

**A COMPREHENSIVE COMPUTATIONAL STUDY ON  $\text{OCH}^+\text{-Rg}$  (Rg = He, Ne, Ar, Kr, Xe) COMPLEXES**Yinghong SHENG<sup>1</sup> and Jerzy LESZCZYNSKI<sup>2,\*</sup>

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Dedicated to Professors Petr Čársky, Ivan Hubač and Miroslav Urban on the occasion of their 60th birthdays.

The equilibrium geometries, harmonic vibrational frequencies, and the dissociation energies of the  $\text{OCH}^+\text{-Rg}$  (Rg = He, Ne, Ar, Kr, and Xe) complexes were calculated at the DFT, MP2, MP4, CCSD, and CCSD(T) levels of theory. In the lighter  $\text{OCH}^+\text{-Rg}$  (Rg = He, Ne, Ar) rare gas complexes, the DFT and MP4 methods tend to produce longer Rg-H<sup>+</sup> distance than the CCSD(T) level value, and the CCSD-calculated Rg-H<sup>+</sup> bond lengths are slightly shorter. DFT method is not reliable to study weak interaction in the  $\text{OCH}^+\text{-He}$  and  $\text{OCH}^+\text{-Ne}$  complexes. A qualitative result can be obtained for  $\text{OCH}^+\text{-Ar}$  complex by using the DFT method; however, a higher-level method using a larger basis set is required for the quantitative predictions. For heavier atom (Kr, Xe)-containing complexes, only the CCSD method predicted longer Rg-H<sup>+</sup> distance than that obtained at the CCSD(T) level. The DFT method can be applied to obtain the semiquantitative results. The relativistic effects are expected to have minor effect on the geometrical parameters, the H<sup>+</sup>-C stretching mode, and the dissociation energy. However, the dissociation energies are sensitive to the quality of the basis set. The nature of interaction between the  $\text{OCH}^+$  ion and Rg atoms was also analyzed in terms of the interaction energy components.

**Keywords:** Rare gases complexes; Weak interaction; Harmonic vibrational frequency; Dissociation energy; Energy decomposition; *Ab initio* calculations; MP2; DFT; CCSD.

Proton-bound complexes are the intermediates of proton transfer reactions which are important in a broad range of chemical and biological environments. In order to better understand the nature of the reaction intermediates, a series of experimental and theoretical investigations have been performed on selected proton-bound complexes such as  $(\text{Ar})_n\text{-HCO}^+$ ,  $(\text{Ar})_n\text{-HSiO}^+$ , and  $(\text{Ar})_n\text{-HN}_2^+$ . The experimental infrared predissociation spectra provide detailed information concerning the interaction between

the contributing moieties and should eventually reveal details of the potential energy surfaces for interactions of ion-neutral species at close range<sup>2</sup>.

Complexes consisting of He, Ne, Ar, and H<sub>2</sub> ligands attached to the linear closed-shell OCH<sup>+</sup> ion have been extensively examined using the IR spectroscopy and different theoretical techniques<sup>4-7</sup>. The OCH<sup>+</sup>-Rg dimers containing rare gas elements (Rg) are determined to be linear with the proton being shared between Rg and CO. The degree to which the properties of the OCH<sup>+</sup> core are altered by the attached ligand and the strength of the intermolecular interaction depend significantly upon the difference between the proton affinities (PA) of CO and the participating ligand,  $\Delta\text{PA}$ <sup>3</sup>. Because the CO molecule has a higher PA value than N<sub>2</sub>, the intermolecular interaction between the OCH<sup>+</sup>-Rg is weaker than in the analogous N<sub>2</sub>H<sup>+</sup>-Rg complexes. Therefore, a smaller red shift of  $\nu_1$  (the C-H<sup>+</sup> stretch) of the OCH<sup>+</sup> fragment, longer intermolecular bonds and lower dissociation energies are expected than in the similar N<sub>2</sub>H<sup>+</sup>-Rg species.

In 1983, the first observation of vibration-rotation transitions in OCH<sup>+</sup> was reported. The  $\nu_1$  absorption band was measured with a color-center laser by modulating the drift velocity of the ion in an ac discharge and the Doppler-shifted absorptions were detected with lock-in techniques. The determined  $\nu_1$  frequency value amounts to  $3088.727 \pm 0.003 \text{ cm}^{-1}$ <sup>4</sup>. The vibrational predissociation spectrum of the OCH<sup>+</sup>-He proton-bound complex has been recorded in the 3  $\mu\text{m}$  (C-H stretch) region by monitoring the OCH<sup>+</sup> photofragment current. A rotationally resolved, parallel band is observed, red-shifted by  $12.4 \text{ cm}^{-1}$  from the  $\nu_1$  transition of the free OCH<sup>+</sup>. Analysis of spectrum bands in terms of a diatomic-like Hamiltonian yields  $\nu_1 = 3076.313 \pm 0.010 \text{ cm}^{-1}$ <sup>5</sup>. The OCH<sup>+</sup>-Ne dimer has been studied by means of infrared photodissociation spectroscopy; the  $\nu_1$  band is red-shifted by  $42.5 \text{ cm}^{-1}$  from the corresponding  $\nu_1$  transition of free OCH<sup>+</sup><sup>6</sup>. Combined experimental and theoretical studies show that the value of  $\nu_1$  in OCH<sup>+</sup>-Ar amounts to  $2815 \text{ cm}^{-1}$ <sup>7</sup>. Therefore, the red shifts are 12.5, 42.5, and  $274 \text{ cm}^{-1}$  for OCH<sup>+</sup>-He, OCH<sup>+</sup>-Ne, and OCH<sup>+</sup>-Ar, respectively.

Currently there are no accurate experimental measurements of the OCH<sup>+</sup>-Rg dissociation energies. The estimation based on *ab initio* calculations (Rg = He, Ar) and RKR/DMA potentials (Rg = Ne) yield the dissociation energies ( $D_0$ ) to be 130–170 ( $242 \text{ cm}^{-1}$ , 0.69 kcal/mol),  $482 \text{ cm}^{-1}$  (1.38 kcal/mol), and 1470–1550  $\text{cm}^{-1}$  (4.202–4.432 kcal/mol) for OCH<sup>+</sup>-He, OCH<sup>+</sup>-Ne, and OCH<sup>+</sup>-Ar, respectively<sup>8-10</sup>.

Scarce experimental vibrational data are available for the Kr- or Xe-containing OCH<sup>+</sup>-Rg, N<sub>2</sub>H<sup>+</sup>-Rg, and OH<sup>+</sup>-Rg complexes. Only one complex involving the heavier krypton atom has been so far studied by high-

resolution spectroscopy<sup>11</sup>; however, the comprehensive information on its structural parameters, vibrational properties is still unknown. A recent theoretical study<sup>12</sup> at the CCSD(T) level using cc-pVQZ basis set provides the value of  $\nu_1$  of about  $2890\text{ cm}^{-1}$ , and the dissociation energy of  $2149\text{ cm}^{-1}$  ( $6.144\text{ kcal/mol}$ ), respectively.

It will be informative to perform the comprehensive study of the molecular structures and the nature of interactions of rare-gas-atoms-containing ions, such as  $\text{N}_2\text{H}^+\text{-(Rg)}_n$ <sup>13</sup> and  $\text{OCH}^+\text{-(Rg)}_n$ ,  $\text{OH}^+\text{-(Rg)}_n$  (Rg = He, Ne, Ar;  $n = 0\text{--}12$ ), *etc.* The choice of the method and basis set reliable for investigating these complexes is of importance since the vibrational properties and the dissociation energies are highly basis-set-dependent and are sensitive to the level of the electron correlation. Therefore, in this paper, we investigate the molecular structures, the thermodynamic, and vibrational properties of  $\text{OCH}^+\text{-Rg}$  (Rg = He, Ne, Ar) using the density-functional theory, MP2, MP4, and CCSD and CCSD(T) methods. It is of less confidence to draw a conclusion which method is reliable for  $\text{OCH}^+\text{-Kr}$  or  $\text{OCH}^+\text{-Xe}$  complexes due to the lack of experimental data. Therefore we will apply the similar strategy as described in our previous study on  $\text{N}_2\text{H}^+\text{-X}$  (X = He, Ne, Ar, Kr, Xe,  $\text{H}_2$ ) complexes<sup>14</sup> to investigate the basis set and electron correlation effects on the properties of the series of  $\text{OCH}^+\text{-Rg}$  (Rg = He, Ne, Ar, Kr, Xe) complexes.

## COMPUTATIONAL

All calculations were carried out using the Gaussian98 program<sup>15</sup>. The molecular structures were optimized by the DFT method with the Becke3LYP functional, the second-order Møller-Plesset (MP2) method<sup>16</sup>, the fourth-order (MP4(SDTQ)) method<sup>17</sup>, and by the coupled-cluster approach using double substitutions from the Hartree-Fock determinant for the CCSD method, and single, double and triple substitutions at the CCSD(T) level<sup>18</sup>. All the geometries were fully optimized without any symmetry constraints. Harmonic vibrational frequency calculations were performed at each level to confirm whether or not the predicted structure is a minimum. The dissociation energies were calculated by applying the DFT, MP2, MP4, CCSD, and CCSD(T) methods.

For  $\text{OCH}^+\text{-Rg}$  complexes where Rg = He, Ne, Ar, the 6-311+G(d,p) basis set<sup>19</sup> was used for calculations at different levels. In addition, the aug-cc-pVXZ (X = D, T, Q) basis sets<sup>20</sup> were also used for  $\text{OCH}^+\text{-Rg}$  (Rg = He, Ne, Ar, Kr) complexes at the MP2 level. Due to the limitation of computational resources, only  $\text{OCH}^+$  and  $\text{OCH}^+\text{-He}$  species have been studied using the aug-cc-pV5Z basis set.

Since the utilized basis sets are not saturated, the basis set extension effects were then examined for the  $\text{OCH}^+\text{-Rg}$  ( $\text{Rg} = \text{He, Ne, Ar}$ ) complexes by the extrapolation formula using the aug-cc-pVXZ ( $X = \text{T, Q}$ ) basis sets<sup>21</sup>:

$$E(X) = E(\text{CBS}) + \frac{A}{X^3}, \quad (1)$$

where CBS denotes complete basis set, as recommended recently by Lee *et al.*<sup>22</sup> The extrapolated dissociation energies are also listed in Tables II and III.

For species involving the heavier rare gas atoms ( $\text{Rg} = \text{Kr and Xe}$ ), different approaches were applied. We used an effective core potential (ECP) which was reported to yield very satisfactory results<sup>23</sup>. The quasirelativistic effective core 6s6p3d1f/4s4p3d1f basis set of the Stuttgart group<sup>24</sup> with 8 valence-electron pseudopotential were used for Kr and Xe in conjunction with the 6-311+G(d,p) basis set for the other atoms (BS-I). The same effective core potentials were used for Kr and Xe, while the aug-cc-pVXZ ( $X = \text{T, Q}$ ) basis sets were used for the  $\text{OCH}^+$  fragment (denoted as BS-T, BS-Q) in order to study basis set effect.

The physical components resulting from interaction energy decomposition were also analyzed applying the modified version<sup>25</sup> of the Gamess program<sup>26</sup>. The total interaction energies ( $\Delta E_{\text{MP2}}$ )

$$\Delta E_{\text{MP2}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} \quad (2)$$

has been decomposed into the Hartree–Fock and electron correlation components

$$\Delta E_{\text{MP2}} = \Delta E_{\text{SCF}} + \varepsilon_{\text{MP}}^{(2)}. \quad (3)$$

The applied SCF energy decomposition was performed within the variational-perturbational scheme, corrected for the basis set superposition error<sup>27</sup>. In the above scheme  $\Delta E_{\text{SCF}}$  was partitioned into the electrostatic ( $\varepsilon_{\text{el}}^{(10)}$ ) and Heitler–London exchange ( $\varepsilon_{\text{ex}}^{\text{HL}}$ ) first-order components and the higher-order delocalization ( $\Delta E_{\text{del}}^{\text{HF}}$ ) term. The delocalization energy accounts for the charge transfer, induction, and other higher-order Hartree–Fock terms<sup>28</sup>. The correlation energy  $\varepsilon_{\text{MP}}^{(2)}$  is the correlation correction to the SCF components<sup>29</sup>. Due to basis sets limitation in the ECP code in

Games Package, the same basis set for Kr and Xe atoms but with the SBKJC effective core potentials, in conjunction with the 6-311+G(d,p), aug-cc-pVTZ, and aug-cc-pVQZ basis sets for C, H, O atoms were tested, and it was found to yield essentially the same geometrical parameters and dissociation energies as the BS-I, BS-T and BS-Q basis sets. Therefore, only SBKJC ECP is applied to energy decomposition analysis.

## RESULTS AND DISCUSSION

The optimized geometrical parameters obtained for  $\text{OCH}^+$  and its rare gas  $\text{OCH}^+\text{-Rg}$  complexes (Rg = He, Ne, Ar, Kr, Xe) with the density-functional, MP2, MP4, CCSD, and CCSD(T) methods are listed in Tables I–III. The corresponding values of selected vibrational modes as well as the dissociation energies are displayed in Tables II and III.

TABLE I

The optimized C–H<sup>+</sup> and C–O bond lengths, and C–H<sup>+</sup> and C–O stretching vibrational frequencies for  $\text{OCH}^+$  at the DFT, MP2, MP4, CCSD, and CCSD(T) levels of theory (units are in Å for bond lengths, kcal/mol for dissociation energies, and  $\text{cm}^{-1}$  for vibrational frequencies)

Method	Size of basis set	H <sup>+</sup> –C	C–O	$\nu_{\text{H}^+\text{-C}}$	$\nu_{\text{C-O}}$
B3LYP/6-311+G(d,p)	50	1.0955	1.1029	3225.7	2270.3
MP2/6-311+G(d,p)	50	1.0927	1.1201	3271.9	2142.3
MP4/6-311+G(d,p)	50	1.0963	1.1273	3226.6	2012.5
CCSD/6-311+G(d,p)	50	1.0950	1.1072	3271.0	2270.6
CCSD(T)/6-311+G(d,p)	50	1.0963	1.1141	3245.8	2202.3
MP2/aug-cc-pVDZ <sup>7b</sup>	55	1.1020	1.1295	3244.2	2098.3
MP2/aug-cc-pVTZ <sup>9</sup>	115	1.0911	1.1192	3236.5	2128.7
MP2/augmented AhlrichsVTZ <sup>10</sup>	138	1.0915	1.1159	3235	2134
MP2/aug-cc-pVQZ	206	1.0906	1.1157	3245.1	2141.6
MP2/aug-cc-pV5Z	334	1.0904	1.1150	3244.2	2142.8
CCSD(T)/cc-pVTZ <sup>4b</sup>	74	1.0936	1.1128	3230	2196
CCSD(T)/cc-pVQZ <sup>4b</sup>	140	1.0935	1.1087	3223	2209
CCSD(T)aug-cc-pVTZ	115	1.0941	1.1127		
CCSD(T)/aug-cc-pVQZ	206	1.0935	1.1089		
CCSD(T)/aug-cc-pV5Z	334	1.0934	1.080		
Exptl. <sup>4c</sup>		1.0929	1.1072		
Exptl. <sup>4a</sup>		1.0972		3089	2184 <sup>4d</sup>

TABLE II

The optimized geometrical parameters for the equilibrium structures for  $\text{OCH}^+\text{-Rg}$  (Rg = He, Ne, and Ar) and their dissociation energies ( $D_e$ ) at the B3LYP, MP2, MP4, CCSD, and CCSD(T) levels of theory. The calculated vibrational frequencies for the C-H<sup>+</sup>, C-O, and Rg-H<sup>+</sup> stretching modes as well as the red shifts of the C-H<sup>+</sup> stretching vibrational frequencies are listed (units are in Å for bond lengths, kcal/mol for dissociation energies, and  $\text{cm}^{-1}$  for vibrational frequencies). The extrapolated complete basis set dissociation energies were estimated based on Eq. (1), E(T-Q) represents the values extrapolated from aug-cc-pVTZ (or BS-T) and aug-cc-pVQZ (or BS-Q) basis sets

OCH <sup>+</sup> -Rg	Method	Size of basis set	Rg-H <sup>+</sup>	H <sup>+</sup> -C	C-O	D <sub>e</sub>	V <sub>ir-c</sub>	V <sub>C-O</sub>	V <sub>Rg-H<sup>+</sup></sub>	ΔV <sub>ir-c</sub>
Rg = He	B3LYP/6-311+G(d,p)	56	1.8532	1.0983	1.1031	1.07	3184.1	2262.3	152.5	42
	MP2/6-311+G(d,p)	56	2.0917	1.0934	1.1201	0.58	3263.3	2142.1	105.6	9
	MP4/6-311+G(d,p)	56	2.0764	1.097	1.1274	0.61	3217.7	2012.7	108.9	9
	CCSD/6-311+G(d,p)	56	2.0863	1.0957	1.1073	0.60	3262.0	2269.2	107.6	9
	CCSD(T)/6-311+G(d,p)	56	2.0773	1.0970	1.1142	0.62	3237.4	2201.1	108.9	8
	MP2/augmented Ahlrichs VTZ <sup>10</sup>	161	1.9440	1.0929	1.1160		3215	2133	139	
	MP2/aug-cc-pVTZ	138	1.9431	1.0921	1.1193	0.87	3219.3	2128.3	139.8	17.2
	MP2/aug-cc-pVQZ	252	1.9601	1.0919	1.1158	0.77	3225.5	2139.8	129.6	19.6
	MP2/aug-cc-pV5Z	414	1.9547	1.0916	1.1148	0.75	3226.1	2143.8	132.1	18.1
	E(T-Q)					0.70				
Rg = Ne	E(Q-5)					0.73				
	QCISD(T)/augmented Ahlrichs VTZ <sup>10</sup>	161	1.9169	1.0964	1.1107					
	QCISD(T)/aug-cc-pVTZ <sup>9</sup>	138	1.9156	1.0958	1.1138					
	CCSD(T)/aug-cc-pVTZ	138	1.9345	1.0850	1.1128	0.95				
	CCSD(T)/aug-cc-pVQZ	252	1.9344	1.0953	1.1090	0.84				
	CCSD(T)/aug-cc-pV5Z <sup>a</sup>	414	/	/	/	0.78				
	E(T-Q)					0.76				
	E(Q-5)					0.72				
	Exptl. <sup>5</sup>		2.00				3076.6			12.4
	B3LYP/6-311+G(d,p)	72	2.0062	1.0997	1.1032	1.30	3166.2	2259.4	99.0	60
MP2/6-311+G(d,p)	72	2.1540	1.0941	1.1201	1.12	3204.9	2011.7	95.6	20	

TABLE II  
(Continued)

OCH <sup>+</sup> -Rg	Method	Size of basis set	Rg-H <sup>+</sup>	H <sup>+</sup> -C	C-O	D <sub>e</sub>	V <sub>H<sup>+</sup>-C</sub>	V <sub>C-O</sub>	V <sub>Rg-H<sup>+</sup></sub>	ΔV <sub>H<sup>+</sup>-C</sub>
	MP4/6-311+G(d,p)	72	2.1341	1.0978	1.1274	1.20	3204.9	2011.7	98.5	22
	CCSD/6-311+G(d,p)	72	2.1590	1.0962	1.1073	1.11	3254.6	2268.3	95.5	16
	CCSD(T)/6-311+G(d,p)	72	2.1417	1.0977	1.1142	1.17	3227.5	2200.1	98.3	18
	MP2/aug-cc-pVTZ	161	1.9798	1.0941	1.1193	1.82	3191.0	2126.9	110.2	46
	MP2/aug-cc-pVQZ	286	1.9714	1.0940	1.1158	1.67	3191.5	2137.6	105.7	54
	Exptl. <sup>7a</sup>		1.98			1.38	3046.1			42.5
	E(T-Q)					1.57				
Rg = Ar	B3LYP/6-311+G(d,p)	80	2.1345	1.1042	1.1179	3.61	2929.4	2191.7	131.9	296
	MP2/6-311+G(d,p)	80	2.2311	1.1045	1.1206	3.28	3083.2	2118.0	141.3	189
	MP4/6-311+G(d,p)	80	2.2101	1.1093	1.1281	3.47	3018.2	1988.8	145.0	208
	CCSD/6-311+G(d,p)	80	2.2504	1.1057	1.1077	3.19	3108.7	2238.7	142.7	162
	CCSD(T)/6-311+G(d,p)	80	2.2221	1.1087	1.1148	3.42	3057.9	2169.0	146.7	188
	MP2/aug-cc-pVDZ <sup>b</sup>	82	2.1871	1.1158	1.1299	4.61	3035.4	2075.2	120.1	255
	MP2/aug-cc-pVTZ	165	2.1230	1.1082	1.1199	5.09	2982.0	2098.2	138.1	255
	MP2/aug-cc-pVQZ	290	2.1223	1.1081	1.1164	4.92	2990.0	2109.4	136.8	255
	MP2/val-1 <sup>b</sup>		2.1306	1.1074	1.1161	4.66				
	E(T-Q)					4.79				
	CCSD(T)/val-2 <sup>b</sup>		2.1333	1.1104	1.1136	4.65				
	CCSD(T)/val-1 <sup>b</sup>		2.1331	1.1105	1.1095	4.70				
	CCSD(T)/val-3 <sup>b</sup>		2.1299	1.1106	1.1088	4.73				
	Exptl.	-	2.134			≈4.4	2815.1 <sup>6</sup>	2135.7 <sup>7d</sup>	131 <sup>7e</sup>	247, 274
	Exptl. <sup>4c</sup>		2.157		1.092					

<sup>a</sup> CCSD(T)/aug-cc-pV5Z. Single-point calculation, based on the CCSD(T)/aug-cc-pVQZ optimized geometry. <sup>b</sup> Refs<sup>7c,8,9</sup>, using 224 cGTOs (aug-cc-pVQZ for argon and cc-pVQZ for HCO<sup>+</sup>), 124 cGTOs (aug-cc-pVTZ for argon and cc-pVTZ for HCO<sup>+</sup>), and 368 cGTOs (aug-cc-pV5Z for argon and cc-pV5Z for HCO<sup>+</sup>), respectively.

TABLE III

The optimized geometrical parameters for the equilibrium structures for  $\text{OCH}^+-\text{Rg}$  (Rg = Kr, Xe) and their dissociation energies ( $D_e$ ) at the B3LYP, MP2, MP4, CCSD, and CCSD(T) levels of theory. The calculated vibrational frequencies for the  $\text{C}-\text{H}^+$ ,  $\text{C}-\text{O}$ , and  $\text{Rg}-\text{H}^+$  stretching modes as well as the red shifts of the  $\text{C}-\text{H}^+$  stretching vibrational frequencies are listed (units are in Å for bond lengths, kcal/mol for dissociation energies, and  $\text{cm}^{-1}$  for vibrational frequencies)

$\text{OCH}^+-\text{Rg}$	Method	Size of basis set	Rg-H <sup>+</sup>	H <sup>+</sup> -C	C-O	$D_e$	$V_{\text{H}^+-\text{C}}$	$V_{\text{C}-\text{O}}$	$V_{\text{Rg}-\text{H}^+}$	$\Delta V_{\text{H}^+-\text{C}}$
Rg = Kr	B3LYP/BS-I	88	2.1745	1.1329	1.1050	6.67	2781.4	2121.0	139.0	444
	MP2/BS-I	88	2.2595	1.1143	1.1210	5.33	2954.7	2096.9	135.4	317
	MP4/BS-I	88	2.2500	1.1192	1.1287	5.48	2888.4	1970.1	136.8	338
	CCSD/BS-I	88	2.2889	1.1143	1.1082	5.00	3002.8	2212.5	135.5	268
	CCSD(T)/BS-I	88	2.2617	1.1182	1.1153	5.34	2941.1	2143.0	136.4	305
	MP2/aug-cc-pVTZ	174	2.1837	1.1184	1.1203	7.66	2848.6	2070.6	142.4	388
	MP2/BS-T	153	2.1898	1.1180	1.1203	7.33	2853.4	2071.3	141.1	383
	MP2/BS-Q	244	2.1362	1.1230	1.1170	8.18	2801.4	2065.9	141.4	444
E(T-Q)					8.79					
Rg = Xe	CCSD(T)/val <sup>a</sup>		2.2323	1.1100	1.1184	6.14	2890	2141	129	
	Exptl. <sup>a</sup>		2.222						129.3	
	B3LYP/BS-I	88	2.3159	1.1498	1.106	8.84	2648.5	2004.8	139.0	577
	MP2/BS-I	88	2.4226	1.1231	1.1215	6.92	2837.3	2066.1	132.2	435
	MP4/PS-I	88	2.4075	1.1296	1.1295	7.21	2748.5	1937.5	133.9	478
	CCSD/BS-I	88	2.4587	1.1223	1.1087	6.57	2903.8	2176.6	131.2	367
	CCSD(T)/BS-I	88	2.4252	1.1276	1.1158	6.99	2825.3	2102.8	134.5	421
	MP2/BS-T	153	2.3065	1.1337	1.1210	9.89	2677.0	2014.2	151.3	560
	MP2/BS-Q	244	2.2606	1.1386	1.1176	11.25	2629.5	1993.6	153.9	616
	E(T-Q)					12.25				
MP2/pp <sup>b</sup>		2.3393	1.1279	1.1171	8.49	2723	2037	161		
CCSD(T)/pp <sup>b</sup>		2.3437	1.1314	1.1106	8.67	2745	2081	160		

<sup>a</sup> Ref.<sup>30</sup>, using 233 cGTOs (aug-cc-pVTZ for krypton and cc-pVTZ for  $\text{HCO}^+$ ). <sup>b</sup> Refs.<sup>12,31</sup>, using 233 cGTOs (cc-pVTZ for  $\text{HCO}^+$  and a scalar-relativistic energy-consistent pseudopotential for xenon from ref.<sup>24</sup>).



### $\text{OCH}^+$ Ion

For the  $\text{OCH}^+$  free ion, all applied methods yield very similar geometrical parameters. The  $\text{H}^+\text{-C}$  distances calculated at the DFT, MP2, MP4, and CCSD levels (using the 6-311+G(d,p) basis set) are 1.0955, 1.0927, 1.0963, and 1.0950 Å, respectively, in good agreement with the CCSD(T) result. Due to the larger PA value of CO than that of the  $\text{N}_2$  molecule, the  $\text{H}^+\text{-C}$  distance is slightly longer than the  $\text{N-H}^+$  distance in the  $\text{N}_2\text{H}^+$  cation (1.038 Å). By comparing with the experimental values, one can conclude that the calculated  $\text{H}^+\text{-C}$  distances at all levels agree very well with the experimental data. The C-O distances calculated at the MP2 and MP4 levels are slightly longer than the CCSD(T) result, while the DFT and CCSD values are slightly shorter.

The vibrational  $\nu_{\text{H}^+\text{-C}}$  frequency calculated at the DFT/6-311+G(d,p) and MP4/6-311+G(d,p) levels are smaller than the  $\nu_{\text{H}^+\text{-C}}$  value obtained from the CCSD(T) calculations by about 0.6%, while MP2/6-311+G(d,p) and CCSD yield a larger by about 0.8% value of  $\nu_{\text{H}^+\text{-C}}$ . The predicted  $\nu_{\text{H}^+\text{-C}}$  values at all levels are in good agreement (with a deviation less than 6%) with the experimental data<sup>4</sup>.

The basis set effect on the predicted properties of the  $\text{OCH}^+$  ion have been studied previously by several groups<sup>4,7,9</sup>. In this work, larger basis sets (aug-cc-pVQZ and aug-cc-pV5Z) were applied at the MP2 level. The calculated results are summarized in Table I. One can see that the differences between the calculated  $\text{H}^+\text{-C}$  and C-O distances using the 6-311+G(d,p) and aug-cc-pVQZ basis sets are only about 0.0021 and 0.0044 Å, respectively. The analogous differences for the  $\nu_{\text{H}^+\text{-C}}$  and  $\nu_{\text{C-O}}$  vibrations are about 27 and 0.7  $\text{cm}^{-1}$ , respectively.

The C-H<sup>+</sup> distance is about to converge at 1.0904 Å as the basis set increases to aug-cc-pV5Z. The difference between the predicted  $\text{H}^+\text{-C}$  values at the MP2/aug-cc-pVQZ and MP2/aug-cc-pV5Z levels is only 0.0002 Å. In addition, the deviations of the  $\text{H}^+\text{-C}$  distances using the aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets are less than 0.6% with respect to the experiments<sup>4</sup>.

Both the MP2/aug-cc-pVTZ and the MP2/aug-cc-pVQZ level  $\nu_{\text{H}^+\text{-C}}$  values are by less than 5% different from the experiment, and expansion of the basis functions to the aug-cc-pV5Z basis set yields essentially the same result. Therefore, we conclude that the further expansion of the basis set is not crucial in the case of  $\text{OCH}^+$ , and the aug-cc-pVTZ basis set is sufficient to obtain a quantitative description of its geometrical parameters and vibrational frequencies.

$OCH^+-He$ 

In the  $OCH^+-He$  complex, the helium atom shares a proton with CO, hence weakens the  $H^+-C$  bond strength. Consequently, the  $H^+-C$  bond length becomes slightly longer (Table II). For instance, the MP2/6-311+G(d,p)-level-calculated  $H^+-C$  distance in the free  $OCH^+$  ion is about 1.0927 Å, while it elongates to 1.0983 Å in the  $OCH^+-He$  complex. The C–O distance is virtually the same as that in free  $OCH^+$  ion.

The DFT/6-311+G(d,p)-optimized He– $H^+$  distance is 1.8532 Å, by 0.224 Å ( $\approx 11\%$ ) shorter than the CCSD(T) result. The MP2, MP4, and CCSD methods yield similar values to the CCSD(T) method.

We noticed that there is still a 4% deviation of the CCSD(T)/6-311+G(d,p) calculated He– $H^+$  distance from the experimental data. One can attribute this to the insufficient basis set. By using larger basis sets, such as the aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z basis sets, the deviation of the He– $H^+$  distance with respect to experiment reduces to 2%.

The decreased bond strength of the  $H^+-C$  bond causes the shift of the  $H^+-C$  stretching mode to a lower vibrational frequency. Experiments reported a red shift of  $12.4\text{ cm}^{-1}$  for the  $\nu_{H^+-C}$  in the  $OCH^+-He$  complex with respect to the free  $OCH^+$  <sup>5</sup>. The B3LYP/6-311+G(d,p)-level calculation predicts a red shift of  $42\text{ cm}^{-1}$ , 240% larger than the experiment. This means that the DFT method cannot describe sufficiently the fairly weak interaction between He and  $OCH^+$ . The DFT/6-311+G(d,p) level overestimates the interaction between the helium atom and  $H^+$ , therefore, a larger red shift of  $\nu_{H^+-C}$  is obtained compared to the CCSD(T) result and the experimental data. With the same basis set, the MP2-, MP4-, and CCSD(T)-calculated  $\nu_{H^+-C}$  values range from  $3217$  to  $3263\text{ cm}^{-1}$  which amounts to about  $140\text{--}180\text{ cm}^{-1}$  deviations from the experiment. This difference may be reduced if the anharmonicity contributions are considered. The corresponding red shifts are predicted to be approximately  $9\text{ cm}^{-1}$ , much closer to the experimental data.

At the MP2 level,  $\nu_{H^+-C}$  values calculated with larger basis sets (aug-cc-pVTZ and aug-cc-pVQZ) are about  $3220\text{ cm}^{-1}$ , which amount to 4% deviation from the experiment. The red shifts  $\Delta\nu_{H^+-C}$  are  $17.2$  and  $19.6\text{ cm}^{-1}$ , respectively, slightly larger than the experimental value.

The dissociation energy  $D_e$  is also dependent upon the level of electron correlation and the basis set. The DFT-predicted  $D_e$  value is about 55% larger than the experiment, while MP2, MP4, CCSD, and CCSD(T) calculated  $D_e$  values are smaller than the experimental result by about 16, 12, 13, and 10%, respectively. However, the dissociation energy amounts to 0.87

and 0.77 kcal/mol when the aug-cc-pVXZ ( $X = \text{T, Q}$ ) basis sets were used. MP2/aug-cc-pV5Z method yields essentially the same dissociation energy as MP2/aug-cc-pVQZ. For comparison, the results of the CCSD(T)/aug-cc-pVXZ ( $X = \text{T, Q}$ ) level calculations performed on the  $\text{OCH}^+$  and  $\text{OCH}^+\text{-He}$  species are reported in Tables I and II. Due to the limitation of computational facilities, only CCSD(T)/aug-cc-pV5Z single-point calculations were carried out for  $\text{OCH}^+$  and  $\text{OCH}^+\text{-He}$  species, and the predicted dissociation energy is also listed in Table II. From Table II one can find that both MP2 and CCSD(T) methods yielded similar optimized geometrical parameters, moreover, the dissociation energies obtained at the MP2/aug-cc-pVXZ ( $X = \text{T, Q, 5}$ ) levels are close to the CCSD(T)/aug-cc-pV5Z results. Therefore one can conclude that the basis set quality does not significantly improve the predicted  $\nu_{\text{H}^+\text{-C}}$  and  $D_e$  values, and MP2/aug-cc-pVQZ can produce the reliable quantitative results.

### $\text{OCH}^+\text{-Ne}$

Similarly to the  $\text{OCH}^+\text{-He}$  complex, the DFT- and MP2-level predicted Ne- $\text{H}^+$  bond length is shorter than the CCSD(T) result, while the MP4 and CCSD methods predicted the longer Ne- $\text{H}^+$  distance. Interestingly, the DFT/6-311+G(d,p)-level-calculated Ne- $\text{H}^+$  distance is close to the reported experimental data ( $\approx 1\%$  error), while all the other methods predict the Ne- $\text{H}^+$  distances which are 6–9% longer than the experiments. This might be due to the fortuitous cancellation of the errors in the DFT calculations.

By using the 6-311+G(d,p) basis set, the dissociation energy obtained at the different levels are around 1.2 kcal/mol, and taking into account the entropies, the  $D_0$  values will be much smaller than the experimental data. The basis set effect was investigated at the MP2 level, the MP2/aug-cc-pVQZ-predicted  $D_e$  amounts to 1.67 kcal/mol, much closer to the experimental data.

Compared to the experiment, the differences in  $\nu_{\text{H}^+\text{-C}}$  values obtained in calculations at different levels using the 6-311+G(d,p) basis set amounts to 7%, while the differences decrease to 5% when the aug-cc-pVXZ ( $X = \text{D, T, Q}$ ) basis sets are used. The basis set effect is significant for the red shift of the  $\text{H}^+\text{-C}$  stretch. The  $\Delta\nu_{\text{H}^+\text{-C}}$  value calculated at the MP2/6-311+G(d,p) level is only  $20\text{ cm}^{-1}$ , about 53% smaller than the experimental data. The improved  $\Delta\nu_{\text{H}^+\text{-C}}$  values are obtained by using the aug-cc-pVXZ ( $X = \text{T, Q}$ ) basis sets, the predicted  $\Delta\nu_{\text{H}^+\text{-C}}$  values are 46 and  $54\text{ cm}^{-1}$ , respectively, which agrees well with the experimental data ( $42.5\text{ cm}^{-1}$ ).

Similarly to the  $\text{OCH}^+\text{-He}$  complex, the difference between the predicted geometrical parameters and the experimental data is also reduced when a larger basis set is used. For instance, the deviations of the  $\text{Ne-H}^+$  distance from the experiment obtained at different levels using the 6-311+G(d,p) basis set are approximately 10%, and they decrease to around 0.4% when the aug-cc-pVXZ ( $X = \text{D, Q}$ ) basis sets are used.

### $\text{OCH}^+\text{-Ar}$

For the  $\text{OCH}^+\text{-Ar}$  complex, the  $\text{Ar-H}^+$  and  $\text{H}^+\text{-C}$  distances predicted at the DFT/6-311+G(d,p) level are smaller than the CCSD(T) values by about 0.088 Å, but close to the experimental data. The MP2 and CCSD methods predicted a longer  $\text{Ar-H}^+$  distance than the CCSD(T) value while it is slightly shorter with the MP4 method.

Combined experimental and theoretical studies show that the value of  $\Delta\nu_{\text{H}^+\text{-C}}$  in  $\text{OCH}^+\text{-Ar}$  falls in the range of 247–274  $\text{cm}^{-1}$ . The DFT-predicted  $\Delta\nu_{\text{H}^+\text{-C}}$  value amounts to 296  $\text{cm}^{-1}$ , semiquantitatively reflecting the red shift effect of the  $\text{C-H}^+$  stretching mode when an argon atom is attached to the proton of the  $\text{OCH}^+$  ion. The MP2, MP4, CCSD, and CCSD(T) levels predicted lower  $\Delta\nu_{\text{H}^+\text{-C}}$  values (189, 208, 162, and 188  $\text{cm}^{-1}$ ) which are significantly smaller than the experimentally obtained result.

The DFT method yielded a better description of the  $\text{Ar-H}^+$  distance and red shift of  $\nu_{\text{H}^+\text{-C}}$ ; however, we believe that this is due to the fortuitous cancellation of the errors. From Table II, it is found that it is necessary to use a larger basis set to obtain a quantitative result for the geometrical parameters and vibrational properties. The MP2/aug-cc-pVTZ and MP2/aug-cc-pVQZ calculations predicted the  $\Delta\nu_{\text{H}^+\text{-C}}$  values of around 255  $\text{cm}^{-1}$ .

Similarly to the cases of the  $\text{OCH}^+\text{-He}$  and  $\text{OCH}^+\text{-Ne}$  complexes, the dissociation energy of  $\text{OCH}^+\text{-Ar}$  is sensitive to the basis set used. One can see (Table II) that the  $D_e$  value increases from 3.28 to 4.92 kcal/mol when the basis set changes from 6-311+G(d,p) to aug-cc-pVQZ at the MP2 level, with the latter being much closer to the experiment.

The size of the basis sets only slightly affects the calculated  $\nu_{\text{H}^+\text{-C}}$  value, as it was also observed for the lighter complexes. At the MP2/6-311+G(d,p) level,  $\nu_{\text{H}^+\text{-N}}$  is about 9.5% smaller than the experimental data; the MP2/aug-cc-pVQZ approach slightly improves the predicted  $\nu_{\text{H}^+\text{-N}}$  value, and it becomes about 6.2% larger than the experimental data<sup>4,6,7</sup>. Our calculated results at the MP2/aug-cc-pVXZ ( $X = \text{T, Q}$ ) levels are in good agreement with the CCSD(T) results by Botschwina *et al.*<sup>7c</sup> using the modified cc-pVTZ and cc-pVQZ basis sets. However, MP2/aug-cc-pVDZ method pre-

dicted a slightly longer  $\text{Ar-H}^+$  distance<sup>7b</sup>, indicating that the double-zeta basis set might not be sufficient to obtain the quantitative description for this system.

In order to further estimate the basis set extension effects, calculations for  $\text{OCH}^+\text{-Rg}$  ( $\text{Rg} = \text{He, Ne, Ar}$ ) dimers were performed using two systematically extended correlation-consistent basis sets. The dissociation energies were then extrapolated to the complete basis set limit. The results of this extrapolation reported in Tables II and III indicate that at the MP2 level of theory the application of the aug-cc-pVTZ or aug-cc-pVQZ basis sets secures a quantitatively correct description of the dissociation energies of those dimers, the dissociation energies obtained at the aug-cc-pVTZ and aug-cc-pVQZ levels are very close to the CBS limits. In addition, the extrapolated dissociation energy of  $\text{OCH}^+\text{-He}$  based on the MP2/aug-cc-pVXZ ( $X = \text{T, Q, 5}$ ) calculations agrees very well with the CCSD(T)/aug-cc-pVXZ ( $X = \text{T, Q, 5}$ ) extrapolated value. Therefore, a further extension of basis set will be of less significance.

#### *$\text{OCH}^+\text{-Kr}$ and $\text{OCH}^+\text{-Xe}$*

The investigated basis set and electron correlation effects on the predicted equilibrium geometries, harmonic vibrational frequencies, and the dissociation energies of the  $\text{OCH}^+\text{-Rg}$  ( $\text{Rg} = \text{He, Ne, and Ar}$ ) complexes allow one to conclude that the MP2 level in combination with aug-cc-pVTZ basis set yields good quantitative results.

So far, only one complex involving the heavier krypton atom,  $\text{OCH}^+\text{-Kr}$ , has been studied by high-resolution spectroscopy<sup>30</sup>, and no experimental data is available for the  $\text{OCH}^+\text{-Xe}$  species. Therefore, the reliable theoretical study could be an alternative way to provide information for these complexes. In addition, there is a lack of systematical investigation of basis set and electronic correction effects on the structures, vibrational frequencies, and the dissociation energies of complexes of the two heaviest rare gas elements. Even though the MP2/aug-cc-pVTZ level provides the quantitative results for their lighter analogues, it might not be suitable for  $\text{OCH}^+\text{-Kr}$  and  $\text{OCH}^+\text{-Xe}$ . In order to find a desirable method to study these heavier-atom-containing systems, a detailed investigation is necessary. Therefore, in the following section, we will discuss the basis set and electron correlation effects on the equilibrium geometries, harmonic vibrational frequencies, and the dissociation energies of the  $\text{OCH}^+\text{-Kr}$  and  $\text{OCH}^+\text{-Xe}$  complexes obtained using the B3LYP density-functional, and MP2, MP4, CCSD, and CCSD(T) methods. In order to study the relativistic effect, the sca-

lar-relativistic energy-consistent pseudopotentials (see Computational) were also applied.

*OCH<sup>+</sup>-Kr*: For OCH<sup>+</sup>-Kr, the BS-I basis set was used to study the differences among the different theoretical levels. The relativistic effects were considered using the quasirelativistic effective core basis set of the Stuttgart group with eight valence-electron pseudopotential. The calculated geometrical parameters, thermodynamic and vibrational properties of the OCH<sup>+</sup>-Kr dimer are shown in Table III.

Similarly to the complexes described above, the DFT method predicts the Kr-H<sup>+</sup> distance of 2.1745 Å, by 0.09 Å shorter than the CCSD(T)-calculated value. This difference is smaller than in the OCH<sup>+</sup>-He and OCH<sup>+</sup>-Ne complexes and close to that in the OCH<sup>+</sup>-Ar complex. Both DFT and Møller-Plesset (MP2, MP4) methods yield a shorter Kr-H<sup>+</sup> distance compared to the CCSD(T) result, while the CCSD method predicts a Kr-H<sup>+</sup> distance which is approximately 0.03 Å longer than the CCSD(T) value. Correspondingly, the DFT-, MP2-, and MP4-level predicted H<sup>+</sup>-C and C-O distances are slightly longer than the CCSD(T) value, while CCSD yields shorter distances.

It has been reported in our previous work<sup>14</sup> that the relativistic effects are insignificant for the N<sub>2</sub>H<sup>+</sup>-Kr complex, only the basis set effect significantly affects the geometrical parameters, thermodynamics, and vibrational properties of N<sub>2</sub>H<sup>+</sup>-Kr. The relativistic effects have the similar impact on OCH<sup>+</sup>-Kr. This can be confirmed by comparing the MP2/BS-T- and MP2/aug-cc-pVTZ-level results. Both MP2/BS-T and MP2/aug-cc-pVTZ methods predicted almost the same Kr-H<sup>+</sup> distance, dissociation energy,  $\nu_{\text{Rg-H}^+}$ , and  $\Delta\nu_{\text{Rg-H}^+}$  values.

From Table III, one can conclude that the basis set effect is crucial for obtaining accurate results. The MP2/aug-cc-pVTZ-level-calculated Kr-H<sup>+</sup> distance amounts to 2.1837 Å, by 0.076 Å smaller than the MP2/BS-I value. The MP2/BS-T approach predicted a similar value of 2.1898 Å. At the MP2/BS-Q level, the predicted Kr-H<sup>+</sup> distance amounts to 2.1362 Å, 0.053 Å shorter than the MP2/BS-T value, indicating a notable basis set dependence.

The MP2/aug-cc-pVTZ level  $\nu_{\text{H}^+-\text{C}}$  value is about 2848 cm<sup>-1</sup>, 4% smaller than the MP2/BS-I result (2955 cm<sup>-1</sup>). The MP2/aug-cc-pVTZ- and MP2/BS-T-calculated  $\nu_{\text{H}^+-\text{N}}$  values are 2849 and 2853 cm<sup>-1</sup>, respectively, with only 4 cm<sup>-1</sup> negligible difference. This further confirms insignificance of relativistic effects on the vibrational properties of the OCH<sup>+</sup>-Kr dimer.

The dissociation energy is sensitive to the quality of basis set. The MP2/aug-cc-pVTZ- and MP2/BS-T-level-calculated  $D_e$  are about 7.66 and

7.33 kcal/mol, about 2 kcal/mol higher than the MP2/BS-I result. The MP2/BS-Q level predicted an even larger  $D_e$  value of 8.18 kcal/mol. A larger value of  $D_e$  obtained using the BS-Q basis set was also observed in the case of  $\text{N}_2\text{H}^+\text{-Kr}$  dimer<sup>14</sup>. Therefore, the quality of basis set is crucial to obtain an accurate prediction of the dissociation energy for the Kr-containing complex.

$\text{OCH}^+\text{-Xe}$ : The DFT/BS-I-calculated  $\text{Xe-H}^+$  distance is 2.3159 Å, 0.109 Å shorter than the CCSD(T) result, while the corresponding differences are 0.224, 0.136, 0.088, and 0.087 Å in the  $\text{OCH}^+\text{-He}$ ,  $\text{OCH}^+\text{-Ne}$ ,  $\text{OCH}^+\text{-Ar}$ , and  $\text{OCH}^+\text{-Kr}$  complexes, respectively. This means that the accuracy of the DFT method on predicting the geometrical parameters for the  $\text{OCH}^+\text{-Xe}$  dimer is similar to the case of the  $\text{OCH}^+\text{-Kr}$  and  $\text{OCH}^+\text{-Ar}$  dimers. Therefore DFT may be applied for qualitative or semiquantitative predictions.

The MP2- and MP4-level- $\text{Xe-H}^+$  distances are 0.003 and 0.018 Å shorter than the CCSD(T) result. The CCSD method yields a  $\text{Xe-H}^+$  distance which is by 0.034 Å longer. Again, the basis set plays a very important role in obtaining accurate results. Within the MP2 scheme, the predicted  $\text{Xe-H}^+$  distance is 2.4226 Å using the BS-I basis set, and the value decreases to 2.3065 Å using the BS-T basis set, and 2.2606 Å at the MP2/BS-Q level. The MP2/BS-T- and MP2/BS-Q-level  $D_e$  values are 9.89 and 11.25 kcal/mol, respectively, much larger than the MP2/BS-I result.

It was reported in our previous study<sup>14</sup> that the basis set effect had minor impact on the vibrational frequencies of the  $\text{N}_2\text{H}^+\text{-Xe}$  complex. However, the value of vibrational frequencies for the  $\text{OCH}^+\text{-Xe}$  dimer is sensitive to the basis set quality. For instance, the MP2/BS-T- and MP2/BS-Q-level predicted  $\nu_{\text{H}^+\text{-C}}$  values are 2677 and 2629  $\text{cm}^{-1}$ , about 210 and 208  $\text{cm}^{-1}$  smaller than the MP2/BS-I-level frequency. The predicted  $\Delta\nu_{\text{H}^+\text{-C}}$  red shifts at the MP2/BS-T and MP2/BS-Q levels are 560 and 616  $\text{cm}^{-1}$ , much larger than MP2/BS-I predicted value (435  $\text{cm}^{-1}$ ). Therefore the quality of basis set is very crucial to obtain an accurate description of the vibrational frequencies for the  $\text{OCH}^+\text{-Xe}$  complex.

The  $\text{OCH}^+\text{-Kr}$  and  $\text{OCH}^+\text{-Xe}$  dimers were also studied by Botschwina *et al.* at the CCSD(T) level using cc-pVQZ basis set<sup>12,31</sup>. Their predicted  $\text{Kr-H}^+$  and  $\text{Xe-H}^+$  distances are 2.2323 and 2.3437 Å, respectively, slightly longer than the MP2/BS-Q level values. As one can see from Table III that the MP2 method tends to predict slightly larger values of the  $\nu_{\text{H}^+\text{-C}}$ ,  $\nu_{\text{C-O}}$  harmonic vibrational frequencies and shorter  $\text{Rg-H}^+$  distances than the CCSD(T) method. The differences between MP2 and CCSD(T) calculated  $\text{Rg-H}^+$  distances are so small (0.002 and 0.003 Å for the  $\text{OCH}^+\text{-Kr}$  and  $\text{OCH}^+\text{-Xe}$  dimers, respectively) that we do not expect noticeable changes in the geo-

metrical parameters and the vibrational properties at the CCSD(T)/BS-Q level. However, similar to the  $N_2H^+-Kr$  and  $N_2H^+-Xe$  complexes, the dissociation energies are sensitive to the quality of the basis set<sup>14</sup>.

### Energy Decomposition Analysis

The nature of interactions in  $OCH^+-Rg$  ( $Rg = He, Ne, Ar, Kr, \text{ and } Xe$ ) dimers were analyzed using interaction energy decomposition (Table IV). The basis set effect on the components of interaction energy is also discussed in this paragraph.

One can conclude from the interaction energy partition that the  $OCH^+-Rg$  ( $Rg = He, Ne, Ar, Kr, \text{ and } Xe$ ) dimers are formed mainly due to the

TABLE IV

The interaction energy decomposition in  $OCH^+-Rg$  ( $Rg = He, Ne, Ar, Kr, \text{ and } Xe$ ) complexes (all values are given in kcal/mol)

$OCH^+-Rg$	Method	$\Delta E^{HL}$	$\epsilon_{el}^{(10)}$	$\epsilon_{ex}^{HL}$	$\Delta E_{del}^{HF}$	$\Delta E_{SCF}$	$\epsilon_{MP}^{(2)}$	$\Delta E_{MP2}$
$OCH^+-He$	MP2/6-311+G(d,p)	0.278	-0.154	0.432	-0.653	-0.375	-0.089	-0.464
	MP2/aug-cc-pVTZ	0.756	-0.092	0.848	-1.203	-0.447	-0.247	-0.694
	MP2/aug-cc-pVQZ	0.611	-0.082	0.693	-1.257	-0.564	-0.290	-0.854
$OCH^+-Ne$	MP2/6-311+G(d,p)	0.456	-0.338	0.794	-0.849	-0.392	-0.155	-0.548
	MP2/aug-cc-pVTZ	1.547	-0.205	1.752	-2.198	-0.651	-0.665	-1.316
	MP2/aug-cc-pVQZ	1.260	-0.281	1.541	-2.254	-0.715	-0.705	-1.420
$OCH^+-Ar$	MP2/6-311+G(d,p)	4.002	-0.348	4.350	-5.337	-1.335	-0.804	-2.139
	MP2/aug-cc-pVTZ	5.912	-0.594	6.509	-8.667	-2.752	-1.825	-4.576
	MP2/aug-cc-pVQZ	5.324	-0.601	5.925	-8.701	-2.776	-1.918	-4.694
$OCH^+-Kr$	MP2/BS-I <sup>a</sup>	6.363	-0.400	6.762	-10.274	-3.513	-1.413	-4.926
	MP2/BS-I <sup>b</sup>	6.380	-0.397	6.777	-10.322	-3.546	-1.419	-4.964
	MP2/BS-T <sup>a</sup>	8.556	-0.524	9.080	-12.309	-3.754	-2.549	-6.303
	MP2/aug-cc-pVTZ	8.852	-0.663	9.515	-12.511	-3.659	-2.474	-6.133
	MP2/BS-Q <sup>a</sup>	9.667	-0.601	10.268	-13.755	-3.487	-3.112	-6.599
$OCH^+-Xe$	MP2/BS-I <sup>a</sup>	7.351	-0.589	7.940	-13.203	-5.262	-1.567	-6.829
	MP2/BS-I <sup>b</sup>	8.296	-0.619	8.915	-14.140	-5.225	-1.697	-6.922
	MP2/BS-T <sup>a</sup>	11.475	-0.384	11.859	-16.998	-5.140	-3.351	-8.491
	MP2/BS-Q <sup>a</sup>	13.553	-0.281	13.834	-18.590	-4.756	-4.032	-8.788

<sup>a</sup> Using SBKJC ECP. <sup>b</sup> Based on geometries optimized using SBKJC ECP.



induction interactions arising from the delocalization energy ( $\Delta E_{\text{del}}^{\text{HF}}$ ) and the correlation component ( $\epsilon_{\text{MP}}^{(2)}$ ). The HF electrostatic contributions are calculated to be quite small. The exchange repulsion ( $\epsilon_{\text{ex}}^{\text{HL}}$ ) causes the instability of the dimers, and this repulsion is cancelled by large delocalization energy ( $\Delta E_{\text{del}}^{\text{HF}}$ ) which, together with the correlation energy ( $\epsilon_{\text{MP}}^{(2)}$ ), stabilizes the whole system.

The energy decomposition components vary with the magnitudes of PA values for the rare gas atoms. Their contributions to the total interaction energy increase with the increasing PA values. Except the minor change of the electrostatic repulsion ( $\epsilon_{\text{el}}^{(10)}$ ), all the other terms increase significantly. For instance, the MP2/6-311+G(d,p)-level contributions from exchange repulsion ( $\epsilon_{\text{ex}}^{\text{HL}}$ ) and the delocalization energy ( $\Delta E_{\text{del}}^{\text{HF}}$ ) increase from 0.432 to 7.94, and from -0.653 to -13.203 kcal/mol, respectively, when Rg atom changes from He to Xe. The electron correlation contribution ( $\epsilon_{\text{MP}}^{(2)}$ ) has a lower increase, and increases from -0.089 to -1.567 kcal/mol.

The basis set effect is crucial to obtain the accurate description of the interaction energy partitions. The size of basis set has less impact on electrostatic repulsion ( $\epsilon_{\text{el}}^{(10)}$ ); however, the exchange repulsion ( $\epsilon_{\text{ex}}^{\text{HL}}$ ) and the delocalization energy ( $\Delta E_{\text{del}}^{\text{HF}}$ ) increase significantly when the aug-cc-pVTZ basis set is used. The MP2/6-311+G(d,p)-calculated  $\epsilon_{\text{ex}}^{\text{HL}}$ ,  $\Delta E_{\text{del}}^{\text{HF}}$ , and  $\epsilon_{\text{MP}}^{(2)}$  values for the  $\text{OCH}^+\text{-He}$  dimer are 0.432, -0.653, and -0.089 kcal/mol, respectively, much smaller than those obtained from MP2/aug-cc-pVTZ calculations (0.848, -1.203, and -0.247 kcal/mol). In addition, the MP2/6-311+G(d,p)-level HF component of  $\text{OCH}^+\text{-He}$  constitutes more than 80% of the total interaction energy, while it contributes only 66% of the total interaction energy when aug-cc-pVQZ basis set is applied. Therefore, for the weakly interacting dimers such as  $\text{OCH}^+\text{-He}$ ,  $\text{OCH}^+\text{-Ne}$ , and  $\text{OCH}^+\text{-Ar}$ , a large basis set is necessary for the quantitative descriptions.

In the heavier (Kr, Xe) rare gas atom containing complexes, the  $\Delta E_{\text{SCF}}$  values for the different basis sets are almost constant, even though the calculated HF components change. The main difference in the interaction energies is attributed to the MP2 contribution ( $\epsilon_{\text{MP}}^{(2)}$ ). Due to the large amount of contribution of HF energy, the MP2/BS-I-predicted interaction energies amount to 75 and 78% of the MP2/BS-Q-predicted interaction energies of  $\text{OCH}^+\text{-Kr}$  and  $\text{OCH}^+\text{-Xe}$  dimers. Therefore, the BS-I basis set might be applied to obtain the qualitative and semiquantitative predictions of the Kr- and Xe-containing complexes.

## CONCLUSIONS

This study provides comprehensive investigation on the basis set and electron correlation dependence on the geometrical parameters, vibrational frequencies and dissociation energies for  $\text{OCH}^+\text{-Rg}$  ( $\text{Rg} = \text{He, Ne, Ar, Kr, and Xe}$ ). From the results of our study, we can draw the following conclusions:

1. In the rare gas complexes  $\text{OCH}^+\text{-Rg}$  ( $\text{Rg} = \text{He, Ne, Ar}$ ), the DFT and MP4 methods tend to produce longer  $\text{Rg-H}^+$  distance than the CCSD(T)-level value, and the CCSD-calculated  $\text{Rg-H}^+$  bond lengths are slightly shorter. For heavier-atom-containing complexes,  $\text{OCH}^+\text{-Rg}$  ( $\text{Rg} = \text{Kr, Xe}$ ), only the CCSD approach predicted longer  $\text{Rg-H}^+$  distance than that obtained at the CCSD(T) level.

2. For the  $\text{OCH}^+$  cation, DFT-, MP2-, MP4-, CCD-, CCSD-, and CCSD(T)-level calculations yield the reliable results in good agreement with experiments. The aug-cc-pVTZ basis set is sufficient to obtain a quantitative description of the  $\text{OCH}^+$  ion geometrical structure. Due to the larger PA value of CO, the predicted  $\text{C-H}^+$  distance is longer than the  $\text{N-H}^+$  in the  $\text{N}_2\text{H}^+$  ion. The predicted results are not altered significantly by the quality of basis set.

3. Due to the lack of appropriate description of the dispersion contributions, the DFT method is not reliable to study the weak interaction in the  $\text{OCH}^+\text{-He}$  and  $\text{OCH}^+\text{-Ne}$  complexes. The accuracy of predicted geometrical parameters, dissociation energies, and red shift of the  $\text{H}^+\text{-C}$  stretching mode ( $\Delta\nu_{\text{H}^+\text{-C}}$ ) are highly dependent upon the level of electronic correlation and the size of basis set. The  $\nu_{\text{H}^+\text{-C}}$  value is less sensitive to the level of electronic correlation and basis set.

4. A qualitative result can be obtained for  $\text{OCH}^+\text{-Ar}$  complexes by using the DFT method. However, the MP2 method in conjunction with the aug-cc-pVTZ basis set is necessary to provide quantitative results in good agreement with the experiments.

5. The effects of basis set and electron correlation on the equilibrium geometries, harmonic vibrational frequencies, and the dissociation energies of the  $\text{OCH}^+\text{-Kr}$  and  $\text{OCH}^+\text{-Xe}$  complexes were systematically investigated. It is noticed that the relativistic effects have minor effect on the geometrical parameters, the  $\text{H}^+\text{-C}$  stretching mode, and the dissociation energy; however, these properties are sensitive to the basis set effect. The calculations using the BS-Q basis set within the MP2 scheme provide reasonable results and might be extended to study the other complexes containing heavier rare gas atoms.

6. The nature of interaction between the  $\text{OCH}^+$  ion and rare gas atoms were analyzed in terms of the interaction energy decomposition. The com-

ponents of the total interaction energy are sensitive to the basis set effect. A large basis set, such as aug-cc-pVTZ basis set, is necessary for the quantitative descriptions of the interaction energy components for lighter rare gas atoms-containing complexes, while the BS-I basis set provided the qualitative and semiquantitative predictions of the Kr- and Xe-containing complexes.

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