Xe-bearing Hydrocarbon Ions: Observation of Xe.Acetylene⁺ and Xe.Benzene⁺ Radical Cations and Calculations of their Ground State Structures

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Abstract

This work reports evidence for novel types of Xe-bearing hydrocarbon radical cations. The Xe.acetylene⁺ radical cation adduct is observed at nearly room temperature using the mass-selected drift cell technique. The irreversible addition of the Xe atom and the lack of back dissociation to HCCH⁺ + Xe is consistent with the calculated binding energy of 0.85 eV to be contrasted with the metastable nature of the neutral Xe.acetylene adduct. The observed Xe.benzene⁺ radical cation appears to be a weakly bound complex stabilized mainly by ion-induced dipole interaction consistent with a calculated binding energy in the range of 0.14-0.17 eV.

TOC Graphic

I. Introduction

Xenon is a trace gas constituting 90 ppb by volume of the atmosphere, about 1/13 of that of krypton. Its varied applications include high-intensity gas discharge and other light sources, propellant for small thrusters used to position satellites in orbit, plasma display panels, anesthesiology, and MRI applications, to name a few of the growing list of commercial uses.¹ Due to diverse applications of xenon, there is a general growth of interest in studying xenon binding and in finding novel ways to produce xenon due to its high price.^{2,3} Great progress is being made in understanding the anesthetic properties of xenon which was approved for use in 2007 in the European community.⁴ While specific binding sites have been discovered⁵, the mechanism of binding remains controversial.⁶ A recent development in nanotechnology made possible the accurate measurement of the binding energy of Xe to carbon nanotubes.⁷

The binding of xenon to various molecules via weak van der Waals (vdW) interactions is expected due to its large polarizability. The binding of Xe by organic materials such as lipids or proteins (e.g. hemoglobin) has been observed decades ago^{8,9} and there is renewed interest in the binding by porous materials.¹⁰⁻¹³ An interesting question is why Xe binds preferentially to specific molecular units via non-directional interactions. Particularly exciting was the discovery of insertion compounds of noble gas atoms into various molecules, first into hydrides and then into organics.¹⁴⁻¹⁸ [Theoretical studies of Xe-containing molecules of the type HXeCCH and HXeC₆H₅ have been reported.](#)¹⁹ The HXeCCH molecule with a Xe atom inserted between the H-C bond, was predicted to be metastable with a large dissociation barrier of 1.5 eV providing sufficient stability against decomposition.¹⁹ Following this theoretical prediction, experimental evidence for the formation of the HXeCCH molecule based on FTIR and EPR spectroscopy in solid Xe matrices was also reported.²⁰ Most of the reported work involves interactions between Xe atoms and neutral molecules and there is no report in the literature on the interaction of Xe atoms with hydrocarbon ions in the gas phase. Only one paper reports formation of ionic complexes of Xe and acetylene by the radiolysis of a mixture of acetylene and Xe gases by 90 eV electrons where the reaction was assumed to take place between the Xe ion and the acetylene neutral molecule.²¹ However, there are no reports on the gas phase reactions between mass-selected acetylene ions and neutral Xe atoms.

Here we report, for the first time, the capture of Xe atoms by the organic radical cations acetylene ($\text{HCCH}^{+\bullet}$) and benzene ($\text{C}_6\text{H}_6^{+\bullet}$) under thermal conditions in the gas phase using the mass-selected drift cell technique. The $\text{Xe.HCCH}^{+\bullet}$ adduct is observed at nearly room temperature in a gas phase reaction between the acetylene radical cation and Xe atoms. The covalent nature of this adduct is indicated by the irreversible addition and the lack of back dissociation to the reactant channels. We also characterize computationally the potential energy surfaces for the interactions of Xe with the $\text{HCCH}^{+\bullet}$ and $\text{C}_6\text{H}_6^{+\bullet}$ cations and identify new covalent and non-covalent minimum energy structures. The results provide direct evidence for the formation of Xe-containing hydrocarbon radical cations and suggest wide prospects for preparing new unusual Xe-containing organic ions in the gas phase and characterizing their structures and chemical properties.

II. Experimental Section

The experiments were performed using the VCU mass-selected ion mobility spectrometer (A Schematic is given in **Figure S1**, Supporting Information). The details of the instrument can be found in several publications²²⁻²⁵ and only a brief description of the experimental procedure is given here. In the experiments, the acetylene ($\text{HCCH}^{+\bullet}$) or the benzene ($\text{C}_6\text{H}_6^{+\bullet}$) molecular ions are formed by electron impact ionization using electron energy of 60-70 eV following the supersonic expansion of 40 psi (≈ 2500 Torr) of ultra-high pure helium seeded with about 1-2% of acetylene gas or benzene vapor through a pulsed supersonic nozzle (500 μm) to the source vacuum chamber maintained at a background pressure of 10^{-7} Torr. The $\text{HCCH}^{+\bullet}$ or the $\text{C}_6\text{H}_6^{+\bullet}$ ions are mass-selected by the first quadrupole mass-filter and injected in (30-50 μs pulses) into the drift cell which contains Xe gas or a mixture of Xe-He at selected pressures typically in the range of 0.1 to 2.0 Torr. The temperature of the drift cell can be controlled to better than $\pm 1\text{K}$ using four temperature controllers. Liquid nitrogen flowing through solenoid valves is used to cool down the drift cell. The reaction products can be identified by scanning a second quadrupole mass filter located coaxially after the drift cell. The injection energies used in the experiments (12 – 15 eV, laboratory frame) are slightly above the minimum energies required to introduce the ions into the cell against the Xe/He outflow from the entrance orifice. Most of the ion thermalization occurs outside the cell entrance by collisions with the Xe/He atoms escaping from the cell entrance orifice. At a cell pressure of 0.2 Torr, the number of collisions that the $\text{HCCH}^{+\bullet}$

or the $\text{C}_6\text{H}_6^{+\bullet}$ encounters with the neutral atoms within the 1.5 millisecond residence time inside the cell is about 10^4 collisions, which is sufficient to ensure efficient thermalization of these ions. The effective temperature of the gas in the drift cell is calculated by accounting for the drift velocity of the ions under the low-field limit defined as $E/N < 6.0$, where E is the electric field intensity and N is the gas number density and E/N is expressed in units of Townsend (Td) where $1 \text{ Td} = 10^{-17} \text{ V} \cdot \text{cm}^2$.²⁶ Under the low-field field, the ion's drift velocity is small compared to the thermal velocity and the effective temperature is found to be about 7 % higher than the thermodynamic temperature.

III. Computational Section

The molecular equilibrium geometries and harmonic frequencies of the dissociated products, local minima and transition structures of the xenon complexes were obtained at the (U)MP2/6-311++G(2d,2p) level.²⁷ The restricted open-shell MP2 (ROMP2) method was also employed due to high spin contamination of the unrestricted MP2 (UMP2) wave function. The structures and relative stabilities of the different isomers as computed using the ROMP2 and the UPM2 methods are not significantly different (see **Tables S1-S4**, Supporting Information). The averaged relativistic core potential by LaJohn was used to describe xenon for all Xe-bearing molecules, denoted as LJ18.²⁸ Local minima are characterized by all real vibrational frequencies and transition structures (TSs) by one imaginary frequency. Each TS was further confirmed by intrinsic reaction coordinate (IRC) calculations to confirm the connections between transition structures and local minima. Relaxed scans provide information on pathways between local minima where we were unable to locate the respective TSs. The Natural Population Analysis (NPA)²⁹ charges, Wiberg bond index (WBI)³⁰ and natural resonance theory (NRT)³¹ analyses were provided at the ROMP2/6-311++G(2d,2p) level. Validation information is provided in **Table S2** using the St/aug-cc-pTVZ basis set for two isomers of $\text{Xe.HCCH}^{+\bullet}$ at both ROMP2 and ROCCSD(T) levels of theory. All computations have been performed with the Gaussian 09 program package.³²

IV. Results and Discussion

1. Mass Spectra at different Temperatures

Figure 1 displays the mass spectrum obtained following the injection of the mass-selected acetylene ion into the drift cell containing 0.76 Torr He at 298 K. When the acetylene cation is

injected into the drift cell containing 0.53 Torr Xe and 0.41 Torr He at 302 K, the major ions observed are the $\text{C}_2\text{H}_4\text{O}^{+\bullet}$, $\text{Xe}^{+\bullet}$, $\text{H}_2\text{O}^{+\bullet}$ in addition to a weak signal corresponding to the $\text{Xe.HCCH}^{+\bullet}$ adduct. The generation of the $\text{Xe}^{+\bullet}$ and $\text{H}_2\text{O}^{+\bullet}$ ions is a result of using higher injection energy to allow the introduction of the $\text{HCCH}^{+\bullet}$ ions against the Xe/He flow from the drift cell. The $\text{C}_2\text{H}_4\text{O}^{+\bullet}$ ion is formed by the irreversible addition reaction of water (present as an impurity in the Xe gas) into the acetylene radical cation. This reaction has been studied previously and the covalent product $\text{C}_2\text{H}_4\text{O}^{+\bullet}$ has been identified as the vinyl alcohol radical cation $\text{H}_2\text{CCH}(\text{OH})^{+\bullet}$.³³ The observation of a small ion signal corresponding to the $\text{Xe.HCCH}^{+\bullet}$ adduct, as shown in Fig. 1-b, suggests another irreversible addition of Xe into the acetylene ion which competes with the more favorable water addition at 302 K. This is confirmed by observing the reaction products at lower temperatures where water can be frozen out of the gas phase, and hence the Xe addition channel becomes predominant at 251 K as shown in Fig. 1-c. Interestingly, by lowering the temperature further, no significant enhancement of the ion signal corresponding to the $\text{Xe.HCCH}^{+\bullet}$ adduct is observed, as shown in Figs 1-d and 1-e, even at very low temperatures such as 185 K (Fig. 1-f). This behavior is consistent with the formation of adduct with large interaction energy where back dissociation into $\text{HCCH}^{+\bullet}$ and Xe may not be possible on the time scale of the drift cell experiment. For example, in a typical reversible association reaction such as $\text{HCCH}^{+\bullet} + \text{HCN} \rightleftharpoons \text{HCCH}^{+\bullet}(\text{HCN})$, equilibrium is readily established within a few microseconds from the injection of the $\text{HCCH}^{+\bullet}$ ion into the drift cell containing HCN vapor under experimental conditions similar to those of Fig. 1.²⁵ For a reversible exothermic association reaction, the intensity of the product ion increases and that of the reactant ion decreases at lower temperatures as the equilibrium shifts more towards the product ion.^{24,25} This behavior is clearly not observed in the reaction of $\text{HCCH}^{+\bullet}$ with Xe where the $\text{HCCH}^{+\bullet}$ ion reacts nearly completely with H_2O forming the $\text{C}_2\text{H}_4\text{O}^{+\bullet}$ covalent product at higher temperatures or with Xe (in the absence of water) forming the $\text{Xe.HCCH}^{+\bullet}$ adduct. The nearly constant ion intensity ratio of $\text{Xe.HCCH}^{+\bullet}/\text{HCCH}^{+\bullet}$ observed at different temperatures as shown in Fig. 1 (c-f) suggests that the $\text{Xe.HCCH}^{+\bullet}$ product ion is a covalently bonded adduct formed by the irreversible addition of Xe into the acetylene radical cation.

No evidence is found for the formation of the dissociative product Xe.HCC^+ as indicated by the comparison of the standard EI mass spectrum of the Xe isotopes obtained from the NIST Database,³⁴ the Xe spectrum obtained by the injection of mass-selected Ar ions into the drift cell

containing a Xe/He mixture, and the spectrum of the $\text{Xe.HCCH}^{+\bullet}$ adduct as shown in **Figure S2** (Supporting Information). The similarity of the relative intensities of the Xe isotopes in the three spectra indicates that the elimination product Xe.HCC^+ is not formed in our experiment of the reaction between the mass-selected $\text{HCCH}^{+\bullet}$ ion and Xe atoms. This is different from the results obtained by the radiolysis of binary mixtures of acetylene and Xe gases where the Xe.HCC^+ product was the most abundant ion at low pressures.²¹ The fact that only the $\text{Xe.HCCH}^{+\bullet}$ adduct is observed in our experiments is consistent with thermalization of the acetylene ion and the lack of excess energy to induce the formation of the dissociation product Xe.HCC^+ .

Figure 1. Mass spectra at different temperatures obtained following the injection of acetylene radical cation ($\text{HCCH}^{+\bullet}$) into the drift cell containing Xe and He vapors at different pressures as indicated.

Figure 2 (a) displays the mass spectrum obtained following the injection of the mass-selected benzene cation into the drift cell containing 0.50 Torr He and 0.58 Torr Xe at 301 K. A significant fragmentation of the benzene cation $\text{C}_6\text{H}_6^{+\bullet}$ is observed due to collisions with the Xe atoms escaping from the drift cell. The role of Xe as efficient collisional dissociation gas in the fragmentation of the benzene cation is clearly established by comparing the mass spectra obtained in the presence of different pressures of Xe in the drift cell, and also in the presence of other carrier gases such as He, Ne and Ar as shown in **Figures S3-1 and S3-2** (Supporting Information).

By lowering the temperature of the drift cell, a weak signal corresponding the $\text{Xe.C}_6\text{H}_6^{+\bullet}$ adduct is observed as shown in Fig. 2-b at 242 K. The extremely low abundance of the $\text{Xe.C}_6\text{H}_6^{+\bullet}$ adduct suggests a very weak binding interaction between the benzene cation and the Xe atom. This is clearly evident by the nearly equal intensity of the benzene cation at different temperatures as shown in Fig. 2 indicating the lack of reactivity towards the addition of the Xe atom. This is very different from the mass spectra shown in Fig. 1 where the intensity of the acetylene cation nearly disappears due to the irreversible addition of the Xe atom forming the covalently bonded $\text{Xe.HCCH}^{+\bullet}$ adduct.

The relative intensities of the Xe isotopes in the $\text{Xe.C}_6\text{H}_6^{+\bullet}$ adduct are similar to those of the Xe spectrum as shown in **Figure S4** (Supporting Information) indicating the absence of elimination products such as $\text{Xe.C}_6\text{H}_5^+$ or $\text{Xe.C}_6\text{H}_4^{+\bullet}$. The fragmentation of benzene is clearly enhanced in the presence of high concentrations of Xe in the drift cell as shown in Figs 2(b), 2(c) and 2(e). It is interesting that the $\text{Xe.C}_2\text{H}_2^{+\bullet}$ is observed at lower temperatures as shown in Figs. 2-d and 2-e at 196 K and 173 K, respectively. This observation suggests the formation of $\text{Xe.C}_2\text{H}_2^{+\bullet}$ adduct by the irreversible addition of the Xe atom into the $\text{C}_2\text{H}_2^{+\bullet}$ fragment formed by the dissociation of the benzene radical cation. This is consistent with the suggested covalent bonding nature of the $\text{Xe.C}_2\text{H}_2^{+\bullet}$ ion formed by the reaction of the acetylene cation and Xe as shown in Fig. 1.

Figure 2. Mass spectra at different temperatures obtained following the injection of the benzene radical cation ($C_6H_6^+$) into the drift cell containing Xe and He vapors at different pressures (Torr): (a) 0.58 Xe + 0.50 He, (b) 0.55 Xe, (c) 0.52 Xe, (d) 0.39 Xe + 0.50 He, (e) 0.45 Xe.

The mass spectrometric results shown in Figs 1 and 2 indicate that acetylene and benzene radical cations react differently with Xe atoms in the gas phase to generate a covalently bonded $\text{Xe.C}_2\text{H}_2^{+\bullet}$ adduct and a much weaker bound $\text{Xe.C}_6\text{H}_6^{+\bullet}$ complex, respectively. The rapid formation of the $\text{Xe.C}_2\text{H}_2^{+\bullet}$ covalent adduct prevents the formation of non-covalent association complexes between the Xe and the acetylene radical cation. However, with the benzene radical cation the formation of the covalent $\text{Xe.C}_6\text{H}_6^{+\bullet}$ adduct appears to be kinetically or energetically unfavorable, and only a very weakly bound association product appears to be formed. The significantly low abundance of the $\text{Xe.C}_6\text{H}_6^{+\bullet}$ complex at temperatures as low as 173 K is consistent with ion-induced dipole and vdW-type interactions which require very low temperatures to form an appreciable amount of the association product.

2. Calculated Structures of the $\text{Xe.HCCH}^{+\bullet}$ and $\text{Xe.C}_6\text{H}_6^{+\bullet}$ Adducts

To understand the nature of chemical bonding in the $\text{Xe.HCCH}^{+\bullet}$ and $\text{Xe.C}_6\text{H}_6^{+\bullet}$ adducts and characterize the potential energy surfaces of the interaction we carried out *ab initio* calculations at the MP2/6-311++G(2d,2p) level.²⁷ Several isomers of the cationic $\text{Xe.HCCH}^{+\bullet}$ and $\text{Xe.C}_6\text{H}_6^{+\bullet}$ complexes have been identified by geometry minimizations. The notation **Am** and **Bm** stand for isomer **m** for the $\text{Xe.HCCH}^{+\bullet}$ (**A**=acetylene) and the $\text{Xe.C}_6\text{H}_6^{+\bullet}$ (**B**=benzene) complexes, respectively.

Insertion Structures H-Xe-CCH^{0/+}

Figure 3 displays the equilibrium insertion structures of the neutral and cationic H-Xe-CCH molecules. The insertion neutral isomer **A1** is a kinetically stable high-energy local minimum, which has been characterized by both theory¹⁹ and experiment.²⁰ As shown in **Figure 3**, our calculations predict the insertion structure **A1**⁺ also to be a local minimum where all bond distances except for the Xe-H bond were elongated in **A1**⁺ compared with **A1**. ROMP2/LJ18/6-311++G(2d,2p) calculations give a significantly longer Xe-C bond distance of 2.819 Å in **A1**⁺ compared with the 2.324 Å in **A1**. The computed harmonic frequencies of **A1**^{0/+} of the Xe-H and Xe-C stretching and the Xe-C-C bending are listed in **Table 1** together with the geometries and relevant vibrational frequencies of the other isomers. At the ROMP2 level, the frequency of the Xe-C-C bending does not significantly differ between **A1** and **A1**⁺, however, the Xe-C stretching frequency is much lower (162.2 cm⁻¹) in **A1**⁺ compared to 326.7 cm⁻¹ in **A1**.

Figure 3. Equilibrium insertion structures of the neutral and cationic $\text{A1}^{0/+}$ and the other isomers of the cationic Xe.HCCH^{+} adduct obtained at the ROMP2/LJ18/6-311++G(2d,2p) level. The distances are given in Å.

Lundell *et. al* described the Xe-C bond in A1 to be highly ionic arising from the positive charge of Xe and negative charge of C bound to the Xe atom.¹⁹ Compared to A1 , in A1^{+} the electrostatic attraction of the Xe-C bond was weakened due to the smaller negative NPA charges (-0.136 |e|) of carbon bound to Xe. Both the analysis of the structural data and the harmonic frequencies showed that the Xe-C bond is weaker in A1^{+} . This assessment is supported by the WBI analysis of the Xe-C bond. Note that the Xe-H bond distance in A1 is 1.750 Å, whereas in A1^{+} it is slightly shorter at 1.612 Å. Moreover, the Xe-H stretching frequency of 2322.1 cm^{-1} in A1^{+} is significantly larger compared to 1735.7 cm^{-1} in A1 . The shorter Xe-H bond distance and

larger Xe-H stretching frequency indicate that the Xe-H bond has a much larger covalent character in **A1**⁺ compared to **A1**, which is also confirmed by the WBI analysis of Xe-H bonds with these WBI values: 0.708 for **A1** vs 0.910 for **A1**⁺ (see **Table 1**). Note that the short Xe-H bond possesses a large covalent character in both **A1** and **A1**⁺. Furthermore, the H-atom bound to Xe has a positive charge of 0.165, indicating the Xe-H bond has a degree of repulsive electrostatic interaction in **A1**⁺, whereas the electrostatic interaction within the Xe-H bond is attractive in **A1**.

Table 1. Computed structural parameters, selected harmonic frequencies, NPA charges and WBI values of the neutral and cationic Xe.HCCH^{0/+} and Xe.C₆H₆^{0/+} at the (RO)MP2/LJ18/6-311++G(2d,2p) level. The structures of these isomers are illustrated in **Figures 3 and 5**.

	Bond distances (Å)			Frequencies (cm ⁻¹)			NBO charges e		WBI		
	R _{C-C}	R _{Xe-C}	R _{Xe-H}	Xe-C-C bend	Xe-C stretch	Xe-H stretch	Xe	C ^a or H ^c	C-C	Xe-C	Xe-H
A1	1.227	2.324	1.750	129.8	326.7	1735.7	0.830	-0.552 -0.151 ^c	2.983	0.363	0.708
A2	1.300	3.822	—	53.9	28.9	—	0.005	0.253	2.055	0.008	—
A3	1.212	—	3.120	51.8 ^b	—	54.3	0.003	0.219 ^c	2.992	—	0.004
A1 ⁺	1.279	2.819	1.612	154.0	162.2	2322.1	0.789	-0.136 0.165 ^c	2.232	0.066	0.910
A2 ⁺	1.300	2.131	—	268.7	457.3	—	0.779	0.087	2.042	0.857	—
A3 ⁺	1.254	—	2.597	78.6 ^b	—	86.3	0.040	0.273 ^c	2.255	—	0.050
A5 ⁺	1.240	2.479	—	153.8	291.3	—	0.405	-0.103	2.299	0.423	—
B1	1.397 ^d	2.350	1.858	—	188.8	1440.7	0.769	-0.362 -0.298 ^c	1.436 ^d	0.453	0.564
B1 ⁺	1.359 ^d	2.525	1.683	—	75.2	1698.7	0.760	0.037 0.151 ^c	1.384 ^d	0.173	0.746
B4 ⁺	1.406 ^d	3.555	—	—	64.1	—	0.015	0.126	1.348 ^d	0.012	—

^a Carbon bound directly to Xe.

^b Values refer to the Xe-H-C bending.

^c Values refer to H bonded directly to Xe.

^d Average values.

Isomers of the Cationic Xe.HCCH⁺ Adduct

We identified and characterized six local minima for the cationic Xe.HCCH⁺ system (**A1**⁺ - **A6**⁺ as shown in **Table S1**, Supporting Information) and the structural parameters of the key isomers **A1**⁺, **A2**⁺, **A3**⁺ and **A5**⁺ along with the neutral isomers **A1**, **A2** and **A3** are listed in **Table 1**. Equilibrium structures for **A2**^{0/+}, **A3**^{0/+} and **A5**⁺ are shown in **Figure 3**. Both **A2**^{0/+} and **A3**^{0/+} are genuine minima of the neutral and cationic Xe.HCCH^{0/+} systems. In the neutral system, the vdW interaction is dominant between Xe and the HCCH fragment in **A2** and **A3** as indicated by the long Xe-C bond distance of 3.822 Å and Xe-H bond distance of 3.120 Å in **A2** and **A3**, respectively. Moreover, **A2** and **A3** possess typical multiple C-C bonds, which is supported by the WBI analysis and bond distances. Also the charge transfer between Xe atom and the CCH₂ or the HCCH fragments can be ignored based on the NPA charges (almost zero) on Xe in **A2** and **A3**. The low computed frequencies in **Table 1** also reflect the fact that the vdW interaction is the dominant interaction between Xe and the HCCH fragment in **A2** and **A3**. In the cationic system, the HCCH fragment receives almost all of the positive charge in **A3**⁺, which weakens the multiple C-C bond due to the partial loss of the bonding π electron pair as indicated by the longer C-C bond distance and the smaller WBI values in **A3**⁺ compared with that of **A3**. However, **A2**⁺ has a totally different situation in that the Xe-C bond possesses a stronger covalent character with the a short Xe-C bond distance of 2.131 Å consistent with the large WBI value of 0.857. Moreover, the harmonic frequencies of the Xe-C-C bending (268.7 cm⁻¹) and the Xe-C (457.3 cm⁻¹) stretching also suggest a strong covalent character of the Xe-C bond in **A2**⁺.

In the cationic system, we found a new isomer **A5**⁺ which does not exist in the neutral system. Starting with an **A5**⁺-like geometry for the neutral system, the geometry optimization produced isomer **A3**. In **A5**⁺, there is a Xe-C bond distance of 2.479 Å with the WBI value of 0.423. Based on the bond distance, harmonic frequency analysis of the Xe-C-C bending and Xe-C stretching and WBI values, the strength of the Xe-C bond in **A5**⁺ is comparable with the one in **A1**. Besides, the electrostatic interaction is less in **A5**⁺ as indicated by the smaller negative charge on C bound directly to Xe. The NRT analyses allowed us to calculate the bond order and its character. The natural bond order of the Xe-C bond in **A5**⁺ is 0.504, which is in agreement with the WBI value (0.423). The NRT analysis provides the covalent and ionic contribution as 0.261 and 0.243 for the bond order, respectively. Note that the covalent character is slightly stronger than the ionic character for the Xe-C bond in **A5**⁺.

Potential Energy Surfaces of the Cationic Xe.HCCH^+ System

To gain insight into the kinetic stability of A5^+ and the other isomers, we have investigated systematically the potential energy surfaces (PES) of the cationic Xe.HCCH^+ system including the isomerism and fragmentation energetics. The PES of the cationic Xe.HCCH^+ system calculated at the ROMP2/LJ18/6-311++G(2d,2p) level is shown in **Figure 4**. The structures of the transition states TS1 and TS2 are shown in **Figure S5** (Supporting Information). In two cases we were unable to identify the TSs and for these pathways we performed relaxed scans by optimizations with fixing one bond angle or bond distance: $\text{A4}^+ \leftrightarrow \text{Scan 1} \leftrightarrow \text{A5}^+$ and $\text{A1}^+ \leftrightarrow \text{Scan 2} \leftrightarrow \text{A6}^+$. Both of these scans are provided in **Figure S6** (Supporting Information) and the maximum points of these scans were indicated as the energies of Scan 1 and Scan 2 in **Figures 4 and S7**. These values serve as approximate energies of the respective transition structures. From a chemical point of view the TS energy along Scan1 is of importance: the barrier from A4^+ to A5^+ should be very small. The PES calculated at the UMP2/LJ18/6-311++G(2d,2p) level is nearly identical as shown in **Figure S7** (Supporting Information).

As shown in **Figure 4**, we found isomer A5^+ to be the global minimum that possesses the extreme kinetic stability against structural transformation and fragmentation. It needs to overcome a barrier of about 0.85 eV toward dissociation to the lowest-energy product, i.e. $\text{Xe} + \text{HCCH}^+$ or at least 1.08 eV to transform to the other high-lying isomers. A1^+ possesses the H-swing process $\text{A1}^+ \rightarrow \text{A3}^+$ via transition state **TS1** with a barrier of 0.44 eV, or the dissociation barrier of 0.61 eV into the $\text{HCC} + (\text{XeH})^+$ product. The $\text{A2}^+ \rightarrow \text{A5}^+$ pathway is an indirect H-transfer process via A4^+ with a total barrier of 0.45 eV via transition state **TS2**. Besides, the dissociation channel of A2^+ is thermodynamically prohibited towards decomposition to the higher-energy $\text{Xe} + \text{CCH}_2^+$ products. The considerable transformation and dissociation barriers indicate that A1^+ and A2^+ have good kinetic stability. The rest of the isomers exhibit less kinetically stable behavior because they possess either low conversion barriers or low-lying dissociation products.

Based on the PES of the cationic Xe.HCCH^+ system, the non-linear structure A5^+ is predicted to be the global minimum with a binding energy of 0.85 eV with respect to dissociation towards $\text{HCCH}^+ + \text{Xe}$. The Xe-C bond distance in this structure (2.479 Å) is comparable to the Xe-C bond distance in the linear neutral isomer **A1** (2.324 Å), and therefore, the Xe-C bond

strength is expected to be similar in both the **A1** and **A5⁺** isomers. It is interesting, however, that the Xe-C bond is significantly weaker in the linear cationic isomer **A1⁺** as compared to the non-linear ground state structure **A5⁺**.

Figure 4. The PES of the cationic Xe.HCCH^+ system at the ROMP2/LJ18/6-311++G(2d,2p). Scan 1 and 2 represent relaxed scans (See **Figure S6**, Supporting Information) using fixed bond angles and distances, respectively. The structures of TS1 and TS2 are shown in **Figure S5** (Supporting Information).

In order to validate the computational approach used to confirm the prediction of the non-linear structure **A5⁺** as the global minimum of the cationic Xe.HCCH^+ system, we performed comparative computations for the **A2⁺** and **A5⁺** isomers by the ROMP2 and ROCCSD(T) methods with two different basis sets and the results are provided in **Table S2** (Supporting Information). Based on these comparisons, we conclude that our approach provided a meaningful compromise between accuracy and computational cost.

The Cationic $\text{Xe.C}_6\text{H}_6^{++}$ System

We have investigated the cationic $\text{Xe.C}_6\text{H}_6^{++}$ system by exploring its potential energy surface at the UMP2/LJ18/6-311++G(2d,2p) level and characterized eight local minima. We present only four of them in **Figure 5** while all the eight structures are described in detail in **Figure S8 and Table S3** (Supporting Information). For the insertion structure, the Xe-C bond is weakened while Xe-H bond is strengthened in **B1**⁺ compared to **B1** as indicated by the bond distances and WBI values (see **Table 1**) similar to the Xe.HCCH system. We found **B2**⁺ and **B4**⁺ to be the lowest-lying isomers that are dominated by vdW interactions between Xe and the C_6H_6 fragment as indicated by the long equilibrium contact distances of 3.179 (Xe $\cdots$ H) and 3.555 (Xe $\cdots$ C) Å, while almost all of the positive charge is localized on the C_6H_6 fragment (NPA charge on Xe is +0.01|e| for **B2**⁺ and +0.01|e| for **B4**⁺ as shown in **Table S4**, Supporting Information). For the lowest-energy isomer **B4**⁺, the Xe-C distance is 3.555 Å, the Xe-C stretching frequency is 64.1 cm⁻¹ and the WBI value is 0.012. Therefore, **B4**⁺ corresponds to a weakly bound $\text{Xe.C}_6\text{H}_6^+$ vdW complex. The insertion structure **B1**⁺ is predicted to be a real minimum with a rather short Xe-C bond distance of 2.525 Å at the UMP2 level. This minimum was further confirmed by the ROMP2 method.

Figure 5. Equilibrium geometries of the key isomers of the cationic $\text{Xe.C}_6\text{H}_6^{+\bullet}$ adduct with the point group assignments obtained at the UMP2/LJ18/6-311++G(2d,2p) level. The $\langle S^2 \rangle$ values are given in brackets. Selected distances are in Å.

ROMP2 single-point calculations were carried out based on the UMP2 geometry (named ROMP2//UMP2). The PES of the cationic $\text{Xe.C}_6\text{H}_6^{+\bullet}$ system obtained at the ROMP2//UMP2/LJ18/6-311++G(2d,2p) level is shown in **Figure 6**. The ROMP2 calculations indicate that the energy of the incoming reactants ($\text{C}_6\text{H}_6^+ + \text{Xe}$) in the mass spectrometric experiment, lies by less than 0.17 eV above **B2⁺** and **B4⁺** which are dominated by vdW interaction. Furthermore, we suspect that **B2⁺** and **B4⁺** are not stable kinetically because only vdW interactions hold the Xe and C_6H_6^+ fragments together. We also found that the insertion structure **B1⁺** was transformed to **B3⁺** in the ROMP2 geometry optimization process (see **Figure 6**). Previous theoretical studies indicated that the electron affinities of the hydrocarbon group

bound directly to the noble gas Ar plays a crucial role in stabilizing the noble-gas inserted hydrocarbon compounds.³⁵ We suspect that the instability with respect to the products for H-Xe-C₆H₅⁺ is due to the insufficient electronegativity of the C₆H₅ group.

Figure 6. The PES of the cationic Xe.C₆H₆⁺⁺ system obtained at the ROMP2//UMP2/LJ18/6-311++G(2d,2p) level. **B1**⁺ is stable only at the UMP2/LJ18/6-311++G(2d,2p) level (see text).

Based on the PES of the cationic Xe.C₆H₆⁺⁺ system shown in **Figure 6**, the vdW-type structure **B2**⁺ and **B4**⁺ are predicted to be the lowest energy structures with relatively small binding energies (0.14 -0.17 eV) with respect to dissociation towards C₆H₆⁺⁺ + Xe. This is consistent with the mass spectrometric observation of a very weak abundance corresponding to the Xe.C₆H₆⁺⁺ complex and the need for significantly lower temperatures (below 170 K) to stabilize the ion-induced dipole complex.

In conclusion, we have presented experimental and computational evidence for novel Xe-bearing hydrocarbon radical cations by combining mass-selected drift cell measurements with computational quantum chemistry. The irreversible addition of the Xe atom in the $\text{HCCH}^+ + \text{Xe}$ reaction leads to a low symmetry (C_s) stable adduct $\text{Xe.HCCH}^{+\bullet}$ consistent with the calculated binding energy of 0.85 eV in contrast to the neutral $\text{HCCH} + \text{Xe}$ reaction which leads only to a metastable adduct. The ground state of the $\text{Xe.HCCH}^{+\bullet}$ adduct is bent with the Xe atom located above a carbon atom of the acetylene cation with a Xe-C bond strength comparable to that of the Xe-C bond formed by Xe insertion at the C-H bond of the neutral acetylene molecule. On the other hand, the observed $\text{Xe.C}_6\text{H}_6^{+\bullet}$ appears to form a weakly bound complex mainly stabilized by ion-induced dipole interaction consistent with a calculated binding energy in the range of 0.14-0.17 eV. In contrast, the neutral analogue forms only a metastable $\text{Xe.C}_6\text{H}_6$ adduct. The high stability of the acetylene adduct and the very different interactions of the Xe atom with the acetylene and benzene radical cations opens possibilities for preparing new unusual Xe-bonded molecular species.

Supporting Information

Supporting Information includes a schematic of the mass-selected ion mobility system (**Figure S1**); mass spectra of the Xe isotopes in $\text{Xe}^{+\bullet}$ and $\text{Xe.HCCH}^{+\bullet}$ (**Figures S2**); mass spectra obtained following the injection of the benzene cation ($\text{C}_6\text{H}_6^{+\bullet}$) into the drift cell containing different carrier gases He, Ne, Ar and Xe (**Figures S3**); mass spectra of the Xe isotopes in $\text{Xe}^{+\bullet}$ and $\text{Xe.C}_6\text{H}_6^{+\bullet}$ (**Figures S4**); structures of transition states TS1 and TS2 for the formation of the $\text{Xe.HCCH}^{+\bullet}$ adduct (**Figure S5**); fully relaxed energy scans at fixed $\angle\text{CCH}$ in $\text{A4}^+ \leftrightarrow \text{A5}^+$ (Scan 1) and fixed C-Xe bond in $\text{A1}^+ \leftrightarrow \text{A6}^+$ (Scan 2) (**Figure S6**); PES of the cationic $\text{Xe.C}_2\text{H}_2^{+\bullet}$ system at the UMP2/LJ18/6-311++G(2d,2p) level (**Figure S7**); structures of eight local minima on the potential energy surfaces of the $\text{Xe.C}_6\text{H}_6^{+\bullet}$ system (**Figure S8**); geometry comparison of the six local minima for the cationic $\text{Xe.HCCH}^{+\bullet}$ system ($\text{A1}^+ - \text{A6}^+$) between the ROMP2 and UMP2 levels of theory using the LJ18/6-311++G(2d,2p) basis set (**Table S1**); comparison of geometries and relative energies of A2^+ and A5^+ computed by ROMP2 and ROCCSD(T) methods with two different basis sets (**Table S2**); calculated energies and spin contamination values for the cationic $\text{Xe.C}_6\text{H}_6^{+\bullet}$ system (**Table S3**); and NPA charges on Xe atom for the eight local minima for the cationic $\text{Xe.C}_6\text{H}_6^{+\bullet}$ system ($\text{B1}^+ - \text{B8}^+$) (**Table S4**).

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