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Noble gas induced surprisingly higher stability of π hydrogen bonded complex: comparative study of hydrogen bonded complexes of HKrCCH and HCCH with H_2O, NH_3, CH_3OH and CH_3NH_2

Saptarsi Mondal and Prashant Chandra Singh*

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Structure, energetics and spectroscopic properties of hydrogen bonded complexes of HKrCCH with H_2O, NH_3, CH_3OH and CH_3NH_2 have been explored as well as compared with the hydrogen bonded complexes of its precursor HCCH. The most stable structure for HKrCCH is the π (O/N–H···π) hydrogen bonded complex, whereas the σ (C–H···O/N) hydrogen bonded complex is most stable for HCCH. Surprisingly, the stabilization energy of the π hydrogen bonded complex of HKrCCH is about two to three fold higher compared to the σ hydrogen bonded complex of HCCH, which is in contrast to the general perception that the strength of π hydrogen bond is less compared to σ hydrogen bond. From the atom in molecule and charge analyses, it has been found that π hydrogen bonded complexes of HKrCCH have a cyclic structure in which O/N–H···π hydrogen bonding takes place along with Kr···O/N interaction. Higher stabilization energy of the π hydrogen bonded complex of HKrCCH is due to a cooperative phenomena in which Kr···O/N interaction contributes to the formation of a strong O/N–H···π hydrogen bonding.

Experimental observation of stable Ar inserted HF, *viz.*, HArF, has enkindled scientific interest in the search of several new types of stable noble gas complexes as well as their chemical properties.[1,2] It has led to the identification of several new noble gas complexes, namely, HNgY, HNgCCY, HCCNgY and HNgCCH (Ng = noble gas molecule and Y is halogen).[3–13] There are also several studies describing the chemical properties such as charge, dipole moment, electron density and vibrational spectrum of these noble gas molecules.[14] The existence of noble gas complexes and their chemical properties are unequivocally established by several theoretical and experimental studies. However, our knowledge about the intermolecular interaction such as hydrogen bonding of the noble gas complexes as well as the effect of insertion of a noble gas on the properties of a hydrogen bond is limited.

Hydrogen bonding, conventionally, is an interaction between a positively charged hydrogen atom attached to oxygen or nitrogen with a lone pair of electrons on electronegative atoms such as oxygen, nitrogen and halogens.[15] Apart from these conventional hydrogen bonds, hydrogen bonds involving unconventional donors and/or acceptors have been reported in the literature.[16–20] These hydrogen bonds include π bond electrons, methyl groups, and basic hydrogen, which act as an acceptor, and C–H groups as a donor. Generally, the strength of these unconventional hydrogen bonded complexes is less than that of conventional hydrogen bonded complexes.[15] Hydrogen bonded complexes of noble gases have been studied theoretically as well as experimentally in low-temperature noble gas matrices, mainly $FArH\cdots N_2$, $FKrH\cdots N_2$, $ClKrH\cdots N_2$, $HXeOH\cdots H_2O$ and $HXeCCH\cdots CO_2$.[21–26] These complexes show blue shift, which is in agreement with theoretical predictions. These investigations have confirmed that noble gas complexes have a similar hydrogen bonding capability as conventional molecules.

Very recently, our group explored the hydrogen bonding capability of the C–H group of noble gas complexes by studying the hydrogen bonding of FKrCCH with typical acceptor molecules such as water, methanol, dimethyl ether, ammonia, methyl ammonia and dimethyl ammonia.[27] Studies of structure, energetics, shift in the C–H stretching frequency as well as topology of electron density provided unambiguous evidence for the formation of C–H···O/N hydrogen bonded complexes. Further, the strength of hydrogen bonding in complexes of FKrCCH was compared with those of precursor FCCH. Surprisingly, it was found that strength of the C–H···O/N hydrogen bonding in the case of FKrCCH is approximately twice that of the parent molecule FCCH. The increase in hydrogen bonding strength of noble gas molecules has been assigned to the increased acidity of C–H group on the insertion of a krypton atom. Our group has also investigated the properties of C–H···H–B dihydrogen bonded complexes of noble gas molecules and found that the strength of the dihydrogen bonded complex is 15% weaker as compared to the hydrogen bonded complex.[28] In another study, it has been shown that the insertion of krypton

Department of Spectroscopy, Indian Association for the Cultivation of Science, Kolkata, 700032, India. E-mail: sppcs@iacs.res.in

in acetylene and hydrogen cyanide increases their ability as a hydrogen bond acceptor and decreases their hydrogen bond donating capability.[29]

In this paper, we have investigated the hydrogen bonding properties of HKrCCH with different solvents: water (H_2O), ammonia (NH_3), methanol (CH_3OH) and methylamine (CH_3NH_2). Furthermore, the effect of insertion of a krypton atom on hydrogen bonding has been investigated by comparing the properties of hydrogen bonded complexes of HKrCCH with its precursor HCCH. HKrCCH is an interesting molecule as it has multiple acceptor and donor groups. It can form an σ hydrogen bond with a Kr–H/C–H donor group and act as a hydrogen bond acceptor because of the π electron density of its C≡C group. In this regard, it will be interesting to investigate which hydrogen binding site of HKrCCH is preferable with different solvents and how the hydrogen bonding properties of HKrCCH are different from those of its precursor HCCH.

Our results show that the most stable complex of HCCH with various solvents is the σ (C–H···O/N) hydrogen bonded complex. Surprisingly, the most stable complex for HKrCCH with all solvents is the cyclic π hydrogen bonded complex in which O/N–H···π hydrogen bonding takes place along with Kr···O/N interaction. The strength of the π hydrogen bonded complex of HKrCCH is about two to three times higher as compared to the σ hydrogen bonded HCCH complex. This surprising higher stability of the π hydrogen bonded complex of HKrCCH is attributed to the cooperative phenomena in which the Kr···O/N interaction contributes to the formation of a strong O/N–H···π hydrogen bond.

Methodology

All structures have been optimized at the MP2 level of method with the aug-cc-pVDZ[30] basis set. In order to confirm the nature of stationary points, subsequent harmonic frequency calculations have been performed for the corresponding optimized structures. For H_2O and NH_3 complexes of HKrCCH, optimization and harmonic frequency calculation has also been performed at the QCISD and CCSD level of theory with the aug-cc-pVDZ basis set and the trends of results are similar to those obtained at the MP2/aug-cc-pVDZ level. Hence, calculation for the hydrogen bonded complexes of HKrCCH with CH_3OH and CH_3NH_2 has been performed only at the MP2/aug-cc-pVDZ level of theory.[17,27,28] In order to get accurate energetics, we have performed single point calculation at the CCSD(T)/aug-cc-pVDZ level of theory for all the structures optimized at the MP2/aug-cc-pVDZ level. All calculations have been performed with frozen core approximation, and optimization has been done with standard convergence criteria.

For all the complexes, stabilization energy (ΔE) was calculated using a supermolecular approach. If A and B form a complex AB, then the stabilization energy of AB is the difference between the total energy of AB and the sum of that of the isolated monomers A and B. The stabilization energy was corrected for basis set superposition error (BSSE) and zero point vibrational energy (ZPVE). The counterpoise method of Boys and Bernardi was used to correct the BSSE.[31] Further, the chemical nature of hydrogen bonding was sketched by using natural bond orbital (NBO)[32] and atoms in molecules (AIM) analysis.[33] All these calculations were performed with Gaussian 09.[34]

Result and discussion

Fig. 1 depicts all the stable hydrogen bonded structures of HKrCCH with H_2O, NH_3, CH_3OH and CH_3NH_2 at the MP2/aug-cc-pVDZ level of theory. HKrCCH forms three stable hydrogen bonded structures (Fig. 1A) with H_2O. First is a C–H···O (σ) hydrogen bonded structure where the C–H group of HKrCCH is donor and interacts with the oxygen of H_2O. Second is a π hydrogen bonded complex in which the O–H group of H_2O is donor and interacts with the π electron density of the CC group of HKrCCH, and third structure is a Kr–H···O (σ) hydrogen bonded system in which the Kr–H group of HKrCCH is donor and interacts with the oxygen of H_2O. In contrast to H_2O complexes, only C–H···O/N and π hydrogen bonded structures were found to be stable for NH_3, CH_3OH, and CH_3NH_2 complexes (Fig. 1A). We have also performed optimization at the CCSD and QCISD level of theory with aug-cc-pVDZ basis set for H_2O as well as NH_3 complexes and obtained the same stable structures. The hydrogen bond distances between donor and acceptor (D_{Hb}) for all the respective complexes of HKrCCH have been shown in Table 1 at various levels of theory. It is evident from the data that D_{Hb} for the C–H···O hydrogen bonded structures lies between 2.23 Å to 2.38 Å, whereas D_{Hb} for the π hydrogen bonded structures is in the range of 2.36 Å to 2.64 Å. D_{Hb} for the Kr–H···O hydrogen bonded structure is ∼1.8 Å. It is important to note that D_{Hb} for the Kr–H···O hydrogen bonded structure of the HKrCCH–H_2O complex is less than that for C–H···O, which shows that the donating capability of Kr–H is higher as compared to the C–H group of HKrCCH. D_{Hb} calculated at QCISD and CCSD method follows the similar trend as MP2, although its value at the QCISD as well as CCSD level of calculation is 0.2 Å higher for the Kr–H···O hydrogen bonded structure. D_{Hb} calculated at the QCISD/CCSD level of theory is 0.05/0.07 Å longer for the C–H···O/N hydrogen bonded structures and 0.03/0.08 Å longer for the O/N–H···π hydrogen bonded structures of HKrCCH as compared to its MP2 value.

Fig. 1 also shows the stable structures of hydrogen bonded complexes of precursor HCCH with the same solvent molecules at the MP2/aug-cc-pVDZ level of theory. HCCH forms C–H···O and a π hydrogen bonded stable structure with H_2O and CH_3OH, whereas with NH_3 and CH_3NH_2, only σ hydrogen bonded structure has been found to be stable. The D_{Hb} for the C–H···O/N hydrogen bonded structure of HCCH varies from 2.17 to 2.26 Å, which is in line with earlier reported experimental and theoretical studies.[35–37] The major structural difference between the C–H···O hydrogen bonded complexes of HCCH and HKrCCH is D_{Hb}, which is longer for HKrCCH complexes. For the π hydrogen bonded complexes, D_{Hb} of HKrCCH complexes is significantly shorter and bent as compared to the HCCH complexes. This indicates the probable role of the krypton atom in hydrogen bonded complexes of HKrCCH.

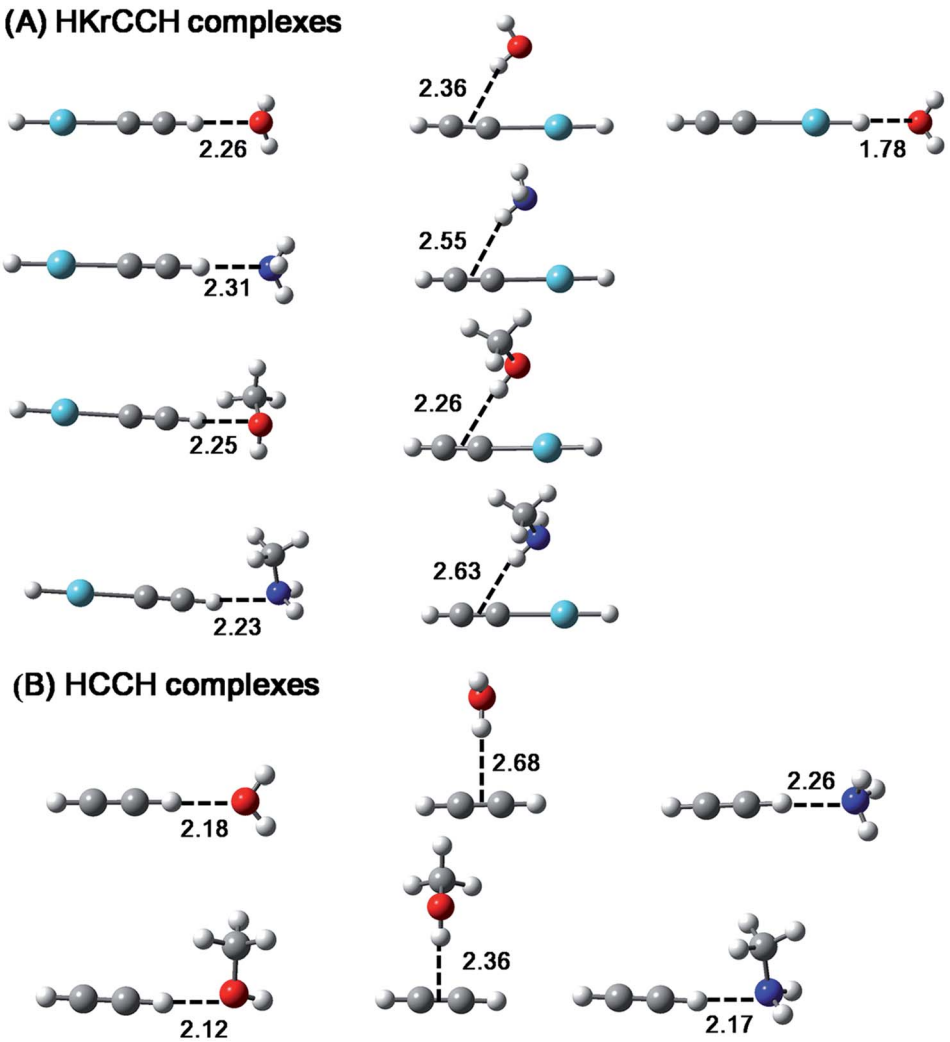

Fig. 1 MP2/aug-cc-pVDZ optimized structure of the hydrogen bonded complexes of HKrCCH (A) and HCCH (B) with H_2O, NH_3, CH_3OH and CH_3NH_2. Distances are depicted in angstroms.

Table 1 also depicts the electronic stabilization energy and corrected (BSSE + ZPE) stabilization energy of HKrCCH and HCCH during complexation at the MP2/aug-cc-pVDZ level of theory along with the value of electronic stabilization energy calculated at the single point CCSD(T)/aug-cc-pVDZ level of theory for all the structures optimized at the MP2/aug-cc-pVDZ level. The calculated values of electronic stabilization energy at the MP2 and CCSD(T) level of theory for the C–H···O/N and π hydrogen bonded complexes of HCCH are approximately close. The value of electronic stabilization energy of the C–H···O/N hydrogen bonded complexes of HKrCCH is approximately the same at the MP2 and CCSD(T) levels of calculation. However, it is overestimated by ~10% and ~28%, respectively, for the π and Kr–H···O hydrogen bonded complexes of HKrCCH at the MP2 level of calculation as compared to its value at the CCSD(T) level of calculation. This could be because of overestimation of dispersion energy at the MP2 level of calculation.[17]

Among all the C–H···O/N hydrogen bonded complexes of HKrCCH, stabilization energies are maximum for CH_3NH_2 and minimum for H_2O, which is very much in line with their respective basicity. It is important to note that the strength of C–H···O hydrogen bonded complex of HKrCCH is less than its precursor HCCH molecule, which is opposite to our earlier study of the hydrogen bonded system for FKrCCH.[27] This can be understood from the change in dipole moment of ($\Delta\mu$) HKrCCH and HCCH during complexation, which is depicted in Table 1. The dipole moment of HKrCCH is 3.36 D at the MP2/aug-cc-pVDZ level of theory and direction of dipole is towards the Kr–H group. In contrast to it, the dipole moment for HCCH is approximately zero. For the C–H···O hydrogen bonded complexes, direction of dipole of HKrCCH and acceptor molecules are opposite, hence, $\Delta\mu$ is negative for these complexes, which renders less stabilization energy. The dipole moment for the hydrogen bonded systems of the precursor HCCH molecule is induced by the acceptors molecules, and hence, it is positive.

The strength of the Kr–H···O hydrogen bonded complex of HKrCCH with H_2O is comparatively higher with respect to its C–H···O hydrogen bonded complex. This is in line with the result for D_{Hb} of the C–H···O and Kr–H···O hydrogen bonded complexes of HKrCCH with H_2O. This is attributed to more

Table 1 The distance between donor hydrogen and acceptor atom (D_{Hb}), stabilization energy (ΔE) and change in dipole moment ($\Delta\mu$) for the hydrogen bonded complexes of HKrCCH and HCCH calculated at various levels of theory with the aug-cc-pVDZ basis set. BSSE as well as ZPE corrected energies are shown in parentheses. Stabilization energy calculated at the CCSD(T) level of theory is a single point energy calculation for the MP2/aug-cc-pVDZ optimized structures

	C–H···O/N			O/N–H···π			Kr–H···O/N		
	D_{Hb} (Å)	ΔE (kJ mol^{-1})	$\Delta\mu$ (D)	D_{Hb} (Å)	ΔE (kJ mol^{-1})	$\Delta\mu$ (D)	D_{Hb} (Å)	ΔE (kJ mol^{-1})	$\Delta\mu$ (D)
HKrCCH···H_2O									
MP2	2.26	10.4 (1.9)	−3.42	2.36	33.1 (18.3)	−2.58	1.78	16.8 (3.4)	5.39
CCSD	2.31	8.9 (0.8)	−2.91	2.39	30.5 (16.2)	−2.56	1.97	15.9 (5.3)	4.15
QCISD	2.31	9.0 (0.9)	−2.91	2.39	30.6 (16.2)	−2.59	1.98	15.6 (5.0)	3.97
CCSD(T)		10.9			30.3			12.0	
HKrCCH···NH_3									
MP2	2.31	14.1(3.1)	−4.39	2.56	26.4 (14.1)	−2.11			
CCSD	2.38	11.0 (0.7)	−4.30	2.64	23.1 (11.2)	−2.06			
QCISD	2.38	11.8 (1.5)	−4.28	2.64	24.0 (12.3)	−2.09			
CCSD(T)		14.3			24.2				
HKrCCH···CH_3OH									
MP2	2.25	14.4 (5.1)	−1.45	2.26	36.5 (21.6)	−1.46			
CCSD(T)		14.4			33.1				
HKrCCH···CH_3NH_2									
MP2	2.23	18.1 (6.6)	−3.50	2.63	32.1 (17.6)	−1.96			
CCSD(T)		17.6			28.7				
HCCH···H_2O									
MP2	2.18	15.1 (2.8)	0.57	2.68	12.7 (0.8)	0.26			
CCSD(T)		15.2			12.4				
HCCH···NH_3									
MP2	2.26	19.7 (5.0)	0.74						
CCSD(T)		19.5							
HCCH···CH_3OH									
MP2	2.12	17.9 (5.1)	0.49	2.36	14.7 (4.1)	0.36			
CCSD(T)		17.6			14.0				
HCCH···CH_3NH_2									
MP2	2.17	23.0 (7.7)	0.75						
CCSD(T)		22.8							

Table 2 Charge on the important atoms of the monomer and the hydrogen bonded complexes of HKrCCH and HCCH calculated at the MP2/aug-cc-pVDZ level of theory. Change in charge of the respective atom during the complexation has been shown in parentheses[a]

	C–H···O/N		O/N–H···π			Kr–H···O	
	H_C	Kr	$H_{O/N}$	O/N	Kr	H_{Kr}	Kr
HKrCCH	0.221	0.532			0.532	0.019	0.532
H_2O	0.237, (0.016)	0.525, (−0.007)	0.495, (0.013)	−0.998, (0.035)	0.557, (0.025)	0.193, (0.174)	0.525, (−0.007)
NH_3	0.241, (0.020)	0.522, (−0.010)	0.386, (0.017)	−1.138, (0.029)	0.551, (0.019)		
CH_3OH	0.228, (0.007)	0.526, (−0.006)	0.492, (0.021)	−0.803, (0.033)	0.553, (0.021)		
CH_3NH_2	0.232, (0.011)	0.522, (−0.010)	0.386, (0.018)	−0.935, (0.028)	0.549, (0.017)		
HCCH	0.233						
H_2O	0.246, (0.013)		0.483, (0.002)	−0.968, (0.005)			
NH_3	0.249, (0.016)						
CH_3OH	0.243, (0.010)		0.480, (0.009)	−0.782, (0.012)			
CH_3NH_2	0.243, (0.010)						

[a] H_C denotes hydrogen attached to carbon, $H_{O/N}$ denotes hydrogen attached to oxygen/nitrogen, H_{Kr} denotes hydrogen attached to krypton.

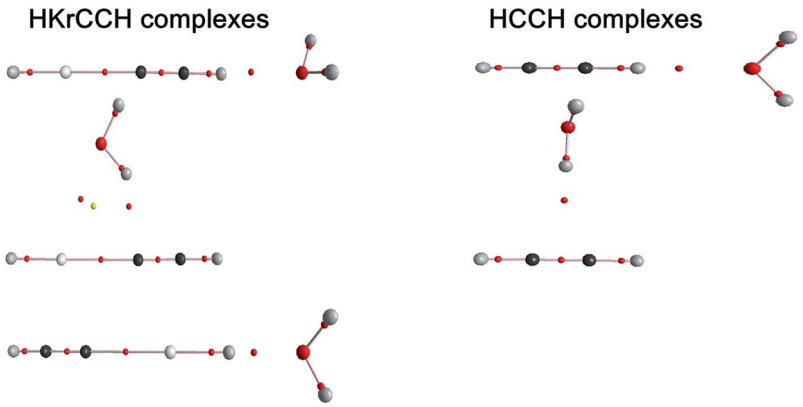

Fig. 2 Molecular graph for the topology of electron density of the hydrogen bonded complexes HKrCCH and HCCH with H_2O at the MP2/aug-cc-pVDZ level of calculation. Bond critical points and ring critical points are shown as red and yellow color balls, respectively.

polarizable nature of Kr–H group compared to the C–H of HKrCCH as the krypton atom is located near to the acceptor molecule. Hence, the effect of the electric field created by the proton acceptor is strong as well as the direction of the dipole for the HKrCCH and acceptor molecules is the same, which results in a positive $\Delta\mu$ and provides higher stabilization.

The most surprising finding for all hydrogen bonded complexes of HKrCCH is that the stabilization energies for π hydrogen bonded complexes are significantly (~3–8 times) higher as compared to its σ hydrogen bonded complexes, which is in contrast to general perception that the strengths of the π hydrogen bonded complexes are half those of the σ hydrogen bonded complexes.[15] In contrast to HKrCCH complexes, σ hydrogen bonded complexes are the most stable structure for precursor HCCH molecule, which is consistent with their earlier experimental and theoretical results.[35–37] Moreover, the stabilization energy of the π hydrogen bonded complexes of HKrCCH (~15 kJ mol^{-1}) is many times higher compared to the most stable σ hydrogen bonded complexes of its precursor HCCH (~4 kJ mol^{-1}). $\Delta\mu$ for the π hydrogen bonded complexes of HKrCCH is negative, whereas the stabilization energy is significantly higher, which is counterintuitive. This shows that apart from

Table 3 Electron density (ρ), Laplacian (∇^2), total electronic energy density (H), local electronic kinetic energy density (G) and local potential energy density (V) for the hydrogen bonded complexes of HKrCCH and HCCH calculated at the MP2/aug-cc-pVDZ level of theory. All the parameters reported in this table are in atomic units[a]

	HKrCCH				HCCH			
C–H···O/N	**H_2O**	**NH_3**	**CH_3OH**	**CH_3NH_2**	**H_2O**	**NH_3**	**CH_3OH**	**CH_3NH_2**
$\rho_{C-H\cdots O/N}$	0.0133	0.0145	0.0152	0.0175	0.0144	0.0163	0.0175	0.0197
$\nabla^2_{C-H\cdots O/N}$	0.0415	0.0380	0.0431	0.0464	0.0492	0.0430	0.0563	0.0522
$G_{C-H\cdots O/N}$	0.0099	0.0091	0.0110	0.0113	0.0113	0.0102	0.0134	0.0126
$V_{C-H\cdots O/N}$	−0.0095	−0.0087	−0.0108	−0.0109	−0.0103	−0.0097	−0.0128	−0.0121
$H_{C-H\cdots O/N}$	0.0004	0.0004	0.0002	0.0004	0.0010	0.0005	0.0006	0.0005
O/N–H···π								
$\rho_{O/N-H\cdots\pi}$	0.0182	0.0126	0.0199	0.0117	0.0116		0.0126	
$\rho_{O/N-Kr}$	0.0094	0.0089	0.0099	0.0106				
ρ_{rcp}	0.0089	0.0078	0.0097	0.0083				
$\nabla^2_{O/N-H\cdots\pi}$	0.0498	0.0352	0.0518	0.0347	0.0318		0.0344	
$\nabla^2_{O/N-Kr}$	0.0396	0.0289	0.0361	0.0335				
∇^2_{rcp}	0.0413	0.0303	0.0381	0.0305				
$G_{O/N-H\cdots\pi}$	0.0118	0.0082	0.0129	0.0079	0.0068		0.0075	
$G_{O/N-Kr}$	0.0085	0.0062	0.0080	0.0075				
G_{rcp}	0.0087	0.0063	0.0083	0.0066				
$V_{O/N-H\cdots\pi}$	−0.0112	−0.0076	−0.0127	−0.0073	−0.0055		−0.0064	
$V_{O/N-Kr}$	−0.0071	−0.0052	0.0071	−0.0066				
V_{rcp}	−0.0070	−0.0051	−0.0071	−0.0056				
$H_{O/N-H\cdots\pi}$	0.0006	0.0006	0.0002	0.0006	0.0013		0.0011	
$H_{O/N-Kr}$	0.0014	0.0010	0.0009	0.0009				
H_{rcp}	0.0017	0.0012	0.0012	0.0010				

[a] The corresponding ρ, ∇^2, G, V, and H values at the (H···O) BCP for the Kr–H···O hydrogen bonded complex are 0.0406, 0.1104, 0.0288, −0.0299, and −0.0011, respectively.

Table 4 Vibrational stretching frequencies (cm^{-1}) of the C–H, Kr–H and O/N–H groups of hydrogen bonded complexes, changes in stretching frequency (cm^{-1}) during complexation and changes in the bond length (angstroms) of respective groups calculated at the MP2/aug-cc-pVDZ level of theory. Changes in stretching frequency during complexation have been shown in parentheses

	ν_{C-H}	ν_{Kr-H}				
HKrCCH	3443	1543	$\nu_{O/N-H}$	Δl_{C-H}	Δl_{Kr-H}	$\Delta l_{O/N-H}$
H_2O						
C–H···O	3389 (−59)	1483 (−54)	3798 (−5)	0.010	0.01	0.0003
			3931 (−6)			0.0002
O–H···π	3435 (−9)	1735(+194)	3653 (−150)	0.001	−0.05	0.0097
			3894 (−43)			−0.0008
Kr–H···O	3425 (−17)	1823 (+280)	3767 (−36)	0.001	−0.07	0.0024
			3898 (−39)			0.0024
NH_3						
C–H···N	3338 (−105)	1464 (−79)	3476 (−5)	0.010	0.02	0.0020
			3631 (−4)			0.0020
			3631 (−4)			−0.0030
N–H···π	3437 (−6)	1681 (+134)	3442 (−41)	0.001	−0.04	0.0020
			3587 (−48)			0.0020
			3624 (−11)			0.0010
CH_3OH						
C–H···O	3380 (−63)	1504 (−39)	3667 (−171)	0.010	0.01	0.0008
O–H···π	3435 (−8)	1717 (+174)	3820 (−18)	0.001	−0.05	0.0080
CH_3NH_2						
C–H···N	3313 (−130)	1467 (−76)	3510 (−3)	0.001	0.02	0.0002
			3609 (+1)			0.0002
N–H···π	3436 (−7)	1673 (+130)	3479 (−34)	0.010	−0.04	0.0040
			3588 (−22)			0.0010
HCCH	3432					
	3519					
H_2O						
C–H···O	3390 (−42)		3802 (−1)	0.0057		−0.0003
	3498 (−21)		3934 (−3)	−0.0005		−0.0003
O–H···π	3423(−10)		3770 (−33)	0.0007		0.0027
	3512(−7)		3912 (−25)	0.0006		−0.0004
NH_3						
C–H···N	3325(−107)		3475 (−6)	0.0094		0.0001
	3487(−32)		3627 (−8)	−0.0005		0.0001
			3627 (−8)			0.0001
CH_3OH						
C–H···O	3364(−68)		3837 (−1)	0.0066		−0.0002
	3492(−27)			−0.0005		
O–H···π	3422(−10)		3798 (−40)	0.0008		0.0020
	3511(−8)			0.0007		
CH_3NH_2						
C–H···N	3288(−144)		3509 (−4)	0.0134		−0.0001
	3483(−36)		3606 (−2)	−0.0005		

electrostatic interaction, dispersion created by the krypton atom plays an important role in stabilization of the π hydrogen bonded complexes of HKrCCH.

In order to gain further insight about the hydrogen bonded complexes of HKrCCH and HCCH, charge on important atoms has been calculated by natural population analysis (NPA) at the MP2/aug-cc-pVDZ level of theory, and the values are depicted in Table 2. For the C–H···O/N hydrogen bonded complexes of HKrCCH and HCCH, there is a slight increase in the positive charge on the hydrogen atom of the C–H group. For the Kr–H···O hydrogen bonded complex of HKrCCH with H_2O, there is a large increase in the positive charge on the hydrogen of Kr–H along with a decrease in the positive charge on the krypton atom as compared to its C–H···O hydrogen bonded complex. This

Table 5 Change in the occupancy of the bonding and antibonding orbitals of the HKrCCH and HCCH molecules during complexation with H_2O at the RHF/aug-cc-pVDZ level of calculation

	HKrCCH			HCCCH	
	CH	HKr	OH	CH	OH
C–H···O (σ) BD	−0.00101	0.00114	−0.00044	−0.00105	−0.00067
BD*	0.00544	0.01886	0.00001	0.00689	0.00003
O–H···π BD	0.00002	0.00096	−0.0028	−0.00001	−0.00019
BD*	0.00068	−0.06845	0.01270	−0.00004	0.00498

indicates that the Kr–H···O hydrogen bonded complex is held by relatively strong electrostatic force, which is also in line with the maximum increase of the dipole moment for these complexes. Apart from H_2O, other acceptor molecules do not form a stable Kr–H···O hydrogen bonded complex with HKrCCH, which could be due to higher electron density on oxygen/nitrogen atom of the respective acceptor molecules.

For the π hydrogen bonded complexes of HKrCCH and HCCH, increase in the positive charge on donor hydrogen atom along with an increase in the negative charge on the oxygen/nitrogen atom has been found. The trend of the data is similar for the π hydrogen bonded complexes of HKrCCH and HCCH. However, the amount of change is higher for HKrCCH as compared to HCCH. It is also important to note that the positive charge on krypton has increased for π hydrogen bonded complexes, which implies that krypton is working as an electron donor. This is in contrast to σ hydrogen bonded complexes of HKrCCH where charge on krypton decreases and it works as an electron acceptor. Decrease in the positive charge on krypton along with high increase in the negative charge on oxygen/nitrogen for the π hydrogen bonded complexes of HKrCCH indicates that there may be an interaction between krypton and oxygen/nitrogen of the solvent molecule. Indeed, the bent structure of the π hydrogen bonded complex of HKrCCH as compared to HCCH complexes also favors this interaction.

In order to ascertain the nature of hydrogen bonding for all the complexes of HKrCCH and HCCH, we have characterized the topology of electron density of each structure by the AIM approach at the MP2/aug-cc-pVDZ level of theory. In present case, the critical points of electron density distribution were obtained and characterized by the rank and trace of the Hessian matrix. A (3, −1) bond critical point (BCP) with a positive Laplacian (∇^2) for the electron density distribution at the BCP indicates the presence of noncovalent interaction, whereas the presence of a (3, +1) ring critical point shows that the corresponding structure is cyclic.[38–41] Fig. 2 shows the molecular graph of electron density for H_2O complexes with HKrCCH and HCCH optimized at the MP2/aug-cc-pVDZ level of calculation, and the obtained values of electron density (ρ), Laplacian (∇^2), total electronic energy density (H) and its component local electronic kinetic energy density (G) as well as local potential energy density (V) at BCP for all the complexes of HKrCCH and HCCH are listed in Table 3. This calculation reveals the presence of a (3, −1) BCP at the H···O/N contact for all the σ hydrogen bonded complexes of HKrCCH and HCCH. The values of ρ and ∇^2 at the BCP (H···O/N) for the C–H···O/N hydrogen bonded complexes lie within the acceptable optimal ranges of 0.002–0.04 and 0.02–0.15 a.u., respectively. The small positive value of H at H···O/N BCP confirms the presence of C–H···O/N hydrogen bonding in these complexes.[42] The value of ρ and ∇^2 are higher for the C–H···O/N hydrogen bonded complexes of HCCH as compared to the HKrCCH complexes, which is in agreement with its D_{Hb} and stabilization energy values. For the Kr–H···O hydrogen bonded complex, the values of ρ and ∇^2 at the Kr–H···O BCP are significantly high for weak noncovalent interaction, and the value of H at that BCP is negative, which is uncommon for complexes having noncovalent interaction.[42] The negative value of H for the Kr–H···O BCP indicates the presence of some degree of electron sharing for this complex.[40] The probable reason for the negative value of H could be high polarization of the hydrogen (H–Kr) of HKrCCH by H_2O molecule due its high dipole moment, which causes a shift in electron density from the hydrogen on to krypton, resulting in the short D_{Hb} (∼1.9 Å) as well as the elongated Kr–C bond (0.17 Å).

AIM calculation for the π hydrogen bonded complexes of HCCH shows a (3, −1) BCP at O/N–H···π contact. All topological parameters for the electron density at this BCP are well in the range of acceptable values for the noncovalent interaction. In contrast to π hydrogen bonded complexes of HCCH, HKrCCH complexes exhibit (3, −1) BCP at O/N–H···π as well as O/N···Kr interactions. The values of ρ, ∇^2 and H for the O/N–H···π and O/N···Kr BCPs are well in the ranges of acceptable values. This study clearly demonstrates that apart from O/N–H···π hydrogen bonding, there is also an additional interaction between oxygen/nitrogen and krypton for the π hydrogen bonded complexes of HKrCCH. This finding is in accordance with earlier appraisal of the charge analysis as discussed above. Interestingly, one (3,+1) RCP is also present between the two (3, −1) BCPs at O/N–H···π and O/N···Kr for the π hydrogen bonded complex of HKrCCH, which indicates that it is a cyclic structure.

AIM analysis shows that the π hydrogen bonded complex of HKrCCH is a cyclic structure in which O/N–H···π and O/N···Kr interactions exist unitedly, and charge analysis depicts that the increase in the positive charge on krypton and negative charge on oxygen induces a comparatively higher increase in positive charge on the donor hydrogen (O/N–H). This clearly indicates that interaction between krypton and oxygen/nitrogen contributes to the formation of strong O/N–H···π hydrogen bonding, and hence, the stabilization energy of these complexes is higher as compared to hydrogen bonded complexes of HCCH as well as σ hydrogen bonded complexes of HKrCCH. In one of the earlier studies, Alkorta and Elguero have shown that HKrCCH forms a

π hydrogen bonded complex with hydrogen fluoride and hydrogen chloride. However, the role of noble gas atom on the higher stability of the π hydrogen bonded complex was not well understood.[29]

It is well known that vibrational spectroscopy and structural change in the donor group during complexation are very sensitive to hydrogen bonded structures and show characteristic frequency shifts upon hydrogen bonding.[15,17] Hence, in order to further understand the role of the noble gas atom in hydrogen bonding, we have explored the shifts in donor's stretching frequencies as well as the stretching frequency of other important modes of hydrogen bonded complexes of HKrCCH and HCCH, and the respective values are shown in Table 4 at the MP2/aug-cc-pVDZ level of theory. For all the hydrogen bonded complexes of HCCH, red shift in donor's vibrational frequencies is observed. The C–H···O/N hydrogen bonded complexes of HKrCCH show a red shift in C–H and Kr–H stretching frequencies. The red shift of the C–H stretching frequency is similar to that in our earlier study for the σ hydrogen bonded complexes of FKrCCH. The red shift in the donor's C–H and Kr–H stretching frequencies is a consequence of the elongation of C–H and Kr–H bonds as evident from the data depicted in Table 4. In contrast to C–H···O/N hydrogen bonded complexes, a blue shift in donor (Kr–H) stretching frequency has been found for the Kr–H···O hydrogen bonded complex of HKrCCH. The blue shift of Kr–H stretching frequency is caused by the contraction of Kr–H bonds. For the π hydrogen bonded complexes of HKrCCH, a red shift in the donor (O/N–H) stretching frequency along with a blue shift in Kr–H stretching frequency takes place during the complexation. This frequency change is a result of the elongation of the O/N–H bond and contraction of the Kr–H bond for the π hydrogen bonded systems of HKrCCH.

In order to understand the role of noble gas in the change of frequency during the complexation, NBO analysis has been performed at the RHF/aug-cc-pVDZ level of theory using structures optimized at the MP2/aug-cc-pVDZ level. The RHF method has been used due to the fact that the NBO analysis yields reliable values only with either HF or DFT methods, since the wavefunction is completely defined.[43] It is well known that red shifted hydrogen bonded complexes show an increase in occupancy of antibonding orbital of donor molecule, whereas it is opposite for blue shifted hydrogen bonded complexes. Table 5 shows the changes of the donor–acceptor's orbital occupancy for the HKrCCH and HCCH complexes with H_2O. For the C–H···O hydrogen bonded complexes of HKrCCH, there is an increase in occupancy for the antibonding orbital of donor C–H, and the same trend is followed for Kr–H also. This is quite consistent with the observed red shift of the stretching frequencies of C–H and Kr–H groups for the C–H···O hydrogen bonded complex of HKrCCH. A similar trend in the occupancy change for the C–H group has been found for the C–H···O hydrogen bonded complex of HCCH. For the π hydrogen bonded complex of HKrCCH, there is an increase in occupancy of antibonding orbital of donor (O–H) group along with a big decrease in the occupancy of antibonding orbital of Kr–H group, which causes red shift in O–H stretching frequency and blue shift in Kr–H stretching frequency during complexation. This shows that Kr–H group acts as an electron acceptor for C–H···O hydrogen bonded complexes and electron donor for π hydrogen bonded complexes of HKrCCH, which is also supported by the charge data. Similar trend of data has been found for other hydrogen bonded complexes of HKrCCH and HCCH.

We have also explored the donor–acceptor orbital interaction for the π hydrogen bonded complexes of HKrCCH and HCCH. It has been found that a major orbital interaction for HCCH complexes is between BD (C≡C) and BD* (O–H), whereas for the HKrCCH complex, there is also an additional interaction between the lone pair of krypton with BD* (O–H) along with BD (C≡C) and BD* (O–H) interaction. This shows that an increase in the BD* occupancy is contributed by the noble gas, and hence, it shows a higher red shift as well as higher stability. AIM, charge and NBO analyses clearly demonstrate that noble gas plays a key role in higher stability of π hydrogen bonded complexes of HKrCCH by virtue of Kr/O···N interaction, which contributes to the formation of strong O/N–H···π hydrogen bond.

Conclusion

The structure, energetics and spectroscopic properties of hydrogen bonded complexes of HKrCCH with H_2O, NH_3, CH_3OH and CH_3NH_2 have been explored and further compared with the hydrogen bonded complexes of its precursor HCCH. HKrCCH forms C–H···O, Kr–H···O (only with H_2O) and O/N–H···π hydrogen bonded complexes, among which the π hydrogen bonded complex has the most stable structure. HCCH forms C–H···O/N and O–H···π (with H_2O and CH_3OH) hydrogen bonded complexes, among which the σ hydrogen bonded complex is the most stable. Surprisingly, the stabilization energy of the π hydrogen bonded complex of HKrCCH is about two to three fold higher compared to the σ hydrogen bonded complex of HCCH. AIM analysis shows (3, −1) critical points at the O/N–H···π and Kr···O/N BCP along with a (3,+1) BCP in between them. This shows that the π hydrogen bonded complex of HKrCCH is a cyclic structure in which Kr···O/N interaction contributes to the formation of strong O/N–H···π hydrogen bonding. This study clearly established that insertion of a noble gas significantly changes the hydrogen bonding nature of its precursor molecule. This result and earlier work by Alkorta and Elguero[29] clearly demonstrates that noble gas contributes to the formation of strong π hydrogen bonded complexes. In the absence of any experiment, the present results hopefully will encourage experimentalists to explore the properties of π hydrogen bonded complexes of noble gas molecules.

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References

1 L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell and M. Rasanen, *Nature*, 2000, **406**, 874–876.
2 L. Khriachtchev, M. Pettersson, A. Lignell and M. Rasanen, *J. Am. Chem. Soc.*, 2001, **123**, 8610–8611.
3 A. Cohen, J. Lundell and R. B. Gerber, *J. Chem. Phys.*, 2003, **119**, 6415–6417.
4 V. I. Feldman, F. F. Sukhov, A. Y. Orlov and I. V. Tyulpina, *J. Am. Chem. Soc.*, 2003, **125**, 4698–4699.
5 L. Khriachtchev, A. Domanskaya, J. Lundell, A. Akimov, M. Rasanen and E. Misochko, *J. Phys. Chem. A*, 2010, **114**, 4181–4187.
6 L. Khriachtchev, A. Lignell, H. Tanskanen, J. Lundell, H. Kiljunen and M. Rasanen, *J. Phys. Chem. A*, 2006, **110**, 11876–11885.
7 L. Khriachtchev, H. Tanskanen, A. Cohen, R. B. Gerber, J. Lundell, M. Pettersson, H. Kiljunen and M. Rasanen, *J. Am. Chem. Soc.*, 2003, **125**, 6876–6877.
8 L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen and M. Rasanen, *J. Am. Chem. Soc.*, 2003, **125**, 4696–4697.
9 T.-Y. Lai, C.-Y. Yang, H.-J. Lin, C.-Y. Yang and W.-P. Hu, *J. Chem. Phys.*, 2011, **134**, 244110.
10 M. Pettersson, L. Khriachtchev, A. Lignell, M. Rasanen, Z. Bihary and R. B. Gerber, *J. Chem. Phys.*, 2002, **116**, 2508–2515.
11 M. Pettersson, L. Khriachtchev, J. Lundell and M. Rasanen, *J. Am. Chem. Soc.*, 1999, **121**, 11904–11905.
12 M. Pettersson, J. Lundell and M. Rasanen, *J. Chem. Phys.*, 1995, **102**, 6423–6431.
13 S. Berski, Z. Latajka, B. Silvi and J. Lundell, *J. Chem. Phys.*, 2001, **114**, 4349–4358.
14 L. Khriachtchev, M. Rasanen and R. B. Gerber, *Acc. Chem. Res.*, 2008, **42**, 183–191.
15 G. A. Jeffery, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, 1994.
16 G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290–296.
17 P. Hobza and Z. K. Havlas, *Chem. Rev.*, 2000, **100**, 4253–4264.
18 P. C. Singh and G. Naresh Patwari, *Chem. Phys. Lett.*, 2006, **419**, 5–9.
19 L. Albrecht, R. J. Boyd, O. Mo and M. Yanez, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14540–14547.
20 I. Rozas, I. Alkorta and J. Elguero, *J. Phys. Chem. A*, 1997, **101**, 9457–9463.
21 A. Lignell, L. Khriachtchev, M. Pettersson and M. Rasanen, *J. Chem. Phys.*, 2003, **118**, 11120–11128.
22 S. A. C. McDowell, *J. Chem. Phys.*, 2004, **120**, 3630–3634.
23 A. V. Nemukhin, B. L. Grigorenko, L. Khriachtchev, H. Tanskanen, M. Pettersson and M. Rasanen, *J. Am. Chem. Soc.*, 2002, **124**, 10706–10711.
24 H. Tanskanen, S. Johansson, A. Lignell, L. Khriachtchev and M. Rasanen, *J. Chem. Phys.*, 2007, **127**, 154313.
25 D. Veldman, S. P. M. A. Chopin, S. C. J. Meskers, M. M. Groeneveld, R. M. Williams and R. A. J. Janssen, *J. Phys. Chem. A*, 2008, **112**, 5846–5857.
26 L. Ma, Z. Huang, X. Niu, T. Shen and L. Guo, *Comput. Theor. Chem.*, 2013, **1017**, 14–21.
27 P. C. Singh, *Chem. Phys. Lett.*, 2011, **515**, 206–209.
28 P. C. Singh, *Chem. Phys.*, 2011, **389**, 96–101.
29 I. Alkorta and J. Elguero, *Chem. Phys. Lett.*, 2003, **381**, 505–511.
30 R. A. Kendall, T. H. Dunning and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796–6806.
31 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.
32 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
33 R. F. W. Bader, *Atoms in Molecules a Quantum Theory*, Oxford University Press, New York, 1990.
34 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, *et al.*, *Gaussian 09 revision B.01*, Gaussian, Inc., Wallingford, CT, 2010.
35 A. Engdahl and B. Nelander, *Chem. Phys. Lett.*, 1983, **100**, 129–132.
36 K. I. Peterson and W. Klemperer, *J. Chem. Phys.*, 1984, **81**, 3842–3845.
37 D. Tzeli, A. Mavridis and S. S. Xantheas, *J. Chem. Phys.*, 2000, **112**, 6178–6189.
38 U. Koch and P. L. A. Popelier, *J. Phys. Chem.*, 1995, **99**, 9747–9754.
39 C. F. Matta, N. Castillo and R. J. Boyd, *J. Phys. Chem. A*, 2005, **109**, 3669–3681.
40 C. F. Matta, N. Castillo and R. J. Boyd, *J. Phys. Chem. B*, 2006, **110**, 563–578.
41 O. Knop, R. J. Boyd and S. C. Choi, *J. Am. Chem. Soc.*, 1988, **110**, 7299–7301.
42 O. Knop, K. N. Rankin and R. J. Boyd, *J. Phys. Chem. A*, 2002, **107**, 272–284.
43 I. V. Alabugin and T. A. Zeidan, *J. Am. Chem. Soc.*, 2002, **124**, 3175–3185.

