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Anharmonic Vibrational Analysis for the Propadienylidene Molecule ($\text{H}_2\text{C}=\text{C}=\text{C}:$)

Qunyan Wu,^{†,‡} Qiang Hao,^{‡,§} Jeremiah J. Wilke,[‡] Andrew C. Simmonett,[‡]
Yukio Yamaguchi,[‡] Qianshu Li,^{†,||} De-Cai Fang,[§] and Henry F. Schaefer III^{*,‡}

*Institute of Chemical Physics, Beijing Institute of Technology, Beijing, P. R. China 100081,
Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602,
College of Chemistry, Beijing Normal University, Beijing, P. R. China 100875, and
Center for Computational Quantum Chemistry, South China Normal University,
Guangzhou, P. R. China 510631*

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Abstract: Maier et al. found that photolysis of singlet cyclopropenylidene (**1S**) in a matrix yields triplet propargylene (**2T**), which upon further irradiation is converted to singlet propadienylidene (vinylidenecarbene, **3S**). Their discovery was followed by interstellar identification of **3S** by Cernicharo et al. An accurate quartic force field for propadienylidene (**3S**) has been determined employing the *ab initio* coupled-cluster (CC) with single and double excitations and perturbative triple excitations [CCSD(T)] method and the correlation-consistent core–valence quadruple- ζ (cc-pCVQZ) basis set. Utilizing vibrational second-order perturbation theory (VPT2), vibration–rotation coupling constants, rotational constants, centrifugal distortion constants, vibrational anharmonic constants, and fundamental vibrational frequencies are determined. The predicted fundamental frequencies for **3S** as well as its ^{13}C and deuterium isotopologues are in good agreement with experimental values. The theoretical zero-point vibration corrected rotational constants \mathbf{B}_0 are consistent with experimental values within 0.3% of errors. The isotopic shifts of \mathbf{B}_0 are in close to exact agreement with experimental observations. The mean absolute deviation between theoretical anharmonic and experimental fundamental vibrational frequencies for 24 modes (excluding CH_2 s-str.) is only 2.6 cm^{-1} . The isotopic shifts of the vibrational frequencies are also in excellent agreement with the available experimental values. However, a large discrepancy is observed for the CH_2 symmetric stretch, casting doubt on the experimental assignment for this mode.

1. Introduction

The singlet state of cyclopropenylidene (**1S**) is known to be the global minimum on the C_3H_2 potential energy surfaces (PESs). The first laboratory detection of **1S** was achieved by Reisenauer et al. in 1984.¹ This was enabled by the *ab initio* prediction of its vibrational frequencies and infrared (IR) intensities provided by Lee et al.² Shortly thereafter,

Reisenauer et al.³ were able to show that, upon irradiation, **1S** is photoisomerized into triplet propynylidene (propargylene, **2T**) and, in a second photostep, into singlet propadienylidene (vinylidenecarbene, **3S**). The second photolysis can be reversed by using shorter wavelength light (254 nm) to regenerate **2T**. By a repeated photolysis of the newly formed **2T** with 313 nm light, complete reversibility of the isomerization to **1S** was demonstrated, as shown in Scheme 1. The same photochemical cycle was observed when the dideuteriocyclopropenylidene (**1S-D**₂) was treated in the same way.^{3,4} **1S** has also been detected in interstellar space, and it appears to be the most abundant of all hydrocarbons and plays an important role in the chemistry of the interstellar

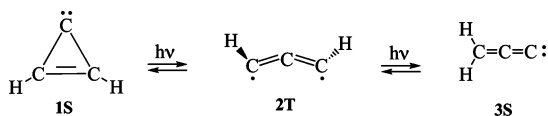
* Corresponding author e-mail: sch@uga.edu.

[†] Beijing Institute of Technology.

[‡] University of Georgia.

[§] Beijing Normal University.

^{||} South China Normal University.

Scheme 1. Interconversion of the Three Lowest-Lying C_3H_2 Species

medium.⁵ Dateo and Lee⁶ reported an *ab initio* quartic force field for cyclopropenylidene (**1S**) at the cc-pVTZ CCSD(T) level of theory. They used second-order vibrational perturbation theory (VPT2) to predict fundamental vibrational frequencies of **1S** and its ^{13}C and deuterium isotopologues. Their theoretical anharmonic quantities were in good agreement with the available experimental observations. Very recently, Lee et al.⁷ also published newer fundamental vibrational frequencies and rovibrational spectroscopic constants for isotopologues of cyclopropenylidene (**1S**) with the cc-pVQZ CCSD(T) method.

Propadienylidene (**3S**) is the first member of the cumulene carbene series to exhibit great stability and has a singlet ground state. It is characterized by carbon–carbon double bonds, terminal nonbonded electrons, and a large dipole moment. Propadienylidene (**3S**) was first detected in the photolysis products of cyclopropenylidene (**1S**) as mentioned above.³ In 1990, **3S** was produced in a laboratory discharge, and its rotational spectrum was determined to high precision by Vrtilek et al.⁸ In the following year (1991), Cernicharo et al. reported the astronomical detection of **3S** in Tmc-1 (one of the best astronomical sources of carbon chains) and tentative detection in the molecular envelope of IRC+10216.⁹ Subsequently, Gottlieb et al.¹⁰ reported the millimeter-wave rotational spectra of four isotopic species of the propadienylidene ($H_2^{13}CCC$, $H_2C^{13}CC$, $H_2CC^{13}C$, and D_2CCC) and the same set of rotational and centrifugal distortion constants. From the observed rotational constants, the r_s structure was determined: $r_s(C_1C_2) = 1.326 \pm 0.003$ Å, $r_s(C_2C_3) = 1.287 \pm 0.003$ Å, $r_s(CH) = 1.084 \pm 0.004$ Å, and $\theta_s(HCH) = 117.7 \pm 0.02^\circ$. Furthermore, vibration–rotation coupling constants calculated in the CEPA-1 approximation were combined with the experimental rotational constants for the five isotopologues to yield an equilibrium geometry:¹⁰ $r_e(C_1C_2) = 1.3283 \pm 0.0005$ Å, $r_e(C_2C_3) = 1.291 \pm 0.001$ Å, $r_e(CH) = 1.083 \pm 0.001$ Å, and $\theta_e(HCH) = 117.6 \pm 0.2^\circ$.

Seburg et al.¹¹ investigated photochemical automerizations and isomerizations of C_3H_2 isomers. Photolysis of [^{13}C] diazopropynes under matrix isolation conditions produced C_3H_2 isomers containing a single ^{13}C label. Monitoring the distribution of the ^{13}C label during photolysis at either $\lambda = 313$ nm or $\lambda > 444$ nm revealed the involvement of two photochemical automerization processes. At $\lambda = 313 \pm 10$ nm, triplet propynylidene (**2T**) and singlet cyclopropenylidene (**1S**) photoequilibrate. The interconversion does not occur by a simple ring-closure/ring-opening mechanism, as hydrogen migration accompanies the interconversion. At $\lambda > 444$ nm, $H_2C=C=^{13}C$ and $H_2C=^{13}C=C$ rapidly equilibrate. Various lines of evidence suggested that the equilibration occurs through a cyclopropyne transition state. Seburg et al.'s *ab initio* theoretical study¹¹ confirmed that the planar isomer of singlet cyclopropyne is the transition state for the

interconversion of two ^{13}C isotopologues. Stanton et al.¹² reported the first electronic absorption spectrum of **3S** in an argon matrix by the striking photochemical automerization of ^{13}C -labeled **3S**. The electronic spectrum of **3S** exhibits rich vibronic structure with absorption maxima that span virtually the visible spectrum. Later, Hodges et al.¹³ reinvestigated the electronic spectrum and recorded the vibrationally resolved spectrum of **3S** in a neon matrix at 6 K. Three electronic transitions were observed: a strong $\tilde{C}-\tilde{X}$ band system in the $39\,051\text{--}47\,156\text{ cm}^{-1}$ range, a weaker $\tilde{B}-\tilde{X}$ transition in the $16\,161\text{--}24\,802\text{ cm}^{-1}$ region, and the hardly detectable (forbidden) $\tilde{A}-\tilde{X}$ transition at $13\,885\text{--}16\,389\text{ cm}^{-1}$. On the basis of these observations, one can search for these absorptions in the gas phase. Recently, the rotationally resolved vibronic bands in the forbidden $\tilde{A}^1A_2-\tilde{X}^1A_1$ electronic transition of **3S** have been observed in the gas phase by cavity ring down (CRD) absorption spectroscopy, through a supersonic planar plasma with allene as a precursor, by Achkasova et al.¹⁴

There have been several theoretical studies^{8–14} on the singlet state of propadienylidene (**3S**). Quite recently, Kloppe's group¹⁵ determined the atomization energies of 19 C_3H_x ($x=0\text{--}4$) molecules and radicals using explicitly correlated coupled-cluster theory. For the singlet propadienylidene (**3S**), they determined harmonic and anharmonic zero-point vibrational energy (ZPVE) at the cc-pCVTZ(C)/cc-pCVDZ(H) CCSD(T) level of theory. On the other hand, Vázquez et al.¹⁶ reported high-accuracy extrapolated *ab initio* thermochemistry (HEAT) of the propargyl radical and the singlet C_3H_2 carbenes. Their HEAT scheme included harmonic and anharmonic contributions to ZPVE correction at the cc-pVQZ CCSD(T) level of theory. However, neither of these two excellent papers presented detailed analyses of rovibrational anharmonic quantities.

In the present study, anharmonic vibrational analyses of the electronic ground state of propadienylidene (**3S**) are performed employing vibrational second-order perturbation (VPT2) theory.^{17–23} The molecular parameters are determined using the *ab initio* coupled cluster with single, double, and perturbative triple excitations [CCSD(T)] method^{24–26} with the correlation-consistent polarized core–valence quadruple- ζ (cc-pCVQZ) basis set.^{27,28} The theoretically determined harmonic and anharmonic rovibrational quantities will be compared with the available experimental measurements. The present research should stimulate further characterization of the propadienylidene molecule (**3S**), which is involved in hydrocarbon chemistry, combustion chemistry, chemical dynamics, interstellar chemistry, and high-resolution spectroscopy.

2. Electronic Structure Considerations

The 1A_1 state of the **3S** isomer arises from the following electronic configuration, when oriented in the yz plane, with the C_2 axis aligned with the z axis:

$$[\text{core}]4a_1^25a_1^26a_1^21b_2^21b_1^27a_1^22b_2^2\tilde{X}^1A_1 \quad (1)$$

where [core] denotes the three lowest-lying core (C: 1s-like) orbitals. In eq 1, the $2b_2$ molecular orbital (MO) describes the $C_2\text{--}C_3$ in-plane π bond, while the $1b_1$ MO is related to

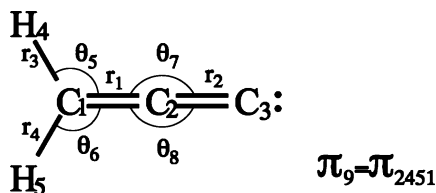


Figure 1. The internal coordinates of the propadienylidene molecule ($\text{H}_2\text{C}=\text{C}=\text{C}:$).

the out-of-plane $\text{C}_1\text{C}_2\text{C}_3$ π bonding. The $7a_1$ MO is associated with the lone-pair orbital localized on the carbene (C_3) atom.

3. Symmetry Internal Coordinates

The vibrational potential energy (\bar{V}) for propadienylidene (**3S**) may be expanded in terms of displacement symmetry internal coordinates (ΔS_i) in the vicinity of the equilibrium point (E_0) as

$$\bar{V} = E_0 + \frac{1}{2} \sum_{ij} F_{ij} \Delta S_i \Delta S_j + \frac{1}{6} \sum_{ijk} F_{ijk} \Delta S_i \Delta S_j \Delta S_k + \frac{1}{24} \sum_{ijkl} F_{ijkl} \Delta S_i \Delta S_j \Delta S_k \Delta S_l \quad (2)$$

In eq 2, F_{ij} , F_{ijk} , and F_{ijkl} denote quadratic, cubic, and quartic force constants. The nine symmetry internal coordinates for C_{2v} species (e.g., C_3H_2 , C_3D_2) are defined by

$$\begin{aligned} S_1(a_1) &= r_1 & \text{C}_1\text{C}_2 \text{ stretch} \\ S_2(a_1) &= r_2 & \text{C}_2\text{C}_3 \text{ stretch} \\ S_3(a_1) &= \frac{1}{\sqrt{2}}(r_3 + r_4) & \text{CH}_2 \text{ s-stretch} \\ S_4(a_1) &= \frac{1}{\sqrt{2}}(\theta_5 + \theta_6) & \text{CH}_2 \text{ scissor} \\ S_5(b_1) &= \theta_8 & \text{CCC bend (oop)} \\ S_6(b_1) &= \pi_9 & \text{CH}_2 \text{ wag} \\ S_7(b_1) &= \frac{1}{\sqrt{2}}(r_3 - r_4) & \text{CH}_2 \text{ a-stretch} \\ S_8(b_2) &= \frac{1}{\sqrt{2}}(\theta_5 - \theta_6) & \text{CH}_2 \text{ rock} \\ S_9(b_2) &= \theta_7 & \text{CCC bend (ip)} \end{aligned} \quad (3)$$

where the internal coordinates (r_1 – r_4 , θ_5 – θ_8 , and π_9) are depicted in Figure 1. The CCC bending coordinates θ_7 and θ_8 are described by linear bending coordinates of the form $\sin^{-1}[\mathbf{e}_\gamma(\mathbf{e}_{23} \times \mathbf{e}_{21})]$, where \mathbf{e}_γ is a fixed unit vector aligned with either the x or y axis and \mathbf{e}_{23} is a unit vector directed from atom C_3 to atom C_2 . The out-of-plane coordinate S_6 can be more explicitly written as $\sin^{-1}[\mathbf{e}_{12}(\mathbf{e}_{14} \times \mathbf{e}_{15})/\sin \theta_{415}]$, where the \mathbf{e} vectors have the previously stated meaning, and θ_{415} is the valence bond angle between atoms H_4 , C_1 , and H_5 . The displacement sizes used for the finite difference procedure (in Å and rad units) are 0.01, 0.01, 0.01, 0.02, 0.03, 0.03, 0.01, 0.02, and 0.03 for coordinates S_1 – S_9 , which yielded a fit with just a 1.9×10^{-9} E_h error.

4. Theoretical Procedures

In the present research, the correlation-consistent polarized core–valence quadruple- ζ (cc-pCVQZ) basis set developed by Dunning and Woon^{27,28} was employed to optimize the

geometry and to determine analytical potentials. The zeroth-order description of the ground state of propadienylidene (**3S**) was obtained using single configuration self-consistent-field (SCF) [restricted Hartree–Fock (RHF)] wave functions. The coupled cluster with single, double, and perturbative triple excitations [CCSD(T)] wave functions^{24–26} were constructed without freezing any core orbitals. In our previous study, it was found that the ground state of **3S**, in the vicinity of the equilibrium point, may be described adequately by the CCSD(T) method, which is based on a single determinant RHF wave function.²⁹

The structure of propadienylidene (**3S**) was optimized using analytic derivative methods.^{30–32} Its dipole moment, harmonic vibrational frequencies, and corresponding IR intensities were determined analytically. Electronic structure computations were carried out using the ACESII (Mainz–Austin–Budapest version),^{33,34} MOLPRO,³⁵ and PSI2³⁶ suites of quantum chemistry software.

The C++ program GRENDL³⁷ was used to generate perturbed geometries and to compute force constants in symmetry internal coordinates. The INTDER 2005^{38,39} code of Allen was employed to perform nonlinear coordinate transformations of quadratic, cubic, and quartic force constants between symmetry internal and Cartesian coordinates. The VPT2 analyses were then performed upon the Cartesian force constants by the ANHARM program.⁴⁰

5. Results and Discussion

5.1. Equilibrium Geometry and Dipole Moment. At the cc-pCVQZ CCSD(T) level of theory, the propadienylidene (**3S**) molecule is predicted to lie 14.5 (13.6) kcal mol^{−1} (the zero-point vibrational energy corrected value in parentheses) above the global minimum on the C_3H_2 PES, cyclopropenylidene (**1S**). At the same level of theory, the structure of propadienylidene (**3S**) has been determined to be $r_e(\text{C}_1\text{C}_2) = 1.3281$ Å, $r_e(\text{C}_2\text{C}_3) = 1.2879$ Å, $r_e(\text{CH}) = 1.0837$ Å, and $\theta_e(\text{HCH}) = 117.45^\circ$. This theoretical r_e structure is in good agreement with the recommended r_e structure (theory + experiment) of Gottlieb et al.:¹⁰ $r_e(\text{C}_1\text{C}_2) = 1.3283 \pm 0.0005$ Å, $r_e(\text{C}_2\text{C}_3) = 1.291 \pm 0.001$ Å, $r_e(\text{CH}) = 1.083 \pm 0.001$ Å, and $\theta_e(\text{HCH}) = 117.6 \pm 0.2^\circ$. Our zero-point corrected structure, which includes the effects of anharmonicity through the cubic terms in the force field is $r_z(\text{C}_1\text{C}_2) = 1.3289$ Å, $r_z(\text{C}_2\text{C}_3) = 1.2870$ Å, $r_z(\text{CH}) = 1.0907$ Å, and $\theta_z(\text{HCH}) = 117.55^\circ$, which compares very favorably with the r_s structure of Gottlieb and co-workers. The dipole moment of isomer **3S** is predicted to be 4.174 debye along the C_2 axis with sign $^+\text{H}_2\text{CCC}^-$. Our value is consistent with the dipole moment of 4.135 debye at the CCSD(T) level of theory with the 131 cGTO basis set of Gottlieb et al.¹⁰ The magnitude of the dipole moment for propadienylidene (**3S**) is larger than that of cyclopropenylidene (**1S**) [3.420 debye at the cc-pCVQZ CCSD(T) level of theory, 3.43(2) debye exptl.⁴¹], probably due to a longer distance (charge separation) between the positive (CH_2) and negative ($\text{C}:$) ends of the molecule.

5.2. Vibration–Rotation Coupling Constants. The vibrational dependence of a rotational constant B_v , v being a vibrational quantum number, has the general form

$$B_v = B_e - \sum_r \alpha_r^B \left(v + \frac{1}{2} \right) + \text{higher terms} \quad (4)$$

where B_e is the equilibrium rotational constant and the sums run over all normal modes. Similar expressions hold for the vibrational dependence of A_v and C_v .

The vibration–rotation coupling constants α_r^B for an asymmetric top from perturbation theory are given by

$$-\alpha_r^B = \frac{2B_e^2}{\omega_r} \left[\sum_{\xi} \frac{3(a_r^{(b\xi)})^2}{4I_{\xi}} + \sum_s (\zeta_{rs}^{(b)})^2 \frac{(3\omega_r^2 + \omega_s^2)}{\omega_r^2 - \omega_s^2} + \pi \left(\frac{c}{h} \right)^{1/2} \sum_s \phi_{rrs} a_s^{(bb)} \left(\frac{\omega_r}{\omega_s^{3/2}} \right) \right] \quad (5)$$

where ω_r is the r th harmonic vibrational frequency, I_{ξ} is the ξ th principal moment of inertia, $\zeta_{rs}^{(b)}$ is the Coriolis coupling constant about the b axis, and ϕ_{rrs} is the cubic force constant. In this equation, the $a_r^{(\alpha\beta)}$ constants are derivatives of the equilibrium moments and products of inertia with respect to the r th normal coordinate Q_r

$$a_r^{(\alpha\beta)} = \left(\frac{\partial I_{\alpha\beta}}{\partial Q_r} \right)_e \quad (6)$$

The vibration–rotation coupling constants (α_r^A , α_r^B , and α_r^C) for six isotopologues of propadienyldiene are presented in Table 1. The second term in the square brackets of eq 5 sometimes suffers from Coriolis resonances when two vibrational frequencies are very close, i.e., $\omega_r \approx \omega_s$. About the a axis of propadienyldiene, strong Coriolis interactions are expected between the CH_2 wagging (ν_5) and CH_2 rocking (ν_8) and between the CCC out-of-plane (ν_6) and in-plane (ν_9) bending vibrations.¹⁰ The corresponding Coriolis coupling constants are determined to be $\zeta_{5,8}^{(a)} = 0.527$ and $\zeta_{6,9}^{(a)} = 0.937$. Anomalous α_r^A constants are indeed observed for these four vibrational modes. In Table 1, therefore, deperturbed values^{20,21} are reported. However, the B_0 constant ($v = 0$) may be determined without Coriolis resonances by taking the sums of α_r^B constants over all normal modes rather than their individual values, as pointed out by East et al.⁴²

5.3. Rotational Constants and Centrifugal Distortion Constants. Since propadienyldiene (**3S**) is a near symmetric top molecule (a highly prolate asymmetric top, $\kappa = -0.9972$),¹⁰ Gottlieb's experiment¹⁰ analyzed the transition frequencies using Watson's S-reduced Hamiltonian.¹⁹ Consequently, the centrifugal distortion constants and the zero-point vibration corrected rotational constants are determined using Watson's S-reduction in the I' representation in our theoretical study. In Table 2, rotational constants and centrifugal distortion constants for the standard H_2CCC species and its four isotopologues are provided. In the following discussion, the equilibrium (A_e , B_e , and C_e) and zero-point vibration corrected (A_0 , B_0 , and C_0) rotational constants are abbreviated as \mathbf{B}_e and \mathbf{B}_0 , respectively. For the standard H_2CCC species, the differences between theoretical equilibrium and zero-point vibration corrected rotational constants are $\Delta[\mathbf{B}_e(\text{theor.}) - \mathbf{B}_0(\text{exptl.})] = (+3484, -15, +1)$ MHz and $\Delta[\mathbf{B}_0(\text{theor.}) - \mathbf{B}_0(\text{exptl.})] = (+999, -8, -7)$ MHz, respectively. Improvement in agreement between theoretical

Table 1. Theoretical Predictions of Vibration–Rotation Coupling Constants (in MHz) for C_3H_2 and Its D and ^{13}C Labeled Isotopologues at the cc-pCVQZ CCSD(T) Level of Theory

	C_3H_2	C_3D_2	C_3HD	$\text{H}_2^{13}\text{CCC}$	$\text{H}_2\text{CC}^{13}\text{C}$	$\text{H}_2\text{C}^{13}\text{CC}$
α_1^A	4785.8	2028.0	1486.4	4711.2	4785.8	4784.7
α_2^A	177.9	76.4	2998.9	194.9	178.8	154.4
α_3^A	−3002.5	−707.0	13.5	−3008.5	−3008.3	−2988.2
α_4^A	134.1	−470.5	−1704.1	162.5	137.4	135.4
α_5^A	3736.3	1210.6	−1378.8	3754.8	3736.8	3747.4
α_6^A	4091.9	1710.6	−3708.1	4058.1	4145.5	3987.9
α_7^A	2867.3	1018.6	−2126.0	2867.7	2867.3	2867.3
α_8^A	−5492.9	−2022.3	3802.1	−5509.4	−5490.7	−5452.2
α_9^A	−2328.8	−1171.0	2655.9	−2281.1	−2367.6	−2223.3
$1/2\sum\alpha_r^A$	2484.5	836.7	1019.9	2475.1	2492.5	2506.8
α_1^B	7.1	14.1	11.1	6.2	6.7	7.1
α_2^B	78.5	61.9	13.6	76.1	75.6	75.6
α_3^B	−18.8	11.1	70.4	−18.6	−17.7	−18.7
α_4^B	27.8	−15.0	−13.1	27.8	26.5	27.8
α_5^B	25.3	24.1	17.8	24.6	23.5	25.3
α_6^B	−64.3	−55.1	−8.1	−62.9	−62.5	−60.6
α_7^B	10.0	16.4	−66.2	8.6	9.4	10.0
α_8^B	−8.5	−9.9	20.3	−8.0	−7.7	−8.6
α_9^B	−70.5	−62.7	−58.3	−67.7	−67.2	−68.8
$1/2\sum\alpha_r^B$	−6.7	−7.6	−6.3	−7.0	−6.7	−5.5
α_1^C	11.8	19.4	12.3	10.6	11.1	11.8
α_2^C	73.3	55.2	17.6	71.1	70.9	70.7
α_3^C	11.9	24.4	64.3	11.0	10.8	11.9
α_4^C	27.7	−0.9	13.0	27.5	26.3	27.7
α_5^C	−2.9	−8.0	18.5	−2.2	−2.5	−2.8
α_6^C	−94.5	−75.7	11.2	−91.5	−90.7	−92.0
α_7^C	11.2	16.6	−28.9	9.8	10.5	11.2
α_8^C	10.3	14.4	−5.1	9.8	9.8	10.3
α_9^C	−32.6	−25.8	−83.5	−32.0	−31.8	−30.6
$1/2\sum\alpha_r^C$	8.2	9.9	9.7	7.0	7.2	9.1

and experimental rotational constants due to zero-point vibration correction is significant; 1.2% deviation for the former $\Delta[\mathbf{B}_e(\text{theor.}) - \mathbf{B}_0(\text{exptl.})]$ and 0.3% for the latter $\Delta[\mathbf{B}_0(\text{theor.}) - \mathbf{B}_0(\text{exptl.})]$. For the dideutero isotopologue (D_2CCC), the corresponding differences are $\Delta[\mathbf{B}_e(\text{theor.}) - \mathbf{B}_0(\text{exptl.})] = (+1091, -15, +3)$ MHz and $\Delta[\mathbf{B}_0(\text{theor.}) - \mathbf{B}_0(\text{exptl.})] = (+253, -8, -6)$ MHz, respectively. Again, the improvement in agreement between theoretical and experimental rotational constants is evident: 0.8% for the former $\Delta[\mathbf{B}_e(\text{theor.}) - \mathbf{B}_0(\text{exptl.})]$ and 0.2% for the latter $\Delta[\mathbf{B}_0(\text{theor.}) - \mathbf{B}_0(\text{exptl.})]$.

The quartic centrifugal distortion constants of the standard H_2CCC species at the cc-pCVQZ CCSD(T) level of theory are predicted to be $D_J = 3.748$ (4.248) kHz, $D_{JK} = 0.5822$ (0.5164) MHz, $D_K = 22.026$ (23.535) MHz, $d_1 = -0.146$ (−0.153) kHz, and $d_2 = -0.054$ (−0.070) kHz, where the experimental values are shown in parentheses. Our predictions are in reasonable agreement with the theoretical values at the CEPA-1/131 cGTO level of theory and experimental observations.¹⁰ For the other four isotopologues, the theoretically determined centrifugal distortion constants are also consistent with the corresponding experimental values. In this light, it should be noted that during their least-squares fit procedures Gottlieb et al. constrained D_k to the values in H_2CCO and D_2CCO , whereas in each of the ^{13}C species, they constrained it to the value in normal H_2CCO .¹⁰

In Table 3, isotopic shifts for rotational constants and centrifugal distortion constants for the four isotopologues with respect to the standard H_2CCC species are presented. Both the theoretical equilibrium rotational constants \mathbf{B}_e (A_e ,

Table 2. Theoretical and Experimental Rotational Constants, and Quartic Centrifugal Distortion Constants (in MHz) for H₂CCC and Its Four Isotopologues at the cc-pCVQZ CCSD(T) Level of Theory

	H ₂ CCC		D ₂ CCC		H ₂ ¹³ CCC		H ₂ C ¹³ CC		H ₂ CC ¹³ C	
	theory	exptl. ^a	theory	exptl. ^a	theory	exptl. ^a	theory	exptl. ^a	theory	exptl. ^a
rotational constants										
A _e	292267		146246		292267		292267		292267	
B _e	10574		9388		10264		10571		10166	
C _e	10205		8821		9916		10202		9824	
A ₀	289782	288783	145408	145155	289792	288880	289760	288610	289774	288860
B ₀	10581	10589	9395	9403	10271	10279	10577	10585	10173	10180
C ₀	10197	10204	8812	8818	9909	9916	10193	10200	9817	9824
quartic centrifugal distortion constants										
10 ³ D _J	3.748	4.248	2.747	3.128	3.552	4.027	3.748	4.240	3.473	3.955
D _{JK}	0.5822	0.5164	0.3848	0.3699	0.5477	0.485	0.5790	0.518	0.5485	0.485
D _K	22.026	23.535	5.272	5.391	22.060	23.535	22.028	23.535	22.060	23.535
10 ³ d ₁	-0.146	-0.153	-0.214	-0.251	-0.133	-0.135	-0.146	-0.147	-0.130	-0.127
10 ³ d ₂	-0.054	-0.070	-0.116	-0.135	-0.048	-0.058	-0.054	-0.078	-0.047	-0.063

^a Ref 10.**Table 3.** Theoretical and Experimental Isotopic Shifts for Rotational Constants and Quartic Centrifugal Distortion Constants (in MHz) of the Four Isotopologues with Respect to Those of the Standard H₂CCC Species at the cc-pCVQZ CCSD(T) Level of Theory

	D ₂ CCC		H ₂ ¹³ CCC		H ₂ C ¹³ CC		H ₂ CC ¹³ C	
	theory	exptl.	theory	exptl.	theory	exptl.	theory	exptl.
rotational constants								
ΔA _e	-146021		0		0		0	
ΔB _e	-1186		-310		-3		-408	
ΔC _e	-1384		-289		-3		-381	
ΔA ₀	-144374	-143628	10	97	-22	-173	-8	77
ΔB ₀	-1186	-1186	-310	-310	-4	-4	-408	-409
ΔC ₀	-1385	-1386	-288	-288	-4	-4	-380	-380
quartic centrifugal distortion constants								
10 ³ ΔD _J	-1.001	-1.12	-0.196	-0.221	0.0	-0.008	-0.275	-0.293
ΔD _{JK}	-0.1974	-0.1465	-0.0345	-0.0314	-0.0032	0.0016	-0.0337	-0.0314
ΔD _K	-16.754	-18.144	0.034	0.0	0.002	0.0	0.034	0.0
10 ³ Δd ₁	-0.068	-0.098	0.013	0.018	0.0	0.006	0.016	0.026
10 ³ Δd ₂	-0.062	-0.065	0.006	0.012	0.0	-0.008	0.007	0.007

B_e, and C_e) and zero-point vibration corrected rotational constants B₀ (A₀, B₀, and C₀) reproduce the experimental isotopic shifts extremely well. Specifically, the isotopic shift predictions for the B₀ and C₀ constants are almost exact for all four isotopologues. The largest deviation between theory and experiment is 151 MHz for the A₀ constant of the H₂C¹³CC isotopologue. However, since experimental uncertainty in determining the A₀ constant for the H₂C¹³CC isotopologue is ±130 MHz, our theoretical isotopic shift is still considered to be in excellent agreement.

Isotopic shifts for the five centrifugal distortion constants relative to those for normal H₂CCC species are largest for D₂CCC, and the magnitudes of these shifts are reasonably consistent with the experimental observations. Among the ¹³C species, the D_J constant is sensitive to ¹³C labeling in the methylene carbon (H₂¹³CCC) and the terminus carbon (H₂CC¹³C). The ¹³C labeling in the central carbon (H₂C¹³CC) is least sensitive for all five constants.

5.4. Harmonic Vibrational Frequencies and Infrared (IR) Intensities. In Tables 4–6, harmonic vibrational frequencies and the associated infrared (IR) intensities for C₃H₂, C₃D₂, and C₃HD are presented. The corresponding quantities for the H₂¹³C=C=C, H₂C=C=¹³C, and H₂C=¹³C=C species are deposited in Tables S1–S3 as

Supporting Information. In these tables, the IR intensities, computed within the double harmonic approximation, are given as units of km mol⁻¹ in parentheses and as ratios relative to the largest intensity in square brackets for direct comparison with Maier's experimental observations.³ For the standard isotopologue of propadienylidene (**3S**), five fundamental frequencies have been observed via matrix isolation IR spectroscopy.³ Our harmonic vibrational frequencies for these five modes are predicted to be (differences from the experimental fundamental values in parentheses): ω₁(a₁) = 3126 (+77), ω₂(a₁) = 2005 (+53), ω₃(a₁) = 1492 (+45), ω₅(b₁) = 1023 (+23), and ω₈(b₂) = 1052 (+27) cm⁻¹. An averaged percent deviation relative to the harmonic vibrational frequencies for the standard H₂CCC (**3S**) isotopologue is 2.6%. For the dideutero isotopologue (D₂CCC), six fundamental vibrational frequencies have been experimentally observed. Theoretical harmonic vibrational frequencies for these six modes are determined to be ω₁(a₁) = 2288 (+87), ω₂(a₁) = 1981 (+48), ω₃(a₁) = 1229 (+20), ω₄(a₁) = 968 (+17), ω₅(b₁) = 816 (+16), and ω₈(b₂) = 846 (+17) cm⁻¹. Average percent deviation relative to the harmonic vibrational frequencies for the dideutero D₂CCC isotopologue is 2.3%.

Table 4. Theoretical Predictions of the Harmonic Vibrational Frequencies (in cm^{-1}), Anharmonic (Fundamental) Vibrational Frequencies (in cm^{-1}), and Infrared Intensities (in km mol^{-1}) [Ratio Relative to the Largest Intensity] for the \tilde{X}^1A_1 State of the Propadienylidene (Vinylidenecarbene, **3S**) C_3H_2 Molecule at the cc-pCVQZ CCSD(T) Level of Theory

mode number (assignment)	harmonic	$\Delta(\text{anh.} - \text{harm.})$	anharmonic	exptl. ^a	$\Delta(\text{harm.} - \text{exptl.})$	$\Delta(\text{anh.} - \text{exptl.})$
1 (a_1) CH_2 s-str.	3126.1(4.4)[0.02]	−135.6	2990.5	3049.5[0.02]	76.6	−59.0
2 (a_1) CC a-str.	2004.8(255.5)[1.00]	−47.0	1957.8	1952.2[1.00]	52.6	5.6
3 (a_1) CH_2 sciss.	1492.0(10.8)[0.04]	−44.4	1447.6	1446.9[0.14]	45.1	0.7
4 (a_1) CC s-str.	1122.3(2.0)[0.01]	−9.6	1112.7			
5 (b_1) CH_2 wag.	1022.5(18.6)[0.07]	−20.3	1002.2	999.5[0.10]	23.0	2.7
6 (b_1) CCC oop-bend	210.7(3.5)[0.01]	−3.5	207.2			
7 (b_2) CH_2 a-str.	3215.6(0.0)[0.00]	−160.0	3055.6			
8 (b_2) CH_2 rock	1051.6(3.4)[0.01]	−28.1	1023.6	1025.0[<0.01]	26.6	−1.4
9 (b_2) CCC ip-bend	273.9(1.4)[0.01]	−3.6	270.3			

^a Ref 3.**Table 5.** Theoretical Predictions of the Harmonic Vibrational Frequencies (in cm^{-1}), Anharmonic (Fundamental) Vibrational Frequencies (in cm^{-1}), and Infrared Intensities (in km mol^{-1}) [Ratio Relative to the Largest Intensity] for the \tilde{X}^1A_1 State of the Dideuterio-Propadienylidene (Vinylidenecarbene, **3S**) C_3D_2 Molecule at the cc-pCVQZ CCSD(T) Level of Theory

mode number (assignment)	harmonic	$\Delta(\text{anh.} - \text{harm.})$	anharmonic	exptl. ^a	$\Delta(\text{harm.} - \text{exptl.})$	$\Delta(\text{anh.} - \text{exptl.})$
1 (a_1) CD_2 s-str.	2287.9(29.2)[0.13]	−82.0	2205.9	2200.5[0.07]	87.4	5.4
2 (a_1) CC a-str.	1981.4(232.4)[1.00]	−43.7	1937.6	1933.4[1.00]	48.0	4.2
3 (a_1) CD_2 sciss.	1228.5(8.5)[0.04]	−18.3	1210.2	1208.7[0.08]	19.8	1.5
4 (a_1) CC s-str.	967.6(0.0)[0.00]	−13.8	953.8	950.8[0.01]	16.8	3.0
5 (b_1) CD_2 wag.	816.3(8.9)[0.04]	−14.2	802.1	800.3[0.06]	16.0	1.8
6 (b_1) CCC oop-bend	203.3(4.5)[0.02]	−2.8	200.5			
7 (b_2) CD_2 a-str.	2395.6(0.7)[0.00]	−92.3	2303.3			
8 (b_2) CD_2 rock	845.7(5.2)[0.02]	−17.5	828.1	829.2[0.02]	16.5	−1.1
9 (b_2) CCC ip-bend	252.5(0.3)[0.00]	−3.4	249.1			

^a Ref 3.**Table 6.** Theoretical Predictions of the Harmonic Vibrational Frequencies (in cm^{-1}), Anharmonic (Fundamental) Vibrational Frequencies (in cm^{-1}), and Infrared Intensities (in km mol^{-1}) [Ratio Relative to the Largest Intensity] for the \tilde{X}^1A_1 State of the Monodeuterio-Propadienylidene (Vinylidenecarbene, **3S**) C_3HD Molecule at the cc-pCVQZ CCSD(T) Level of Theory

mode number (assignment)	harmonic	$\Delta(\text{anh.} - \text{harm.})$	anharmonic	exptl. ^a	$\Delta(\text{harm.} - \text{exptl.})$	$\Delta(\text{anh.} - \text{exptl.})$
1 (a') CH str.	3173.9(1.9)[0.01]	−154.5	3019.4			
2 (a') CD str.	2337.2(13.2)[0.05]	−80.7	2256.5	2254.5[0.02]	82.7	2.0
3 (a') CC a-str.	1994.4(246.3)[1.00]	−44.8	1949.6	1940.6[1.00]	53.8	9.0
4 (a') CH bend	1367.1(9.1)[0.04]	−34.7	1332.4	1331.6[0.07]	35.5	0.8
5 (a') CC s-str.	1109.3(1.8)[0.01]	−17.5	1091.8			
6 (a') CD bend	882.5(4.1)[0.02]	−18.8	863.7	865.4[0.03]	17.1	−1.7
7 (a') CCC ip-bend	262.0(0.7)[0.00]	−3.5	258.5			
8 (a'') CHD wag.	925.0(13.7)[0.06]	−17.6	907.4	904.0[0.03]	21.0	3.4
9 (a'') CCC oop-bend	207.9(3.9)[0.02]	−3.1	204.8			

^a Ref 3.

Five fundamental vibrational frequencies have been identified for the monodeutero isotopologue (HDCCC). For this isotopologue, the experimental assignments of the CD in-plane bending (ν_6 , a') at 904.0 cm^{-1} and the CD out-of-plane bending (ν_8 , a'') at 865.4 cm^{-1} should be reversed as the CD in-plane bending (ν_6 , a') at 865.4 cm^{-1} and the CD out-of-plane bending (ν_8 , a'') at 904.0 cm^{-1} . Predicted harmonic vibrational frequencies for these five modes are $\omega_2(a') = 2337 (+83)$, $\omega_3(a') = 1994 (+54)$, $\omega_4(a') = 1367 (+36)$, $\omega_6(a') = 883 (+17)$, and $\omega_8(a'') = 925 (+21)\text{ cm}^{-1}$. An averaged percent deviation relative to the harmonic vibrational frequencies for the monodeutero HDCCC isotopologue is 2.6%. The differences between the theoretical (harmonic) and experimental (fundamental) vibrational frequencies may be mainly attributed to the anharmonicity of molecular vibrations. The anharmonicity effect for the vibrational frequencies will be addressed in the following three sections.

The IR intensity of the $\omega_2(a_1)$ mode is extraordinarily strong compared to those of the other eight modes, since it corresponds to a CC antisymmetric stretching motion with a large change in dipole moment.³ In Maier et al.'s paper,³ this I_2 intensity is regarded as a reference to determine relative intensities of other vibrational modes. In Seburg's experimental work, they were able to observe the three fundamental frequencies (ν_2 , ν_3 , and ν_5) with the strongest intensities in an argon matrix at 8 K.¹¹ Theoretically predicted relative intensities provided in Tables 4–6 and Tables S1–S3 are in reasonable agreement with experimentally observed values.

5.5. Vibrational Anharmonic Constants. The r th anharmonic (fundamental) vibrational frequency (ν_r) is determined using the following equation:

$$\nu_r = \omega_r + 2\chi_{rr} + \frac{1}{2} \sum_{s \neq r} \chi_{rs} \quad (7)$$

Table 7. Theoretical Predictions of Anharmonic Vibrational Constants (in cm^{-1}) for the C_3H_2 , C_3D_2 , and C_3HD Molecules at the cc-pCVQZ CCSD(T) Level of Theory

	C_3H_2	C_3D_2	C_3HD		C_3H_2	C_3D_2	C_3HD
χ_{11}	-30.197	-14.725	-63.988	χ_{34}	-2.827	-4.767	-5.689
χ_{22}	-10.543	-9.262	-33.096	χ_{35}	-4.202	-1.022	-10.707
χ_{33}	-10.527	-0.146	-10.015	χ_{36}	-0.021	5.367	-5.815
χ_{44}	-2.054	-1.071	-6.335	χ_{37}	-21.493	-2.881	-7.510
χ_{55}	-0.965	-2.004	-2.431	χ_{38}	-14.767	-9.523	-3.694
χ_{66}	-0.559	-0.572	-1.736	χ_{39}	-0.131	2.599	-8.377
χ_{77}	-35.583	-21.117	-0.414	χ_{45}	-3.182	-1.758	-3.857
χ_{88}	-2.593	-1.058	-1.898	χ_{46}	10.091	5.294	-11.609
χ_{99}	-0.516	-0.344	-0.561	χ_{47}	-1.403	-8.943	0.158
χ_{12}	-2.722	-7.578	-1.152	χ_{48}	-3.064	-2.987	-0.433
χ_{13}	1.863	-15.354	-2.383	χ_{49}	4.511	1.676	0.594
χ_{14}	-1.843	-6.489	-17.477	χ_{56}	-1.239	-1.620	-6.961
χ_{15}	-8.242	-3.988	-7.394	χ_{57}	-19.980	-12.215	-1.069
χ_{16}	-2.240	-2.288	-5.725	χ_{58}	4.545	1.733	-2.491
χ_{17}	-123.602	-61.080	-1.308	χ_{59}	1.397	0.902	7.835
χ_{18}	-12.206	-6.874	-15.224	χ_{67}	-2.292	-1.761	4.601
χ_{19}	-1.443	-1.393	-2.352	χ_{68}	-0.309	-0.585	0.368
χ_{23}	-5.022	-10.435	-5.318	χ_{69}^a	0.0	0.0	0.631
χ_{24}	-13.223	-5.311	-5.800	χ_{78}	-9.674	-6.682	1.134
χ_{25}	-5.835	-2.465	-0.665	χ_{79}^b	-1.403	-1.220	0.0
χ_{26}	-8.845	-7.673	-6.138	χ_{89}	0.068	-1.133	-0.443
χ_{27}	2.200	-5.342	-1.298				
χ_{28}	-10.374	-4.791	-6.794				
χ_{29}	-8.094	-6.813	-1.894				

^a $\chi_{69} = \chi_{96} = 0.0$ (adjusted) for C_3H_2 and C_3D_2 , whose original values were 17.7 and 8.1 cm^{-1} , respectively. ^b $\chi_{79} = \chi_{97} = 0.0$ (adjusted) for C_3HD , whose original value was 11.3 cm^{-1} .

where ω_r is an r th harmonic vibrational frequency and χ_{rs} are anharmonic vibrational constants. During the anharmonicity analyses, it was found that the anharmonic vibrational constant χ_{69} , the coupling constant between two CCC bending modes, is unphysically too large, probably due to the very low frequencies. Therefore, we adjusted this χ_{69} constant to be zero, i.e., $\chi_{69} = \chi_{96} = 0$ for the isotopologues with C_{2v} point group symmetry and $\chi_{79} = \chi_{97} = 0$ for the HDCCC isotopologue. The anharmonic vibrational constants (χ_{rs}) for C_3H_2 , C_3D_2 , and C_3HD are presented in Table 7, whereas those for the three ^{13}C labeled isotopologues are reported in Table S4 (Supporting Information).

5.6. Fundamental Vibrational Frequencies. In Tables 4–6, anharmonic vibrational frequencies for C_3H_2 , C_3D_2 , and C_3HD are included, while those for $\text{H}_2^{13}\text{C}=\text{C}=\text{C}$, $\text{H}_2\text{C}=\text{C}=\text{C}$, and $\text{H}_2\text{C}=\text{C}=\text{C}$ are shown in Tables S1–S3. In the last column of Table 4, the anharmonic vibrational frequencies for the standard H_2CCC species are compared with the experimentally observed fundamental vibrational frequencies. The largest discrepancy (59.0 cm^{-1}) is seen for the CH_2 symmetric stretching mode, possibly due to higher anharmonicity, or an experimental misassignment, given that our computed value for the CC antisymmetric stretch lies only 5.6 cm^{-1} away from the experimentally assigned CC antisymmetric stretching frequency. Given the close agreement between experiment and theory for the C–D stretching frequencies in the deuterated isotopologs, further spectroscopic studies of the C_3H_2 (3S) species are highly desirable, to confirm the laboratory assignment.

For the dideutero isotopologue (D_2CCC), the agreement between theoretical anharmonic and experimental fundamental frequencies is again excellent, as shown in Table 5. The largest deviation is 5.4 cm^{-1} for the CD_2 symmetric

stretching mode. In the last column of Table 6, a similar comparison has been made for the monodeutero isotopologue (HDCCC). The largest difference of 9.0 cm^{-1} is seen for the CC antisymmetric stretching mode. The theoretical anharmonic vibrational frequencies well reproduce the experimental fundamental frequencies. Specifically, our new assignments for the CD in-plane bending (ν_6 , a') and CD out-of-plane bending (ν_8 , a'') modes, as mentioned above (in section 5.4), are in excellent agreement with the experimental observations.

In the last columns of Tables S1–S3 (Supporting Information), the differences between the theoretical anharmonic and experimental fundamental vibrational frequencies for the three ^{13}C -labeled C_3H_2 isotopologues are presented. For each of the three isotopologues, the largest deviation is seen for the CC antisymmetric stretching mode (ν_2): 4.4 ($\text{H}_2^{13}\text{C}=\text{C}=\text{C}$), 4.7 ($\text{H}_2\text{C}=\text{C}=\text{C}$), and 4.6 cm^{-1} ($\text{H}_2\text{C}=\text{C}=\text{C}$). The mean absolute deviation between theoretical anharmonic and experimental fundamental vibrational frequencies for 24 modes of the six isotopologues (excluding CH_2 symmetric stretching) is only 2.6 cm^{-1} .

5.7. Isotopic Shifts of Vibrational Frequencies. In Table 8, theoretical isotopic shifts (in cm^{-1}) for the harmonic and anharmonic vibrational frequencies of the D_2CCC and HDCCC isotopologues with respect to the standard H_2CCC species are compared with the corresponding shifts of the experimental fundamental vibrational frequencies. Upon deuteration, the five vibrational modes involving the H atoms [mode 1 (a_1 , CH_2 s-str.), mode 3 (a_1 , CH_2 sciss.), mode 5 (b_1 , CH_2 wag.), mode 7 (b_2 , CH_2 a-str.), and mode 8 (b_2 , CH_2 rock)] are significantly red-shifted, as expected. Isotopic shifts from the theoretical harmonic vibrational frequencies are reasonably consistent with the experimental observations. On the other hand, isotopic shifts based on the theoretical anharmonic vibrational frequencies are in excellent agreement with the experimental values, within 2 cm^{-1} of deviations except for the ν_1 (a_1 , CH_2 s-str.) mode of D_2CCC and ν_2 (a_1 , CC str.) mode of HDCCC.

In Table 9, theoretical isotopic shifts for harmonic and anharmonic vibrational frequencies of the $\text{H}_2^{13}\text{C}=\text{C}=\text{C}$, $\text{H}_2\text{C}=\text{C}=\text{C}$, and $\text{H}_2\text{C}=\text{C}=\text{C}$ isotopologues with respect to the standard H_2CCC molecule are compared with those of the experimental fundamentals. The ^{13}C -labeling is most significant for the antisymmetric CC stretching mode (ν_2 , a_1) of the $\text{H}_2\text{C}=\text{C}=\text{C}$ and $\text{H}_2\text{C}=\text{C}=\text{C}$ isotopologues. On the other hand, the CH_2 scissoring mode (ν_3 , a_1) and CH_2 wagging mode (ν_5 , b_1) are affected notably by the ^{13}C -labeling of the CH_2 group ($\text{H}_2^{13}\text{C}=\text{C}=\text{C}$). Isotopic shifts from both theoretical harmonic and anharmonic vibrational frequencies are in excellent agreement with the experimental measurements of the ^{13}C -labeled isotopologues.

Concluding Remarks

Anharmonic rotational–vibrational analysis has been carried out for the electronic singlet state of the propadienylidene (3S) molecule employing vibrational second-order perturbation theory (VPT2). The equilibrium geometry and a quartic

Table 8. Theoretical and Experimental Isotopic Shifts of Vibrational Frequencies (cm^{-1}) for C_3D_2 and C_3HD with Respect to C_3H_2 at the cc-pCVQZ CCSD(T) Level of Theory

mode (symmetry)	$\text{D}_2\text{C}=\text{C}=\text{C}$ theory	$\text{D}_2\text{C}=\text{C}=\text{C}$ exptl.	mode (symmetry)	$\text{HDC}=\text{C}=\text{C}$ theory	$\text{HDC}=\text{C}=\text{C}$ exptl.
$\Delta\omega_1(a_1)$	-838.2		$\Delta\omega_1(a')$		
$\Delta\omega_2(a_1)$	-23.4		$\Delta\omega_2(a')$	-10.4	
$\Delta\omega_3(a_1)$	-263.5		$\Delta\omega_3(a')$	-124.9	
$\Delta\omega_4(a_1)$	-154.7		$\Delta\omega_4(a')$	-13.0	
$\Delta\omega_5(b_1)$	-206.2		$\Delta\omega_5(a'')$	-97.5	
$\Delta\omega_6(b_1)$	-7.4		$\Delta\omega_6(a'')$	-2.8	
$\Delta\omega_7(b_2)$	-820.0		$\Delta\omega_7(a')$		
$\Delta\omega_8(b_2)$	-205.9		$\Delta\omega_8(a')$	-169.1	
$\Delta\omega_9(b_2)$	-21.4		$\Delta\omega_9(a')$	-11.9	
$\Delta\nu_1(a_1)$	-784.6	-849.0	$\Delta\nu_1(a')$		
$\Delta\nu_2(a_1)$	-20.2	-18.8	$\Delta\nu_2(a')$	-8.2	-11.6
$\Delta\nu_3(a_1)$	-237.4	-238.2	$\Delta\nu_3(a')$	-115.2	-115.3
$\Delta\nu_4(a_1)$	-158.9		$\Delta\nu_4(a')$	-20.9	
$\Delta\nu_5(b_1)$	-200.1	-199.2	$\Delta\nu_5(a'')$	-94.8	-95.5
$\Delta\nu_6(b_1)$	-6.7		$\Delta\nu_6(a'')$	-2.4	
$\Delta\nu_7(b_2)$	-752.3		$\Delta\nu_7(a')$		
$\Delta\nu_8(b_2)$	-195.5	-195.8	$\Delta\nu_8(a')$	-159.9	-159.6
$\Delta\nu_9(b_2)$	-21.2		$\Delta\nu_9(a')$	-11.8	

Table 9. Theoretical and Experimental Isotopic Shifts of Vibrational Frequencies (cm^{-1}) for $\text{H}_2^{13}\text{C}=\text{C}=\text{C}$, $\text{H}_2\text{C}=\text{C}=\text{C}^{13}\text{C}$, and $\text{H}_2\text{C}=\text{C}=\text{C}^{13}\text{C}$ with Respect to C_3H_2 at the cc-pCVQZ CCSD(T) Level of Theory

mode (symmetry)	$\text{H}_2^{13}\text{C}=\text{C}=\text{C}$ theory	$\text{H}_2^{13}\text{C}=\text{C}=\text{C}$ exptl.	$\text{H}_2\text{C}=\text{C}=\text{C}^{13}\text{C}$ theory	$\text{H}_2\text{C}=\text{C}=\text{C}^{13}\text{C}$ exptl.	$\text{H}_2\text{C}=\text{C}=\text{C}^{13}\text{C}$ theory	$\text{H}_2\text{C}=\text{C}=\text{C}^{13}\text{C}$ exptl.
$\Delta\omega_2(a_1)$	-9		-16		-52	
$\Delta\omega_3(a_1)$	-8		-2		-1	
$\Delta\omega_5(b_1)$	-10		0		-1	
$\Delta\nu_2(a_1)$	-9	-8	-16	-15	-50	-49
$\Delta\nu_3(a_1)$	-9	-9	-2	-2	-1	-2
$\Delta\nu_5(b_1)$	-9	-7	0	2	-1	-3

force field have been determined at the all-electron cc-pCVQZ CCSD(T) level of theory. The predicted fundamental frequencies for propadienylidene as well as its ^{13}C and deuterium isotopologues are in good agreement with available experimental values. The mean absolute deviation between theoretical anharmonic and experimental fundamental vibrational frequencies for 24 modes of seven isotopologues (excluding CH_2 s-str.) is only 2.6 cm^{-1} . The isotopic shifts of the vibrational frequencies are also in excellent agreement with the available experimental values, agreeing within 2.0 cm^{-1} . It has been unambiguously demonstrated that second-order vibrational perturbation theory (VPT2) using a highly accurate quartic force field accompanied with careful detailed analysis does provide quite reliable information for a penta-atomic molecule (C_3H_2) and its ^{13}C and deuterium isotopologues. We hope that the present research will aid further characterization of the propadienylidene molecule and encourage theoretical and experimental studies in the areas of hydrocarbon chemistry, combustion chemistry, chemical dynamics, interstellar chemistry, and high-resolution spectroscopy. We encourage experimental reinvestigation of the CH_2 symmetric stretch to confirm its assignment.

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Note Added in Proof. We recently became aware of a complimentary study of the vibrational modes of propadienylidene [Botschwina, P.; Oswald, R. *J. Phys. Chem. A* **2010**, *114*, 9782], performed independently of our work, but at the same time. Their results are in very good agreement with ours, and a thorough analysis of the ν_1 fundamental misassignment is provided.

Supporting Information Available: Theoretical predictions of the harmonic vibrational frequencies, anharmonic vibrational frequencies, and infrared intensities and theoretical predictions of anharmonic vibrational constants. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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