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## The electronic spectrum of the $C_s$ - $C_{11}H_3$ radical

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The electronic gas-phase absorption spectrum of the bent carbon-chain radical,  $HC_4CHC_6H$  with  $C_s$  symmetry, is recorded in the 595 nm region by cavity ring-down spectroscopy through an expanding hydrogen plasma. An unambiguous spectroscopic identification becomes possible from a systematic deuterium labeling experiment. A comparison of the results with recently reported spectra of the nonlinear  $HC_4CHC_4H$  and  $HC_4C(C_2H)C_4H$  radicals with  $C_{2v}$  symmetry provides a more comprehensive understanding of the molecular behavior of  $\pi$ -conjugated bent carbon-chain systems upon electronic excitation. We find that the electronic excitation in the bent carbon-chain  $HC_4CHC_{2n}H$  ( $n = 1-4$ ) series exhibits a similar trend as in the linear  $HC_{2n+1}H$  ( $n = 3-6$ ) series, shifting optical absorptions towards longer wavelengths for increasing overall bent chain lengths. The  $\pi$ -conjugation in bent  $HC_4CHC_{2n}H$  ( $n = 1-4$ ) chains is found to be generally smaller than in the linear  $HC_{2n+1}H$  ( $n = 3-6$ ) case for equivalent numbers of C-atoms. The addition of an electron-donating group to the bent chain causes a slight decrease of the effective conjugation. © 2012 American Institute of Physics. [doi:10.1063/1.3681259]

### I. INTRODUCTION

Free hydrocarbon-chain radicals with delocalized  $\pi$ -electrons, such as finite polyene ( $-(CH=CH)_n-$ ), polyyne ( $-(C\equiv C)_n-$ ) chains, and cumulene carbenes ( $H_2C(=C)_n-$ ) are important reactive intermediates in the synthesis of new materials such as  $\pi$ -conjugated polymers, carbon nanotubes, and nanowires.<sup>1-4</sup> These reactive species play a role as precursors in the formation of polycyclic aromatic hydrocarbons (PAHs) and fullerenes in hydrocarbon combustion,<sup>5</sup> in plasma environments,<sup>6-8</sup> in terrestrial processes,<sup>9,10</sup> and in dense interstellar clouds.<sup>11-15</sup> Consequently, experimental and theoretical studies dedicated to the nature and unusual electronic and dynamical properties of reactive  $\pi$ -conjugated hydrocarbon chains have attracted much interest.

Recent improvements in the detection sensitivity of optical techniques have made it possible to record electronic gas-phase spectra of carbon-chain radicals in direct absorption and to study the molecular behavior upon electronic excitation.<sup>16</sup> The majority of these species  $XC_nY$  ( $X, Y = H, N, O, \dots$ ) has a linear carbon-chain structure. Subsequent members of the even  $XC_{2n}Y$  (or odd  $XC_{2n+1}Y$ ) chain series have similar electronic configurations. Also several of the spectroscopic parameters depend in a systematic way on the number of C-atoms in the chain, most noticeably the optical absorption wavelength of the electronic origin band in homologous series. This is a consequence of the well known particle-in-a-box behaviour—the longer the chain the more corresponding absorption wavelengths shift to the red.<sup>16-20</sup>

In recent years, several nonlinear planar carbon-chain species have been studied in the gas phase.<sup>21-28</sup> Systematic data for different  $n$ -values are available for chains of the form  $C_{2n+1}H_3$ . It was found that the  $n = 3-6$  species detected in a mass-selective REMPI-TOF experiment<sup>23,24</sup> absorb at very similar energies, and do not shift monotonically with increasing C-atom number. It has become clear that this is at least partially a consequence of the fact that not all the observed spectra correspond to homologues of the same series; the carrier of the  $C_7H_3$  spectrum was unambiguously identified as the 2-(buta-1,3-dienyl)cycloprop-2-ylidene radical containing a three-member ring,<sup>24</sup> whereas the carriers of the  $C_9H_3$  and  $C_{11}H_3$  spectra were determined as nonlinear  $HC_4CHC_4H$  and  $HC_4C(C_2H)C_4H$  structures with  $C_{2v}$  symmetry, respectively.<sup>28</sup> These structures, shown in Figs. 1(a) and 1(b), have similar effective bent chain lengths and consequently absorb at rather comparable wavelengths. Another isomeric structure of  $C_{11}H_3$ — $HC_4CHC_6H$  with  $C_s$  symmetry—has a two-C-atom longer chain length and here an effective redshift is expected. For this reason, in the present work, the optical absorption spectrum of the bent  $C_s$ - $C_{11}H_3$  radical has been searched for in the wavelength range to the red with respect to the origin band transition of  $C_{2v}$ - $C_9H_3$ .<sup>28</sup> An unambiguous identification of the observed bands is possible by applying deuterium labeling as an effective analytical tool to determine the molecular structure. The observed spectra are compared to spectra previously reported for the symmetric and bent  $C_{2v}$ - $C_9H_3$  and  $C_{2v}$ - $C_{11}H_3$ <sup>28</sup> series, as well as for the linear  $HC_{2n+1}H$  ( $n = 3-6$ ) series.<sup>19,29</sup> Based on these experimental findings, the  $\pi$ -conjugation in bent odd-carbon-chain systems will be discussed.

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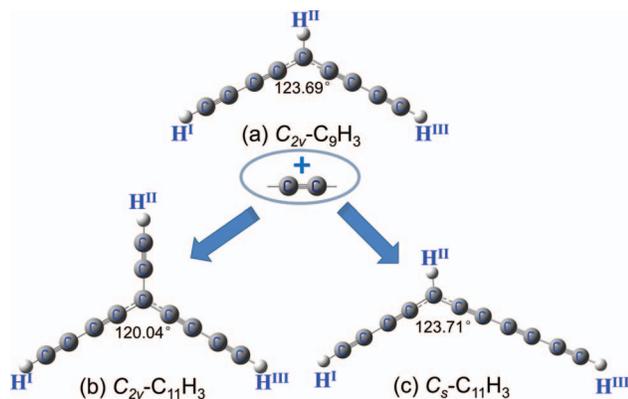


FIG. 1. The molecular structure of (a)  $C_{2v}\text{-C}_9\text{H}_3$ , (b)  $C_{2v}\text{-C}_{11}\text{H}_3$ , as derived in Ref. 28 and (c)  $C_s\text{-C}_{11}\text{H}_3$ . The angles of bent carbon-chain structures are calculated at the B3LYP/6-311G(d, p) level.

## II. EXPERIMENTAL AND THEORETICAL METHODS

### A. Experimental setup

Optical spectra of nonlinear carbon chains are recorded by pulsed cavity ring-down spectroscopy through a supersonically expanding hydrocarbon plasma. The experimental setup has been described in detail before.<sup>28,30</sup> Carbon-chain species are produced in a plasma source by discharging an acetylene/helium gas mixture in a pinhole discharge nozzle, which is specifically suitable for the study of larger carbon-chain species. The precursor gas mixture is expanded with a backing pressure of  $\sim 10$  bar into a vacuum chamber that is pumped by a roots blower system with a total capacity of  $1000\text{ m}^3/\text{hr}$ . The typical stagnation pressure in the chamber during jet operation amounts to  $\sim 0.04$  mbar. Three gas mixtures, 0.4%  $C_2H_2/He$ , 0.2%  $C_2D_2/He$ , and ( $\sim 0.2\%$   $C_2H_2 + 0.15\%$   $C_2D_2)/He$ , are used to create C/H, C/D, and C/H/D plasma jets, respectively. A high voltage pulse ( $\sim 300\ \mu\text{s}$  and  $-1200\text{ V}$ ) is applied to the electrodes of the discharge nozzle and coinciding with a gas pulse of  $\sim 800\ \mu\text{s}$  duration generated by a pulsed valve (General Valve, Series 9) mounted on top of the pinhole discharge body.<sup>28</sup>

The plasma expansion perpendicularly crosses the optical axis of a 58 cm long cavity, approximately 7 mm downstream. This optical cavity consists of two plano-concave mirrors (Research Electro-Optics, two sets of mirrors with reflectivity  $>99.99\%$  at 580 nm and  $>99.998\%$  at 532 nm, respectively) mounted on high-precision alignment tools. Cavity ring-down events are obtained by injecting a dye-laser pulse into the high-finesse optical cavity. Light leaking out of the cavity is detected by a photomultiplier tube and typical ring-down times are in the range of 10–20  $\mu\text{s}$ . The setup is operated at 10 Hz, determined by the repetition rate of a Nd: YAG laser (532 nm and 355 nm) that is used to pump the dye laser (Sirah, Cobra-Stretch, bandwidth  $\sim 0.06\text{ cm}^{-1}$ ). A trigger scheme allows optimizing the timing of the ring-down event with respect to the discharge pulse. The absolute laser frequency is calibrated with an absolute precision better than  $0.02\text{ cm}^{-1}$  using an  $I_2$  absorption reference spectrum that is recorded simultaneously.

### B. Density functional theory calculations

The analysis of the experimental data is supported by density functional theory (DFT) calculations. The calculations are carried out using the GAUSSIAN 03 software package.<sup>31</sup> Apart from  $HC_4CHC_2H$ , all species calculated in this work, including the bent  $HC_4CHC_{2n}H$  ( $n = 2\text{--}4$ ) and linear  $HC_{2n+1}H$  ( $n = 3\text{--}6$ ) chains, have been theoretically studied previously using smaller basis sets.<sup>32,33</sup> In the present work, these carbon-chain species are (re)calculated at the DFT-B3LYP<sup>34</sup> level with larger basis sets. Specifically, the 6-311G (d, p) basis set is employed for the structural optimization and for the calculation of vibrational frequencies. Previous studies have shown that this basis set predicts rotational constants of conjugated carbon chains with reasonably high precision.<sup>28,33,35</sup> The resulting molecular structures are subsequently employed to predict the vertical electronic transition energy by time-dependent density functional response theory (TD-DFT/B3LYP)<sup>36</sup> employing a 6-311++G(2d, p) basis set. Complete active space multiconfiguration SCF calculations<sup>37</sup> with seven electrons and eight orbitals in the active space (CASSCF(7, 8)) are performed for the bent  $HC_4CHC_{2n}H$  ( $n = 1\text{--}4$ ) chains to characterize the role of the active molecular orbitals upon electronic excitation.

TD-DFT predicted values for vertical excitation energies of conjugated hydrocarbons have been argued to be not of highest accuracy because of substantial configuration interaction, while the trend of decreasing excitation energies with increasing chain lengths is nevertheless correctly reproduced.<sup>29,33,38,39</sup> Previous work showed that TD-DFT calculated absorption wavelengths for the bent  $HC_4CHC_4H$  species yielded values very comparable to the experimental ones.<sup>28,32</sup> Therefore, for the purpose of this study the TD-DFT/B3LYP method should be sufficiently accurate to predict electronic transition energies for members of the bent  $HC_4CHC_{2n}H$  ( $n = 1\text{--}4$ ) chains, and to verify the trend in this homologous series.

## III. RESULTS AND ANALYSIS

### A. Experimental spectrum of $C_s\text{-C}_{11}\text{H}_3$

Spectra of the  $C_s\text{-C}_{11}\text{H}_3$  molecule have not been reported so far and here the search for its optical (electronic) absorption spectrum is performed in the 530–620 nm wavelength range by comparing spectra recorded through both C/H and C/D plasma. A strong absorption band is observed at  $\sim 16784\text{ cm}^{-1}$  (labeled as  $h_0$ ) in the C/H plasma, with a corresponding D-isotopically shifted band (labeled as  $d_0$ ) observed at  $\sim 16828\text{ cm}^{-1}$  in the C/D plasma, as shown in Figs. 2(a) and 2(b), respectively. Besides the bands  $h_0$  and  $d_0$ , also two weak bands (labeled as  $h_1$  and  $d_1$  in Fig. 2) are observed in the C/H and C/D plasma, blue shifted by  $\sim 27.2\text{ cm}^{-1}$  and  $26.3\text{ cm}^{-1}$  with respect to  $h_0$  and  $d_0$ , respectively.

Both the  $h_0$  and  $d_0$  bands reflect unresolved P- and R-branch profiles separated by  $\sim 1.0\text{ cm}^{-1}$ . A K-stack structure cannot be resolved. The band  $h_0$  in the C/H plasma exhibits a similar band contour as the electronic origin band of  $C_{2v}\text{-C}_9\text{H}_3$ <sup>28</sup> but is  $\sim 2100\text{ cm}^{-1}$  ( $\sim 66\text{ nm}$ ) red-shifted. The red-shifted wavelength is close to the value of the observed

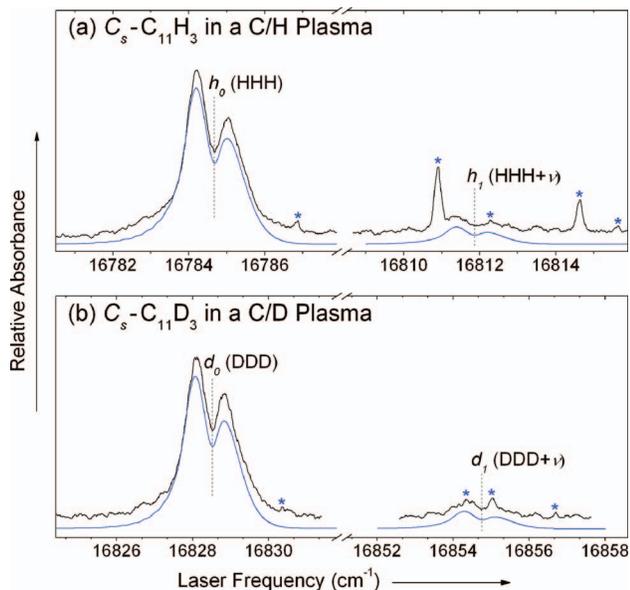


FIG. 2. Experimental spectra of  $C_s-C_{11}H_3$  and  $C_s-C_{11}D_3$  recorded through: (a) C/H and (b) C/D plasma. The simulated spectra are shown by lower blue traces in each panel.  $\nu$  denotes the excitation of a low-frequency vibration in the upper electronic state. A rotational temperature of  $\sim 14$  K and a Gaussian linewidth of  $\sim 0.1$   $cm^{-1}$  are used in the spectral simulations. Irregular features marked by asterisks in both panels are overlapping absorptions from small species, such as  $C_2$ , CH/CD... etc.

two-C-atom interval ( $\sim 72$  nm) in the linear  $HC_{2n+1}H$  homologous series.<sup>19,29</sup> Other bands with comparable or larger intensities have not been found in the searched wavelength range. The similar band contour and the red-shift value of band  $h_0$  with respect to the  $C_{2\nu}-C_9H_3$  electronic origin band are therefore taken as an indication that this band originates from the electronic origin band of  $C_s-C_{11}H_3$  (Fig. 1(c)).

A spectral contour fit, assuming an  $a$ -type electronic transition for a nonlinear molecule, is applied to the bands  $h_0$  and  $d_0$ . This method has been previously used to derive the indicative rotational constants of  $C_{2\nu}-C_9H_3$  and  $C_{2\nu}-C_{11}H_3$ .<sup>28</sup> The fit is performed using the PGOPHER software,<sup>40</sup> and the resulting simulated spectra are shown in the bottom traces of Figs. 2(a) and 2(b), respectively. From the fits, a set of indicative values of the molecular constants

$$A'' \approx 0.15 \text{ cm}^{-1}, \quad B'' \approx C'' \approx 0.009 \text{ cm}^{-1},$$

$$\Delta \left( A - \frac{B+C}{2} \right) = \left( A' - \frac{B'+C'}{2} \right) - \left( A'' - \frac{B''+C''}{2} \right) \approx 0.011 \text{ cm}^{-1}$$

is obtained. The values of the derived rotational constants have a ratio of

$$A'' : \left( \frac{B'' + C''}{2} \right) \approx 1 : 0.07,$$

very similar to those found for  $C_{2\nu}-C_9H_3$ ,<sup>28</sup> but the absolute values are substantially smaller.

The number and geometrical location of the hydrogen atoms in the carrier of band  $h_0$  is determined by deuterium labeling in a C/H/D plasma jet. A H/D ratio of  $\sim 1:0.8$  is

used in the  $C_2H_2/C_2D_2/He$  gas mixture for the discharge. The recorded spectra are shown in Fig. 3(a). The S/N ratio of the individual spectra is lower than for the pure hydrogenated or deuterated species as the total number of molecules is now shared over several isotopic combinations. In addition, the spectra coincide with overlapping absorption lines of small species, such as  $C_2$ , CH/CD... etc. Therefore, in order to inspect the origin of the overlapping absorption lines, additional measurements with a lower backing pressure of  $\sim 2$  bar were performed, and the resulting spectra are shown in Fig. 3(b). The experimental conditions with much lower backing pressure in the plasma expansion do not favor the formation of carbon chains, whereas smaller compounds are still present in the plasma. Figure 3(c) shows the resulting spectra by subtracting the overlapping absorption lines due to small carbon species from the spectra displayed in Fig. 3(a), revealing the overlap between spectra of small radicals and long carbon-chain species. Four separated absorption features with unresolved rotational contours can be seen in between or along the  $h_0$  and  $d_0$  bands. These features are ascribed to partially deuterated isotopologue bands of  $C_s-C_{11}H_3$ .

For large molecules with relatively small rotational constants, the difference between rotational constants of different D-isotopologues is expected to be very small (see the DFT-calculated constants for  $C_s-C_{11}H_3$  in Table I as an example). The experimentally derived rotational constants from the fits of bands  $h_0$  and  $d_0$  are therefore also used in the spectral simulations of the individual absorption bands in Fig. 3(c). The simulated spectra, as well as the individual bands, are shown in the middle and lower traces of Fig. 3(c), respectively. From the spectral simulations, in total eight isotopologue bands can be obtained, with quantitatively determined intensity ratios of  $\sim 0.8 : 1 : 0.6 : 0.8 : 0.6 : 0.8 : 0.5 : 0.6$ , among which the second and seventh band are  $h_0$  and  $d_0$ , respectively. The derived band origins are listed in Table I. The estimated uncertainty of the band intensity is less than  $\pm 5\%$ . The number of bands is specific for the case of a tri-hydride in which three hydrogen atoms are non-interchangeable (see the supplementary material<sup>42</sup> and Ref. 28 for more details), and consistent with the expected molecular structure of  $C_s-C_{11}H_3$ . We label the three hydrogen positions in the spectral carrier as  $H^I$ ,  $H^{II}$ , and  $H^{III}$  (as indicated in Fig. 1), and employ  $H^I H^{II} H^{III}$  as an overall label. Using the band positions derived from the spectral simulation in Fig. 3(c), values for three fundamental H/D isotopic shifts, i.e., H/D isotopic shifts by mono-deuteration of HHH, are determined as  $\sim 30.6$   $cm^{-1}$  ( $\Delta^I$ ),  $-0.7$   $cm^{-1}$  ( $\Delta^{II}$ ), and  $13.5$   $cm^{-1}$  ( $\Delta^{III}$ ), respectively.

## B. Structure determination of $C_s-C_{11}H_3$

The ground-state structure of  $C_s-C_{11}H_3$  is optimized at the B3LYP/6-311G level. The optimized structure is shown in Fig. 1(c) and the resulting rotational constants are listed in Table I. It is found that the rotational constants of the DFT-calculated  $C_s-C_{11}H_3$  structure are in good agreement with the experimentally derived values. Further, TD-DFT calculations predict that  $C_s-C_{11}H_3$  has an allowed  $1^2A'' - X^2A''$  electronic transition ( $a$ -type) with vertical excitation energy of

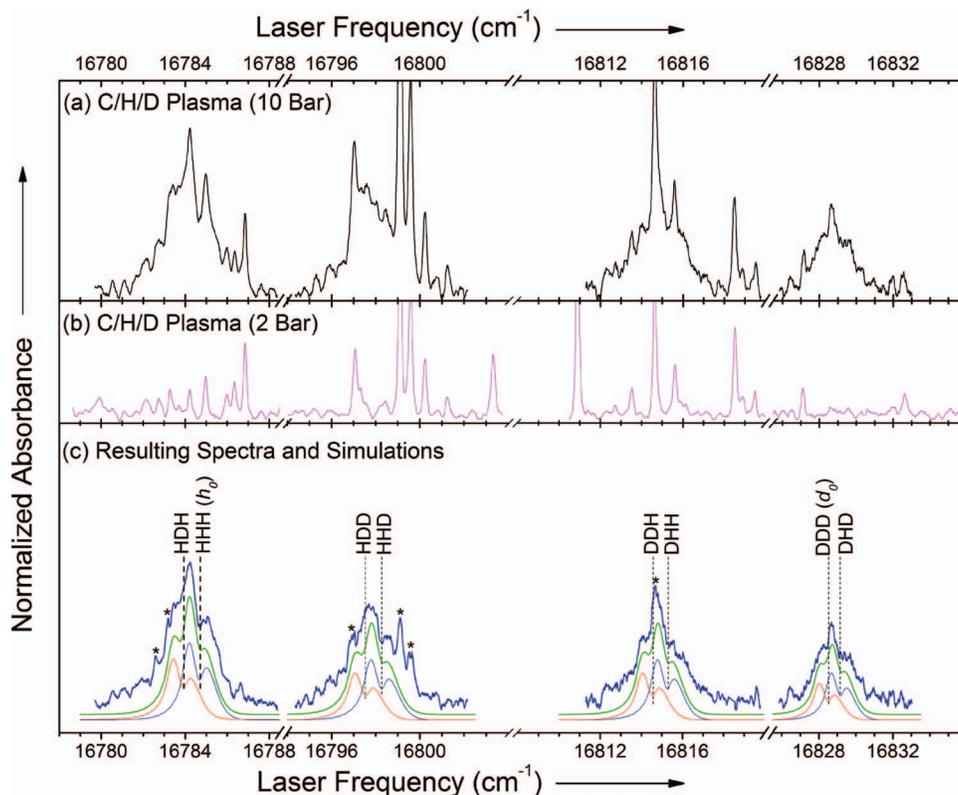


FIG. 3. Experimental spectra recorded through a C/H/D plasma (H/D ratio  $\sim 1:0.8$ ). The backing pressure used for the jet expansion is (a)  $\sim 10$  bar and (b)  $\sim 2$  bar. The upper blue lines in panel (c) illustrate the resulting spectra of D-isotopologues of  $C_5-C_{11}H_3$  by subtracting spectra in panel (b) from panel (a). The simulated spectra are shown by bold green lines in the middle trace of panel (c). The individual simulations of eight D-isotopologues are shown by blue and red lines in the lower traces of panel (c). A rotational temperature of  $\sim 14$  K and a Gaussian linewidth of  $\sim 0.1$   $cm^{-1}$  are used in the spectral simulations. Irregular features marked by asterisks in panel (c) indicate the residuals of the subtraction.

$\sim 2.20$  eV, which is rather close to the experimentally observed absorption band position of  $h_0$  ( $\sim 16784.7$   $cm^{-1}$ , i.e., 2.08 eV).

From the comparison between the experimental observations and supporting DFT calculations, the assignment of the optical absorption band  $h_0$  to  $C_5-C_{11}H_3$ , i.e.,  $HC_6CHC_4H$  (Fig. 1(c)), therefore, is a logical step, even though the present experiment is not mass selective. Furthermore this assignment is consistent with the following observations that are characteristic for a  $C_5-C_{11}H_3$  structure:

- (1) As discussed in Ref. 28, structural similarities between different unsaturated carbon chains can be derived from their H/D isotopic shifts. The experimentally determined H/D isotopic shifts (see Table I) can be compared to shifts in other carbon chains to further confirm the isomeric structure of  $C_5-C_{11}H_3$  as the carrier of the band  $h_0$ . It is found that, (a) the experimentally determined fundamental H/D isotopic shifts of band  $h_0$ ,  $\Delta^I \sim 30.6$   $cm^{-1}$  and  $\Delta^{II} \sim -0.7$   $cm^{-1}$ , are close to the values of  $\Delta^I \sim 34.9$   $cm^{-1}$  and  $\Delta^{II} \sim -1.0$   $cm^{-1}$  for  $C_{2v}-C_9H_3$ ,<sup>28</sup>

TABLE I. Spectroscopic parameters (in  $cm^{-1}$ ) of the eight isotopologues of  $C_5-C_{11}H_3$ .

| Isotopologues<br>( $H^I H^{II} H^{III}$ ) <sup>a</sup> | DFT/B3LYP-6-311G(d, p) |         |         |         | Expt.       |                  |            |         |
|--|------------------------|---------|---------|---------|-------------|------------------|------------|---------|
|  | A                      | B       | C       | $\nu^b$ | $T_0$       | $\Delta_{H/D}^c$ | $T_v$      | $\nu^d$ |
| HDH  | 0.1407                 | 0.00886 | 0.00834 | 29.5    | 16784.0(1)  | -0.7(1)          |            |         |
| HHH  | 0.1490                 | 0.00887 | 0.00838 | 29.6    | 16784.71(5) | 0.0              | 16811.9(2) | 27.2(2) |
| HDD  | 0.1387                 | 0.00864 | 0.00814 | 29.1    | 16797.6(1)  | +12.9(1)         |            |         |
| HHD  | 0.1470                 | 0.00865 | 0.00817 | 29.2    | 16798.3(1)  | +13.6(1)         |            |         |
| DDH  | 0.1357                 | 0.00867 | 0.00815 | 28.9    | 16814.6(1)  | +29.9(1)         |            |         |
| DHH  | 0.1435                 | 0.00868 | 0.00819 | 29.0    | 16815.3(1)  | +30.6(1)         |            |         |
| DDD  | 0.1338                 | 0.00846 | 0.00796 | 28.5    | 16828.55(5) | +43.9(1)         | 16854.8(2) | 26.3(2) |
| DHD  | 0.1414                 | 0.00847 | 0.00800 | 28.6    | 16829.2(1)  | +44.5(1)         |            |         |

<sup>a</sup>D-isotopologue formulas are indicated by the permutation  $H^I H^{II} H^{III}$  instead of  $H^I C_4 CH^{II} C_6 H^{III}$ .

<sup>b</sup>Values in the ground state, scaled by a factor of 0.968.<sup>41</sup>

<sup>c</sup> $\Delta$  denotes the H/D isotopic shift with respect to the main isotopologue HHH, i.e.,  $HC_4CHC_6H$ .

<sup>d</sup>Experimentally determined values in the electronically excited state.

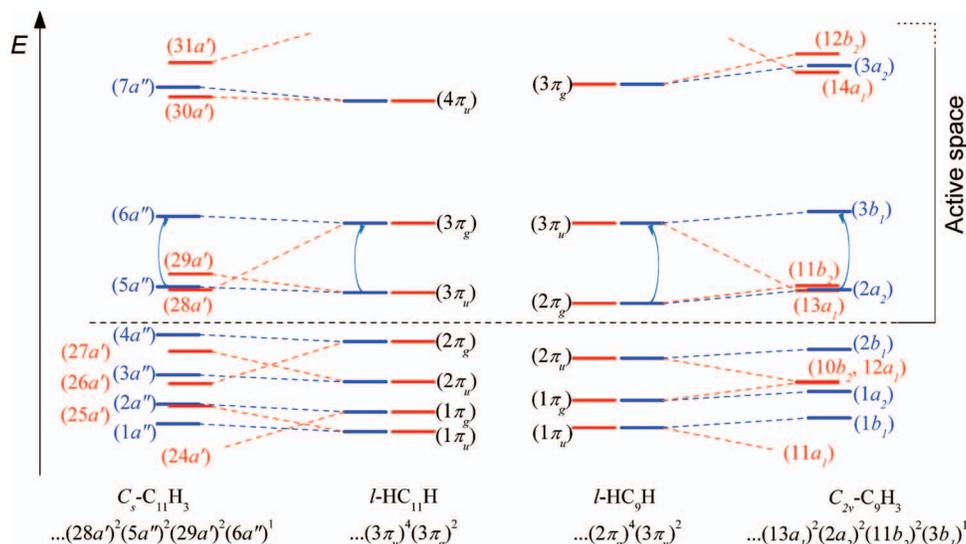


FIG. 4. Schematic diagram of relative molecular orbital energies and correlations between linear and bent nine/eleven-carbon chains. For the bent  $C_{2v}$ - $C_9H_3$  and  $C_s$ - $C_{11}H_3$  chains, orbitals colored blue and red are the  $\pi$ -orbitals with orientations perpendicular and parallel to the molecular plane, respectively. The blue arrows denote the electronic excitations as observed in the optical spectra.

indicating that the substructure containing  $H^I$  and  $H^{II}$  atoms between the spectral carrier of band  $h_0$  and  $C_{2v}$ - $C_9H_3$  must be similar; (b) the value of  $\Delta^{III} \sim 13.5 \text{ cm}^{-1}$  is close to the H/D isotopic shift of  $C_7H$  ( $\sim 19 \text{ cm}^{-1}$  for  $C_7D$ ),<sup>43</sup> indicating that the likely substructure containing  $H^{III}$  may be of the form  $H^{III}C_6C$ -; and (c) the value of  $\Delta^{I+III} \sim 44.5 \text{ cm}^{-1}$ , i.e., the H/D isotopic shift of DHD with respect to the main isotopologue HHH, is close to the H/D isotopic shift of  $HC_{11}H$  ( $\sim 50 \text{ cm}^{-1}$  for  $DC_{11}D$ ),<sup>19</sup> indicating that the substructure containing  $H^I$  and  $H^{III}$  is likely a bent  $H^I$ - $C_{11}$ - $H^{III}$  chain. As illustrated in Fig. 1(c), all these spectral (and consequently structural) similarities are consistent with an isomeric  $C_s$ - $C_{11}H_3$  structure.

- (2) Two weak bands, labeled as  $h_I$  and  $d_I$  in Fig. 2, are observed in the C/H and C/D plasma, and  $\sim 27 \text{ cm}^{-1}$  blue shifted with respect to the bands  $h_0$  and  $d_0$ . These bands are assigned as vibronic transitions involving excitation of the lowest-frequency vibrational mode in the upper electronic state of  $C_s$ - $C_{11}H_3$  and  $C_s$ - $C_{11}D_3$ . Generally, for both linear and non-linear carbon-chain species, the lowest-frequency vibration ( $C \cdots C \cdots C$  bending mode) depends on the overall chain length, as well as the bend angle (see supplementary material<sup>42</sup>). Here the experimentally determined vibrational energy of  $\nu'$  in the upper state,  $27.2 \text{ cm}^{-1}$  for  $C_s$ - $C_{11}H_3$  and  $26.3 \text{ cm}^{-1}$  for  $C_s$ - $C_{11}D_3$ , is  $\sim 10 \text{ cm}^{-1}$  lower than the experimental values found for  $C_{2v}$ - $C_9H_3$  and  $C_{2v}$ - $C_9D_3$ ,<sup>28</sup> respectively. Further, the difference between the experimentally determined upper state vibrational energies and DFT-predicted ground-state values is  $\sim 9\%$  (see Table I, and Fig. S1 in the supplementary material<sup>42</sup>), nearly the same as that in  $C_{2v}$ - $C_9H_3$ .<sup>28</sup> This is consistent with the fact that the bend angle ( $\sim 123.7^\circ$ ) in  $C_s$ - $C_{11}H_3$  is nearly the same as for  $C_{2v}$ - $C_9H_3$  but the overall chain length of the former molecule is longer by two-C atoms.

- (3) The  $\sim 67 \text{ nm}$  red-shift of band  $h_0$  with respect to the electronic origin band of  $C_{2v}$ - $C_9H_3$ , is very close to the TD-DFT predicted value ( $\sim 65 \text{ nm}$ ) (see Table S3 in the supplementary material<sup>42</sup>), and also resembles the red-shift ( $\sim 72 \text{ nm}$ ) of the electronic origin band of linear  $HC_{11}H$  with respect to  $HC_9H$ .<sup>19,29</sup> According to the ‘particle-in-a-box’ (PIB) model which treats the delocalized  $\pi$ -electron as a particle in a one dimensional box of conjugated hydrocarbon chain,<sup>20,44</sup> similar  $\pi$ -electron excitations in different linear homologous series of conjugated carbon chains should exhibit a similar trend. Molecular orbital (MO) analysis shows that the orbital configurations in the ground state of  $C_s$ - $C_{11}H_3$  and  $C_{2v}$ - $C_9H_3$  are very similar. This is summarized in Fig. 4. Specifically, the conjugated  $\pi$ -bonding MOs in the active space of  $C_s$ - $C_{11}H_3$  and  $C_{2v}$ - $C_9H_3$  are closely correlated to the degenerated  $\pi$ -orbitals in linear  $HC_{11}H$  and  $HC_9H$ , respectively. Further, the electronic transitions corresponding to the observed spectra,  $1^2A'' - X^2A''$  for  $C_s$ - $C_{11}H_3$  and  $1^2A_2 - X^2B_1$  for  $C_{2v}$ - $C_9H_3$ , have similar  $\pi \leftarrow \pi$  electronic excitations as in the  $A^3\Sigma_u^- - X^3\Sigma_g^-$  transitions of linear  $HC_{11}H$  and  $HC_9H$ , respectively. These correlations are consistent with a picture in which the carrier of the band  $h_0$  is a homologue of the conjugated carbon-chain series including  $C_{2v}$ - $C_9H_3$ .

All arguments discussed above lead to the conclusion that the spectral carrier of the observed band  $h_0$  must be the  $C_s$ - $C_{11}H_3$  radical with a  $H^I C_4 C H^{II} C_6 H^{III}$  structure as illustrated in Fig. 1(c).

## IV. DISCUSSION

### A. $\pi$ -conjugation in a bent odd-carbon-chain system

The present results allow a comparison between the electronic origin-band positions of  $C_s$ - $C_{11}H_3$ , the previously

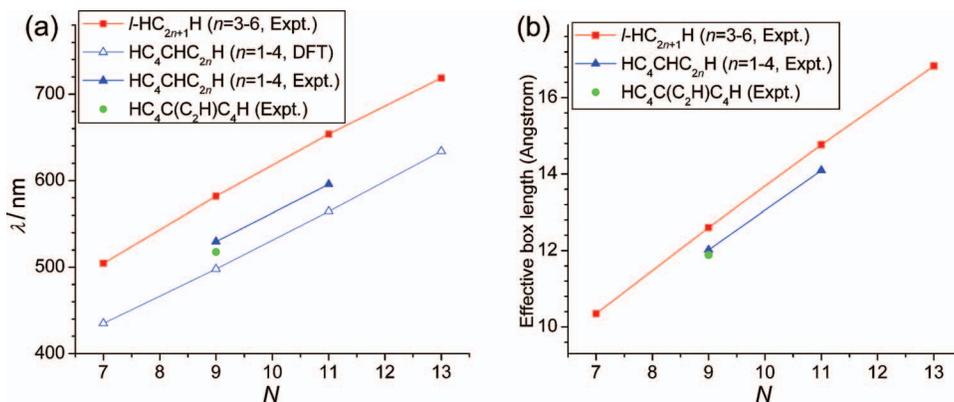


FIG. 5. (a) Calculated and experimentally determined optical absorption wavelengths, (b) effective box length vs total number of C-atoms ( $N$ ) in linear and bent chains. (■: linear  $\text{HC}_{2n+1}\text{H}$  chains for  $n = 3-6$  and  $N = 2n+1$ ; ▲ and △: bent  $\text{HC}_4\text{CHC}_{2n}\text{H}$  chains for  $n = 1-4$  and  $N = 2n+5$ .) The results of  $\text{C}_{2v}\text{-C}_{11}\text{H}_3$  (●:  $N = 9$ ) are also shown in both panels for comparison.

reported bent carbon chains  $\text{C}_{2v}\text{-C}_9\text{H}_3$  and  $\text{C}_{2v}\text{-C}_{11}\text{H}_3$ ,<sup>28</sup> and the linear  $\text{HC}_{2n+1}\text{H}$  ( $n = 3-6$ ) chains.<sup>19,29</sup> This is summarized in Fig. 5(a). Results of DFT-calculated optical absorption wavelengths for the bent homologous carbon chains  $\text{HC}_4\text{CHC}_{2n}\text{H}$  ( $n = 1-4$ ) are also included in Fig. 5(a). The comparison shows that the optical absorption wavelengths for the bent homologous carbon chains  $\text{HC}_4\text{CHC}_{2n}\text{H}$  ( $n = 1-4$ ) follow an approximate linear relationship, exhibiting a similar trend as in the linear  $\text{HC}_{2n+1}\text{H}$  ( $n = 3-6$ ) chains.

The MO analysis shows that for bent  $\text{HC}_4\text{CHC}_{2n}\text{H}$  ( $n = 1-4$ ) and linear  $\text{HC}_{2n+1}\text{H}$  ( $n = 3-6$ ) carbon chains, the MOs in the active space are all  $\pi$ -bonding orbitals formed by combinations of  $2p$  orbitals of carbon atoms. These  $\pi$ -orbitals constitute a purely  $\pi$ -conjugation space in which no  $\sigma$ -orbitals are involved. This makes it possible to discuss the  $\pi$ -conjugation in a bent odd-carbon-chain system using the well known PIB model.<sup>44</sup> Using the experimentally observed value of  $\lambda_{\text{abs}}$ , the effective box length ( $L_{\text{eff}}$ ) of a conjugated carbon-chain system can be calculated by<sup>42</sup>

$$L_{\text{eff}} = \sqrt{\frac{\hbar N_C \lambda_{\text{abs}}}{8mc}}, \quad (1)$$

where  $N_C$  is the number of conjugated C-atoms. Here, the  $\pi$ -conjugation in the bent carbon-chain system is evaluated in terms of this effective box length  $L_{\text{eff}}$ .

In Fig. 5(b), it is illustrated that the effective  $\pi$ -conjugation length ( $L_{\text{eff}}$ ) in both linear and bent odd-carbon chains increases quasi-linearly upon increasing the number of  $\pi$ -conjugated C-atoms. In the bent geometric configuration of  $\text{C}_{2v}\text{-C}_9\text{H}_3$  and  $\text{C}_s\text{-C}_{11}\text{H}_3$ , the effective  $\pi$ -conjugation length is generally somewhat shorter than in the linear geometric configurations of  $\text{HC}_9\text{H}$  and  $\text{HC}_{11}\text{H}$ , respectively. This may arise from the change of the hybrid type of the carbon atom at the inflexion point, which is due to typical  $sp^1$  hybridization in a linear carbon chain while it changes to  $sp^2$  hybridization in a  $\sim 120^\circ$  bent chain structure. DFT calculations show that  $\text{C}_{2v}\text{-C}_9\text{H}_3$  and  $\text{C}_s\text{-C}_{11}\text{H}_3$  exhibit nearly the same bend angle of  $123.70 \pm 0.01^\circ$ . This angle indicates that compared to linear carbon chains, the combinations of  $\pi$ -MOs in the bent chains involve nearly one less  $2p$  atomic orbital, yielding weaker  $\pi$ -conjugation. This is consistent with the fact that

the effective  $\pi$ -conjugation lengths ( $L_{\text{eff}}$ ) for the two bent carbon chains undergo similar shortenings compared to linear  $\text{HC}_9\text{H}$  and  $\text{HC}_{11}\text{H}$ , respectively. Another possible reason for the smaller effective  $\pi$ -conjugation length in the bent geometric configuration of  $\text{C}_{2v}\text{-C}_9\text{H}_3$  and  $\text{C}_s\text{-C}_{11}\text{H}_3$  is that the bent  $\text{HC}_4\text{CHC}_{2n}\text{H}$  ( $n = 1-4$ ) and linear  $\text{HC}_{2n+1}\text{H}$  ( $n = 3-6$ ) carbon chains have different configuration interactions between their low-lying electronic states. This may affect the effective  $\pi$ -conjugation in highly unsaturated hydrocarbons.

On the other hand, when adding a  $-\text{C}_2\text{-H}^{\text{II}}$  group in  $\text{C}_{2v}\text{-C}_9\text{H}_3$ , the effective  $\pi$ -conjugation length for  $\text{C}_{2v}\text{-C}_{11}\text{H}_3$  becomes slightly smaller, as shown in Fig. 5(b). DFT calculations for the charge distribution in  $\text{C}_{2v}\text{-C}_9\text{H}_3$  and  $\text{C}_{2v}\text{-C}_{11}\text{H}_3$  show that the  $-\text{C}_2\text{-H}^{\text{II}}$  group plays a role as an electron-donating group and provides additional electron density (see Fig. S3 in the supplementary material<sup>42</sup>). As a result, the effective ‘one-dimensional-box’ length ( $L_{\text{eff}}$ ) slightly decreases.

## B. H/D isotopic shifts

In our previous work,<sup>28</sup> it was concluded that the structural similarities between different unsaturated hydrocarbons can be derived from their H/D isotopic shifts. This implies that the H/D isotopic shifts of bent carbon chains like  $\text{C}_{2v}\text{-C}_9\text{H}_3$  and  $\text{C}_s\text{-C}_{11}\text{H}_3$  should exhibit a similar behavior as in the case of linear  $\text{HC}_{2n+1}\text{H}$  chains, i.e., the dependence of the H/D isotopic shift on the chain length or the number of C-atoms.<sup>19</sup> Here, similarities between the experimentally determined H/D isotopic shifts of bent  $\text{C}_{2v}\text{-C}_9\text{H}_3$  and  $\text{C}_s\text{-C}_{11}\text{H}_3$  chains with shifts compared to linear  $\text{HC}_{2n+1}\text{H}$  ( $n = 3-6$ ) chains are discussed (see Fig. S4 and Table S4 in the supplementary material<sup>42</sup>).

From the comparison, a similar dependence of the H/D isotopic shift on the overall chain length can be found for both mono- and di-deuteration of the bent chain structure ( $\text{H}^{\text{I}}\text{-C}_4\text{CC}_{4(6)}\text{-H}^{\text{III}}$ ). Specifically, the values of  $\Delta^{\text{I+III}}$  and  $\Delta^{\text{III}}$  of bent  $\text{C}_{2v}\text{-C}_9\text{H}_3$ , and  $\text{C}_s\text{-C}_{11}\text{H}_3$  chains exhibit a similar trend as for linear chains with an equivalent number of C-atoms, but their absolute values are slightly smaller. Further, for  $\text{H}^{\text{I}}$ -deuteration of the same  $\text{H}^{\text{I}}\text{-C}_4\text{C}$  substructure in  $\text{C}_{2v}\text{-C}_9\text{H}_3$  and  $\text{C}_s\text{-C}_{11}\text{H}_3$ , the value of  $\Delta^{\text{I}}$  also slightly decreases upon increase of the overall bent chain length.

The H/D isotopic shift of the electronic origin band of bent carbon chains also depends on the position of deuteration in the molecule. For example, in the case of the bent carbon chains C<sub>2v</sub>-C<sub>9</sub>H<sub>3</sub>, C<sub>2v</sub>-C<sub>11</sub>H<sub>3</sub>, and C<sub>s</sub>-C<sub>11</sub>H<sub>3</sub>, the value of Δ<sup>II</sup> from H<sup>II</sup>/D<sup>II</sup> substitution is nearly zero, and much smaller than Δ<sup>I</sup> and Δ<sup>III</sup> that take values as large as 34.9 cm<sup>-1</sup>.

The H/D isotopic shift in an electronic transition originates from the change of the vibrational zero-point energy (ZPE) upon electronic excitation, i.e.,

$$\begin{aligned} \Delta^{H/D} &= \Delta(ZPE)^D - \Delta(ZPE)^H \\ &= \left[ \frac{1}{2} \left( \sum_i v_i^D \right)' - \frac{1}{2} \left( \sum_i v_i^D \right)'' \right] \\ &\quad - \left[ \frac{1}{2} \left( \sum_i v_i^H \right)' - \frac{1}{2} \left( \sum_i v_i^H \right)'' \right] \\ &= \frac{1}{2} \left( \sum_i v_i^D - \sum_i v_i^H \right)' - \frac{1}{2} \left( \sum_i v_i^D - \sum_i v_i^H \right)'' \end{aligned} \quad (2)$$

where ' and '' denote upper and lower electronic states, respectively, and  $v_i$  are the frequencies of all vibrational modes. According to Eq. (2), the value of Δ<sup>H/D</sup> comprises contributions from all molecular vibrations and is consequently difficult to predict. The Δ<sup>H/D</sup> value, however, reflects the overall change of the molecular structure or substructure upon electronic excitation. It is worth to note that the vibrational motions and electronic excitations of homologues of the same series of carbon chains are always very similar. Larger molecules have more normal vibrational modes and larger ground state ZPEs than smaller molecules. Therefore, the observation of smaller H/D isotopic shifts in longer linear or bent carbon chains implies that the change of the molecular structure upon electronic excitation in longer carbon-chain molecules is generally smaller than in shorter chains. Similarly, for non-linear carbon chains C<sub>2v</sub>-C<sub>9</sub>H<sub>3</sub>, C<sub>2v</sub>-C<sub>11</sub>H<sub>3</sub> and C<sub>s</sub>-C<sub>11</sub>H<sub>3</sub>, the nearly zero value of Δ<sup>II</sup> upon H<sup>II</sup>/D<sup>II</sup> substitution implies that the H<sup>II</sup> containing substructures (i.e., C-H<sup>II</sup>, or C-C≡CH<sup>II</sup>) nearly do not change upon electronic excitation.

## V. CONCLUSION

In conclusion, a new isomer of the C<sub>11</sub>H<sub>3</sub> radical, HC<sub>4</sub>CHC<sub>6</sub>H with C<sub>s</sub> symmetry, has been detected and identified using deuterium labeling in the gas phase. A comparison has been made between the present results and available experimental data for bent HC<sub>4</sub>CHC<sub>4</sub>H, HC<sub>4</sub>C(C<sub>2</sub>H)<sub>4</sub>H, and linear HC<sub>2n+1</sub>H (n = 3–6) molecules. The spectroscopic parameters have been interpreted from the perspective of π-conjugations in highly unsaturated carbon chains. The dependence of the H/D isotopic shifts on the chain length or the number of C-atoms in the optical spectra of bent C<sub>2v</sub>-C<sub>9</sub>H<sub>3</sub> and C<sub>s</sub>-C<sub>11</sub>H<sub>3</sub> has been discussed as well.

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