

## Theoretical investigation on the interactions between HRnCCH and X(X=N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>)

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**Abstract.** We have investigated the structures and properties of the hydrogen bonded complexes formed between HRnCCH and X (X stand for nitrogen, oxygen, water and ammonia) using MP2 (full) theoretical method at the aug-cc-pVTZ-pp for Rn atom and aug-cc-pVTZ for other atoms. In this study, as for the complexes between HRnCCH and X, three stationary structures are located (one annular and two linear structures) corresponding to the true energy minima on the potential energy surface. In these complexes, the red shift of the H-Rn stretch in the linear structure C<sub>XA</sub>, whereas the blue shift of the H-Rn stretch in the structure linear C<sub>XB</sub> and the structure circular C<sub>XC</sub>, the biggest red shift is -35.71 cm<sup>-1</sup> in C<sub>NH3A</sub> and the biggest blue shift is 76.45 cm<sup>-1</sup> in C<sub>H2OB</sub>. In addition, we found a tremendous red shift in C<sub>H2OC</sub> (-154.7 cm<sup>-1</sup> in O-H bond) and C<sub>NH3A</sub> (-96.15 cm<sup>-1</sup> in C-H bond). The most stable structure is the circular structure between HRnCCH and H<sub>2</sub>O, whose interaction energies is -27.4 kJ/mol. The origin of the frequency shift and charge transfer in these complexes has been analyzed by the natural bond orbital analysis and atom in molecule. The natural bond orbital analysis indicates the C→σ<sub>H-Rn</sub><sup>\*</sup> orbital interaction plays a key role in the stabilization energy. The atom in molecule shows the largest the absolute value of  $V = 0.0220$  a.u and the most negative the value of  $H = -0.0055$  a.u corresponding the most stabilization of the circular structure between HRnCCH and H<sub>2</sub>O.

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## 1 Introduction

Hydrogen bonding is one of the weak forces between van der Waals force and covalent bond, which plays an important role in chemistry, biology and physics [1–3]. The type of the hydrogen bond is  $X-H\cdots Y$ , where X and Y are electronegative atoms (such as F, O, and N [4–6]) or groups. For the past decades, the hydrogen bonding has been extensively studied by experimental [7] and computational methods. The first studies focused on the hydrogen bond (H–X) for the characteristics of the red-shift of stretch vibration. For example, ab initio methods have been employed to investigate the relations among bond distances, interaction energies and frequency shifts [8]. Later, researchers began to study their characteristics of structure, the charge transfer and interaction energy [9]. In particular, the blue shift hydrogen bonds have obtained an increasing interest for recent years [10–13]. In addition, hydrogen bonding has been applied to the macromolecular, such as the hydrogen bonding changes in stresses environmental [14] and the application in molecular recognition [15–17]. Additionally, one has explored the natures and features of hydrogen bond and halogen bond [18, 19].

On the other hand, although it is well known that the single noble-gas cannot participate in chemical reaction, it can be inserted into other molecules, leading to formation of the metastable complex by photolyzing HY molecules at the low temperature rare gas and thermally mobilizing H atoms [20]. In 1962, the first noble-gas compound has been discovered by Barlett [21]. Some natures and features of neutral noble-gas molecules  $HNgY$  (Ng = noble gas atom, Y = electronegative atom or group) have been explored. The  $HNgY$  molecule has an ionic bond (Ng–Y) and a covalent bond (H–Ng), and has a very large dipole moment. Thus, these molecules are very easy to form hydrogen bonded complexes [22]. After the first stable neutral noble-gas compound  $HArF$  [23, 24] studied, the complexes between  $HKrF$  [25],  $HKrCl$  [26] and  $N_2$  [27],  $P_2$  and  $CO$  had been studied by theoretical and experimental methods. Large red-shift in the  $HArF\cdots P_2$  [28] complex was unveiled. Recently, the features and natures of  $FArCCH$  [29, 30],  $HArCCH$  and  $HArCCF$  [31] have been explored by theoretical methods. The gigantic blue-shift ( $574\text{ cm}^{-1}$ ) of the H–Ar stretching frequency in  $C_2H_2\cdots HArCCF$  complex [32] was observed. Hanna Tanskanen have studied the  $HXeCCH\cdots CO_2$  complex [33] using theoretical calculations, which have found blue-shift and red-shift, respectively. According to the latest reports,  $HRnCCH$  [34] was probably existed in the atmosphere by theoretical investigation.

In this study, the complexes formed between  $HRnCCH$  and X (X= $N_2$ ,  $O_2$ ,  $H_2O$ ,  $NH_3$ ) using the MP2 theoretical method at the aug-cc-pVTZ-pp level for the first time. In addition, the natures and characters of the bond critical points have been analyzed using the natural bond theory and quantum theory of atom in molecules. The purpose of this study is to elucidate the structures of these complexes and obtain the stabilization energies of the complexes reported here. Furthermore, this study provides a new insight on the Rn atom to affect the natures of the molecule.