THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

High-Resolution Spectroscopy of C_3 around 3 μm

Jürgen Krieg,*[,†] Volker Lutter,[†] Christian P. Endres,[†] Imke H. Keppeler,[‡] Per Jensen,[‡] Michael E. Harding,[¶,§] Juana Vázquez,[§] Stephan Schlemmer,[†] Thomas F. Giesen,[∥] and Sven Thorwirth*[,†]

[†]I. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, 50937 Köln, Germany

[‡]Physikalische und Theoretische Chemie, Bergische Universität Wuppertal, Gaussstrasse 20, 42097 Wuppertal, Germany

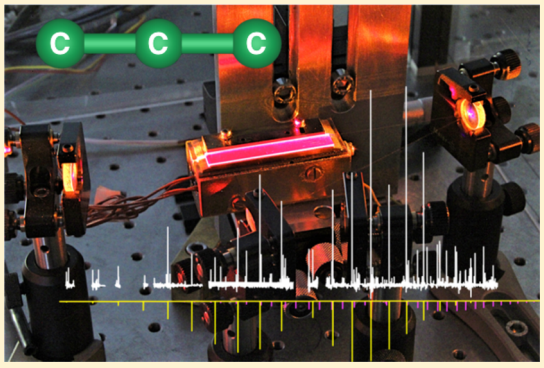
[¶]Institut für Nanotechnologie, Karlsruher Institut für Technologie, Campus Nord, Postfach 3640, 76021 Karlsruhe, Germany

[§]Center for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Texas 78712, United States

[∥]Universität Kassel, Fachbereich 10-Physik, Heinrich-Plett-Strasse 40, 34132 Kassel, Germany

Supporting Information

ABSTRACT: We report on the detection of the $(10^01) \leftarrow (00^00)$ vibrational band of gas-phase C_3 and the two of its mono ^{13}C substituted isotopologs in the infrared region around 3200 cm^{-1}. Additionally, the associated hot band $(11^11) \leftarrow (01^10)$ has been assigned for the parent isotopolog. Spectra have been recorded using a supersonic jet spectrometer with a laser ablation source in combination with a continuous-wave optical parametric oscillator as radiation source. High-level quantum-chemical ab initio calculations have been performed and used to assist the assignment. A combined fit for the vibrational states of C_3 found in this study has been done together with previously reported high-resolution data to increase the accuracy of the molecular parameters, especially for the ground state. The vibrational energies are 3260.126, 3205.593, and 3224.751 cm^{-1} for the (10^01) state of C_3, $^{12}C^{13}C^{12}C$, and $^{13}C^{12}C^{12}C$, respectively. The (11^11) state of C_3 has been found to be at 3330.509 cm^{-1}.



INTRODUCTION

The carbon cluster C_3 is of fundamental interest for its role in combustion processes and molecular astrophysics, and it also serves as a benchmark system for quantum chemistry. Among the known linear pure carbon clusters, it is the only "floppy" one; i.e. its bending motion has a very shallow, highly anharmonic potential. This gives rise to a large amplitude bending motion which complicates the description of the internal dynamics. For this reason, C_3 has been subject to several theoretical treatments using different approaches,[1,2] and different experimental methods have been applied to analyze its rotational and vibrational energy levels.

The first spectroscopic detection of C_3 by assignment of cometary features around 4050 Å to lab spectra goes back to Douglas in 1951.[3] Gausset et al. analyzed these bands in more detail in 1965,[4] obtaining ground state combination differences. The first high-resolution (10^{-3} cm^{-1}, $\Delta\nu/\nu = 5 \times 10^{-7}$) rovibrational detection of C_3 in its $^1\Sigma_g^+$ electronic ground state was performed in 1988 by Matsumura et al. using tunable diode laser absorption spectroscopy.[5] C_3 was produced via photolysis of the precursor molecules diacetylene and allene and probed in its ν_3 vibrational fundamental around 2040 cm^{-1}. Soon after, the same group published measurements of associated hot bands[6] involving the singly and doubly excited bending vibrational mode ν_2. C_3 has also been detected in space via the antisymmetric stretch ν_3.[7] The ν_2 bending mode in the far-infrared has also been observed in space[8,9] as well as in the laboratory.[10]

Methods like laser-induced fluorescence spectroscopy and stimulated emission pumping (SEP) were used to measure a significant number of additional vibrational levels.[11,12] Because of the high frequency of the applied lasers (typically in the UV), frequency resolution and accuracy are of the order of 10^{-2} cm^{-1} or worse. However, infrared-inactive transitions were measured this way, for example, the energy of the ν_1 vibrational fundamental at 1226 cm^{-1}.[13]

The region of the combination bands involving the two stretching modes around 3250 cm^{-1} remained largely unexplored thus far, except for C_3 trapped in inert-gas matrices. There, values of 3245.2 and 3255.6 cm^{-1} were obtained for the (10^01) mode in solid argon[14] and solid neon,[15] respectively.

In the experiment described in the following, a supersonic jet spectrometer featuring a home-built optical parametric oscillator (OPO) providing output around 3 μm wavelength

Received: December 4, 2012
Revised: March 8, 2013
Published: March 11, 2013

 © 2013 American Chemical Society

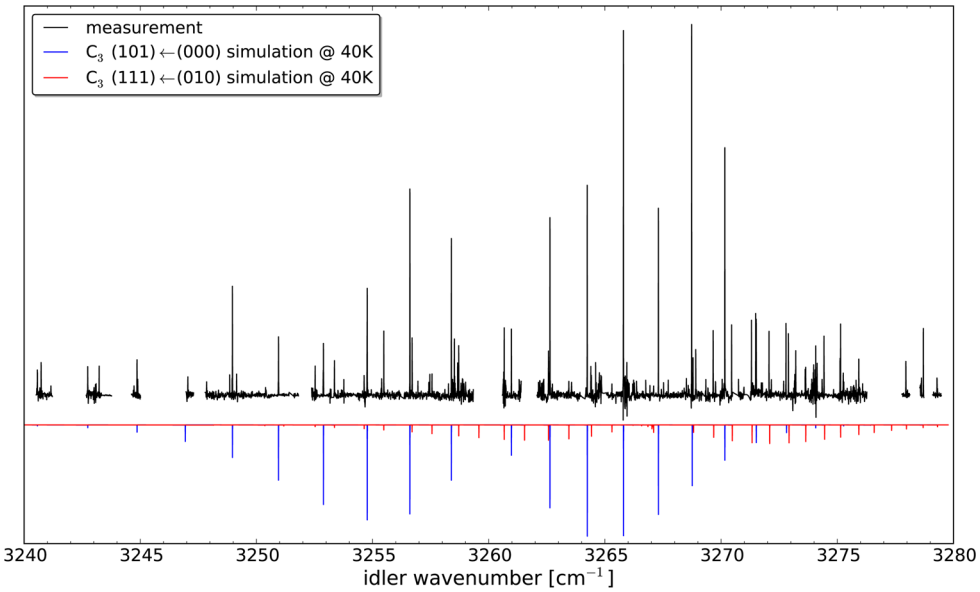


Figure 1. Overview of the experimental spectrum of $^{12}C_3$ in the range 3240−3280 cm^{-1}. The simulations of the two vibrational bands assigned here has been performed using the PGOPHER program.[16]

as radiation source has been used to perform high-resolution rovibrational spectroscopy of gas-phase C_3 in the wavenumber range from 3190 to 3280 cm^{-1}.

■ EXPERIMENT

The experimental setup used for the present study is a combination of an optical parametric oscillator serving as infrared radiation source, a laser ablation setup for production of C_3 in a pulsed supersonic jet, and a sensitive detection unit comprising liquid nitrogen-cooled HgCdTe detectors. Ablation precursors were solid rods of graphite which are commercially available (Sigma Aldrich). For measurements of ^{13}C isotopologs, sample rods enriched in ^{13}C to 25% were used which were obtained by compressing appropriate powder mixtures of graphite and amorphous ^{13}C (99%, Sigma Aldrich) and little corn starch solution acting as glue.

In the laser-ablation process, the solid precursor is target to a high-energy pulse from a Q-switched Nd:YAG laser which is frequency multiplied to its third harmonic at λ = 355 nm. At a backing pressure of helium buffer gas of approximately 15 bar, the ablated material is transported through a reaction channel with a rectangular cross section (slit nozzle length 10 mm, cross section 1 mm × 15 mm), in which carbon clusters form. After passing this channel, the cluster pulse expands adiabatically into a vacuum chamber kept at a background pressure around 10^{-2} mbar. Using this method, rotational temperatures typically reach values of 20 to 40 K in the jet, while vibrational temperatures usually are significantly higher.

The infrared probe beam intersects the cluster pulse orthogonally to its direction of propagation, and the transmitted intensity is recorded as a function of frequency. The spectrometer reaches a wavenumber accuracy on the order of a few times 10^{-4} cm^{-1}, while the C_3 absorption lines exhibit typical widths of roughly 100 MHz, limited by the jet expansion along the line of sight. Spectra are recorded using a classical absorption spectroscopy scheme. Details about the radiation source can be found in the Supporting Information.

The frequency calibration has been performed as described in detail in the Supporting Information. However, due to the rather sparse spectra of suitable reference gases (NH_3 and H_2O) and the limited continuous tuning range of the OPO idler frequency, a calibration in the mentioned way was not possible for every individual scan. Transitions have been assigned a somewhat larger uncertainty (0.002 cm^{-1}), when no water vapor or ammonia absorption line was covered in a given scan. The uncertainty of 0.002 cm^{-1} for those lines was estimated conservatively from the maximum wavemeter offsets observed in the present study.

■ MEASUREMENT AND RESULTS

$^{12}C^{12}C^{12}C$ Main Isotopolog. In the present investigation, a total of 57 rovibrational transitions has been measured in the wavenumber range covering more than 45 cm^{-1} between 3233.8 and 3280.6 cm^{-1}. The data were reduced applying least-squares-fitting using a standard linear molecule Hamiltonian. An overview spectrum including a simulation of the C_3 transitions is shown in Figure 1. Table 1 lists all 23 measured transitions which have been assigned to the $(10^01) \leftarrow (00^00)$ combination band of C_3. The 6*B* spacing between the *P*(2) and *R*(0) transitions is a characteristic feature of a σ-vibrational band of a molecule with Bose-Einstein statistics and zero-spin nuclei. The spacing between adjacent lines in the *P*- and *R*-branch is 4*B* for the same reason. This finding makes the presented assignment unambiguous. Thirty-four transitions accompanying the $(10^01) \leftarrow (00^00)$ band were assigned to the $(11^11) \leftarrow (01^10)$ hot band, as listed in Table 2. Such a hot band originating from a degenerate bending mode is of π symmetry and exhibits an almost regular spectrum. The spacing between lines is 2*B* in a first approximation, but close inspection reveals so-called staggering; i.e., the spacing between neighboring lines alternates as a result of Bose-Einstein nuclear spin statistics, and *l*-type doubling leading to separate *e* and *f* states. A weak *Q*-branch is characteristic of these bands at the band origin. Figure 2 features the observed *Q*-branch of the $(11^11) \leftarrow (01^10)$ hot band together with the much stronger *R*(8) transition of the $(10^01) \leftarrow (00^00)$ combination band and gives an impression of the intensity ratios. The hot band

Table 1. Transition Wavenumbers of the (101) ← (000) Band of C_3 (in cm^{-1})

J	$P(J)^a$	$o-c^b$ ($\times 10^3$)	$R(J)^a$	$o-c^b$ ($\times 10^3$)
0	–	–	3260.9744(6)	−1.0
2	3258.3915(5)	−0.6	3262.6340(20)	0.1
4	3256.6061(5)	−0.3	3264.2415(5)	0.3
6	3254.7701(5)	−0.5	3265.7983(5)	1.0
8	3252.8857(5)	0.5	3267.3032(20)	0.6
10	3250.9513(5)	0.4	3268.7595(20)	2.3
12	3248.9690(20)	0.5	3270.1620(5)	0.4
14	3246.9399[c]	–	3271.5163(5)	0.1
16	3244.8634(5)	0.2	3272.8208(5)	−0.8
18	3242.7418(5)	−0.3	3274.0776(5)	−0.6
20	3240.5760(20)	−0.4	3275.2857[c]	–
22	3238.3673(7)	0.4	3276.4472[c]	–
24	3236.1143(5)	0.0	3277.5579[c]	–
26	3233.8189(5)	0.2	3278.6059(5)[d]	−17.5

[a]Experimental uncertainties are given in parentheses in units of the last significant digits. [b]Best fit residuals. Fit parameters are listed in Table 3. [c]Calculated using best fit parameters from Table 3. [d]Line excluded from fit due to large deviation from the calculated value.

roughly has 15−20% of the intensity found for the combination band originating from the ground vibrational state.

The new data from the present study have been included into a combined fit also taking into account data from previous high-resolution studies involving the (00^00), (01^10), (00^01), (01^11), (10^01), and (11^11) vibrational states (Table 3). A corresponding vibrational energy level diagram is given in Scheme 1, where all vibrational transitions included in the present fit have been indicated and states common to different experimental studies can easily be identified.

A least-squares fit has been performed using the PGOPHER[16] program using a standard linear molecule Hamiltonian. For the σ states (00^00), (00^01), and (10^01) the rovibrational energies are determined by

$$E(J)/h = \nu + BF - DF^2 + HF^3 + LF^4 + \ldots \quad (1)$$

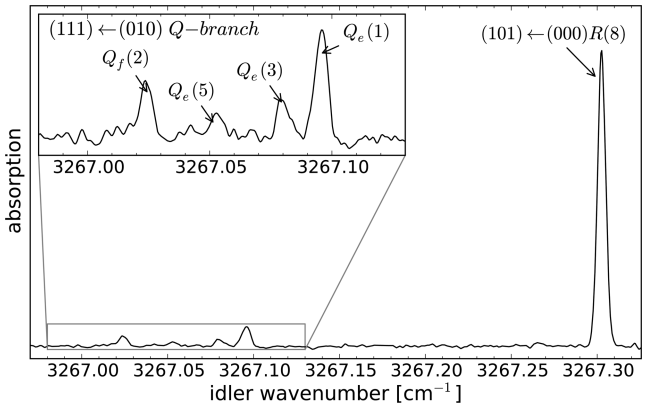


Figure 2. Q-branch of the (11^11) ← (01^10) hot band of C_3 together with the $R(8)$ transition of the (10^01) ← (00^00) band.

with $F = J(J + 1)$, where J is the rotational angular momentum quantum number. Energy levels for the π states (01^10), (01^11), and (11^11) are expressed as

$$E_{\pm}(J)/h = \nu + BF_l - DF_l^2 + HF_l^3 + LF_l^4 + \ldots \pm \frac{1}{2}\{qF + q_JF^2 + q_{JJ}F^3 + \ldots\} \quad (2)$$

with $F_l = J(J + 1) - l^2$, F defined as for eq 1, and l as the vibrational angular momentum quantum number. E_+ (E_-) refers to states with even (odd) parity.

The overall agreement of the combined fit with previously reported values is very good, and the parameters have been determined very precisely, especially for the ground state. In general, there is also good agreement between the experimental parameter values and those calculated with the MORBID program (see below). However, for the band centers of the bands reported here, the deviations are as large as 15 cm^{-1}, corresponding to a relative deviation of about 0.5%. The overall average deviation of calculated to measured values for the

Table 2. Transition Wavenumbers of the (11^11) ← (01^10) Hot Band of C_3 (in cm^{-1})

J	$P(J)^a$	$o-c^b$ ($\times 10^3$)	$Q(J)^a$	$o-c^b$ ($\times 10^3$)	$R(J)^a$	$o-c^b$ ($\times 10^3$)
1e	–	–	3267.0962(20)	0.3	3268.8181(20)	1.3
2f	3265.3039(5)	0.3	3267.0249(20)	0.4	3269.6834(5)	0.1
3e	3264.4199(5)	−1.5	3267.0807(20)	0.4	3270.4783(20)	−2.1
4f	3263.4510(5)	0.2	3266.8499(20)	−1.0	3271.3342(5)	1.0
5e	3262.5698(20)	0.0	3267.0536(20)	1.5	3272.0907(5)	0.9
6f	3261.5413[c]	–	3266.5786(20)	−0.4	3272.9241(5)	−0.4
7e	3260.6648(8)	−0.6	–	–	3273.6445(5)	−0.2
8f	3259.5762[c]	–	–	–	3274.4576(5)	0.4
9e	3258.7078(5)	−1.1	–	–	3275.1458(5)	0.7
10f	3257.5567(5)	0.2	–	–	3275.9302(10)	−1.4
11e	3256.7012(5)	0.4	–	–	3276.5911[c]	–
12f	3255.4817(9)	−1.4	–	–	3277.3478[c]	–
13e	3254.6373(5)[d]	−4.6	–	–	3277.9794(5)[d]	−3.1
14f	3253.3574(5)	0.0	–	–	3278.7060(5)	−0.1
15e	3252.5309(20)	−1.7	–	–	3279.3192(5)	−0.2
16f	3251.1804(5)	0.1	–	–	3280.0066[c]	–
17e	3250.3733[c]	–	–	–	3280.6030(20)	1.5
18f	3248.9538(20)	1.0	–	–	3281.2493[c]	–

[a]Experimental uncertainties are given in parentheses in units of the last significant digits. [b]Best fit residuals. Fit parameters are listed in Table 3. [c]Calculated using best fit parameters from Table 3. [d]Line excluded from fit due to large deviation from the calculated value.

Table 3. Best Fit Molecular Parameters of C_3 (in cm^{-1})

vibrational state	parameter	this work (combined fit)[a,b]	Gendriesch et al. (2003)[b,c]	refit of Kawaguchi et al. (1989)[b,d]	theoretical estimate[e]	MORBID[f]
(00^00)	B	0.4305728(19)	0.4305726(47)	0.430584(24)	0.42418	0.43035
	$D \times 10^6$	1.471(13)	1.478(13)	1.479(28)	–	1.39
	$H \times 10^9$	0.1330(75)	0.136(61)	0.1351(96)	–	–
(01^10)	ν	63.4165946(77)	63.4165889(54)	63.4165889	61.8	62.2
	B	0.4424042(16)	0.4424043(36)	0.442383(18)	0.44397	0.44155
	$D \times 10^6$	2.336(11)	2.346(13)	2.323(27)	–	2.09
	$H \times 10^9$	0.244(10)	0.257(12)	0.248(12)	–	–
	$q \times 10^3$	5.6930(12)	5.6935(25)	5.616(27)	–	5.68
	$q_J \times 10^6$	−0.886(26)	−0.879(30)	−0.758(23)	–	−0.849
	$q_{JJ} \times 10^{12}$	60.(23)	40.(26)	–	–	–
(00^01)	ν	2040.019278(67)	–	2040.01930(66)	2052.3	2039.9
	B	0.4356969(56)	–	0.435708(26)	0.42086	0.43544
	$D \times 10^6$	4.312(59)	–	4.321(38)	–	3.66
	$H \times 10^9$	0.984(85)	–	0.987(26)	–	–
	$L \times 10^{12}$	−0.176(41)	–	−0.1765(92)	–	–
	$M \times 10^{15}$	0.0165(68)	–	0.0166(14)	–	–
(01^11)	ν	2078.500541(67)	–	2078.50052(57)	2092.6	2077.3
	B	0.4499179(35)	–	0.449896(18)	0.44064	0.44911
	$D \times 10^6$	4.919(18)	–	4.905(29)	–	4.38
	$H \times 10^9$	0.738(18)	–	0.740(18)	–	–
	$L \times 10^{12}$	−0.0483(66)	–	−0.0483(53)	–	–
	$q \times 10^3$	8.2483(40)	–	8.172(28)	–	8.21
	$q_J \times 10^6$	−2.002(22)	–	−1.879(25)	–	−1.67
	$q_{JJ} \times 10^{12}$	277.(18)	–	221.5(43)	–	–
(10^01)	ν	3260.127048(91)	–	–	3256.7	3277.6
	B	0.4241990(25)	–	–	0.41943	0.42423
	$D \times 10^6$	1.0760(99)	–	–	–	0.447
(11^11)	ν	3330.508589(68)	–	–	3328.0	3349.7
	B	0.4354153(62)	–	–	0.43921	0.43427
	$D \times 10^6$	1.955(30)	–	–	–	1.68
	$q \times 10^3$	5.1794(99)	–	–	–	4.99
	$q_J \times 10^6$	−0.655(44)	–	–	–	−0.678

[a]Combined fit, see text. Measurements performed in this work comprise the (11^11) and (10^01) states. [b]Standard deviations are given in parentheses in units of the last significant digits. [c]Reference 17. [d]Refit of data from ref 6 with the ν_2 band center kept fixed at the value given in ref 17. [e]Computed at the ae-CCSD(T)/cc-pCVTZ level of theory. See text for details. [f]Calculated using the MORBID program[1] with potential energy parameter values given by Špirko et al.[2]

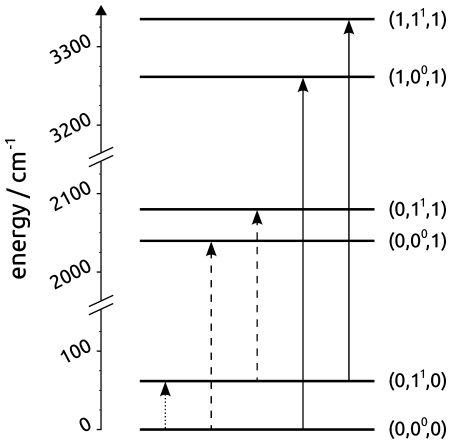
combined fit is 1.34×10^{-3} cm^{-1}, and the dimensionless average-weighted deviation is 1.32.

$^{12}C^{13}C^{12}C$ Isotopolog. Using ^{13}C-enriched samples as described above, we were able to measure the spectrum of the centrally substituted isotopolog of C_3. This is the first high-resolution measurement of this species in the gas phase, and 12 transitions of the $(10^01) \leftarrow (00^00)$ band have been observed (Table 4). Initially, an improved prediction of the location of the band center was calculated by scaling the matrix value reported by Szczepanski and Vala[18] with a correction factor obtained from the matrix- and gas-phase values of the parent isotopolog. Table 5 summarizes all parameters determined by least-squares analysis using the energy expression given in eq 1 for the (00^00) and (10^01) states.

Since $^{12}C^{13}C^{12}C$ is also a centrosymmetric linear molecule with Bose-Einstein statistics and zero-spin nuclei at the two ends, in analogy to its parent isotopic species, one observes a $4B$ spacing of the transitions within the P- and R-branches which are separated by $6B$ at the band origin. Since the $P(2)$ transition has not been measured here, the assignment is in principle ambiguous in one shift of $4B$ ($2J$). However, possible ambiguities in the assignment have been resolved using calculations at different levels of theory in conjunction with a simple second-order vibrational perturbation theory (VPT2)[19] approach (see upcoming section). These numbers have been scaled using the ratio of the experimental and calculated parameters of the main isotopic species. A comparison of the resulting value with the experimental rotational constants for both possible assignments yielded deviations of roughly 10% for one assignment and less than 1% for the second one, hence speaking strongly in favor of the latter assignment (Table 4). This assignment was later additionally confirmed by computations using the MORBID approach. The average deviation of observed and calculated transitions is 0.6×10^{-3} cm^{-3} (dimensionless weighted 0.42).

$^{13}C^{12}C^{12}C$ Isotopolog. Following the strategy applied for the $^{12}C^{13}C^{12}C$ species, the detection and assignment of lines from the $^{13}C^{12}C^{12}C$ species in the $(10^01) \leftarrow (00^00)$ combination band was accomplished in a straightforward manner. Sixteen transitions have been measured; they are listed in Table 6. Since this isotopolog is not centrosymmetric, a regular spectrum common to linear molecules with a $2B$ spacing of the P- and R-branch transitions, and a $4B$ spacing at the band center is observed. The $P(3)$ to $R(0)$ transitions could not be observed, and therefore the assignment of the band center is again based on scaled quantum chemical calculations.

Scheme 1. Vibrational Energy Level Scheme of C_3 with Transitions Included in the Combined Fit Presented Here[a]



[a]The interplay of these transitions can be recognized by shared states. For better comparability of energy differences, the energy scales are the same for all three axis segments. Transitions indicated with a dotted arrow are taken from Gendriesch et al.[17] and those with a dashed arrow from Kawaguchi et al.[6] Solid arrows designate transitions measured in this work.

Table 4. Transition Wavenumbers of the $(10^01) \leftarrow (00^00)$ Band of $^{12}C^{13}C^{12}C$ (in cm^{-1})

J	$P(J)^a$	$o-c^b$ ($\times 10^3$)	$R(J)^a$	$o-c^b$ ($\times 10^3$)
0	–	–	3206.4418(10)	0.1
2	3203.8601[c]	–	3208.1020(20)	−0.3
4	3202.0786(15)	−0.4	3209.7142(20)	−0.4
6	3200.2508(10)	0.5	3211.2776(20)	−0.7
8	3198.3737(20)	−0.8	3212.7938(10)	0.0
10	3196.4519(10)	−0.4	3214.2615(10)	0.4
12	3194.4845(10)	0.2	3215.6799(20)	−0.8

[a]Experimental uncertainties are given in parentheses in units of the last significant digits. [b]Best fit residuals. Fit parameters are listed in Table 5. [c]Calculated using best fit parameters from Table 5.

Similar to the case of $^{12}C^{13}C^{12}C$, calculations have been used to test all five assignments possible by shifting the band center at intervals of 2*B*. Again, only the assignment given in Table 7 results in very good agreement with the calculations and is therefore considered secure.

Moazzen-Ahmadi and McKellar[20] were the first to investigate gas-phase $^{13}C^{12}C^{12}C$ at high resolution in their study of the $(00^01) \leftarrow (00^00)$ fundamental band around 2000 cm^{-1}. These data, along with seven transitions from the far-infrared ν_2 bending mode measured very recently at Cologne using the SuJeSTA Instrument,[21,22] have been used to perform a combined fit of all data as described by eqs 1 and 2. The study of the ν_2 fundamental of $^{13}C^{12}C^{12}C$ will be presented elsewhere. Seventy-six transition frequencies have been used as input, and 15 parameters have been optimized to get a weighted average error of 1.33, corresponding to an unweighted average error of 0.0015 cm^{-1}. The fit parameters are listed in Table 7.

Table 6. Transition Wavenumbers of the $(10^01) \leftarrow (00^00)$ Band of $^{13}C^{12}C^{12}C$ (in cm^{-1})

J	$P(J)^a$	$o-c^b$ ($\times 10^3$)	$R(J)^a$	$o-c^b$ ($\times 10^3$)
0	–	–	3225.5661[c]	–
1	3223.9235[c]	–	3226.3700(10)	1.1
2	3223.0837[c]	–	3227.1603(10)	0.9
3	3222.2317[c]	–	3227.9361(20)	−1.5
4	3221.3654(20)	−2.2	3228.7025(10)	−0.9
5	3220.4872(20)	−4.1	3229.4566(20)	−0.3
6	3219.5997(20)	−3.3	3230.1982(10)	0.1
7	3218.7039(10)	1.2	3230.9261(20)	−1.0
8	3217.7917(10)	1.1	3231.6438(10)	−0.1
9	3216.8658(20)	−1.0	3232.3485[c]	–
10	3215.9316(10)	0.3	3233.0410[c]	–
11	3214.9840(10)	−0.2	3233.7216[c]	–

[a]Experimental uncertainties are given in parentheses in units of the last significant digits. [b]Best fit residuals. Fit parameters are listed in Table 7. [c]Calculated using best fit parameters from Table 7.

CALCULATIONS

Estimates from Vibrational Perturbation Theory. In a preliminary approach to the C_3 problem, the vibrational levels and the rotational constants were computed via VPT2. While VPT2 has conceptual difficulties with the description of large amplitude motions (and with vibrationally floppy molecules in general), the following approach was chosen to assist the spectroscopic line search in the present study—at the beginning of this work no MORBID results were available for the latter purpose.

We computed quadratic, cubic, and semidiagonal quartic force constants as required for the application of VPT2 via numerical differentiation of analytic second derivatives[23] at the coupled-cluster singles and doubles level extended by a perturbative correction for the contribution from triple excitations (CCSD(T)).[24] This procedure was then applied to the parent isotopolog employing a variety of standard basis sets, i.e., ANO1,[25] ANO2,[25] cc-pVTZ,[26] cc-pVQZ,[26] cc-pCVTZ,[27] and cc-pCVQZ.[27] ANO1, ANO2, cc-pVTZ, and cc-pVQZ were used together with the valence-only approximation, and additional results were obtained correlating all electrons with the cc-pVTZ, cc-pVQZ, cc-pCVTZ, and cc-pCVQZ basis sets. C_3 shows difficulties not only in its

Table 5. Best Fit Molecular Parameters of $^{12}C^{13}C^{12}C$ (in cm^{-1})

vibrational state	parameter	this work[a]	theoretical estimate[b]	scaled matrix[c]	MORBID[d]
(00^00)	B	0.430276(27)	0.42387	–	0.43006
	$D \times 10^6$	1.30(12)	–	–	1.38
(10^01)	ν	3205.59319(33)	3202.0	3205.8	3221.8
	B	0.424243(27)	0.41923	–	0.42418
	$D \times 10^6$	1.00(12)	–	–	0.812

[a]Standard deviations are given in parentheses in units of the last significant digits. [b]Computed at the ae-CCSD(T)/cc-pCVTZ level of theory. See text for details. [c]Matrix values in argon from ref 18 are 3245.2 cm^{-1} for C_3 and 3191.1 cm^{-1} for $^{12}C^{13}C^{12}C$. The krypton values yield a very similar result. [d]Calculated from the MORBID program[1] with potential energy parameter values given by Špirko et al.[2]

Table 7. Best Fit Molecular Parameters of $^{13}C^{12}C^{12}C$ (in cm^{-1})

vibrational state	parameter	this work (combined fit)[a,b]	refit of Moazzen- Ahmadi (1993)[b,c]	theoretical estimate[d]	scaled matrix[e]	MORBID[f]
(00^00)	B	0.413741(19)	0.413743(23)	0.40761	–	0.41351
	$D \times 10^6$	1.394(40)	1.398(47)	–	–	1.30
	$H \times 10^9$	0.129(25)	0.130(28)	–	–	–
(01^10)	ν	60.747687(38)	–	61.8	–	61.8
	B	0.424619(22)	–	0.42660	–	0.42427
	$D \times 10^6$	2.50(25)	–	–	–	1.95
	$q \times 10^3$	5.781(35)	–	–	–	5.27
	$q_J \times 10^6$	–	–	–	–	−0.773
(00^01)	ν	2027.20779(53)	2027.20780(57)	2039.4	2027.3	2026.9
	B	0.418741(22)	0.418743(26)	0.40442	–	0.41852
	$D \times 10^6$	4.164(60)	4.168(69)	–	–	3.59
	$H \times 10^9$	1.044(71)	1.047(78)	–	–	–
	$L \times 10^{12}$	−0.197(31)	−0.197(35)	–	–	–
(10^01)	ν	3224.7509(11)	–	3221.4	3224.6	3241.4
	B	0.407586(52)	–	0.40308	–	0.40764
	$D \times 10^6$	0.94(42)	–	–	–	0.270

[a]All states listed here have been included in the combined fit. Measurements of the (10^01) state have been done within the scope of this study, and the (01^10) state has been detected by our group recently.[21] [b]Statistical standard deviations are given in parentheses in units of the last significant digits. [c]Refit of data given in ref 20. [d]Computed at the ae-CCSD(T)/cc-pCVTZ level of theory. See text for details. [e]Argon matrix values for ν_3 from ref 18 are 2038.9 cm^{-1} for C_3 and 2026.2 cm^{-1} for $^{13}C^{12}C^{12}C$. For the $\nu_1 + \nu_3$ band, 3245.2 cm^{-1} for C_3 and 3209.8 cm^{-1} for $^{13}C^{12}C^{12}C$ has been reported. The krypton values yield a very similar result. [f]Calculated from the MORBID program as described by Jensen[1] with potential energy parameter values given by Špirko et al.[2]

vibrational-rotational behavior but also has peculiarities in the description of its electronic structure. A rather unusual basis set dependence was found which results in significant discrepancies with the available experimental data if, e.g., the cc-pCVQZ or larger basis sets are employed. Therefore, we resorted to a more empirical choice of basis and selected the method/basis set combination which resembled best the experimental findings for the parent isotopolog. We then computed the ratios between the spectroscopic features obtained for the parent species and the isotopolog and used these factors to scale the experimental results of $^{12}C^{12}C^{12}C$ to assist the spectroscopic determination of the isotopologs by narrowing the frequency range. For simplicity only the results at the unscaled ae-CCSD(T)/cc-pCVTZ level of theory are reported in Tables 3, 5, and 7.

All calculations were carried out using the quantum-chemical program package CFOUR (coupled-cluster techniques for computational chemistry).[28]

MORBID Calculations. For theoretical prediction of the molecular rotation-vibration parameters of C_3 and its monosubstituted isotopologs, calculations using the MORBID program described by Jensen[1] were carried out with the refined values for the required molecular potential energy surface as given by Špirko et al.[2]

To calculate the rotation-vibration energies with MORBID the following basis set was used: The Morse oscillator functions $|n_1 n_3\rangle$, which are used to diagonalize the stretching Hamiltonian, should obey the equation $n_1 + n_3 \leq N_{\text{Stretch}} = 10$. Furthermore we used the $N_{\text{Bend}} = 13$ lowest bending basis functions and the $N = 9(6)$ lowest stretching basis functions of A_1 (B_2) symmetry to diagonalize the final Hamiltonian. For unsymmetrical isotopologs we used the $N = 15$ lowest stretching basis functions of A_1 symmetry. Molecular parameter values were then determined by fitting eqs 1 or 2 through the MORBID-calculated energies for $J \leq 20$.

The potential energy surface used for the MORBID calculations is based on the *ab initio* surface calculated in 1992 by Jensen et al.[29] with the complete-active-space self-consistent-field (CASSCF) method,[29] using the computational resources available at the time. The parameters of this surface were subsequently slightly refined in a least-squares fitting to the experimental wavenumber data available in 1992 to produce the parameter values given by Špirko et al.[2]

DISCUSSION

The combined fit of high-resolution data available for C_3 performed here shows that the weighted deviations for the $(10^01) \leftarrow (00^00)$ band are somewhat smaller than those of the $(11^11) \leftarrow (01^10)$ band, even though the same procedure has been performed to calibrate the transition wavenumbers. The fact that the fit gets worse for the $(11^11) \leftarrow (01^10)$ band may be indicative of shortcomings in a standard Hamiltonian applied to pathological molecules such as C_3.

The detection of the new bands of C_3 at high resolution in the gas phase provides new valuable data for this fundamental molecule especially on the vibrational energies and allows deducing information about the molecular potential. In the customary approach, the vibrational energy levels G of C_3 can be expressed as follows:[30,31]

$$G(v_1, v_2, v_3) = \sum_r \omega_r \left(v_r + \frac{d_r}{2}\right) + \sum_{r \leq s} x_{rs} \left(v_r + \frac{d_r}{2}\right)\left(v_s + \frac{d_s}{2}\right) + \sum_{r \leq s} g_{rs} l_r l_s \ldots \quad (3)$$

with the harmonic frequencies ω and the anharmonicity constants x_{rs} and g_{rs}, the latter of which are only relevant in the case of at least two quanta excited in the bending mode. The indices r and s represent the vibrational modes of the molecule, v is the corresponding vibrational quantum number, d the degeneracy of that mode, and $l\hbar$ the associated vibrational

angular momentum. In the present case of a binary combination band of two vibrational modes ν_1 and ν_3 with the frequencies $\nu_1 = G(1,0,0) - G(0,0,0)$ and $\nu_3 = G(0,0,1) - G(0,0,0)$, its frequency $\nu_{1+3} = G(1,0,1) - G(0,0,0)$ simplifies using the above equation to

$$\nu_{1+3} = \nu_1 + \nu_3 + x_{13} \tag{4}$$

neglecting higher-order terms in the anharmonic potential. Since both of the fundamental wavenumbers ν_1 = 1226.6(10) cm^{-1} and ν_3 = 2040.0198(8) cm^{-1} are known from experiments,[5,13,32] the anharmonicity constant x_{13} can be estimated from the present measurements of ν_{1+3} = 3260.1265(8) cm^{-1} as x_{13} = −6.5(10) cm^{-1}. The large uncertainty is due to the measurement of the ν_1 band using emission pumping spectra in the UV and visible, where the frequency accuracy is not as high as in the present infrared work.

The energy difference of the hot band $(11^11) \leftarrow (01^10)$ has been determined from the fit precisely to be ν_{1+2+3} = 3330.50860(1) cm^{-1}. Using eqs 3 and 4 neglecting higher order terms, one obtains for the frequency ν_{1+2+3} of the combination band (11^11)

$$\begin{aligned}\nu_{1+2+3} &= \nu_1 + \nu_2 + \nu_3 + x_{12} + x_{23} + x_{13}\\ &= \nu_{1+3} + \nu_2 + x_{12} + x_{23}\end{aligned} \tag{5}$$

so that with the known frequencies ν_{1+3}, ν_{1+2+3}, ν_2 (see Table 3) one obtains a very accurate value for the sum $x_{12} + x_{23}$ = +6.9655(2) cm^{-1}. Using data from the $(01^11) \leftarrow (01^10)$ hot band by Kawaguchi et al.,[6] the value of x_{23} = −38.930(4) cm^{-1} can be calculated and by eliminating that number, one obtains an estimate of x_{12} = +45.896(4) cm^{-1}.

The 20-year-old CASSCF potential energy surface,[29] which serves as the starting point for the MORBID calculations of the present work, is clearly less accurate than the new ae-CCSD(T)/cc-pCVTZ force field reported above, as witnessed by the fact that the band centers calculated directly from the CASSCF surface[29] are only in fair agreement with the corresponding experimental values available. By refining the CASSCF surface in a least-squares fitting to the experimental band center values available in 1992, good agreement with experiment was achieved for the vibrational energies of the corresponding states (Table 3). As experimentally derived values for the (10^01) and (11^11) band centers were not available at the time of the least-squares fitting, their agreement with experiment is still essentially determined by the information from the CASSCF surface and therefore comparatively poor. One way of remedying this would be a new least-squares fitting to the experimental wavenumber data currently available. It is remarkable, however, that even with this somewhat deficient potential energy surface, MORBID produces B values whose deviations from experiment are typically an order of magnitude smaller than the deviations of the B values calculated from the CCSD(T) force field in the present work. This may suggest that the curvilinear bending coordinate used by MORBID (almost, but not quite, equal to the bond angle supplement 180° − ∠(CCC)) gives a better description of the large-amplitude bending motion than the rectilinear normal coordinates used in the VPT2 model (which describe motion of the nuclei along straight lines). However, it is currently hard to determine if the approaches to the nuclear motion problem of C_3 used are well suited or not, as neither the semiempirical potential energy surface used with the MORBID program nor the current CCSD(T) force field can be considered accurate enough for this comparison.

CONCLUSIONS

The $(10^01) \leftarrow (00^00)$ and $(11^11) \leftarrow (01^10)$ vibrational bands of gas-phase C_3 in its electronic ground state have been measured at high spectral resolution and high accuracy for the first time. Rotational and centrifugal distortion constants have been determined for these states, which are in good agreement with theoretical estimates. The relative accuracy $\Delta\nu/\nu$ of the measured transition wavenumbers is of the order of 1.7×10^{-7} cm^{-1} (absolute accuracy 5×10^{-4} or 15 MHz) and even slightly better than the precision of previous far-infrared measurements ($\Delta\nu/\nu = 2.5 \times 10^{-7}$).[17] The broad wavenumber coverage of our OPO-based system resulted in a large number of observable transitions. In all, the present experiment results in a significant extension of the available data set for the C_3 molecule.

In the jet, we do not find any evidence for any ^{13}C enrichment in the terminal position as suggested elsewhere.[33] From our experiment, we conclude that the ^{13}C and ^{12}C isotopes are partitioned statistically in the C_3 molecule to the extent of our sensitivity.

Searches for other infrared-active vibrational bands of C_3 are worth conducting in the future, and, as shown in this study, the combination of the jet spectrometer with an OPO is an ideal tool for such broadband experiments. For example, the bands $(12^01) \leftarrow (00^00)$ or other hot bands $(1\ 2x\ 1) \leftarrow (0\ 2x\ 0)$, with x = 2, 4, ..., are promising targets at 3 μm wavelength. In the future, a combined fit of even more rovibrational measurements as well as a new, more reliable and accurate ab initio potential energy surface of C_3 will provide an excellent basis for an improved understanding of this peculiar molecule.

ASSOCIATED CONTENT

Supporting Information

Detailed descriptions of the home-built continuous-wave optical parametric oscillator used in this study as well as the detection technique and frequency calibration. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: krieg@ph1.uni-koeln.de (J.K.); sthorwirth@ph1.uni-koeln.de (S.T.). Phone: +49 (0)221 470-1936. Fax: +49 (0)221 470-5162.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge support by the Deutsche Forschungsgemeinschaft (DFG grants TH 1301/3-1 and JE 144/24-1) and additional funding by DFG grant SFB 956. Support for M.E.H. and J.V. was provided by grants from the U.S. National Science Foundation (Grant CHE0710146), the U.S. Department of Energy, BasicEnergy Sciences (Contract FG02-07ER15884), and the Robert A. Welch Foundation (Grant F-1283) to Professor John F. Stanton of the University of Texas at Austin.

REFERENCES

(1) Jensen, P. A New Morse Oscillator-Rigid Bender Internal Dynamics (MORBID) Hamiltonian for Triatomic Molecules. *J. Mol. Spectrosc.* **1988**, *128*, 478−501.

(2) Špirko, V.; Mengel, M.; Jensen, P. Calculation of Rotation-Vibration Energy Levels in Ground State C_3 by a Born-Oppenheimer-Type Separation of the Vibrational Motions. *J. Mol. Spectrosc.* **1997**, *183*, 129−138.

(3) Douglas, A. E. Laboratory Studies of the λ 4050 Group of Cometary Spectra. *Astrophys. J.* **1951**, *114*, 466−468.

(4) Gausset, L.; Herzberg, G.; Lagerqvist, A.; Rosen, B. Analysis of the 4050-Å Group of the C_3 Molecule. *Astrophys. J.* **1965**, *142*, 45−76.

(5) Matsumura, K.; Kanamori, H.; Kawaguchi, K. Infrared Diode Laser Kinetic Spectroscopy of the ν_3 Band of C_3. *J. Chem. Phys.* **1988**, *89*, 3491−3494.

(6) Kawaguchi, K.; Matsumura, K.; Kanamori, H.; Hirota, E. Diode Laser Spectroscopy of C_3: The $\nu_2 + \nu_3 - \nu_2$, $2\nu_2 + \nu_3 - 2\nu_2$, and $2\nu_2 + \nu_3$ Bands. *J. Chem. Phys.* **1989**, *91*, 1953−1957.

(7) Hinkle, K. H.; Keady, J. J.; Bernath, P. F. Detection of C_3 in the Circumstellar Shell of IRC+10216. *Science* **1988**, *241*, 1319−1322.

(8) Giesen, T. F.; van Orden, A.; Cruzan, J. D.; Provencal, R. A.; Saykally, R. J.; Gendriesch, R.; Lewen, F.; Winnewisser, G. Interstellar Detection of CCC and High-Precision Laboratory Measurements Near 2 THz. *Astrophys. J.* **2001**, *551*, L181−L184.

(9) Mookerjea, B.; Giesen, T.; Stutzki, J.; Cernicharo, J.; Goicoechea, J. R.; de Luca, M.; Bell, T. A.; Gupta, H.; Gerin, M.; Persson, C. M.; et al. Excitation and Abundance of C_3 in Star Forming Cores. Herschel/HIFI Observations of the Sight-Lines to W31C and W49N. *Astron. Astrophys.* **2010**, *521*, L13−L13−5.

(10) Schmuttenmaer, C. A.; Cohen, R. C.; Pugliano, N.; Heath, J. R.; Cooksy, A. L.; Busarow, K. L.; Saykally, R. J. Tunable Far-IR Laser Spectroscopy of Jet-Cooled Carbon Clusters: The ν_2 Bending Vibration of C_3. *Science* **1990**, *249*, 897−900.

(11) Baker, J.; Bramble, S. K.; Hamilton, P. A. A Hot Band LIF Study of the $A^1\Pi_u$−$X^1\Sigma_g^+$ Transition in C_3. *Chem. Phys. Lett.* **1993**, *213*, 297−302.

(12) Rohlfing, E. A. Laser-Induced-Fluorescence Spectroscopy of Jet-Cooled C_3. *J. Chem. Phys.* **1989**, *91*, 4531−4542.

(13) Northrup, F. J.; Sears, T. J. Stimulated-Emission Pumping Spectroscopy Study of Jet-Cooled C_3: Pure Bending Levels and Bend-Symmetric-Stretch Combination Levels of $\tilde{X}^1\Sigma_g^+$. *J. Opt. Soc. Am. B* **1990**, *7*, 1924−1934.

(14) Ortman, B. J.; Hauge, R. H.; Margrave, J. L.; Kafafi, Z. H. Reactions of Small Carbon Clusters with Water in Cryogenic Matrixes. The FTIR Spectrum of Hydroxyethynyl Carbene. *J. Phys. Chem.* **1990**, *94*, 7973−7977.

(15) Gonzalez, E.; Rittby, C. M. L.; Graham, W. R. M. Isotopic Study of New Fundamentals and Combination Bands of Linear C_5, C_7, and C_9 in Solid Ar. *J. Phys. Chem. A* **2011**, *115*, 2533−2539.

(16) Western, C. M. PGOPHER, a Program for Simulating Rotational Structure, version 7.1, http://pgopher.chm.bris.ac.uk.

(17) Gendriesch, R.; Pehl, K.; Giesen, T.; Winnewisser, G.; Lewen, F. Terahertz Spectroscopy of Linear Triatomic CCC: High Precision Laboratory Measurement and Analysis of the Ro-Vibrational Bending Transitions. *Z. Naturforsch., A: Phys. Sci.* **2003**, *58*, 129−138.

(18) Szczepanski, J.; Vala, M. The $\nu_1 + \nu_3$ Combination Mode of C_3 in Ar and Kr Matrices: Evidence for a Bent Structure. *J. Chem. Phys.* **1993**, *99*, 7371−7375.

(19) Mills, I. M. In *Molecular Spectroscopy: Modern Research*; Rao, K. N., Mathews, C. W., Eds.; Academic Press Inc.: New York, 1972.

(20) Moazzen-Ahmadi, N.; McKellar, A. R. W. Infrared Diode Laser Spectroscopy of the ν_3 Fundamental and $\nu_3 + \nu_2 - \nu_2$ Sequence Bands of $^{13}C_3$ and of the ν_3 Fundamental Band of $^{12}C^{12}C^{13}C$. *J. Chem. Phys.* **1993**, *98*, 7757−7762.

(21) Endres, C. Unpublished results.

(22) Caris, M.; Giesen, T. F.; Duan, C.; Müller, H. S. P.; Schlemmer, S.; Yamada, K. M. T. Sub-Millimeter Wave Spectroscopy of the C_3H Radical: Ro-Vibrational Transitions from Ground to the Lowest Bending State. *J. Mol. Spectrosc.* **2009**, *253*, 99−105.

(23) Stanton, J. F.; Lopreore, C. L.; Gauss, J. The Equilibrium Structure and Fundamental Vibrational Frequencies of Dioxirane. *J. Chem. Phys.* **1998**, *108*, 7190−7196.

(24) Gauss, J.; Stanton, J. F. Analytic CCSD(T) Second Derivatives. *Chem. Phys. Lett.* **1997**, *276*, 70−77.

(25) Almlöf, J.; Taylor, P. R. General Contraction of Gaussian Basis Sets. I. Atomic Natural Orbitals for First- and Second-Row Atoms. *J. Chem. Phys.* **1987**, *86*, 4070−4077.

(26) Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron Through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(27) Woon, D. E.; Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. V. Core-Valence Basis Sets for Boron Through Neon. *J. Chem. Phys.* **1995**, *103*, 4572−4585.

(28) CFOUR, Coupled-Cluster Techniques for Computational Chemistry, a quantum-chemical program package by Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G., with contributions from Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; Cheng, L.; Christiansen, O.; Heckert, M.; Heun, O.; Huber, C.; Jagau, T.-C.; Jonsson, D.; Jusélius, J.; Klein, K.; Lauderdale, W. J.; Matthews, D. A.; Metzroth, T.; Mück, L. A.; O'Neill, D. P.; Price, D. R.; Prochnow, E.; Puzzarini, C.; Ruud, K.; Schiffmann, F.; Schwalbach, W.; Stopkowicz, S.; Tajti, A.; Vázquez, J.; Wang, F.; Watts, J. D., and the integral packages MOLECULE (Almlöf, J. and Taylor, P. R.), PROPS (Taylor, P. R.), ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; and Olsen, J.), and ECP routines by Mitin, A. V. and van Wüllen, C. For the current version, see http://www.cfour.de.

(29) Jensen, P.; Rohlfing, C. M.; Almlöf, J. Calculation of the Complete-Active-Space Self-Consistent-Field Potential-Energy Surface, the Dipole Moment Surfaces, the Rotation-Vibration Energies, and the Vibrational Transition Moments for $C_3(\tilde{X}^1\Sigma_g^+)$. *J. Chem. Phys.* **1992**, *97*, 3399−3411.

(30) Bernath, P. E. *Spectra of Atoms and Molecules*, 2nd ed.; Oxford University Press, New York, 2005.

(31) Duncan, J. L. The Determination of Vibrational Anharmonicity in Molecules from Spectroscopic Observations. *Spectrochim. Acta, Part A* **1991**, *47*, 1−27.

(32) Merer, A. J. Absorption Spectra of C_3 and C_3H_2 from the Flash Photolysis of Diazopropyne. *Can. J. Phys.* **1967**, *45*, 4103−4111.

(33) McAnoy, A. M.; Dua, S.; Schröder, D.; Bowie, J. H.; Schwarz, H. The Formation of Neutral CCC and Its Radical Cation from the CCC Radical Anion in the Gas Phase. A Joint Experimental and Theoretical Study. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1647−1652.