Infrared spectroscopic and theoretical study of the $\text{HC}_{2n+1}\text{O}^+$ ($n = 2-5$) cations

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The carbon chain cations, $\text{HC}_{2n+1}\text{O}^+$ ($n = 2-5$), are produced via pulsed laser vaporization of a graphite target in supersonic expansions containing carbon monoxide and hydrogen. The infrared spectra are measured via mass-selected infrared photodissociation spectroscopy of the CO “tagged” $[\text{HC}_{2n+1}\text{O}\cdot\text{CO}]^+$ cation complexes in the 1600–3500 cm^{-1} region. The geometries and electronic ground states of these cation complexes are determined by their infrared spectra compared to the predications of theoretical calculations. All of the $\text{HC}_{2n+1}\text{O}^+$ ($n = 2-5$) core cations are characterized to be linear carbon chain derivatives terminated by hydrogen and oxygen, which have the closed-shell singlet ground states with polyynes-like carbon chain structures. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4984084>]

I. INTRODUCTION

Carbon chains and its derivatives are highly active species, which widely exist as reactive intermediates in many chemical processes including atmospheric chemistry,¹ hydrocarbon compounds’ dissociation and combustion,^{2,3} as well as interstellar chemistry.⁴⁻⁶ Carbon chain derivatives terminally capped by hydrogen, nitrogen, or oxygen have been the subject of intensive experimental and theoretical studies.⁷⁻¹¹ Short chain species such as HCO, HCO^+ , HCCO ,¹²⁻¹⁴ and HC_nN ($n = 1-4$),¹⁵⁻¹⁸ as well as long chain cyanopolynes including HC_5N , HC_7N , and HC_9N ,¹⁹⁻²¹ have been observed in space by radio-astronomy.

The neutral molecules HC_nO ($n = 1-9$) have been studied by rotational spectroscopy in the gas phase. The first four members of this series were determined to possess planar bent structures due to a strong Renner-Teller interaction. The bending angle increases as the carbon number increases.²²⁻²⁹ The Renner-Teller interaction is weak for longer members of the series because the orbital angular momentum is not quenched.³⁰ Thus, the HC_nO radicals with $n = 5$ and 7 were characterized by Fourier transform microwave spectroscopy to have linear structures and $^2\Pi$ electronic ground states.³⁰ Compared to the neutral species, the HC_nO^+ ions, which are isoelectronic with the HC_nN neutrals, have received much less attention. The charged HC_nO^+ ions have been produced in the gas phase, and their thermochemistry and ion chemistry have been probed with mass spectrometry.^{31,32} Only the first member HCO^+ has been well studied spectroscopically in the gas phase.³³⁻³⁵ In addition, a vibrationally resolved electronic absorption spectrum of the HC_7O^+ cation has been recorded in a 6 K neon matrix after the mass-selected deposition of the cations produced in the gas phase.³⁶

The cation was determined to have a singlet electronic ground state with a linear structure.³⁶ In this paper, the carbon chain cation derivatives with the odd number of carbon atoms, $\text{HC}_{2n+1}\text{O}^+$ with $n = 2-5$, are produced via pulsed laser vaporization of a graphite target in supersonic expansions containing carbon monoxide and hydrogen. These cations are investigated via mass-selected infrared photodissociation spectroscopy as well as theoretical calculations.

II. EXPERIMENTAL AND THEORETICAL METHODS

The infrared photodissociation spectra of the carbon chain cations were measured by a collinear tandem time-of-flight mass spectrometer as described in detail previously.^{37,38} The cations were produced by a pulsed laser vaporization ion source using the second harmonic of a pulsed Nd:YAG laser (532 nm; 10 Hz repetition rate). The pulsed laser was focused onto a graphite target which was loaded on a two-dimensional translation stage. The expansion gas is helium seeded with 1% H_2 and 5%-10% CO at a backing pressure of 0.6–1.2 MPa. After free expansion and cooling, the ions were skimmed to a second chamber, where they were mass-separated by a primary time-of-flight mass spectrometer. The ions of interest were mass-selected and decelerated into the extraction region of a second collinear time-of-flight mass spectrometer, where they were subjected to photodissociation by a tunable IR laser. The infrared light was generated by an optical parametric oscillator/amplifier system (OPO/OPA, LaserVision) pumped by a Nd:YAG laser, producing about 0.6–1.2 mJ/pulse laser beam in the range of 1600–2200 cm^{-1} with AgGaSe_2 crystal, and about 1.3–5.0 mJ/pulse in the range of 2100–3500 cm^{-1} without AgGaSe_2 crystal. The IR photodissociation spectrum was obtained by monitoring the yield of the fragment ions as a function of the IR laser wavelength. The spectra were recorded by scanning the dissociation laser in steps of 2 cm^{-1} and averaging over 500 laser shots at each step.

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Quantum chemical calculations were performed using the density functional theory (DFT) method with the Gaussian 09 program.³⁹ Geometry optimizations and harmonic and anharmonic frequency calculations⁴⁰ were carried out using the hybrid B3LYP functional.^{41,42} The empirical dispersion correction^{43,44} was added to increase the accuracy in predicting the weak interactions between the tagging ligands and the carbon chain cations. Dunning's correlation consistent basis set with polarized triple-zeta plus diffuse functions (aug-cc-pVTZ) was used for all atoms.⁴⁵ The harmonic vibrational frequencies were scaled by a factor of 0.968 according to the Computational Chemistry Comparison and Benchmark Database.⁴⁶ Bonding analyses were performed by the natural bond orbital (NBO) analysis^{47,48} and the adaptive natural density partitioning (AdNDP)⁴⁹ methods using the density generated from the B3LYP-D3 calculations. The AdNDP analysis was performed using the Multiwfn package.⁵⁰

III. RESULTS AND DISCUSSION

The mass spectrum of the cations in the m/z range of 70–190 generated from laser vaporization of graphite target in the expansion of helium gas seeded with 10% carbon monoxide and 1% molecular hydrogen is displayed in Fig. 1. Peaks due to HC_nO^+ ($n = 5$ –9) are observed to be the most intense peaks in the mass spectrum, suggesting that these cations are formed preferentially. Large variations in the relative abundance of cations with odd and even numbers of carbon atoms are observed. The ions with odd numbers of carbon atoms are more intense than the ions with even numbers of carbon atoms. A similar behavior with odd-even intensity alternation has been observed in previous spectroscopic studies of the HC_nO neutrals.³⁰ The intense $\text{HC}_{2n+1}\text{O}^+$ ($n = 2$ –5) cations with odd numbers of carbon atoms are mass-selected for infrared photodissociation. It is found that these cations do not dissociate when excited with infrared light. To obtain the infrared spectra of the $\text{HC}_{2n+1}\text{O}^+$ ($n = 2$ –5) cations, the message atom “tagging” technique is employed.^{51–54} The $\text{HC}_{2n+2}\text{O}_2^+$ ($n = 2$ –5) cation complexes are formed by adjusting the timing between the vaporization laser and supersonic expansion to favor the formation of weakly bound complexes due

to cold supersonic beam conditions and are mass-selected for infrared photodissociation. It is found that these cation complexes dissociate efficiently via the loss of a CO ligand with unfocused infrared laser, indicating that the $\text{HC}_{2n+2}\text{O}_2^+$ ($n = 2$ –5) cations are weakly bound “CO-tagged” $[\text{HC}_{2n+1}\text{O-CO}]^+$ ($n = 2$ –5) complexes involving strongly bound $\text{HC}_{2n+1}\text{O}^+$ ($n = 2$ –5) core ions. As discussed previously,^{55–57} CO-tagging usually has a negligible effect on the structure and low-resolution, rotationally unresolved vibrational spectrum of the core ion.

The infrared spectra of the $[\text{HC}_{2n+1}\text{O-CO}]^+$ ($n = 2$ –5) cation complexes in the 1600–3500 cm^{-1} frequency region are displayed in Fig. 2. The band positions are listed in Table I. The spectral features imply that the observed bands can be assigned to the vibrations of the $\text{HC}_{2n+1}\text{O}^+$ core ions, which have linear or near linear structures involving a carbon chain terminally capped by hydrogen and oxygen. Each cation spectrum exhibits a band in the 3250–3300 cm^{-1} region: 3262 cm^{-1} for $n = 2$; 3284 cm^{-1} for $n = 3$; 3292 cm^{-1} for $n = 4$; and 3296 cm^{-1} for $n = 5$. The band positions are appropriate for terminal C—H stretching vibrations, which increase monotonically by increasing the number of carbon atoms. The bands in the 2200–2300 cm^{-1} region at 2286 cm^{-1} for $n = 2$, 2272 cm^{-1} for $n = 3$, 2276 cm^{-1} for $n = 4$, and 2266 cm^{-1} for $n = 5$ can be assigned to terminal CO stretching vibrations of the $\text{HC}_{2n+1}\text{O}^+$ core ions. The bands in the 1900–2200 cm^{-1} region can be attributed to the stretching vibrations of the carbon chains. No bands are observed above 3300 cm^{-1} and below 1900 cm^{-1} , suggesting that other isomers involving either OH or bridge-bonded C=O moieties can clearly be ruled out. The spectral features also indicate that for each complex the weakly tagged CO group is coordinated neither to the hydrogen atom nor to the oxygen atom of the $\text{HC}_{2n+1}\text{O}^+$ core ions. CO coordination to hydrogen or oxygen is expected to induce quite large red-shifts of the CH or CO stretching vibrational frequencies of the $\text{HC}_{2n+1}\text{O}^+$ core ions. The observed bands show non-symmetric band shapes with varying widths in the range of 8–16 cm^{-1} . A similar band shape has been observed, which was interpreted as stemming from unresolved rotational excitation.^{58,59}

FIG. 1. Mass spectrum of the cations in the m/z range of 70–190 from pulsed laser evaporation of a graphite target in expansion of helium seeded with 1% H_2 and 10% CO at a backing pressure of 1.0 MPa.

FIG. 2. The infrared photodissociation spectra of the $[\text{HC}_{2n+1}\text{O-CO}]^+$ ($n = 2$ –5) cation complexes in the 1600–3500 cm^{-1} region. (a) $n = 2$, (b) $n = 3$, (c) $n = 4$, and (d) $n = 5$.

TABLE I. The experimental vibrational frequencies and the calculated vibrational frequencies (cm^{-1} , unscaled) and intensities (km/mol in parentheses) as well as the calculated dissociation energy (D_0 , in kcal/mol) for “tagging” CO of the $[\text{HC}_{2n+1}\text{O}\cdot\text{CO}]^+$ ($n = 2-5$) cation complexes.

Species	D_0	Expt.	Calcd. (harmonic)	Calcd. (anharmonic)	Assignment
$[\text{HC}_5\text{O}\cdot\text{CO}]^+$	3.4	3262	3397.9(134)	3328.0(102)	CH str. (ν_1)
		2286	2369.4(2399)	2323.8(2337)	CO str. (ν_2)
		2186	2282.5(542)	2238.7(259)	CC str. (ν_3)
			2247.8(79)	2219.0(78)	Tagging CO str. (ν_4)
		2028	2113.6(125)	2077.8(184)	Chain str. (ν_5)
$[\text{HC}_7\text{O}\cdot\text{CO}]^+$	2.9	3284	3413.4(164)	3302.2(156)	CH str. (ν_1)
		2272	2362.8(1775)	2313.5(27)	CO str. (ν_2)
		2158	2263.7(3633)	2223.7(2880)	CC str. (ν_3)
			2241.3(206)	2214.8(302)	Tagging CO str. (ν_4)
		2122	2213.3(1050)	2178.4(1267)	CC str. (ν_5)
$[\text{HC}_9\text{O}\cdot\text{CO}]^+$	2.6	2014	2087.4(14)	2056.0(21)	Chain str. (ν_6)
		3292	3424.0(196)	3294.2(206)	CH str. (ν_1)
		2290 ^a			
		2276	2354.9(2331)	2309.9(1730)	CO str. (ν_2)
			2276.4(0)	2225.9(8)	CC str. (ν_3)
$[\text{HC}_{11}\text{O}\cdot\text{CO}]^+$	2.3		2238.1(80)	2211.3(68)	Tagging CO str. (ν_4)
		2066	2195.4(8064)	2148.8(6890)	CC str. (ν_5)
			2171.2(1090)	2134.7(1479)	CC str. (ν_6)
		2002	2066.1(208)	2033.7(205)	Chain str. (ν_7)
$[\text{HC}_{11}\text{O}\cdot\text{CO}]^+$	2.3	3296	3431.4(230)	3297.9(183)	CH str. (ν_1)
		2266	2345.1(3530)	2292.0(2846)	CO str. (ν_2)
			2278.3(84)	2226.5(14)	CC str. (ν_3)
			2240.0(3)	2202.6(1)	CC str. (ν_4)
		2178	2235.2(73)	2204.8(70)	Tagging CO str. (ν_5)
$[\text{HC}_{11}\text{O}\cdot\text{CO}]^+$	2.3	2066	2150.8(2676)	2114.6(7633)	CC str. (ν_6)
		1996	2121.3(12 248)	2084.8(8004)	CC str. (ν_7)
			2050.5(9)	2015.5(7)	Chain str. (ν_8)

^aThis band is tentatively assigned as an overtone of the low CC stretching mode that is in Fermi resonance with the CO stretching mode.

Quantum chemical calculations have been carried out to investigate the geometries, bond dissociation energies, and vibrational frequencies of the cation complexes. Calculations have been performed on both the $[\text{HC}_{2n+1}\text{O}\cdot\text{CO}]^+$ ($n = 2-5$) cation complexes and the bare $\text{HC}_{2n+1}\text{O}^+$ core ions. For each $\text{HC}_{2n+1}\text{O}^+$ core ion, geometry optimizations have been performed on various possible structures, and the results are shown in Figs. S1 and S2 of the [supplementary material](#), respectively. For each ion, the global minimum structure has a closed-shell singlet ground state with a linear carbon chain terminally capped by hydrogen and oxygen. The corresponding triplet state is predicted to lie 30-50 kcal/mol higher in energy than the singlet state. The energy gap between singlet and triplet spin states decreases monotonically upon increasing the carbon chain length. The other structural isomers are predicted to lie much higher ($>50 \text{ kcal/mol}$) in energy above the linear singlet ground state structure. The CO-tagged $[\text{HC}_{2n+1}\text{O}\cdot\text{CO}]^+$ ($n = 2-5$) cation complexes are also calculated. Since the global minimum structure is much lower in energy than the other isomers for each $\text{HC}_{2n+1}\text{O}^+$ core ion system, only the complexes tagged to the global minimum singlet ground state $\text{HC}_{2n+1}\text{O}^+$ core ions are considered. Figure 3 shows the optimized geometries of the bare $\text{HC}_{2n+1}\text{O}^+$ core ions as well as

the CO-tagged $[\text{HC}_{2n+1}\text{O}\cdot\text{CO}]^+$ ($n = 2-5$) cation complexes at the B3LYP-D3/aug-cc-pVTZ level. For each $[\text{HC}_{2n+1}\text{O}\cdot\text{CO}]^+$ complex, the CO ligand is tagged to the carbon atom of the terminal CO moiety of the $\text{HC}_{2n+1}\text{O}^+$ core ion, resulting in an $^1\text{A}'$ electronic ground state with C_s symmetry. The distances between the tagged CO ligand and the core ions are predicted to lie in the range of 3.073-3.191 Å. Very small changes of the bond angles and bond lengths are observed for the core ions upon CO tagging. The carbon chain remains essentially linear with only the OCC angle being slightly bent (177.9° for HC_5O^+ to 178.9° for HC_{11}O^+). The dissociation energies of the tagged CO are predicted to be quite small (2.3-3.4 kcal/mol , Table I).

Table I shows the experimental and calculated vibrational frequencies of the $[\text{HC}_{2n+1}\text{O}\cdot\text{CO}]^+$ cation complexes. The calculated values of the harmonic frequencies are uniformly higher than the experimental values as expected.⁶⁰ The simulated vibrational spectra based on the scaled vibrational frequencies and intensities of the most stable structures of the $\text{HC}_{2n+1}\text{O}^+$ core ions as well as the CO-tagged $[\text{HC}_{2n+1}\text{O}\cdot\text{CO}]^+$ cation complexes are compared with the experimental spectra in Figs. 4-7, respectively. The simulated IR spectra of the $\text{HC}_{2n+1}\text{O}^+$ ions with and without CO-tagging are

FIG. 3. Optimized geometries of $[\text{HC}_{2n+1}\text{O-CO}]^+$ and $\text{HC}_{2n+1}\text{O}^+$ ($n=2-5$) (bond lengths in angstroms and bond angles in degrees), the NBO natural charges and Wiberg bond orders (values in brackets) for $\text{HC}_{2n+1}\text{O}^+$ ($n=2-5$) calculated at the B3LYP-D3/aug-cc-pVTZ level.

essentially the same except that the band positions of the CO-tagged complexes are slightly red-shifted from those of untagged ions. The shifts are in general less than 20 cm^{-1} . The stretching mode of tagged CO is predicted to be weak and slightly blue-shifted from that of free CO calculated at the same level (2207 cm^{-1}) due to weak electrostatic interactions. This mode could either be overlapped by the strong CC stretching mode in the $2140\text{--}2200\text{ cm}^{-1}$ region or too weak to be observed experimentally. As shown in Figs. 4–7, the agreement between experimental and computed band positions is in general satisfactory. As listed in Table I, the evolution of both the CH and CO stretch frequencies with the chain length is qualitatively reproduced by the harmonic calculations. Besides the CO stretching mode at 2276 cm^{-1} , an

additional band at 2290 cm^{-1} is observed for the $[\text{HC}_9\text{O-CO}]^+$ cation. This band is tentatively assigned to an overtone of the low CC stretching mode (ν_9) that is in Fermi resonance with the CO stretching mode. The anharmonic frequency calculations were also performed and the results are listed in Table I. The C–H stretching modes have the largest anharmonic corrections, with the anharmonic values $70\text{--}130\text{ cm}^{-1}$ lower than the corresponding harmonic values. The anharmonic corrections are in the range of $27\text{--}53\text{ cm}^{-1}$ for the other modes with the tagged CO stretching mode having the smallest corrections.

There are some substantial deviations regarding the observed and calculated relative IR intensities. It should be pointed out that although the infrared photodissociation spectrum often resembles the linear absorption spectrum, the

FIG. 4. The experimental infrared photodissociation spectrum of the [HC₅O-CO]⁺ cation complex [trace (a)] and the simulated spectra of the most stable [HC₅O-CO]⁺ (b) and HC₅O⁺ (c) cations at the B3LYP-D3/aug-cc-pVTZ level. The harmonic vibrational frequencies are scaled by a factor of 0.968 and are given an 8 cm⁻¹ full width at half-maximum.

intensities depend not only on the cross section for photon absorption but also on the efficiency of intramolecular vibrational relaxation and laser intensity. The infrared laser intensity is varied with wavelength (Fig. S7 of the [supplementary material](#)), and such a variation is not corrected in the experimental spectra. The harmonic and anharmonic calculations give dramatically different intensity predictions in some cases, for example, in the CO stretching mode of [HC₇O-CO]⁺. The harmonic calculation gives a value of 1775 km/mol, whereas the anharmonic calculations predict a value of only 27 km/mol. This suggests that the intensity predictions at the DFT levels are not very reliable for these quasi-linear chain species. The simulated spectra of other high-lying structural isomers are shown in Figs. S3-S6, respectively. None of them match with the experimental spectra and can clearly be ruled out.

The HC₇O⁺ cation was produced from 1,2,3,4,5-benzenepentacarboxylic acid in an ion source and has been studied recently by vibrationally resolved electronic absorption spectroscopy after mass-selected deposition in the 6 K

FIG. 5. The experimental infrared photodissociation spectrum of the [HC₇O-CO]⁺ cation complex [trace (a)] and the simulated spectra of the most stable [HC₇O-CO]⁺ (b) and HC₇O⁺ (c) cations at the B3LYP-D3/aug-cc-pVTZ level. The harmonic vibrational frequencies are scaled by a factor of 0.968 and are given an 8 cm⁻¹ full width at half-maximum.

FIG. 6. The experimental infrared photodissociation spectrum of the [HC₉O-CO]⁺ cation complex [trace (a)] and the simulated spectra of the most stable [HC₉O-CO]⁺ (b) and HC₉O⁺ (c) cations at the B3LYP-D3/aug-cc-pVTZ level. The harmonic vibrational frequencies are scaled by a factor of 0.968 and are given an 8 cm⁻¹ full width at half-maximum.

neon matrix.³⁶ The observed spectrum is consistent with the linear structure, which was predicted to be the global minimum structure.³⁶

As shown in Fig. 3, the HC_{2n+1}O⁺ cations are predicted to have polyyne-like carbon chain structures with alternating long and short C—C bond lengths. The long bonds have bond lengths in the range of 1.300–1.338 Å, which are slightly shorter than typical C=C double bond length (1.34 Å).⁶¹ The short bonds have bond lengths in the range of 1.210–1.234 Å, which are slightly longer than the typical C≡C triple bond length (1.20 Å).⁶² This pattern of bond length deviates from the traditional Lewis structure of polyynes with alternating single and triple bonds, suggesting a strong delocalized bonding character of the carbon chains in the linear HC_{2n+1}O⁺ cations. The Wiberg bond orders for the HC_{2n+1}O⁺ cations are also calculated and displayed in Fig. 3. The long C—C bonds have bond orders of 1.3–1.5, whereas the short C—C bonds are calculated to have values in the range of 2.1–2.6. The terminal CO bond distance increases from 1.134 Å in HC₅O⁺ to 1.143 Å in HC₁₁O⁺, consistent with the observed trend of the

FIG. 7. The experimental infrared photodissociation spectrum of the [HC₁₁O-CO]⁺ cation complex [trace (a)] and the simulated spectra of the most stable [HC₁₁O-CO]⁺ (b) and HC₁₁O⁺ (c) cations at the B3LYP-D3/aug-cc-pVTZ level. The harmonic vibrational frequencies are scaled by a factor of 0.968 and are given an 8 cm⁻¹ full width at half-maximum.

CO stretching vibrational frequency, which decreases from 2286 cm^{-1} for HC_5O^+ to 2266 cm^{-1} for HC_{11}O^+ .

Natural population analysis shows that the positive charge is largely distributed on the CO and CH moieties (Fig. 3). In each cation, the carbon atom of the CO unit has the largest positive charge. This explains why the tagged CO prefers to coordinate with the carbon atom of the CO moiety. The charge of the carbon atom decreases monotonically from $+0.81e$ in HC_5O^+ to $+0.77e$ in HC_{11}O^+ , in accord with the predicted dissociation energy of the tagged CO, which decreases monotonically from 3.4 kcal/mol for $[\text{HC}_5\text{O-CO}]^+$ to 2.3 kcal/mol for $[\text{HC}_{11}\text{O-CO}]^+$ due to a reduced electrostatic interaction.⁶³ To understand the bonding in the linear $\text{HC}_{2n+1}\text{O}^+$ cations, we performed the Adaptive Natural Density Partitioning (AdNDP) analysis, which has the ability to recover simultaneously both localized and delocalized bonding in chemical species. The results are shown in Fig. 8. Besides the oxygen lone pair and two-center-two-electron (2c-2e) localized C—O, C—C, and C—H σ bonds, there are delocalized multicenter-two-electron π bonds. The HC_5O^+ cation contains two three-center-two-electron (3c-2e) π bonds in the CCO moiety, two four-center-two-electron (4c-2e) π bonds in the carbon chain, and two

six-center-two-electron (6c-2e) π bonds along the C_5O structural motif. The two degenerate 6c-2e π bonds are bonding in character for the first, second, and fourth C—C bonds but are antibonding in character for the C—O bond as well as the third C—C bond with respect to the CO bond. Besides the degenerate 3c-2e and 4c-2e π bonds, the HC_7O^+ cation contains additional two 5c-2e and two 8c-2e π bonds; the HC_9O^+ cation exhibits additional two 5c-2e, two 6c-2e, and two 10c-2e π bonds; while the HC_{11}O^+ cation involves additional four 5c-2e, two 6c-2e, and two 12c-2e π bonds. These delocalized π orbitals are responsible for alternating long and short C—C bond lengths in these linear carbon chain cations.

The linear $\text{HC}_{2n+1}\text{O}^+$ cation species characterized here are isoelectronic to the linear HC_{2n+1}N neutral molecules, which have been identified in dense interstellar clouds by millimeter-wave spectroscopy.^{19–21} One would expect that the $\text{HC}_{2n+1}\text{O}^+$ cation species may also be presented in the interstellar medium, as both oxygen and nitrogen are among the most abundant elements in the interstellar medium. It is well known that the C^+ , CH , CH^+ , CO , and CO^+ species are among the most important building blocks of interstellar organic molecules. The carbon chain species such as C_nH have also

FIG. 8. Chemical bonding pattern of the $\text{HC}_{2n+1}\text{O}^+$ ($n = 2-5$) cations by the AdNDP analyses. ON stands for occupation number. Only one of the doubly degenerate π bonds is shown.

been identified in space environments.⁶⁴ These species can act as potential reactants for the generation of oxygen containing organic cations such as $\text{HC}_{2n+1}\text{O}^+$ via ion-molecular reactions or photo-induced association reactions driven by cosmic rays in a dense interstellar cloud environment.⁶⁵

IV. CONCLUSIONS

The carbon chain cations $\text{HC}_{2n+1}\text{O}^+$ ($n=2-5$) are produced via pulsed laser vaporization of a graphite target in supersonic expansions containing carbon monoxide and hydrogen. Their infrared spectra are measured via mass-selected infrared photodissociation spectroscopy of the “CO-tagged” $[\text{HC}_{2n+1}\text{O-CO}]^+$ cation complexes in the 1600–3500 cm^{-1} frequency region. Spectroscopic combined with quantum chemical calculations indicate that the $\text{HC}_{2n+1}\text{O}^+$ ($n=2-5$) core ions are linear carbon chain derivatives terminally capped by hydrogen and oxygen, which have closed-shell singlet ground states with polyyne-like carbon chain structures with regular alternating long and short C—C bonds. The AdNDP bonding analysis indicates that along with the localized two-center-two-electron σ bonds, there are pairs of multiple-center-two-electron delocalized π bonds on the C_nO chains, which are responsible for the alternating bond lengths. The linear $\text{HC}_{2n+1}\text{O}^+$ cation species characterized here are potential species in the interstellar medium. The present infrared spectral data offer the laboratory evidence and support for future interstellar spectroscopic detection.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for calculated geometries for all structural isomers and vibrational spectra of the $\text{HC}_{2n+1}\text{O}^+$ cations.

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