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Gas Phase Hydrogenated and Deuterated Fullerene Cations

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Abstract

H/D accretion, especially onto ionized fullerenes, is expected to be very efficient in space. In this work, we study hydrogenated and deuterated fullerene cations and their photodissociation behavior in the gas phase. The experimental results show that hydrogenated fullerene cations (i.e., $[C_{60}H_n]^+$ and $[C_{70}H_n]^+$, n up to 30) and deuterated fullerene cations (i.e., $[C_{60}D_n]^+$ and $[C_{70}D_n]^+$, n up to 21) are formed efficiently through the ion-atom collision reaction pathway. Upon irradiation, the hydrogenated and deuterated fullerene cations dissociate into fullerene cations and H/H_2 or D/D_2 species. The structures of the newly formed hydrogenated and deuterated fullerene cations (C_{58} and C_{60}) and the bonding energies for these reaction pathways are investigated by means of quantum chemical calculations. The competition between hydrogenation and dehydrogenation is confirmed, and the hydrogenation-to-dehydrogenation ratio in the accretion processes in the gas phase is determined. We infer that the proportion of accreted hydrogen and deuterium atoms on the surface of fullerenes is similar to that of hydrogen and deuterium atoms in the interstellar environment where these fullerenes are located, especially when the interstellar environments are similar to our experimental conditions, i.e., the hot environment.

Key words: astrochemistry – methods: laboratory: molecular – ultraviolet: ISM – ISM: molecules – molecular processes

1. Introduction

The buckminsterfullerene (C₆₀) molecule was first "discovered" in 1985 in a laboratory (Kroto et al. 1985). An important breakthrough came in 2010, when the infrared spectra of circumstellar and interstellar sources revealed the presence of buckminsterfullerene (C₆₀) in space (Cami et al. 2010; Sellgren et al. 2010). Importantly, several near-infrared diffuse interstellar bands (DIBs) were linked for the first time to the electronic transitions of C_{60}^+ (Campbell et al. 2015; Walker et al. 2015; Cordiner et al. 2017). The confirmation of interstellar buckminsterfullerene represents a breakthrough in our understanding of chemical complexity in the interstellar medium (ISM), providing new understanding of the types of complex molecules that may be responsible for the remaining (unidentified) DIBs in space (Campbell & Maier 2018; Cordiner et al. 2019).

As an important component of the interstellar organic inventory, extensive experimental and theoretical investigations aiming at revealing the formation mechanism of C₆₀ in the interstellar environments have been performed (Berné & Tielens 2012; Zhen et al. 2014; Omont 2016; Candian et al. 2018). These studies have shown that the formation of C_{60} may start from a simple carbon-rich seeded gas, following a bottom-

up route (Jäger et al. 2009, 2011), or proceed through the photodissociation of large polycyclic aromatic hydrocarbon (PAH) molecules, following a top-down route (Berné & Tielens 2012; Zhen et al. 2014; Candian et al. 2019).

It is known that the carbon cage of fullerene is very difficult to destroy or modify, which is especially true for the buckminsterfullerene (C₆₀) molecule (Zimmerman et al. 1991; Handschuh et al. 1995). Experiments and molecular dynamics simulations of low-energy (10-30 eV) H interactions with the C₆₀ molecule have been carried out to investigate the possible chemical combinations at these energies (Beardmore et al. 1994). However, minor modifications that preserve the cage size and composition, such as ionization, isomerization, exohedral addition of atoms, and other chemical reactions including association with PAHs (Dunk et al. 2013; García-Hernández & Díaz-Luis 2013; García-Hernández et al. 2013; Sato et al. 2013; Bohme 2016; Hu et al. 2021a, 2021b), are much easier. Therefore, fullerene species, such as C₆₀, exist in different ionization or chemical states in the ISM. Based on these findings, to calculate the total abundance of each fullerene species, the abundances of all the different ionization and chemical states were added together rather than considering the abundance in only a single state (Tielens 2013). In

addition, the different ionization and chemical states of fullerene species are affected by the physical and chemical conditions, so it is critical to understand the reactivity of fullerenes with other molecules (Omont 2016; Zhen et al. 2019; Hu et al. 2021a, 2021b).

Hydrogen and deuterium may be bound on the outer surface of fullerenes by opening their double bonds to form strong C-H or C-D alkane bonds (Petrie et al. 1992; Bohme 2016; Omont 2016). A mass spectrometric study of the hydrogenation of pure C₆₀ in thin solid films was conducted, resulting in $C_{60}H_n$ (n = 2 up to 24), with a wide distribution of n values for a given exposure (Brühwiler et al. 1993). In a study by Cataldo and Iglesias-Groth, when hydrogen atoms were mixed in solvents, C₆₀ was quickly hydrogenated to form C₆₀H₃₆ (Cataldo & Iglesias-Groth 2009; Iglesias-Groth et al. 2012), which have been recognized as major members of the fullerane family (Webster 1992; Le Page et al. 2001; Iglesias-Groth 2006; Cataldo & Iglesias-Groth 2009). In particular, the vibrational IR spectrum of $[C_{60}H]^+$ and $[C_{70}H]^+$ was recently reported (Palotás et al. 2020, 2021). In C₆₀ and C₇₀, which has a very sparse IR spectrum, all vibrational normal modes become IR allowed upon protonation, resulting in a rich spectrum for $[C_{60}H]^+$ and $[C_{70}H]^+$ (Palotás et al. 2020, 2021), in their work, an atmospheric pressure chemical ionization (APCI) is used to produce the gas-phase $[C_{60}H]^+$ and $[C_{70}H]^+$.

Interstellar PAHs, fullerene and their-related species are expected to be substantially influenced by their chemicalphysical conditions (Bakes & Tielens 1994; Le Page et al. 2001). Interestingly, these hydrogenated fullerene species may also be candidates of interest for the IR interstellar bands that could motivate spectroscopic studies (Tielens 2013). To understand the co-evolution of interstellar fullerene chemistry, by tracking the H/D atoms accretion processes on fullerene cations, in this work, we present an investigation of the chemical reactivity of fullerene (C60 and C70) cations and smaller fullerene ($C_{56/58}$ and $C_{66/68}$) cations with hydrogen or deuterium atoms, as well as their photochemical behaviors in the gas phase. Experiments are carried out using a quadrupole ion trap in combination with time-of-flight mass spectrometry. Quantum chemical calculations are also performed to determine the molecular structures and the formation mechanisms.

2. Methods

2.1. Experimental Methods

A brief description of the experiment is provided, and more detailed information on the experimental procedures is available in Zhen et al. (2019). First of all, fullerene (C₆₀, or C₇₀) containing ¹³C and ¹²C with a natural isotopic ratio is evaporated by heating the powder (J&K Scientific, with purity better than 99%) in oven at a temperature of ~613 K. Subsequently, evaporated C₆₀ or C₇₀ molecules are ionized using electron impact ionization and transported into the ion

trap via an ion gate and a quadrupole mass filter. The third harmonic of an Nd: YAG laser (INDI, Spectra-Physics), 355 nm, \sim 6 ns, operated at 10 Hz, is used to irradiate the trapped cations. A beam shutter was used to determine the interaction time of the light with the trapped ions. The shutter is externally triggered to guarantee that the ion cloud is irradiated only for a specified amount of time during each cycle. A high-precision delay generator controls the full-timing sequence.

A hydrogen atom beam source (HABS) (MBE-Komponenten GmbH) (Tschersich & von Bonin 1998) was installed on top of the ion trap, and used to produce the hydrogen or deuterium atoms. The hydrogen or deuterium atoms were formed by cracking D_2 and H_2 gas (with purity better than 99.99%) using a tungsten capillary at 1973 and 2113 K, respectively. The chamber pressure during the hydrogen atom beam exposure was $\sim 1.2 \times 10^{-6}$ mbar with D₂ or H₂ flowing through the HABS (the typical background pressure in the chamber is $\sim 6.0 \times 10^{-7}$ mbar with helium gas). The working distance from the end of tungsten capillary in the HABS to the ion trap was \sim 5.0 cm. The hydrogen and deuterium atom flux was incident into the ion trap through a 2.4 mm aperture in the ring electrode. The hydrogen and deuterium atoms were expected to have a flux of $\sim 5.0 \times 10^{14}$ H atoms cm⁻²s⁻¹, and $\sim 4.0 \times 10^{14}$ D atoms cm⁻²s⁻¹ based on the operating conditions.

Two-time strategies are used here: (1) without laser irradiation: our setup operates with a frequency of 0.5, 0.2, 0.1, and 0.05 Hz, i.e., one full measuring cycle lasts 2.0, 5.0, 10.0, and 20.0 s, respectively. At each experiment, the ion gate opens, allowing the ion trap to fill for a certain amount of ions. In the ion trap, the hydrogenated and deuterated fullerene cations are formed. During this procedure, helium gas is introduced continuously into the trap via a leaking valve to thermalize the ion cloud through collisions (~ 300 K). Adduct formation presumably occurs under our experimental operating conditions. At the end of each cycle, the resulting mass fragments are measured; (2) with laser irradiation: our setup operates with a frequency of 0.2 Hz, i.e., one full measuring cycle lasts 5.0 s. At the leading edge of the master trigger, the ion gate is opened (0.0-4.6 s), allowing the ion trap to fill for a certain amount of ions. During this time, the trapped ion reacts with hydrogen or deuterium atoms to form new cations. Afterward, the beam shutter is opened that allowed the 355 nm laser to irradiate the ion cloud (4.6-4.9 s). At the end of irradiation, a negative square pulse is applied to the end cap of the ion trap to accelerate the ions moving out of the trap and diffusing into the field-free TOF region, where the mass fragments can be measured.

2.2. Theoretical Chemistry Calculations Methods

The theoretical chemistry calculations are carried out with density functional theory (DFT) with the hybrid density

functional B3LYP (Lee et al. 1988; Becke 1992) as implemented in the Gaussian 16 program (Frisch et al. 2016). The basis set of 6-311++G(d, p) is used for all calculations. All species' geometries were optimized at the local minimum of their potential energy surface in the calculation. The zeropoint energy and thermal corrections can be obtained from the frequency calculation to correct the molecular energy.

3. Experimental Results

In the experiments, the high energy of the impacting electrons (\sim 82 eV) led to the formation of fullerene (C₆₀ and C₇₀) cations and smaller fullerene (C_{56/58} and C_{66/68}) cations through C₂ loss (Handschuh et al. 1995; Lifshitz 2000; Zhen et al. 2014). The mass spectrum results are shown in Figures 1–5.

3.1. The Hydrogenated and Deuterated Fullerene ($C_{56/58}$ and C_{60}) Cations

The mass spectrum of the evolution of hydrogenated and deuterated fullerene (C56/58 and C60) cations with increasing H/D exposure time is shown in Figure 1: (A) with H atoms; (B) with D atoms. Clearly, a series of peaks corresponding to hydrogenated and deuterated fullerene cations were observed. Upon H/D exposure, the m/z distribution exhibited the expected shift to higher masses, accompanied by a broadening of the distribution. By varying the exposure time (2.0, 5.0, 10.0, and 20.0 s), the degree of hydrogenation or deuteration of the fullerene ($C_{56/58}$, and C_{60}) cations changed. In particular, with an exposure time of 20.0 s, the largest hydrogenated and deuterated fullerene cations, $[C_{60}H_{30}]^+$, m/z = 750, and $[C_{60}D_{21}]^+$, m/z = 762, were observed. The series of peaks shown in the mass spectrum (m/z > 720 for $C_{60}^+)$ are composed of $[{}^{12}C_{60}H_n]^+$ and $[{}^{13}C^{12}C_{60}H_{n-1}]^+$. In addition, the zoom in mass spectrum of the evolution of hydrogenated and deuterated fullerene (C56/58) cations with increasing H/D exposure time are presented in Figure 2: (A) with H atoms; (B) with D atoms. The experiments showed that smaller fullerene $(C_{56/58})$ cations exhibited reaction behavior with H/D atoms very similar to that of C_{60} cations.

From the obtained mass spectrum, we can see that the deuteration ion of fullerenes ($C_{56/58}$, and C_{60}) was lower than the hydrogenation on the same reaction timescale, which was attributed mainly to the flux of D atom being lower than the flux of H atoms (the hydrogen and deuterium atoms were expected to have a flux of ~5.0 × 10¹⁴ H atoms cm⁻²s⁻¹, and ~4.0 × 10¹⁴ D atoms cm⁻²s⁻¹ based on the operating conditions). Under natural conditions, the abundance of neutral ¹²C is higher than ¹³C; i.e., the peak intensity of m/z = 720 ($^{12}C_{60}^+$) was stronger than that of m/z = 721 ($^{13}C^{12}C_{59}^+$). However, we also noted that the peak intensity of m/z = 721 ($^{13}C^{12}C_{59}^+$) was stronger than that of m/z = 720 ($^{12}C_{60}^+$), as shown in Figure 1, which is related to the natural carbon element abundance; i.e., ¹³C-containing species gave rise to a

stronger peak intensity than pure 12 C species, possibly due to the experimental setup conditions (quadrupole ion trap).

For the hydrogenation and deuteration pathway of fullerene (C₆₀) cations, these hydrogenated and deuterated fullerene cations were formed through ion-atom reaction pathways, i.e., C_{60}^+ H/D atoms. The reaction between fullerene cations and H/D atoms occurs through sequential steps, with repeated addition of H/D atoms on the surface of fullerene cages. In addition, in previous studies (Petrie et al. 1992; Le Page et al. 2001), competition between hydrogenation and dehydrogenation or deuteration and deduteration was observed in the ion-atom reaction pathways; i.e., H_2/D_2 formed as a secondary product through $[C_{60}H_n]^+ + H \rightarrow [C_{60}H_{n-1}]^+ + H_2$, or $[C_{60}D_n]^+ + D \rightarrow [C_{60}D_{n-1}]^+ + D_2$. We will discuss the adduct behavior with theoretical chemistry calculations in the next section.

Based on the above findings, the reaction pathways between fullerene (C_{60}) cations and H/D atoms are summarized as follows:

$$C_{60}^+ \xrightarrow{H} [C_{60}H_n]^+ + H_2, \quad n \text{ up to } 30$$
$$C_{60}^+ \xrightarrow{D} [C_{60}D_n]^+ + D_2, \quad n \text{ up to } 21$$

Figure 3 shows the resulting mass spectrum of trapped hydrogenated and deuterated fullerene ($C_{56/58}$, and C_{60}) cations upon 355 nm irradiation at a laser energy of 0.9 mJ (irradiation times amounting to 0.3 s; i.e., typically ~3 pulses): (A) with H atoms; (B) with D atoms. The intensity of the lower-mass peaks increased while that of the higher-mass peaks decreased upon laser irradiation (Figure 3, middle blue spectrum). For clarity, a difference spectrum was plotted for comparison (lowest trace in Figure 3), and it was found that only dehydrogenation products were formed, with no evidence of other fragmentation channels. In addition, H/H₂, or D/D₂ loss channels exist, and we will discuss the adduct behavior with theoretical chemistry calculations in the next section.

Accordingly, we propose the following photodissociation pathway for the hydrogenated and deuterated fullerene ($C_{56/58}$, and C_{60}) cations:

$$[C_{56/58/60}H_n]^+ \xrightarrow{h\nu} H/H_2 + C^+_{56/58/60}$$
$$[C_{56/58/60}D_n]^+ \xrightarrow{h\nu} D/D_2 + C^+_{56/58/60}$$

3.2. The Hydrogenated and Deuterated Fullerene ($C_{66/68}$ and C_{70}) Cations

Similar to the fullerene ($C_{56/58}$, and C_{60}) cation system, the mass spectrum of the evolution of hydrogenated and deuterated fullerene ($C_{66/68}$, and C_{70}) cations with increasing H/D exposure time is shown in Figure 4: (A) with H atoms; (B) with D atoms. Clearly, a series of peaks attributed to hydrogenated and deuterated fullerene cations were observed. Upon H/D exposure, the m/z distribution exhibited the



Figure 1. The mass spectrum of the evolution of hydrogenated and deuterated fullerene ($C_{56/58}$ and C_{60}) cations with increasing H/D exposure time: (A) with H atoms; (B) with D atoms.

expected shift to higher masses, accompanied by a broadening of the distribution. By varying the exposure time (2.0, 5.0, 10.0, and 20.0 s), the degree of hydrogenation or deuteration of fullerene (C_{66/68}, and C₇₀) cations changed. In particular, at an exposure time of 20.0 s, the largest hydrogenated and deuterated fullerene cations, $[C_{70}H_{25}]^+$, m/z = 865, and $[C_{70}D_{21}]^+$, m/z = 882, were observed. The series of peaks shown in the mass spectrum (m/z > 840 for C⁺₇₀) are composed of $[{}^{12}C_{70}H_n]^+$ and $[{}^{13}C{}^{12}C_{70}H_{n-1}]^+$. In addition, the experiments

showed that smaller fullerene (C_{66/68}) cations exhibited reaction behavior with H/D atoms very similar to that of C_{70}^+ .

From the obtained mass spectrum, we can see that the degree of deuteration of fullerenes ($C_{66/68}$, and C_{70}) was lower than the hydrogenation at the same reaction timescale, which was attributed mainly to the flux of D atom being lower than the flux of H atom. Similarly, under natural conditions, the abundance of neutral ¹²C is higher than ¹³C; i.e., the peak intensity of m/z = 840 ($^{12}C_{70}^{+}$) was stronger than that of



Figure 2. The zoom in mass spectrum of the evolution of hydrogenated and deuterated fullerene ($C_{56/58}$) cations with increasing H/D exposure time: (A) with H atoms; (B) with D atoms.

m/z = 841 (${}^{13}C^{12}C_{69}^+$). However, we noted that the peak intensity of m/z = 841 (${}^{13}C^{12}C_{69}^+$) was stronger than of m/z = 840 (${}^{12}C_{70}^+$), as shown in Figure 4, which is related to the natural carbon element abundance; i.e., ${}^{13}C$ -containing species gave rise to a stronger peak intensity than pure ${}^{12}C$ species, possibly due to the experimental setup conditions.

In terms of the hydrogenation and deuteration pathway of fullerene (C_{70}) cations, similar to the fullerene (C_{60}) cation

system, these hydrogenated and deuterated fullerene cations were formed through ion-atom reaction pathways, i.e., C_{70}^+ + H/D atoms. The reaction between fullerene cations and H/D atoms occurred through sequential steps with repeated addition of H/D atoms on the surface of the fullerene cages. Similarly, H₂/D₂ also formed as a secondary product through $[C_{70}H_n]^+$ + H $\rightarrow [C_{70}H_{n-1}]^+$ + H₂ or $[C_{70}D_n]^+$ + D $\rightarrow [C_{70}D_{n-1}]^+$ + D₂ (Petrie et al. 1992; Le Page et al. 2001).



Figure 3. Mass spectrum of hydrogenated and deuterated fullerene ($C_{56/58}$ and C_{60}) cations trapped in QIT upon 355 nm irradiation at a laser energy of 0.9 mJ (irradiation times amounting to 0.3 s, from 4.6–4.9 s): without irradiation (red), with irradiation (blue), and the difference spectrum (black) of the irradiation and without irradiation experiments: (A) with H atoms; (B) with D atoms.

Based on these findings, the reaction pathways between fullerene (C_{70}) cations and H/D atoms are summarized as follows:

$$C_{70}^{+} \xrightarrow{\mathbf{H}} [C_{70}\mathbf{H}_{n}]^{+} + \mathbf{H}_{2}, \ n \text{ up to } 25$$

$$C_{70}^{+} \xrightarrow{\mathbf{D}} [C_{70}\mathbf{D}_{n}]^{+} + \mathbf{D}_{2}, \ n \text{ up to } 21$$

Figure 5 shows the resulting mass spectrum of trapped hydrogenated and deuterated fullerene ($C_{66/68}$, and C_{70}) cations upon 355 nm irradiation at a laser energy of 0.9 mJ (irradiation times amounting to 0.3 s; i.e., typically ~3 pulses): (A) with H atoms; (B) with D atoms. The intensity of the lower-mass peaks increased while that of the higher-mass peaks decreased upon laser irradiation (Figure 5, middle blue spectrum). For clarity, a difference spectrum was plotted for comparison (lowest trace in Figure 5), which showed that only dehydrogenation products are formed, with no evidence of other fragmentation channels. In addition, H/H_2 , or D/D_2 loss channels were found to exist.

Accordingly, we propose the following photodissociation pathway for the hydrogenated and deuterated fullerene ($C_{66/68}$, and C_{70}) cations:

$$[C_{66/68/70}H_n]^+ \xrightarrow{n\nu} H/H_2 + C_{66/68/70}^+$$
$$[C_{66/68/70}D_n]^+ \xrightarrow{h\nu} D/D_2 + C_{66/68/70}^+$$

4. Theoretical Chemistry Calculation Results

To understand the obtained experimental results, we take the reaction pathway of C_{60}^+ + H/D, $[C_{60}H]^+$ + H or $[C_{60}D]^+$ + D, $[C_{60}H]^+$ + D or $[C_{60}D]^+$ + H, and C_{58}^+ + H/D, as a typical

example to theoretically study the H/D accretion process. In addition, we note that all the calculation results are based on the electronic ground state. For PAH and fullerene molecules, it is commonly accepted that excitation to an excited electronic state is followed by internal conversion (IC) to a highly excited vibrational state of the electronic ground state. Intramolecular vibrational redistribution (IVR) then quickly equilibrates the excess energy among all available vibrational states. IC and IVR leave the PAH and fullerene molecules in the electronic ground state and available for further photon absorption through the same transition. IC occurs on a timescale of picoseconds. Studies on PAH molecules reveal an IVR timescale of less than 10–50 ps if the internal energy exceeds 1000 cm⁻¹ (Felker & Zewail 1988; Heikal et al. 1991).

We carried out the calculation for the fullerene (C_{60}) cation system and defective fullerene (C_{58}) cation system due to their similarity to other fullerene systems. The molecular geometry of C_{58} was obtained by C_2 unit loss between two hexagons of C_{60} , assuming that there is no carbon skeleton rearrangement (except for the C_2 loss at a local position) during the electron impact ionization and fragmentation process (Candian et al. 2019; Zhen et al. 2019). As shown in Figure 6, the energy for the reaction pathways was obtained. The molecular geometry and the truncated icosahedral graph of fullerene (C_{58} and C_{60}) cations are also presented in Figures 6, and the numbers indicating the carbon sites were categorized into the same groups.

In the reaction between $[C_{60}]^+ + H/D$, only one reaction pathway for $[C_{60}H]^+$ and $[C_{60}D]^+$ was obtained, with



Figure 4. The mass spectrum of the evolution of hydrogenated and deuterated fullerene ($C_{66/68}$ and C_{70}) cations with increasing H/D exposure time: (A) with H atoms; (B) with D atoms.

exothermic energies of 2.3 and 2.5 eV, respectively (Petrie et al. 1992). According to the work of others (Palotás et al. 2020), the optimized geometry of endohedral hydrogenation sites of fullerene is higher in energy than the exohedral hydrogenation sites of fullerene. Moreover, the predicted spectrum of endohedral hydrogenation is in poorer agreement with the experimental spectrum. So we only consider the exohedral hydrogenation sites of fullerene. For the reaction between $[C_{60}H]^+$ + H and $[C_{60}D]^+$ + D, based on the

structural symmetry of fullerene (C₆₀) cations, the remaining 59 carbon sites were categorized into 22 different groups, as presented in Figure 6. Then, 22 different reaction pathways for $[C_{60}H]^+$ + H, and $[C_{60}D]^+$ + D were obtained, with exothermic energies in the range of 1.5–2.4 and 1.7–2.6 eV, respectively. In all the 22 different reaction pathways, two types of reaction were observed: first, for the groups of 1-2($[C_{60}H_2]^+$) to 1-23($[C_{60}H_2]^+$) and 1-2($[C_{60}D_2]^+$) to 1-23($[C_{60}D_2]^+$), H/D and C₆₀ units were connected by one



Figure 5. Mass spectrum of the hydrogenated and deuterated fullerene ($C_{66/68}$ and C_{70}) cations trapped in QIT upon 355 nm irradiation at a laser energy of 0.9 mJ (irradiation times amounting to 0.3 s, from 4.6–4.9 s): without irradiation (red), with irradiation (blue), and the difference spectrum (black) of the irradiation and without irradiation experiments: (A) with H atoms; (B) with D atoms.

C-H bond; second, for the groups of $1-1(C_{60}^+ + H_2)$ and $1-1(C_{60}^+$ + D₂), H₂/D₂ was formed through a reaction of the hydrogen atom with the C-H unit. For the reaction between C_{58}^+ + H and C_{58}^+ + D, based on the structural symmetry of fullerene (C_{58}) cations from previous theoretical results (Zhen et al. 2019; Hu et al. 2021a, 2021b), we focused on all of its carbon sites, as presented in Figures 6. Based on that, 31 different reaction pathways for C_{58}^+ + H and C_{58}^+ + D were obtained, as shown in Figure 6, with exothermic energies in the range of 1.3–2.9 and 1.4-3.1 eV, respectively. The exothermic energy for each accretion pathway was relatively higher, which is consistent with the experimental results, indicating that the ion-atom reactions between fullerene cations and hydrogen or deuterium atoms readily occur. We also propose that the hydrogenated and deuterated fullerene cations formed in the laboratory are a mixture of cation types. The C58 cations have a very similar reaction behavior when compare with C₆₀ cations.

We note that, for the ion-atom collision reactions that under the gas phase conditions, we consider the reaction collision can be happened if the exothermic energy is around or higher than 1.0 eV. In this way, from our obtained theoretical calculation results, the exothermic energy is all around or higher than 1.0 eV, so we treat the reaction formation rate are same as the ion-atom collision reaction rate between fullerene cations and H/D atoms in the gas phase. Based on that, from the calculation results, we can conclude that the different accretion carbon sites have little effect on the binding energy; the fluctuation between them is not obvious, which means that the addition of H/D atoms on the carbon skeleton of fullerenes is a relatively independent event. In the case of the lower degree of hydrogenation or deuteration of fullerene cations, no difference between fullerenes (e.g., $C_{56/58}^+$, $C_{66/68}^+$) was observed; however, in the case of the higher degree of hydrogenation or deuteration of fullerene cations, defective fullerenes may have some advantages due to the higher reactivity of the newly formed C-rings. This reaction behavior is different from that observed in a previous study (Zhen et al. 2019; Hu et al. 2021a, 2021b). For fullerene react with large molecules (e.g., anthracene, $C_{14}H_{10}$), all these large molecules are evenly distributed on the carbon skeleton of $C_{56/58/60}^+$ due to the space steric effect. However, H/D atoms have no spatial hindrance effect, so these H/D atoms can combine with the different carbon sites of $C_{56/58/60}^+$ relatively independently.

For the subsequent dissociation pathway initiated by laser irradiation, as shown in Figures 3 and 5, the hydrogenated and deuterated fullerene cations evolve toward breaking the C-H/C-D bonds. In the process of photolysis, if two CH/CD units are not adjacent, then the photolysis product will be H/D atoms.

If two CH/CD units are adjacent, it is possible to have a sufficiently close distance during the continuous vibration of the C-H/C-D bonds, then the photolysis product will be H_2/D_2 molecules (energy allowed; the endothermic energy is very small, lower than 1.0 eV). But it is difficult to have an impact on each other between two nonadjacent C-H/C-D bonds due to the relatively long distance between them, even though energy allowed. Two typical types of H_2/D_2 molecule loss channels





$C_{60}^{+} + H$	$C_{60}^{+} + D$					
$1 ([C_{60}H]^+)$ -2.32 eV	$1 ([C_{60}D]^+)$ -2.49 eV					
$[C_{60}H]^+ + H$	$[C_{60}D]^+ + D$					
1-1 ($C_{60}^{+} + H_2$) -1.91 eV	$1-1 (C_{60}^{+} + D_2) - 1.90 \text{ eV}$					
$1\text{-}2\;([C_{60}H_2]^+) \text{-}2.44\;\text{eV} 1\text{-}10\;([C_{60}H_2]^+) \text{-}2.00\;\text{eV} 1\text{-}18\;([C_{60}H_2]^+) \text{-}1.66\;\text{eV}$	$1-2 ([C_{60}D_2]^+) -2.63 \text{ eV} 1-10 ([C_{60}D_2]^+) -2.18 \text{ eV} 1-18 ([C_{60}D_2]^+) -1.83 \text{ eV}$					
$1\text{-}3\ ([C_{60}H_2]^+) \text{-}1.59\ \text{eV} 1\text{-}11\ ([C_{60}H_2]^+) \text{-}1.81\ \text{eV} 1\text{-}19\ ([C_{60}H_2]^+) \text{-}1.81\ \text{eV}$	$1-3 ([C_{60}D_2]^+) -1.76 \text{ eV} 1-11 ([C_{60}D_2]^+) -1.98 \text{ eV} 1-19 ([C_{60}D_2]^+) -1.99 \text{ eV}$					
$1\text{-}4 \ ([C_{60}H_2]^+) \qquad -2.13 \ \text{eV} \qquad 1\text{-}12 \ ([C_{60}H_2]^+) \qquad -1.75 \ \text{eV} \qquad 1\text{-}20 \ ([C_{60}H_2]^+) \qquad -1.81 \ \text{eV}$	$1-4 ([C_{60}D_2]^+) -2.31 \text{ eV} 1-12 ([C_{60}D_2]^+) -1.92 \text{ eV} 1-20 ([C_{60}D_2]^+) -1.99 \text{ eV}$					
$1\text{-}5\ ([C_{60}H_2]^+) \text{-}2.00\ eV 1\text{-}13\ ([C_{60}H_2]^+) \text{-}1.71\ eV 1\text{-}21\ ([C_{60}H_2]^+) \text{-}1.76\ eV$	$1-5 ([C_{60}D_2]^+) -2.18 \text{ eV} 1-13 ([C_{60}D_2]^+) -1.88 \text{ eV} 1-21 ([C_{60}D_2]^+) -1.93 \text{ eV}$					
$1\text{-}6 \ ([\mathrm{C}_{60}\mathrm{H}_2]^+) -1.49 \ \mathrm{eV} 1\text{-}14 \ ([\mathrm{C}_{60}\mathrm{H}_2]^+) -1.79 \ \mathrm{eV} 1\text{-}22 \ ([\mathrm{C}_{60}\mathrm{H}_2]^+) -1.67 \ \mathrm{eV}$	$1-6 ([C_{60}D_2]^+) -1.67 \text{ eV} 1-14 ([C_{60}D_2]^+) -1.97 \text{ eV} 1-22 ([C_{60}D_2]^+) -1.85 \text{ eV}$					
$1\text{-7} ([\mathrm{C}_{60}\mathrm{H}_2]^+) \text{-1.93 eV} 1\text{-15} ([\mathrm{C}_{60}\mathrm{H}_2]^+) \text{-1.75 eV} 1\text{-23} ([\mathrm{C}_{60}\mathrm{H}_2]^+) \text{-1.58 eV}$	1-7 ($[C_{60}D_2]^+$) -2.11 eV 1-15 ($[C_{60}D_2]^+$) -1.93 eV 1-23 ($[C_{60}D_2]^+$) -1.75 eV					
1-8 ($[C_{60}H_2]^+$) -1.76 eV 1-16 ($[C_{60}H_2]^+$) -1.74 eV	1-8 ($[C_{60}D_2]^+$) -1.94 eV 1-16 ($[C_{60}D_2]^+$) -1.92 eV					
1-9 ([$C_{60}H_2$] ⁺) -1.79 eV 1-17 ([$C_{60}H_2$] ⁺) -1.90 eV	$1-9([C_{60}D_2]^+)$ -1.97 eV $1-17([C_{60}D_2]^+)$ -2.08 eV					
[C ₆₀ H]++ D	$[C_{60}D]^+ + H$					

 $1-1 (C_{60}^{+} + HD) -1.98 eV$





C ₅₈ ⁺ +H					$C_{58}^{+} + D$						
1 ([C ₅₈ H] ⁺)	-1.25 eV	12 ([C ₅₈ H] ⁺)	-2.22 eV	23 ([C ₅₈ H] ⁺)	-1.69 eV	1 ([C ₅₈ D] ⁺)	-1.42 eV	12 ([C ₅₈ D] ⁺)	-2.40 eV	23 ([C ₅₈ D] ⁺)	-1.87 eV
2 ([C ₅₈ H] ⁺)	-2.02 eV	13 ([C ₅₈ H] ⁺)	-1.72 eV	24 ([C ₅₈ H] ⁺)	-1.74 eV	2 ([C ₅₈ D] ⁺)	-2.19 eV	13 ([C ₅₈ D] ⁺)	-1.90 eV	$24 ([C_{58}D]^+)$	-1.91 eV
3 ([C ₅₈ H] ⁺)	-2.88 eV	14 ([C ₅₈ H] ⁺)	-1.87 eV	25 ([C ₅₈ H] ⁺)	-1.95 eV	3 ([C ₅₈ D] ⁺)	-3.06 eV	$14([C_{58}D]^+)$	-2.04 eV	25 ([C ₅₈ D] ⁺)	-2.12 eV
4 ([C ₅₈ H] ⁺)	-1.65 eV	15 ([C ₅₈ H] ⁺)	-2.16 eV	26 ([C ₅₈ H] ⁺)	-1.86 eV	4 ([C ₅₈ D] ⁺)	-1.82 eV	15 ([C ₅₈ D] ⁺)	-2.33 eV	26 ([C ₅₈ D] ⁺)	-2.03 eV
5 ([C ₅₈ H] ⁺)	-2.24 eV	16 ([C ₅₈ H] ⁺)	-1.82 eV	27 ([C ₅₈ H] ⁺)	-1.85 eV	5 ([C ₅₈ D] ⁺)	-2.42 eV	16 ([C ₅₈ D] ⁺)	-1.99 eV	27 ([C ₅₈ D] ⁺)	-2.02 eV
6 ([C ₅₈ H] ⁺)	-2.28 eV	17 ([C ₅₈ H] ⁺)	-2.05 eV	28 ([C ₅₈ H] ⁺)	-1.95 eV	6 ([C ₅₈ D] ⁺)	-2.46 eV	17 ([C ₅₈ D] ⁺)	-2.22 eV	28 ([C ₅₈ D] ⁺)	-2.12 eV
7 ([C ₅₈ H] ⁺)	-1.76 eV	18 ([C ₅₈ H] ⁺)	-2.00 eV	29 ([C ₅₈ H] ⁺)	-1.82 eV	7 ([C ₅₈ D] ⁺)	-1.93 eV	18 ([C ₅₈ D] ⁺)	-2.17 eV	29 ([C ₅₈ D] ⁺)	-1.99 eV
8 ([C ₅₈ H] ⁺)	-2.94 eV	19 ([C ₅₈ H] ⁺)	-2.03 eV	30 ([C ₅₈ H] ⁺)	-1.81 eV	8 ([C ₅₈ D] ⁺)	-3.11 eV	19 ([C ₅₈ D] ⁺)	-2.20 eV	30 ([C ₅₈ D] ⁺)	-1.98 eV
9 ([C ₅₈ H] ⁺)	-2.46 eV	20 ([C ₅₈ H] ⁺)	-2.11 eV	31 ([C ₅₈ H] ⁺)	-1.82 eV	9 ([C ₅₈ D] ⁺)	-2.63 eV	20 ([C ₅₈ D] ⁺)	-2.28 eV	31 ([C ₅₈ D] ⁺)	-1.99 eV
10 ([C ₅₈ H] ⁺)	-2.57 eV	21 ([C ₅₈ H] ⁺)	-1.91 eV			10 ([C ₅₈ D] ⁺)	-2.75 eV	21 ([C ₅₈ D] ⁺)	-2.08 eV		
11 ([C ₅₈ H] ⁺)	-1.99 eV	22 ([C ₅₈ H] ⁺)	-2.06 eV			11 ([C ₅₈ D] ⁺)	-2.16 eV	22 ([C ₅₈ D] ⁺)	-2.23 eV		

Figure 6. The energies for the reaction pathways of fullerene (C_{60}) and defective fullerene (C_{58}) cations with H/D atoms, and the red atoms represent carbon atoms on the seven C-ring.

are obtained: forming groups of $[C_{60}H_2]^+$ (1,2) and $[C_{60}H_2]^+$ (1,5) and forming groups of $[C_{60}D_2]^+$ (1,2) and $[C_{60}D_2]^+$ (1,5). The calculation results are presented below:

$$(1 - 2)[C_{60}H_2]^+ \longrightarrow H_2 + C_{60}^+ - 0.5 \text{ eV} (1 - 5)[C_{60}H_2]^+ \longrightarrow H_2 + C_{60}^+ - 0.1 \text{ eV} (1 - 2)[C_{60}D_2]^+ \longrightarrow D_2 + C_{60}^+ - 0.7 \text{ eV} (1 - 5)[C_{60}D_2]^+ \longrightarrow D_2 + C_{60}^+ - 0.3 \text{ eV}$$

In the photolysis process, possible dynamical processes play an important role, and further studies will be required to address this issue.

5. Discussion

As presented in Figure 6, the occurrence of dehydrogenation $(1-1 \ (C_{60}^+ + H_2), -1.9 \ eV)$ or dedeuteration $(1-1 \ (C_{60}^+ + D_2), -1.9 \ eV)$ reactions has been proved in the H/D accretion process, and the exothermic energies of the hydrogenation and dehydrogenation reactions are similar. In addition, we also calculated the reaction pathway of $[C_{60}H]^+ + D \rightarrow C_{60}^+ + HD$, $-2.0 \ eV$ and $[C_{60}D]^+ + H \rightarrow C_{60}^+ + HD$, $-1.8 \ eV$.

Since both hydrogenation and dehydrogenation events are relatively independent and random, the chance of their occurrence is completely determined by the sites of the already hydrogenated and still unhydrogenated carbon sites on the fullerene surface (Tielens 2013; Omont 2016). The free H-D exchange (energy allowed) processes suggest that the proportion of accreted hydrogen and deuterium atoms on the surface of fullerenes is similar to that of hydrogen and deuterium atoms in the interstellar environment where these fullerenes are located (Le Page et al. 2001; Montillaud et al. 2013; Omont 2016). The flux density of H-atoms in our laboratory studies is expected $\sim 10^5$ times higher than the photodissociation regions (PDRs, e.g., NGC 7023), which means 20 s in our experiments, equals to the reaction time of ~ 20 days in PDRs (Tielens 2013). Nevertheless, in the present, we assume that the formation and photochemistry of hydrogenated and deuterated fullerene cations in space follow the similar mechanism with our experiments.

A previous study indicated that the H₂ form from PAHs may be an important pathway for the formation of H₂ in PDRs (Boschman et al. 2012; Montillaud et al. 2013; Croiset et al. 2016). In addition, in solvents, heat treatment of C₆₀ H₃₆ can cause dehydrogenation and easily release H₂ molecules (Cataldo & Iglesias-Groth 2009; Iglesias-Groth et al. 2012). Given the results presented in this work, the potential for fullerene cations to react with H/D atoms to form hydrogenated and deuterated fullerene cations must also be considered, which provides a catalytic pathway for molecular H₂/D₂ formation, and it is also important to consider the reaction between graphene molecules and H/D atoms (Pantazidis et al. 2019; Thrower et al. 2019).

Overall, the theoretical chemistry calculation results are consistent with the experimental results. We can conclude that ion-atom reactions between fullerene cations and hydrogen or deuterium atoms readily occur, producing a large number of hydrogenated fullerene cations (i.e., $[C_{60}H_n]^+$ and $[C_{70}H_n]^+$, n up to 30) and deuterated fullerene cations (i.e., $[C_{60}D_n]^+$ and $[C_{70}D_n]^+$, n up to 21) in experiments, also resulting in a very large number of reaction pathways. These newly formed hydrogenated and deuterated fullerene cations can be quite stable (binding energy of ~ 2.0 eV). Smaller fullerene cations (e.g., $C_{56/58}^+$ and $C_{66/68}^+$) have reactivity similar to that of larger fullerene cations (e.g., C_{60}^+ and C_{70}^+) in the adduction process with hydrogen or deuterium atoms. Additionally, the competition between hydrogenation and dehydrogenation or between deuteration and dedeuteration was confirmed, and the hydrogenation and deuteration channel ratios of fullerene cations in the accretion reaction in the gas phase were determined. Subsequent photoprocessing (355 nm was used here) can diminish these cations to their most stable forms and convert them back to fullerene cations and H/H₂ or D/D₂ species again. We note that we did not perform all possible related theoretical chemistry calculations (this was not a full survey); when the amount of hydrogen or deuterium addition is higher (e.g., $[C_{60}H_{30}]^+$, and $[C_{60}D_{21}]^+$), there may be some intramolecular interactions or other reaction formation pathways and photodissociation channels (Omont 2016; Zhen et al. 2019). In addition, during the formation process, possible dynamical processes play an important role, and further studies will be required to address this issue.

Furthermore, these hydrogenated and deuterated fullerene cations may also be promising candidates of interest for the IR interstellar bands (Zhang et al. 2017). Because the structure of hydrogenated and deuterated fullerene cations initially formed is diverse, their contribution to the spectral profile and the spectral features for detections in the ISM should be investigated.

6. Conclusions

In summary, we have investigated the formation and photochemistry of hydrogenated and deuterated fullerene cations both experimentally and theoretically. Fullerene cations (e.g., $C_{56/58}$, $C_{66/68}$ and $C_{60/70}$ cations) form adducts with hydrogen or deuterium atoms much more readily; i.e., hydrogenated fullerene cations (i.e., $[C_{60}H_n]^+$ and $[C_{70}H_n]^+$, *n* up to 30) and deuterated fullerene cations (i.e., $[C_{60}D_n]^+$ and $[C_{70}D_n]^+$, *n* up to 21) are formed efficiently through ion-atom reactions. Smaller fullerene cations (e.g., $C_{56/58}^+$ and $C_{66/68}^+$) have reactivities similar to or higher than those of larger fullerene cations (e.g., C_{60}^+ and C_{70}^+) during the adduction with hydrogen or deuterium atoms. Hence, if these fullerenes are present in space, the formation of hydrogenated and deuterated fullerene could produce an extended family of large molecules.

Likewise, these types of hydrogenated and deuterated fullerene may play a role in the IR spectral complexity of circumstellar environments where C_{60} is prominent.

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