3	1/3	1.07
C	1/3	2/3	1.20
D	0	1	1.35

flow of a helium gas pulse at 2 bar stagnation pressure which pre-expanded into a reaction channel of 3 mm length and 10×1 mm² cross section. The reaction channel allowed the formation of small and medium sized carbon clusters by re-condensing at moderate temperatures before the gas flow expanded adiabatically into a vacuum chamber at typically 10^{-3} mbar background pressure in the form of a supersonic jet. The adiabatic expansion reduced the rotational temperature of the carbon clusters to a few tens Kelvin. A schematic sketch of the experiment is shown in Figure 1. Radiation in the range of 9 to 14 GHz was produced by a tunable synthesizer, and the output signal was amplified and frequency multiplied by a factor of 144 in a cascaded multiplier chain (Virginia Diodes) to generate radiation between 1.8 and 1.9 THz. The terahertz-beam intersected the supersonic jet perpendicularly 20 mm downstream the slit-nozzle exit in a multi-pass optics (arrangement: folded Herriott type). The transmitted THz-radiation was focused onto a liquid-He cooled InSb hot-electron bolometer (QMC instruments). The data were recorded during a 100 μ s time frame allowing for the background subtraction of the signal shortly before the pulsed absorption signal appeared. A low-noise amplifier and band-pass filter (SR560, Scientific Instruments) was used to reduce the low frequency noise of the signal before storing the time-dependent signal on a computer. An absorption spectrum was obtained when tuning the THz-frequency in steps of 0.25 MHz over the entire spectral range, by taking the averaged 100 μ s time-signals of 30 laser shots

TABLE II. Molecular parameters of the ground and lowest bending states of the C_3 isotopologues (in MHz).

Parameter	¹² C ¹² C ¹² C ^a	¹² C ¹³ C ¹² C ^b	¹² C ¹² C ¹³ C ^b	¹³ C ¹³ C ¹² C ^c	¹³ C ¹² C ¹³ C	¹³ C ¹³ C ¹³ C ^d
(0,0 ⁰ ,0)						
$B'' \times 10^{-3}$	12.908 678(4)	12.900 325(96)	12.403 170(11)	12.395 038(86)	11.910 794(31)	11.903 524(32)
D''	0.046 68(24)	0.042 57(128)	0.040 97(66)	0.043 74 ^e	0.042 10 ^e	0.038 39(51)
$H'' \times 10^6$	6.95(39)		3.42(57)			4.05(46)
$L'' \times 10^9$	-0.95(16)					
(0,1 ¹ ,0)						
$\nu \times 10^{-3}$	1901.181 630(9)	1830.243 173(69)	1892.864 561(18)	1821.165 337(63)	1884.687 261(57)	1812.201 110(22)
$B' \times 10^{-3}$	13.263 270(5)	13.245 166(74)	12.743 487(12)	12.725 848(65)	12.237 327(36)	12.220 861(22)
D'	0.070 62(22)	0.081 71(128)	0.061 60(116)	0.069 11 ^e	0.075 26(15)	0.060 28(44)
$H' \times 10^6$	6.55(60)			4.51(19)		8.63(47)
$L' \times 10^9$	1.33(46)					
q	170.938(6)	176.495(47)	158.614(9)	164.148(43)	146.893(26)	152.381(22)
q_J	-0.031 19(32)		-0.030 70(126)	-0.021 78(7)		-0.022 90(62)
$q_{JJ} \times 10^6$	11.5(11)					
$q_{JJJ} \times 10^9$	-5.48(87)					

^aGlobal fit including high resolution ¹²C₃ data.^{13,14,16,19}

^bGlobal fit including data from Krieg *et al.*¹⁹ and Haddad *et al.*²¹

^cGlobal fit including optical data set.²¹

^dGlobal fit including data from Moazzen-Ahmadi and McKellar.²⁰

^eFixed estimated D values.³⁰

at each frequency position. The accuracy of line center positions was typically 50 kHz with line widths (FWHM) around 4 MHz.

For measurements on C_3 isotopologues, ^{13}C -enriched target samples were produced in stoichiometric mixtures. Sample pellets of 10 mm in diameter and of 10 mm length were sintered from ^{12}C - and ^{13}C -amorphous powders (Sigma Aldrich, 99% grade) at the Tycho Sinterlab, Rostock, using a HP D5 unit (FCT Systeme GmbH). To achieve homogeneous samples of reproducible high quality, the field assisted sintering technique (FAST) was used, applying a force of 5 kN on the sample at 1700 °C final temperature and a previous heating rate of 100 K/min (for technical details, see Garay²³). The sample density depends linearly on the ^{13}C mole fraction, which has been used as a sample quality parameter (see Table I).

III. MEASUREMENTS AND DATA REDUCTION

In the present study, sixty-five ro-vibrational transitions of the ν_2 fundamental bending mode, $(0,1^1,0)$ - $(0,0^0,0)$, were measured in the frequency region between 1.8 and 1.9 THz

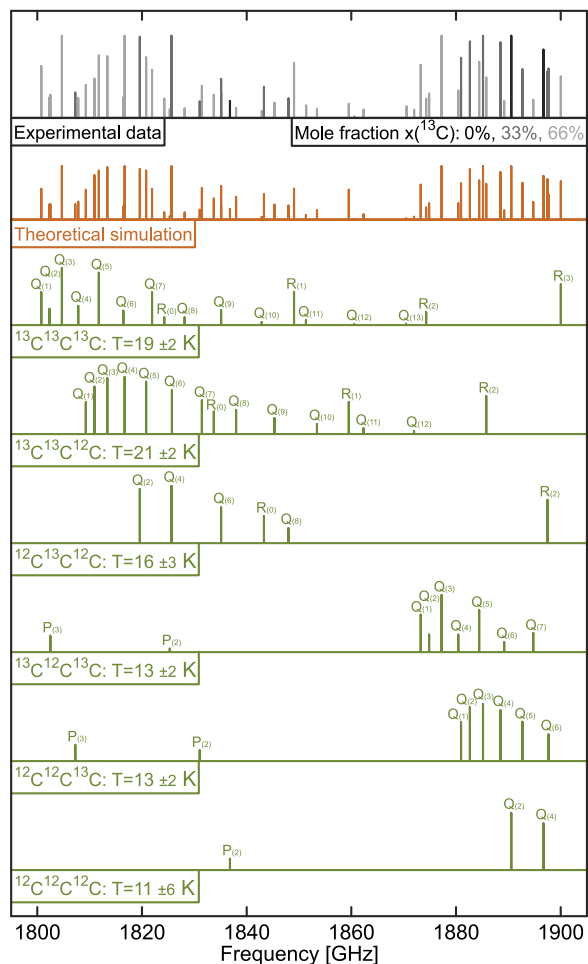


FIG. 2. Stick diagram of measured ν_2 bending mode transitions, $(0,1^1,0)$ - $(0,0^0,0)$, for C_3 and its isotopologues; in gray, spectra of ^{13}C enriched samples. The second plot from the top (in orange) shows the simulated spectra for all isotopologues with the parameters and temperatures determined from the present study. The lower six plots (in green) show the simulations of each assigned C_3 isotopologue with respect to the fitted rotational temperature.

and assigned to six different C_3 isotopologues. Table III lists line positions for the main isotopologue as well as those from the singly, doubly, and fully ^{13}C -substituted C_3 isotopologues. For transitions outside the covered frequency range, we give calculated values based on a least squares fit analysis using a standard Hamiltonian for a linear molecule from all available data from the literature. We used the PGOPHER program²⁴ to derive molecular parameters for all six C_3 isotopologues in the ground and vibrational excited states as given in Table II. Ground state and excited bending state energies are given by

$$E_0(J)/h = B''f - D''f^2 + H''f^3 + L''f^4, \quad (1)$$

for the $(0,0^0,0)$ ground state, and

$$E_{\pm}(J)/h = \nu + B'f_{\ell} - D'f_{\ell}^2 + H'f_{\ell}^3 + L'f_{\ell}^4 \pm \frac{1}{2} (qf + q_Jf^2 + q_{JJ}f^3 + q_{JJJ}f^4), \quad (2)$$

for the $(0,1^1,0)$ excited state, with $f = J(J+1)$ and $f_{\ell} = J(J+1) - \ell^2$ the squared angular momenta. B'' , D'' , H'' , and L'' denote the rotational ground state constant and centrifugal distortion constants, B' , D' , H' , and L' the corresponding excited state constants, ν the band center, q the ℓ -type doubling constant with q_J , q_{JJ} , and q_{JJJ} the higher order correction terms. The sign convention of ℓ -type doubling constants follows the definition given in Yamada²⁵ (positive q for e(lower) and f(upper) states). Each isotopologue was fitted separately including the new measured data and available data from the literature. A stick spectrum of measured C_3 lines in the frequency region of 1.8–1.9 THz and simulated spectra based on best fit parameters are shown in Figure 2.

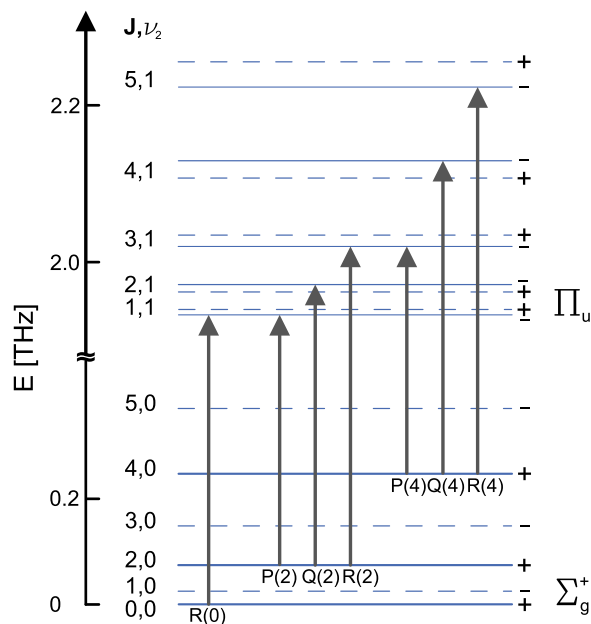


FIG. 3. Combination differences of the low C_3 -transitions. The lower state rotational constant B'' is derived from the $R(0)$ - $P(2)$ combination difference, and the upper state B' is derived from the $R(2)$ - $P(2)$ combination difference.

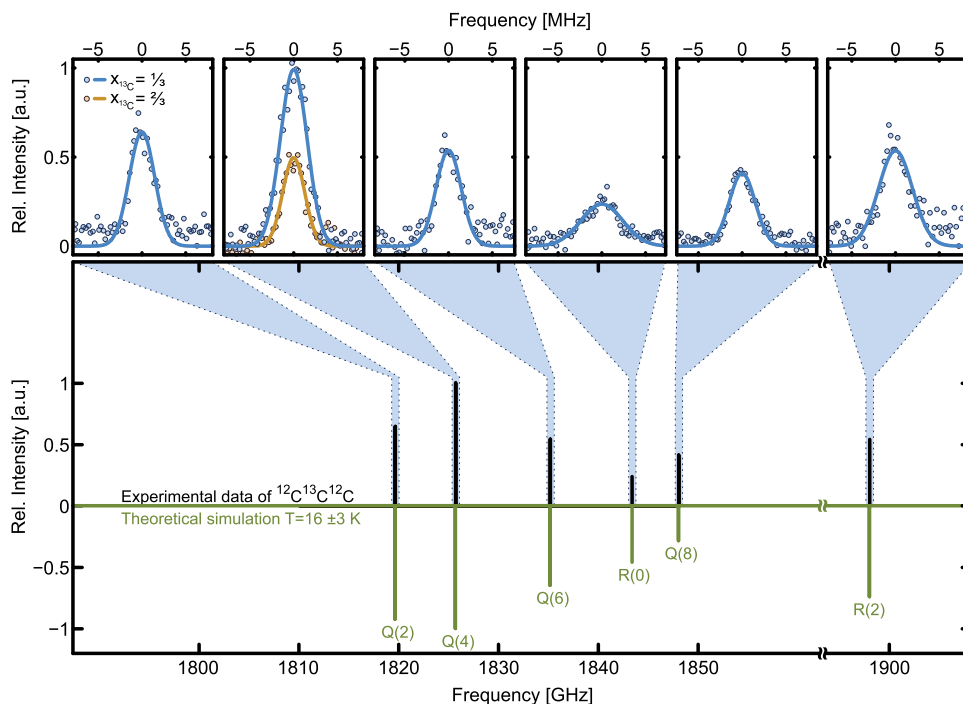


FIG. 4. Stick spectrum of measured $^{12}\text{C}^{13}\text{C}^{12}\text{C}$ lines and calculated line intensities at $T = 16$ K featuring a 0:1 statistical weight alternation of odd/even J transitions. Upper trace frames show recorded spectra from 33% ^{13}C -enriched samples (blue) and fitted Gaussian line shapes. A weaker signal (orange) is recorded when samples of 67% ^{13}C were used.

A. $^{12}\text{C}^{12}\text{C}^{12}\text{C}$

In order to improve the accuracy of the main isotopologue data, we re-measured the transitions $P(2)$, $P(4)$, $Q(2)$, $Q(4)$, $Q(8)$, $Q(10)$, and $R(0)$, which in combination with our previous measurement of the $R(2)$ line^{15,16} allow for a separate determination of upper and lower state constants, B' , q' , and B'' via combination differences (see Figure 3). The re-measured $P(2)$ line was found 2 MHz higher in frequency than the value given by Schmuttenmaer *et al.*,¹⁴ a finding which may

explain the deviations of astrophysically detected $P(J)$ transitions from line positions given in the *Cologne Database for Molecular Spectroscopy* (CDMS).²⁶ From the improved data set, an accurate line list for $^{12}\text{C}^{12}\text{C}^{12}\text{C}$ bending mode transitions was derived from a weighted global fit analysis of all available data. As a result, improved rotational constants and the band center position were obtained which are in excellent agreement with recent *ab initio* results published by Schröder and Sebald²² and which reproduce the astrophysical data within the error limits. The obtained molecular parameters

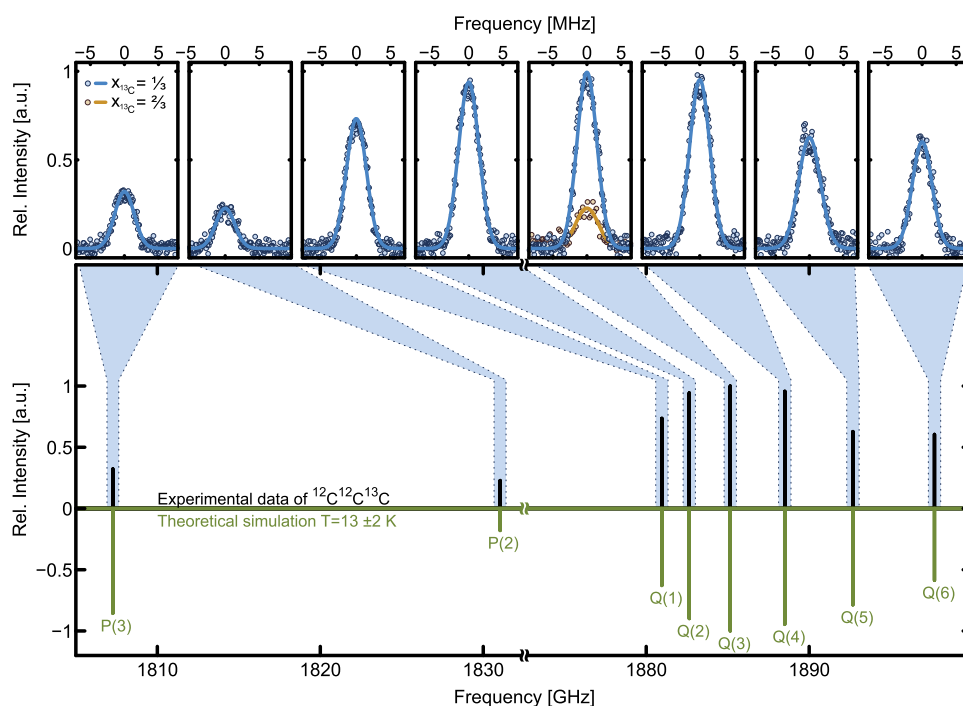


FIG. 5. The lower frame shows the measured experimental transitions (black downwards) in the ν_2 band of $^{12}\text{C}^{12}\text{C}^{13}\text{C}$ in the frequency range 1.8–1.9 THz and the simulation (green downwards) at a rotational temperature of 13 K as stick spectrum. The upper frames show measured line profiles (dots) with a mole fraction of 1/3 ^{13}C in the ablation target (sample B) and their Gaussian fits (blue solid line). The isotopologue assignment, $^{12}\text{C}^{12}\text{C}^{13}\text{C}$, is confirmed by the $Q(3)$ -transition, which was much weaker using a 2/3 ^{13}C (sample C), i.e., at a higher ^{13}C mole fraction as indicated in orange.

TABLE III. Transition frequencies of the $(0, 1^1, 0)-(0, 0^0, 0)$ bending mode (in MHz) of $^{12}\text{C}_3$ and for ^{13}C substituted C_3 isotopologues. Experimental uncertainties are given in parentheses with 1σ deviation.

Isotopologue	J	$P(J)^a$	o.-c.	$Q(J)^a$	o.-c.	$R(J)^a$	o.-c.
$^{12}\text{C}^{12}\text{C}^{12}\text{C}$	0					1 914 273.912(13)	-0.010
	2	1 836 823.502(25)	-0.028	1 890 558.188(11)	+0.020	1 968 595.391(200) ^b	+0.299
	4	1 787 890.534(14)	+0.003	1 896 706.838(9)	-0.008	2 025 051.586(899) ^c	-0.043
	6	1 741 122.646(6895) ^c	-1.275	1 906 337.903(250) ^b	-0.103	2 083 626.535(899) ^c	-0.586
	8	1 696 525.363(801)		1 919 410.791(7)	+0.001	2 144 301.38(158)	
	10	1 654 087.90(209)		1 935 870.390(158)	-0.068	2 207 049.97(342)	
	12	1 613 805.25(435)		1 955 648.963(200) ^b	-0.301	2 271 843.88(652)	
	14	1 575 661.17(795)		1 978 667.579(150) ^b	+0.049	2 338 649.4(115)	
	16	1 539 634.2(134)		2 004 835.934(3000) ^b	+1.031	2 407 428.6(193)	
$^{12}\text{C}^{13}\text{C}^{12}\text{C}$	0					1 843 311.778(215)	+0.016
	2	1 765 911.343(490)		1 819 596.013(89)	-0.014	1 897 470.722(103)	-0.001
	4	1 716 881.67(136)		1 825 647.312(49)	+0.007	1 953 647.368(599)	
	6	1 669 898.28(277)		1 835 125.454(65)	-0.008	2 011 799.71(186)	
	8	1 624 935.55(493)		1 847 989.176(128)	+0.007	2 071 870.74(401)	
	10	1 581 952.80(809)		1 864 182.073(210)		2 133 788.40(729)	
	12	1 540 894.3(125)		1 883 632.789(558)		2 197 465.6(120)	
$^{12}\text{C}^{12}\text{C}^{13}\text{C}$	0					1 905 449.403(31)	
	1			1 880 960.405(18)	+0.012	1 931 298.897(62)	-0.000
	2	1 831 031.852(111)	-0.002	1 882 638.282(15)	-0.008	1 957 668.258(142)	
	3	1 807 272.923(38)	+0.000	1 885 152.952(16)	-0.021	1 984 556.117(451)	
	4	1 784 038.758(42)	-0.000	1 888 501.875(15)	+0.035	2 011 960.97(110)	
	5	1 761 329.936(195)		1 892 681.327(30)	-0.083	2 039 881.18(225)	
	6	1 739 146.880(605)		1 897 687.328(28)	+0.015	2 068 314.95(409)	
	7	1 717 489.85(140)		1 903 514.278(57)		2 097 260.31(685)	
	8	1 696 358.93(277)		1 910 156.118(131)		2 126 715.1(108)	
	9	1 675 753.99(493)		1 917 605.715(269)		2 156 677.1(162)	
	10	1 655 674.71(814)		1 925 854.996(513)		2 187 143.6(235)	
	11	1 636 120.5(127)		1 934 894.914(921)		2 218 111.8(330)	
	12	1 617 090.6(189)		1 944 715.45(158)		2 249 578.8(452)	
$^{13}\text{C}^{13}\text{C}^{12}\text{C}$	0					1 833 727.029(135)	+0.040
	1			1 809 265.353(47)	+0.013	1 859 510.580(340)	-0.256
	2	1 759 358.370(435)		1 810 916.271(46)	-0.040	1 885 789.206(51)	+0.002
	3	1 735 566.630(777)		1 813 390.624(32)	+0.027	1 912 559.993(182)	
	4	1 712 274.65(120)		1 816 685.578(28)	-0.024	1 939 820.765(435)	
	5	1 689 482.42(172)		1 820 797.925(40)	+0.046	1 967 568.758(775)	
	6	1 667 189.60(231)		1 825 723.103(52)	-0.041	1 995 800.91(120)	
	7	1 645 395.54(299)		1 831 456.425(142)	+0.148	2 024 513.85(171)	
	8	1 624 099.24(375)		1 837 991.464(284)	+0.042	2 053 703.98(231)	
	9	1 603 299.66(460)		1 845 321.794(80)	-0.049	2 083 367.42(300)	
	10	1 582 994.66(552)		1 853 440.173(129)	+0.054	2 113 500.12(379)	
	11	1 563 183.09(653)		1 862 338.136(137)	+0.047	2 144 097.83(470)	
	12	1 543 862.77(763)		1 872 006.862(164)	-0.038	2 175 156.16(575)	
$^{13}\text{C}^{12}\text{C}^{13}\text{C}$	0					1 896 777.619(91)	
	1			1 873 249.945(28)	-0.042	1 921 609.918(120)	+0.003
	2	1 825 315.282(1000)	+0.908	1 874 849.468(62)	+0.021	1 946 944.145(378)	
	3	1 802 507.865(137)	-0.009	1 877 246.689(20)	+0.041	1 972 776.911(601)	
	4	1 780 208.360(389)		1 880 439.089(76)	-0.113	1 999 104.018(874)	
	5	1 758 414.455(596)		1 884 423.867(34)	-0.059	2 025 920.48(120)	
	6	1 737 123.985(855)		1 889 196.899(92)	+0.058	2 053 220.51(159)	
	7	1 716 333.98(117)		1 894 753.384(157)	-0.213	2 080 997.52(204)	
	8	1 696 040.68(154)		1 901 087.345(444)		2 109 244.14(258)	
	9	1 676 239.52(199)		1 908 192.997(803)		2 137 952.20(323)	
	10	1 656 925.15(252)		1 916 062.96(133)		2 167 112.73(403)	
	11	1 638 091.41(316)		1 924 689.29(206)		2 196 715.96(502)	
	12	1 619 731.36(396)		1 934 063.21(303)		2 226 751.33(625)	

TABLE III. (Continued.)

Isotopologue	J	$P(J)^a$	o.-c.	$Q(J)^a$	o.-c.	$R(J)^a$	o.-c.
$^{13}\text{C}^{13}\text{C}^{13}\text{C}$	0					1 824 269.584(67)	+0.031
	1			1 800 767.425(28)	+0.050	1 849 040.217(34)	-0.002
	2	1 752 849.792(174)		1 802 341.000(40)	+0.051	1 874 290.759(52)	-0.012
	3	1 730 010.350(313)		1 804 699.272(15)	-0.043	1 900 019.564(46)	+0.005
	4	1 707 655.383(473)		1 807 840.160(34)	+0.075	1 926 224.713(133)	
	5	1 685 785.055(651)		1 811 760.101(18)	+0.007	1 952 904.156(406)	
	6	1 664 399.291(878)		1 816 455.333(58)	-0.077	1 980 055.627(928)	
	7	1 643 497.78(125)		1 821 921.380(26)	+0.032	2 007 676.70(180)	
	8	1 623 080.01(190)		1 828 152.253(386)	-0.244	2 035 764.81(313)	
	9	1 603 145.23(297)		1 835 142.712(38)	-0.023	2 064 317.29(506)	
	10	1 583 692.55(459)		1 842 885.099(155)	-0.161	2 093 331.39(774)	
	11	1 564 720.90(690)		1 851 372.802(245)	+0.181	2 122 804.3(113)	
	12	1 546 229.1(100)		1 860 597.147(402)	+0.400	2 152 733.3(160)	
13	1 528 215.8(141)		1 870 548.993(79)	+0.007	2 183 115.6(220)		

^aValues without o.-c. values are calculated values from a best fit analysis based on measured frequencies.

^bTaken from Gendriesch *et al.*¹⁶

^cTaken from Schmuttenmaer *et al.*¹⁴

are listed in Table II. Figure 2 shows a stick spectrum of $^{12}\text{C}^{12}\text{C}^{12}\text{C}$ with only even J quantum numbers, featuring Bose-Einstein statistical weights of two identical carbon nuclei of spin $I(^{12}\text{C}) = 0$.

B. $^{12}\text{C}^{13}\text{C}^{12}\text{C}$

Using ^{13}C -enriched target rods, a new band at 1.830 THz appeared 71 GHz below the main isotopologue band center. Strongest line intensities were observed when one-third of the carbon sample was of amorphous ^{13}C , i.e., presumably favoring the formation of singly ^{13}C -substituted C_3 species, see Figure 4. The lack of odd-numbered J -transitions in the measured spectrum was in support of assigning two R -branch and four Q -branch transitions to centro-symmetric $^{12}\text{C}^{13}\text{C}^{12}\text{C}$.

These new data together with IR-data reported by Krieg *et al.*¹⁹ and optical data from Haddad *et al.*²¹ were analyzed in a weighted least squares fit to derive molecular parameters as given in Table II. We found excellent agreement with *ab initio* data of Schröder and Sebald,²² in particular the measured and calculated line center positions agree within 6 GHz. For transitions of $J > 8$, line intensities became rather faint due to an unfavorable Boltzmann-population of rotational levels at temperatures below 20 K.

C. $^{12}\text{C}^{12}\text{C}^{13}\text{C}$

A second band at 1.893 THz was found only 8 GHz below the main isotopologue band when a 33% ^{13}C -enriched sample was used. We assigned one R -branch, two P -branch,

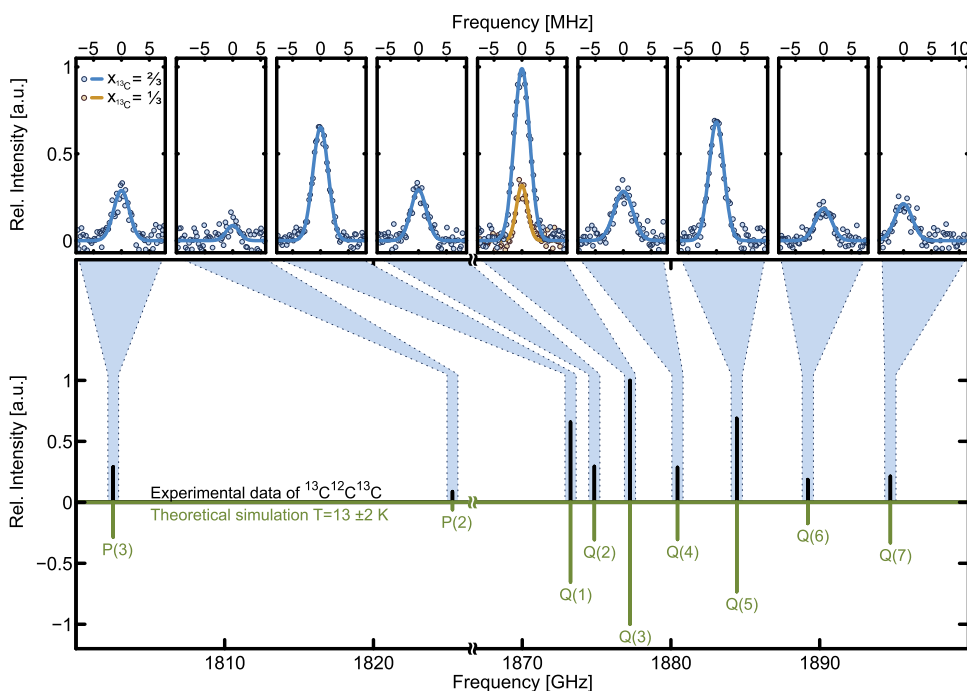


FIG. 6. Stick spectrum of measured $^{13}\text{C}^{12}\text{C}^{13}\text{C}$ lines and calculated line intensities at $T = 13$ K featuring a 3:1 statistical weight alternation of odd/even J transitions. Upper trace frames show recorded spectra from 67% ^{13}C -enriched samples (blue) and fitted Gaussian line shapes. A weaker signal (orange) is recorded when samples of 33% ^{13}C were used.

and six Q -branch transitions of the ν_2 -bending mode to $^{12}\text{C}^{12}\text{C}^{13}\text{C}$ (see Figure 5). Even and odd numbered transitions were found of comparable intensities, according to an asymmetric molecule of point group $C_{\infty v}$. All measured line positions were determined very precisely with uncertainties of less than 100 kHz. Accurate line positions are given in Table III, and molecular parameters derived from a weighted global fit analysis including IR-data published by Krieg *et al.*¹⁹ and optical data by Haddad *et al.*²¹ can be found in Table II.

D. $^{13}\text{C}^{13}\text{C}^{12}\text{C}$

In order to identify the lowest rotation-vibrational transitions of the doubly ^{13}C -substituted asymmetric $^{13}\text{C}^{13}\text{C}^{12}\text{C}$ species, a 67% ^{13}C -enriched target sample was used. The strongest lines of a band originating at 1.821 THz were assigned to three R - and twelve Q -branch transitions of this molecule. For a global fit analysis, optical measurements by Haddad *et al.* were included. The lack of high J -transitions did not allow us to determine the centrifugal distortion constants of $^{13}\text{C}^{13}\text{C}^{12}\text{C}$. Instead we used ground and excited state centrifugal parameters of $^{13}\text{C}^{13}\text{C}^{13}\text{C}$ and scaled these with the corresponding ratios of $^{12}\text{C}^{12}\text{C}^{12}\text{C}$ and $^{12}\text{C}^{12}\text{C}^{13}\text{C}$.

E. $^{13}\text{C}^{12}\text{C}^{13}\text{C}$

A set of ten lines around the band center at 1.885 THz showed maximum intensity when using a sintered target rod of 67% ^{13}C -enriched carbon. In addition to the standard Boltzmann thermal population, individual lines follow an intensity alternation with an odd numbered J -transition being three times stronger than the even numbered ones. These findings led to the assignments of these lines to $^{13}\text{C}^{12}\text{C}^{13}\text{C}$. Here the line intensities are affected by Dirac-spin statistical weights of two identical nuclei of spin $I(^{13}\text{C}) = 1/2$. Figure 6 shows the recorded $^{13}\text{C}^{12}\text{C}^{13}\text{C}$ spectrum at temperatures around

13(2) K. We scaled the ground state centrifugal distortion constants of $^{13}\text{C}^{12}\text{C}^{13}\text{C}$ with ground state centrifugal parameters of $^{13}\text{C}^{13}\text{C}^{13}\text{C}$, $^{12}\text{C}^{12}\text{C}^{12}\text{C}$, and $^{12}\text{C}^{13}\text{C}^{12}\text{C}$ due to the lack of measured higher J -transitions.

F. $^{13}\text{C}^{13}\text{C}^{13}\text{C}$

In order to identify the bending mode of the fully ^{13}C -substituted C_3 isotopologue, we used a 67% ^{13}C -enriched sample. Four R -branch and thirteen Q -branch transitions of a 3:1 intensity alternation were measured in the accessible range of the radiation source. Molecular parameters were obtained from a least squares fit analysis including IR-data published by Moazzen-Ahmadi and McKellar.²⁰

In total 65 transitions were assigned to the six isotopologues of C_3 . Accurate line center positions, rotational constants for ground and excited states as well as the ℓ -type doubling parameters were derived. Higher centrifugal parameters were obtained when rotationally resolved IR-data of high J -transitions were introduced to the global fit.

The experimental observation shows that the band centers have to be predicted theoretically with an accuracy better than half percent to distinguish different isotopologues, see Figure 7. The *ab initio* calculated band centers of Schröder and Sebald²² are systematically lower by 6 GHz (0.3%) compared to experimental values. The calculated excited state rotational constants $B^{(0,1,1)}$ and the ℓ -type doubling constants q agree almost perfectly well with the corresponding experimental values. In Table IV experimental vibration-rotation coupling constants α_2 for the ν_2 bending mode are given.

IV. MOLECULAR STRUCTURE

The structure parameters, bond lengths r_1, r_2 and bending angle ρ , are not directly observable. In good approximation C_3 is thought to be a linear molecule with two equivalent bond lengths $r_1 = r_2 = r$ and bending angle $\rho = 0$. As a first approach, the bond length r can be estimated by using the experimentally determined $B^{(0)}$ -values of the isotopologues, resulting in the so-called “ $r^{(0)}$ -structure.” Because of the unharmonicity of the potential even at the ground vibrational level, the $r^{(0)}$ -distance between the outer and inner carbon atoms does not correspond to the equilibrium distance. In Sections IV B and IV C, the structural parameter r is approximated by two methods. First, Watson’s mass-dependent structure $r^{(m)}$ is calculated using experimental data only. Second, the vibrational correction α_2 of the bending mode is used to derive an approximated value $r^{(0e0)}$ for the equilibrium structure $r^{(e)}$. It is expected that $r^{(m)}$ and $r^{(0e0)}$ are close to theoretical values as discussed in Section V.

A. Effective vibrational ground state structure, $r^{(0)}$

The effective moment of inertia for the vibrational ground state, $I^{(0)}$, can be derived from the rotational ground state constant $B^{(0)}$,

$$I^{(0)} = \frac{\hbar}{4\pi B^{(0)}}. \quad (3)$$

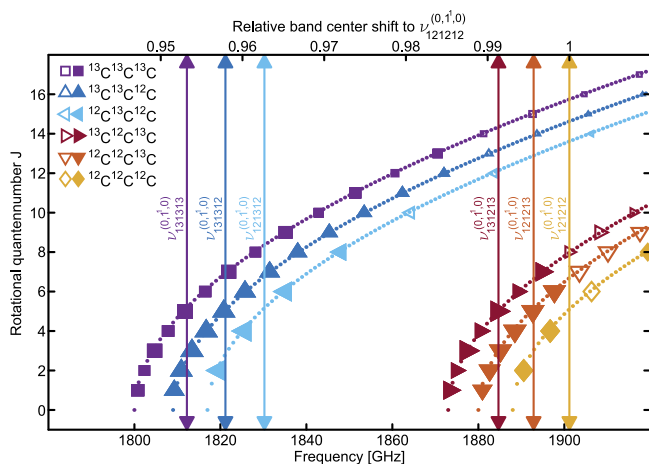


FIG. 7. Measured (filled symbols) and calculated (open symbols) Q -transitions of all C_3 isotopologues are shown. The band center $\nu_{\text{xyz}}^{(0,1,0)}$ of the respective isotopologues are marked with a vertical double arrow. The Q -branches of isotopologues split up into two groups at 1.82 and 1.89 THz, which are defined by the centro-symmetric atom of each molecule. The deviation within the groups is less than one percent of the band center frequency. The symbol size represents the transition intensity at 30 K.

TABLE IV. Comparison of experimental and calculated molecular parameters (in MHz) of all ^{13}C substituted C_3 isotopologues.

Parameter	This work	Previous expt. work	Theo. calc. ^a
$^{12}\text{C}^{12}\text{C}^{12}\text{C}$			
$B^{(0,0,0)} \times 10^{-3}$	12.908 678(4)	12.908 248(57) ^b	12.909 963
$\nu^{(0,1,0)} \times 10^{-3}$	1901.181 630(9)	1901.181 677(231) ^b	1896.487
$B^{(0,1,0)} \times 10^{-3}$	13.263 270(5)	13.262 944(48) ^b	13.263 718
$q^{(0,1,0)}$	170.938(6)	170.672(36) ^b	170.8
α_2	-354.592(6)	-354.696(75)	-353.755
$^{12}\text{C}^{13}\text{C}^{12}\text{C}$			
$B^{(0,0,0)} \times 10^{-3}$	12.900 325(96)	12.899 350(809) ^b	12.902 168
$\nu^{(0,1,0)} \times 10^{-3}$	1830.243 173(69)		1824.537
$B^{(0,1,0)} \times 10^{-3}$	13.245 166(74)		13.246 030
$q^{(0,1,0)}$	176.495(47)		177.2
α_2	-344.841(121)		-343.862
$^{12}\text{C}^{12}\text{C}^{13}\text{C}^b$			
$B^{(0,0,0)} \times 10^{-3}$	12.403 170(11)	12.403 643(507) ^b	12.404 213
$\nu^{(0,1,0)} \times 10^{-3}$	1892.864 561(18)		1888.093
$B^{(0,1,0)} \times 10^{-3}$	12.743 487(12)		12.743 878
$q^{(0,1,0)}$	158.614(9)		158.6
α_2	-340.317(16)		-339.665
$^{13}\text{C}^{13}\text{C}^{12}\text{C}$			
$B^{(0,0,0)} \times 10^{-3}$	12.395 038(86)	12.420 4(360) ^c	12.396 418
$\nu^{(0,1,0)} \times 10^{-3}$	1821.165 337(63)	1821.169 84(114) ^b	1815.543
$B^{(0,1,0)} \times 10^{-3}$	12.725 848(65)	12.729 757(660) ^b	12.726 789
$q^{(0,1,0)}$	164.148(43)	173.31(104) ^b	164.3
α_2	-330.810(108)		-330.371
$^{13}\text{C}^{12}\text{C}^{13}\text{C}$			
$B^{(0,0,0)} \times 10^{-3}$	11.910 794(31)	11.9413(258) ^c	11.911 654
$\nu^{(0,1,0)} \times 10^{-3}$	1884.687 261(57)		1879.999
$B^{(0,1,0)} \times 10^{-3}$	12.237 327(36)		12.237 528
$q^{(0,1,0)}$	146.893(26)		147.2
α_2	-326.533(48)		-325.874
$^{13}\text{C}^{13}\text{C}^{13}\text{C}$			
$B^{(0,0,0)} \times 10^{-3}$	11.903 524(32)	11.902 480(450) ^d	11.904 759
$\nu^{(0,1,0)} \times 10^{-3}$	1812.201 110(2)		1806.549
$B^{(0,1,0)} \times 10^{-3}$	12.220 861(22)		12.221 639
$q^{(0,1,0)}$	152.381(22)		152.6
α_2	-317.337(39)		-316.880

^aTaken from Schröder and Sebald.²²^bTaken from Krieg *et al.*¹⁹ Note that the experimental values given for $^{13}\text{C}^{13}\text{C}^{12}\text{C}$ were originally assigned to the $^{12}\text{C}^{12}\text{C}^{13}\text{C}$ isotopologue.^cTaken from Haddad *et al.*²¹^dTaken from Moazzen-Ahmadi and McKellar.²⁰

The effective structure parameter in the vibrational ground state, $r^{(0)}$, can be determined by

$$\begin{aligned}
 I^{(0)} &= \sum_{i=1}^3 m_i (z_i^{(0)})^2 \\
 &= \frac{(r^{(0)})^2}{M^2} \left[m_1(m_2 + 2m_3)^2 \right. \\
 &\quad \left. + m_2(m_1 - m_3)^2 + m_3(2m_1 + m_2)^2 \right], \quad (4)
 \end{aligned}$$

where $z_i^{(0)}$ and m_i are the coordinate of the i th atom with mass m_i in the molecule-fixed center of the mass coordinate system, $r^{(0)}$ is the C–C bond length, and $M = m_1 + m_2 + m_3$ is the total mass. The derived $r^{(0)}$ values are listed in Table V for each isotopologue.

B. Watson's mass-dependent structure, $r^{(m)}$

Another approximation to the bond length r can be made by using the approach by Watson.²⁷ First, the so-called

TABLE V. Experimental structure parameters^a of the C₃ isotopologues.

Parameter	Units	¹² C ¹² C ¹² C	¹² C ¹³ C ¹² C	¹² C ¹² C ¹³ C	¹³ C ¹³ C ¹² C	¹³ C ¹² C ¹³ C	¹³ C ¹³ C ¹³ C
$B^{(0)}$	GHz	12.908 678(4)	12.900 325(96)	12.403 170(11)	12.395 038(86)	11.910 794(31)	11.903 524(32)
$I^{(0)}$	uÅ ²	39.150 330(12)	39.175 680(292)	40.745 955(36)	40.772 687(283)	42.430 337(110)	42.456 252(22)
$r^{(0)}$	Å	1.277 209(0)	1.277 623(10)	1.277 261(1)	1.277 661(9)	1.277 308(3)	1.277 698(3)
$I^{(s)}$	uÅ ²	39.541 03(851)	39.554 09(964)	41.137 86(851)	41.154 73(955)	42.825 36(882)	42.843 82(973)
$I^{(m)}$	uÅ ²	39.931 72(1702)	39.932 50(1928)	41.529 77(1703)	41.536 77(1909)	43.220 38(1764)	43.231 38(1909)
$r^{(m)}$	Å	1.289 89(27)	1.289 90(31)	1.289 49(26)	1.289 58(30)	1.289 14(26)	1.289 31(29)
$B^{(0e0)}$	GHz	12.554 086(8)	12.555 484(155)	12.062 853(20)	12.064 228(138)	11.584 261(57)	11.586 187(50)
$I^{(0e0)}$	uÅ ²	40.256 137(24)	40.251 655(496)	41.895 479(68)	41.890 704(479)	43.626 349(214)	43.619 097(189)
$r^{(0e0)}$	Å	1.295 121(1)	1.295 049(16)	1.295 152(2)	1.295 060(15)	1.295 185(6)	1.295 077(6)

^aFor conversion of the units, the recommended values from CODATA³¹ were used.

“ $r^{(s)}$ -structure” has to be evaluated by applying the Kraitchman equation, e.g., see Chapter XIII in Gordy and Cook.²⁸ It is well known that the Kraitchman coordinates fail in determining the position of atoms close to the center-of-mass. For the central carbon atom, the $z^{(s)}(2)$ coordinates are expected to be very small but the values obtained here are in fact noticeably large and positive for all isotopologues, i.e., about 0.16 Å. Thus the $r^{(s)}$ -structure could not be determined in the present study. Although the Kraitchman coordinates are of less significance than the coordinates of the atoms themselves; the substitution moment of inertia, $I^{(s)}$, calculated with the $[z^{(s)}(i)]^2$ for $i = 1, 2, 3$ can be used to evaluate the $I^{(m)}$ defined by Watson,²⁷ which is $I^{(m)} = 2I^{(s)} - I^{(0)}$. The values of $I^{(s)}$ and $I^{(m)}$ are listed in Table V. Because $I^{(m)}$ is a good approximation of the equilibrium moment of inertia $I^{(e)}$ at least for molecules built of heavy atoms, the structure parameter $r^{(m)}$ for the mass-dependent structure proposed by Watson²⁷ can be derived by replacing $I^{(0)}$ and $r^{(0)}$ in Eq. (4) by $I^{(m)}$ and $r^{(m)}$. The obtained $r^{(m)}$ values are listed in Table V for each isotopologue. The variances of the $r^{(m)}$ values for isotopologues are larger than those of the $r^{(0)}$ values by one order of magnitude. This may be due to the model errors, which are enhanced in the process estimating the $I^{(s)}$. The $r^{(m)}$ values are systematically and noticeably larger than $r^{(0)}$ for all isotopologues.

C. Vibrational corrected equilibrium structure, $r^{(0e0)}$

The effective rotational constant of a linear molecule for a given vibrational state (v_1, v_2^ℓ, v_3) can be denoted as $B^{(v_1, v_2^\ell, v_3)}$.

TABLE VI. Bond length parameter of C₃ in Å.

C–C length	r
$r^{(0)}$	1.277 46(22)
$r^{(m)}$	1.289 55(31)
$r^{(0e0)}$	1.295 11(5)
$r^{(e)}$	1.294 71(5) ^a
$r_{\text{exp}}^{(e)}$	1.294 07(10) ^b
$r_{\text{mix}}^{(e)}$	1.293 97(10) ^b
$r_{\text{theo}}^{(e)}$	

^aDerived from rotational constants of ¹²C¹²C¹²C only: $B^{(0,0,0)}$, $B^{(0,1,0)}$, $B^{(0,0,1)}$ (see the supplementary material), and $B^{(1,0,0)}$ (see Zhang *et al.*²⁹).

^bValues taken from Schröder and Seibald;²² $r_{\text{theo}}^{(e)}$ (*ab initio* calculation) and $r_{\text{mix}}^{(e)}$ (mixed experimental/theoretical approach).

The effective rotational constant for the ground vibrational state is thus denoted as $B^{(0,0,0)}$ or simply as $B^{(0)}$ (as in Section IV A). In the first approximation, the equilibrium rotational constant $B^{(e)}$, i.e., the rotational constant for the $r^{(e)}$ -structure, is related to the effective rotational constant of a vibrational state by

$$B^{(v_1, v_2^\ell, v_3)} = B^{(e)} - \sum_{i=1}^3 \alpha_i (v_i + d_i/2), \quad (5)$$

where α_i and d_i represent the vibration-rotation interaction constant and the degeneracy of the i th vibrational mode. The equilibrium moment of inertia $I^{(e)}$ is readily obtained as the inverse of $B^{(e)}$, see Eq. (3). The equilibrium moment of inertia of C₃ derived in this manner is expressed by a simple function of the mass m_i and coordinate z_i of each atom, see Eq. (4). The structure parameters $r^{(e)}$ for each isotopologue are thus determined from the corresponding values of $I^{(e)}$.

In the present study, experimental values $B^{(0)}$ and α_2 were very accurately determined for all isotopologues. For the ν_1 and ν_3 symmetric and antisymmetric stretching mode of ¹²C¹²C¹²C, the values $\alpha_1 = 169.160(630)$ MHz (derived from $B^{(1,0,0)} = 12\,739.681$ MHz²⁹) and $\alpha_3 = -153.023(208)$ MHz have almost the same value but with opposite signs. Thus, the effect of α_1 and α_3 in Eq. (5) nearly cancels out; the *ab initio* calculation also supports this cancellation.²² Hence, taking only the α_2 contribution into consideration, we obtained $B^{(0e0)}$ values for each isotopologue. The thus-derived $r^{(0e0)}$ values are listed in Table V. The value of α_2 is smaller than $B^{(0)}$ by a factor of approximately 3/100, which is larger than that of a semi-rigid molecule. We estimate the higher order contribution neglected in the approximate relation of Eq. (5) to be on the order of $(3/100)^2 \approx 1/1000$. Thus, the relative uncertainty of $r^{(0e0)}$ may be in the order of 0.001 Å. They show very little deviation among the isotopologues.

V. CONCLUSION

We observed the ν_2 fundamental band of the C₃ radical at high resolution for all isotopologues: ¹²C¹²C¹²C, ¹²C¹³C¹²C, ¹²C¹²C¹³C, ¹³C¹³C¹²C, ¹³C¹²C¹³C, and ¹³C¹³C¹³C. From the rotational constants of the ground state and the $\nu_2 = 1$ state, we determined experimentally the bond length of the C₃ radical

to high precision. The C–C nuclear distances were determined using various models, see Table VI. In this table, the $r^{(0)}$, $r^{(m)}$, and $r^{(0e0)}$ values are the averages over those obtained for the isotopologues as listed in Table V. Their estimated uncertainties reflect the variance of the parameters among these isotopologues. For example, since the differences between the $r^{(0)}$ values of the isotopologues are very small, its calculated standard deviation of the mean value is underestimated. It is important to note that the $r^{(0)}$ value in Table VI is indeed smaller than the $r^{(m)}$ value and that the relation $r^{(0e0)} > r^{(m)} > r^{(0)}$ holds. This might be explained as an effect of a bending vibration with a large amplitude, which is not negligible even in the vibrational ground state through the zero-point vibration. Furthermore the probability of finding a carbon atom perpendicular to the molecular axis is expected to be distributed in a fairly large area. Thus, the effective rotational constant in the ground state should be significantly affected by these off-axis contributions. As mentioned in Section IV, the $r^{(0e0)}$ value should be a good approximation of the $r^{(e)}$ value in the present case. For $^{12}\text{C}^{12}\text{C}^{12}\text{C}$, where experimental values of α_1 , α_2 , and α_3 are available, the derived $r_{\text{exp}}^{(e)} = 1.294\,71(5)$ Å value using Eq. (3) is slightly smaller than the $r^{(0e0)} = 1.295\,11(5)$ Å value. Thus, we expect the experimentally determined $r^{(0e0)}$ from all isotopologues to slightly overestimate the true bond length. This is also confirmed by the theoretically determined value of $r_{\text{theo}}^{(e)} = 1.293\,97(10)$ Å by a recent *ab initio* calculation by Schröder and Sebald.²² The agreement between the two values is excellent, if we take into account the uncertainty of 0.001 Å in $r^{(0e0)}$ mentioned at the end of Section IV C.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for a complete list of fitted molecular parameters and line lists for all C₃ isotopologues.

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