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A Comprehensive Computational Study of N_2H^+-X (X = He, Ne, Ar, Kr, Xe, and H_2) Complexes

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The equilibrium geometries, harmonic vibrational frenquencies, and the dissociation energies of the N_2H^+-X (X = He, Ne, Ar, Kr, Xe, and H_2) complexes were calculated at the DFT, MP2, MP4, CCD, CCSD, and CCSD(T) levels of theory. In all of the rare gas complexes, the DFT, MP2, and MP4 methods tend to produce longer $X-H^+$ (X = He, Ne, Ar, Kr, Xe, and H_2) distances than the CCSD(T)-level-predicted value, while the CCD- and CCSD-level $X-H^+$ bond lengths are slightly shorter. For the free N_2H^+ ion, all level calculations yield reliable results and are congruous with experiments. The predictions of geometrical parameters, dissociation energies, and the red shift of the H^+-N stretching mode ($\Delta\omega_{H^+-N}$) in N_2H^+-He and N_2H^+-Ne complexes are highly dependent upon the level of electron correlation and the size of the basis set. The DFT method is not reliable for studies of fairly weak interactions between He, Ne and N_2H^+, however, may be used to obtained the qualitatively correct results for N_2H^+-Ar and $N_2H^+-H_2$. For complexes involving heavier atoms, N_2H^+-X (X = Kr and Xe), the relativistic effects have a minor effect on the geometrical parameters and the H^+-N stretching mode. However, the dissociation energy is highly dependent upon the relativistic effects. Moreover, the dissociation energies and the geometrical parameters are sensitive to the size of the basis set.

I. Introduction

Proton bound complexes are the intermediates of proton-transfer reactions which are important in a broad range of chemical and biological environments. 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 $OCH^+-(Ar)_n$, $OSiH^+-(Ar)_n$, and $N_2H^+-(Ar)_n$.[1−6,8−12] The experimental infrared predissociation spectra give detailed information concerning the interaction between the contributing moieties and should eventually provide details of the potential energy surfaces for interactions of ion−neutral species at close range.[2]

Complexes consisting of He,[3] Ne,[4] Ar,[5] and H_2[6] ligands attached to the linear closed-shell N_2H^+ ion have been extensively examined using the IR spectroscopy and different theoretical techniques. The N_2H^+-Rg dimers containing rare gas atoms (Rg) are determined to be linear with the proton being shared between Rg and N_2. However, the $N_2H^+-H_2$ complex is T-shaped with the shared proton attached to the midpoint of the H−H bond.

The degree to which the properties of the N_2H^+ core are altered by the attached ligand and the strength of the intermolecular interaction depend significantly upon the difference between the proton affinities (PAs) of N_2 and the participating ligand, ΔPA.[7] Different ligands lead to changes in the H^+-N and N−N bond distances and consequently a shift to a lower vibrational frequency for ν_1 (the $N-H^+$ stretch) of the N_2H^+ fragment. This results in the observed red shift for the N_2H^+-X complexes as compared to the N_2H^+ cation.

The experimental value of the ν_1 frequency in the free N_2H^+ amounts to 3233.95 cm^{-1}.[8] On the basis of the modified Rydberg−Klein−Rees procedure, the ν_1 frequency in the N_2H^+-He dimer is predicted to be about 3158 cm^{-1}; therefore, the red shift is about 75.5 cm^{-1}. The dissociation energy D_e for N_2H^+-He complexes is predicted to be about 540.7 cm^{-1} (1.55 kcal/mol).[3] The rotational structures of the N_2H^+-Ne and N_2H^+-Ar complexes are more complicated than the rotational structure of N_2H^+-He due to perturbation of the upper-state rotational manifolds. Combined experimental and theoretical studies show that the values of ν_1 in N_2H^+-Ne and N_2H^+-Ar amount to 3053.5 and 2505.5 cm^{-1}, respectively. For the latter complex, the D_e value calculated at the CCSD(T) using modified cc-pV5Z basis set[9] amounts to 8.06 kcal/mol, while the experimental D_0 is about 2781.5+1.5 cm^{-1} (7.95 kcal/mol). A combined experimental and theoretical study at the MP2 level[10] reveals that the dissociation energy D_e of N_2H^+-Ne is approximately 996 cm^{-1} (2.85 kcal/mol).[4] The D_0 for $N_2H^+-H_2$ is estimated to be around 2000 cm^{-1} (5.72 kcal/mol). So far no experimental data is available for the N_2H^+-Kr or N_2H^+-Xe complexes because their binding energies are too high to be dissociated in the experiments. It has also been reported that the effects of vibrational anharmonicity were particularly pronounced for the intramolecular stretching vibrations of N_2H^+-Kr and N_2H^+-Xe.[11]

We are in the process of investigating the size-dependent of the molecular structures and the nature of interactions of $N_2H^+-(X)_n$ (X = He, Ne, Ar, and H_2; n= 0−13).[12] It is of importance to be able to choose a reliable method and basis set to investigate these complexes since the vibrational properties and the dissociation energies are highly basis-set dependent and are sensitive to the level of electron correlation. Therefore, in this paper, we investigate the molecular structures and the thermodynamic and vibrational properties of N_2H^+-X (X = He, Ne, Ar, and H_2) using the density functional theory, MP2, MP4, CCD, and CCSD, and CCSD(T) methods with different basis sets. Using the approach that has been proven to be reliable for these complexes, the molecular structures and properties of unknown N_2H^+-Kr and N_2H^+-Xe complexes are also predicted and discussed.

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TABLE 1: Optimized N−H$^+$ and N−N Bond Lengths and the Harmonic Vibrational Frequencies of the N−H$^+$ and N−N Stretching Modes for N_2H^+ at the DFT, MP2, MP4, CCD, CCSD, and CCSD(T) Levels of Theory[a]

method	no. of basis functions	H$^+$−N	N−N	ω_{H^+-N}	ω_{N-N}
B3LYP/6-311+G(d,p)	50	1.0398	1.0905	3382.9	2378.7
MP2/6-311+G(d,p)	50	1.0384	1.1145	3410.4	2131.9
MP4/6-311+G(d,p)	50	1.0383	1.1152	3414.5	2113.1
CCD/6-311+G(d,p)	50	1.0360	1.0956	3464.1	2369.8
CCSD/6-311+G(d,p)	50	1.0369	1.0980	3447.8	2344.6
CCSD(T)/ 6-311G(d,p)	50	1.0378	1.1052	3429.7	2270.9
MP2/aug-cc-pVDZ	55	1.0447	1.1254	3361.8	2111.0
MP2/6-311++G(3df,3pd)	96	1.0354	1.1075	3400.7	2149.1
MP2/aug-cc-pVTZ	115	1.0355	1.1084	3380.2	2141.5
MP2/aug-cc-pVQZ	206	1.0346	1.1050	3392.1	2157.7
MP2/aug-cc-pV5Z	334	1.0347	1.1042	3387.3	2161.1
CCSD(T)/aug-cc-pVTZ	115	1.0353	1.0993	/	/
exptl		1.0336[b]	1.0928[b]	3233.95[b] 3405.5[c]	2257.9[b] 2266.8[c]

[a] Units are in angstroms for bond distances, kcal/mol for dissociation energies, and cm^{-1} for vibrational frequencies. [b] Reference 8a,b. [c] Reference 8c.

II. Computational Methods

All calculations were carried out using the Gaussian98 program.[13] The molecular structures were optimized by the DFT method with the Becke3LYP functional, the second-order Møller−Plesset (MP2),[14] the fourth-order (MP4(SDTQ)),[15] and by the coupled-cluster methods using double substitutions from the Hartree−Fock determinant for CCD,[16] CCSD, and single, double, and triple substitutions at the CCSD(T) level.[17] All of the geometries were fully optimized without any symmetry constraints. Harmonic vibrational frequency calculations were performed at each level to confirm whether the predicted structure is a minimum. The dissociation energies were calculated by applying the DFT, MP2, MP4, CCD, CCSD, and CCSD(T) methods.

For N_2H^+−X complexes where X = He, Ne, Ar, and H_2, the 6-311+G(d,p) basis set[18] was used for calculations at different levels. In addition, the aug-cc-pV*X*Z (*X* = D, T, Q) basis sets[19] were also used for N_2H^+−X (X= He, Ne, Ar, and Kr) complexes at the MP2 level. We also compared the basis set effect for N_2H^+−X (X = He, Ne, and H_2) using the 6-311++G(3df,3dp)[12] basis set. Only N_2H^+ and N_2H^+−He have been studied by using the aug-cc-pV5Z basis set due to the limitation of computational resources.

For species involving the heavier rare gas atoms (X = Kr and Xe), different approaches were applied. We used an effective core potential (ECP) which was reported to yield very satisfactory results.[20] The quasirelativistic effective core 6s6p3d1f/4s4p3d1f basis set of the Stuttgart group[21] with eight 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 different aug-cc-pV*X*Z (X = D, T, and Q) basis sets were used for the N_2H^+ fragment (denoted as **BS-D**, **BS-T**, and **BS-Q**) in order to study basis set effect. In addition, the SDB-cc-pVQZ Martin/Sundermann Stuttgart relativistic, large core VQZ ECP[22] basis set (14s10p3d2f1g/4s4p3d2f1g) for Xe[23] and the 6-311+G(d,p) basis set for N and H atoms (**BS-II**) was also used for N_2H^+−Xe. Another basis set (**BS-III**) which uses the DZVP basis set[24] for Xe and the 6-311+G(d,p) basis set for H and N atoms without ECP was used to compare the relativistic effects of N_2H^+−Xe.

III. Results and Discussion

The optimized geometrical parameters obtained for N_2H^+ and its rare gas N_2H^+−X complexes (X = He, Ne, Ar, Kr, Xe, and H_2) with the density functional, MP2, MP4, CCD, CCSD, and CCSD(T) methods are listed in Tables 1−5. The corresponding values of the stretching harmonic vibrational frequencies as well as the dissociation energies are displayed in Tables 2−5.

III.A. N_2H^+ Ion. For the N_2H^+ free ion, all applied methods yield very similar geometrical parameters. The H$^+$−N distances calculated at the DFT, MP2, and MP4 levels (using the 6-311+G(d,p) basis set) are 1.0398, 1.0384, and 1.0383 Å, respectively, approximately 0.002, 0.001, and 0.001 Å longer than the CCSD(T) results. The CCD- and CCSD-level H$^+$−N distances are only 0.001 Å shorter than the CCSD(T) value. Correspondingly, the N−N distances calculated at the MP2 and MP4 levels are slightly longer, while the CCD and CCSD values are slightly shorter than the CCSD(T) results. By comparing with the experimental values, one can conclude that the calculated H$^+$−N distances at the different levels agree very well with the experimental data.

The harmonic vibrational frequency ω_{H^+-N} calculated at the DFT/6-311+G(d,p), MP2/6-311+G(d,p), and MP4/6-311+G(d,p) levels is smaller than ω_{H^+-N} value obtained from the CCSD(T) calculation, by about 1.4%, 0.6%, and 0.4%, respectively, while CCD and CCSD yield a larger values (by about 1% and 0.5%). The predicted ω_{H^+-N} values at all levels are in good agreement with the experimental arharmonic frequency (deviation less than 7%). However, when compared with the harmonic frequency (3405.5 cm^{-1}) obtained by employing an effective spectroscopic Hamiltonian to simulate experimental data, the agreement of the calculated values with the experiment is within 2%.

To study the effect of the basis set on the properties of the N_2H^+ ion, a series of larger basis sets were applied at the MP2 level. It can be seen from Table 1 that the differences between the calculated H$^+$−N and N−N distances, which were obtained using the 6-311+G(d,p) and aug-cc-pV5Z basis sets, are only about 0.004 and 0.010 Å, respectively. The similar dependence for the predicted ω_{H^+-N} and ω_{N-N} vibrations is observed, the differences are about 23 and 29 cm^{-1}, respectively. It is also noticed that the aug-cc-pVDZ basis set yields slightly longer H$^+$−N and N−N distances, indicating that the double-ζ basis set might not be sufficient for this system.

The H$^+$−N distance is about to converge at 1.0347 Å as the basis set increases to aug-cc-pV5Z. The MP2/aug-cc-pVTZ- and MP2/aug-cc-pVQZ-predicted N−H$^+$ values are only 0.01% larger than the MP2/aug-cc-pV5Z result. In addition, the deviations of the H$^+$−N and N−N distances obtained from the

TABLE 2: Optimized Geometrical Parameters for the Equilibrium Structures for $N_2H^+{-}X$ (X = He, Ne, and Ar) and Their Dissociation Energies D_e at the B3LYP, MP2, MP4, CCD, CCSD, and CCSD(T) Levels of Theory[a]

$N_2H^+{-}X$	method	no. of basis functions	$X{-}H^+$	$H^+{-}N$	N−N	D_e	ω_{X-H^+}	ω_{H^+-N}	ω_{N-N}	$\Delta\omega_{H^+-N}$
X = He	B3LYP/6-311+G(d,p)	56	1.5600	1.0490	1.0904	2.03	141.7	3227.3	2363.9	156
	MP2/6-311+G(d,p)	56	1.7073	1.0420	1.1143	1.09	159.0	3338.8	2130.9	72
	MP4/6-311+G(d,p)	56	1.7206	1.0417	1.1150	1.23	157.3	3347.3	2113.3	67
	CCD/6-311+G(d,p)	56	1.7408	1.0388	1.0956	1.04	151.9	3407.6	2366.3	57
	CCSD/6-311+G(d,p)	56	1.7387	1.0397	1.0980	1.05	152.5	3391.8	2342.0	56
	CCSD(T)/ 6-311+G(d,p)	56	1.7282	1.0415	1.1051	1.08	157.0	3362.1	2268.6	68
	MP2/6-311++G(3df,3pd)	114	1.6458	1.0400	1.1074	1.51	197.5	3309.4	2147.0	91
	MP2/aug-cc-pVTZ	138	1.6465	1.0403	1.1083	1.65	205.7	3291.6	2139.4	87
	MP2/aug-cc-pVQZ	252	1.6466	1.0396	1.1050	1.54	205.7	3299.5	2155.3	93
	MP2/aug-cc-pV5Z	414	1.6467	1.0398	1.1042	1.51	204.8	3293.2	2158.3	94
	CCSD(T)/aug-cc-pVTZ	138	1.6474	1.0400	1.0991	1.68	/	/	/	/
	exptl		1.63[a]			1.5[a]	163.0[b]	3158.4[b]		76[b,c]
X = Ne	B3LYP/ 6-311+G(d,p)	72	1.7762	1.0499	1.0904	2.33	144.5	3212.8	2362.3	170
	MP2/ 6-311+G(d,p)	72	1.8668	1.0434	1.1142	1.93	111.5	3313.8	2130.8	97
	MP4/ 6-311+G(d,p)	72	1.8605	1.0434	1.1150	2.14	114.2	3316.4	2113.5	98
	CCD/ 6-311+G(d,p)	72	1.9010	1.0400	1.0950	1.78	106.9	3395.0	2367.1	69
	CCSD/6-311+G(d,p)	72	1.8943	1.0406	1.0979	1.83	125.5	3375.7	2341.8	72
	CCSD(T)/6-311+G(d,p)	72	1.8731	1.0428	1.1050	1.94	112.1	3338.7	2268.1	91
	MP2/aug-cc-pVDZ	78	1.7310	1.0543	1.1250	3.08	152.0	3190.4	2106.6	171
	MP2/6-311++G(3df,3pd)	135	1.7087	1.0458	1.1073	3.48	154.4	3206.3	2142.1	194
	MP2/aug-cc-pVTZ	161	1.7282	1.0455	1.1082	3.14	145.4	3200.6	2134.7	180
	MP2/aug-cc-pVQZ	286	1.7090	1.0454	1.1050	3.09	158.4	3197.6	2150.0	195
	CCSD(T)/aug-cc-pVTZ	161	1.7313	1.0443	1.0990	3.16				
	exptl		1.7561[d]			2.85[d]	135.0[d]	3053.5		181
X = Ar	B3LYP/ 6-311+G(d,p)	80	1.8681	1.0909	1.0935	7.14	198.1	2716.9	2160.9	666
	MP2/ 6-311+G(d,p)	80	1.8390	1.0880	1.1160	7.23	193.7	2636.0	2020.6	774
	MP4/ 6-311+G(d,p)	80	1.8469	1.0869	1.1157	7.25	191.9	2646.1	2017.5	768
	CCD/ 6-311+G(d,p)	80	1.8933	1.0752	1.0959	6.29	174.5	2856.6	2248.7	608
	CCSD/ 6-311+G(d,p)	80	1.8898	1.0771	1.0982	6.39	176.2	2828.5	2225.2	619
	CCSD(T)/6-311+G(d,p)	80	1.8625	1.0840	1.1054	6.89	166.5	2733.0	2146.0	697
	MP2/aug-cc-pVDZ	82	1.8714	1.0892	1.1258	8.24	189.6	2663.4	2027.4	698
	MP2/aug-cc-pVTZ	165	1.8500	1.0827	1.1092	9.18	202.0	2662.9	2045.6	717
	MP2/aug-cc-pVQZ	290	1.8489	1.0823	1.1059	8.98	201.9	2665.0	2056.8	727
	CCSD(T)/aug-cc-pVTZ	165	1.8798	1.0777	1.0993	8.67	/	/	/	/
	exptl					7.95[e]		2505.5[f]	2041.2[f]	729

[a] The calculated harmonic vibrational frequencies for the $N{-}H^+$, N−N, and $X{-}H^+$ stretching modes as well as the red shift of the $N{-}H^+$ stretching vibrational frequencies are listed. (Units are in angstroms for bond distances, kcal/mol for dissociation energies, and cm^{-1} for vibrational frequencies.) [b] Reference 3a. [c] Reference 3c. [d] Reference 4a. [e] Reference 5a,b. [f] Reference 5c.

TABLE 3: Optimized Geometrical Parameters for the Equilibrium Structure and the Dissociation Energies *D*) and Harmonic Vibrational Frequencies for the $N{-}H^+$, N−N, $X{-}H^+$, and H−H Stretching Modes, as Well as the Red Shift of $N{-}H^+$ Stretching Vibrational Frequencies Calculated at the B3LYP, MP2, MP4, CCD, CCSD, and CCSD(T) Levels of Theory[a]

$N_2H^+{-}X$	method	no. of basis functions	$X{-}H^+$	$H^+{-}N$	N−N	D_e	ω_{X-H^+}	ω_{H^+-N}	ω_{N-N}	ω_{H-H}	$\Delta\omega_{H^+-N}$
X = H_2	B3LYP/6-311+G(d,p)	74	1.4066	1.0914	1.1180	9.36	623.5	2610.9	1943.7	4201.2	772
	MP2/6-311+G(d,p)	74	1.4487	1.0957	1.1155	7.96	575.3	2568.8	1989.9	4320.0	842
	MP4/6-311+G(d,p)	74	1.4709	1.0903	1.1158	7.81	564.7	2619.0	2008.6	4262.7	796
	CCD/6-311+G(d,p)	74	1.5017	1.0812	1.0961	7.15	538.5	2803.8	2219.5	4262.5	660
	CCSD/6-311+G(d,p)	74	1.5280	1.0780	1.0984	7.12	504.3	2824.9	2222.8	4281.9	623
	CCSD(T)/6-311+G(d,p)	74	1.4848	1.0873	1.1056	7.42	553.6	2708.0	2132.3	4245.2	722
	MP2/6-311++G(3df,3pd)	132	1.4447	1.0943	1.1087	8.53	566.1	2538.5	1981.5	4298.6	858
	MP2/aug-cc-pVTZ	161	1.4445	1.0945	1.1093	8.70	553.9	2537.9	1978.4	4298.3	842
	MP2/aug-cc-pVQZ	298	1.4443	1.0939	1.1061	8.51	557.3	2542.3	1987.0	4299.8	850

[a] Units are in angstroms for bond distances, kcal/mol for dissociation energies, and cm^{-1} for vibrational frequencies.

aug-cc-pVTZ and aug-cc-pVQZ basis sets are less than 0.1% with respect to the experiments. The calculated ω_{H^+-N} value show less than 5% deviation from the experiment in either the aug-cc-pVTZ, the aug-cc-pVQZ, or the aug-cc-pV5Z basis sets. Therefore, the expansion of the basis set is of less significance in the case of N_2H^+, and the aug-cc-pVTZ basis set is sufficient to obtain a quantitative description for the geometrical parameters and vibrational frequencies of the N_2H^+ ion.

III.B. $N_2H^+{-}He$. In the $N_2H^+{-}He$ complex, the helium atom shares a proton with N_2 and weakens the $H^+{-}N$ bond strength. Consequently, the $H^+{-}N$ bond length becomes slightly longer than in the isolated N_2H^+ ion. For instance, the MP2/6-311+G(d,p)-level-calculated $H^+{-}N$ distance in the free N_2H^+ ion is about 1.0384 Å, while it elongates to 1.0420 Å in the $N_2H^+{-}He$ complex. The helium atom does not affect the N−N distance significantly: this distance becomes only slightly shorter from 1.1145 to 1.1143 Å.

The DFT/6-311+G(d,p)-optimized $He{-}H^+$ distance is 1.560 Å. It is 0.168 Å (∼10%) shorter than the CCSD(T) result. A longer He−H distance is obtained using the MP2-, MP4-, CCD-, and CCSD-level calculations; the predicted $He{-}H^+$ distance agrees well with the CCSD(T) result.

TABLE 4: Optimized Geometrical Parameters for the Equilibrium Structures for $N_2H^+{-}Kr$ and Their Dissociation Energies D_e at the B3LYP, MP2, MP4, CCD, CCSD, and CCSD(T) Levels of Theory[a]

$N_2H^+{-}Kr$	method	no. of basis functions	$X{-}H^+$	$H^+{-}N$	$N{-}N$	D_e	ω_{X-H^+}	ω_{H^+-N}	ω_{N-N}	$\Delta\omega_{H^+-N}$
	B3LYP/BS-I	88	1.9321	1.0913	1.1239	11.39	197.9	2588.6	1887.9	794
	MP2/BS-I	88	1.9629	1.1004	1.1159	10.11	183.4	2521.8	1966.6	889
	MP4/BS-I	88	1.9827	1.0969	1.1162	9.78	178.2	2545.8	1977.9	869
	CCD/BS-I	88	2.0314	1.0833	1.0960	8.62	164.0	2779.9	2206.8	684
	CCSD/BS-I	88	2.0276	1.0853	1.0984	8.70	165.1	2751.6	2183.3	696
	CCSD(T)/BS-I	88	2.0023	1.0926	1.1056	9.29	172.7	2656.0	2102.7	774
	B3LYP/6-311+G(d,p)	98	1.9450	1.0913	1.1217	11.68	196.6	2593.8	1909.8	789
	MP2/6-311+G(d,p)	98	1.9778	1.0988	1.1159	9.76	179.8	2529.5	1969.1	881
	MP4/6-311+G(d,p)	98	1.9819	1.1007	1.1163	9.25	177.8	2530.9	1982.4	884
	CCD/6-311+G(d,p)	98	2.0381	1.0843	1.0960	8.03	161.9	2767.9	2195.7	696
	CCSD(T)/6-311+G(d,p)	98	2.0054	1.0948	1.1056	8.78	171.0	2634.2	2082.7	796
	MP2/aug-cc-pVTZ	174	1.9112	1.1098	1.1102	13.04	202.3	2422.4	1885.0	958
	MP2/aug-cc-pVQZ	299	1.8884	1.1066	1.1141	12.98	207.6	2408.8	1856.6	983
	MP2/BS-Q	244	1.8765	1.1067	1.1183	14.09	217.3	2390.2	1825.4	1002
	CCSD(T)/aug-cc-pVTZ	174	1.9488	1.1022	1.0996	12.25				
	CCSD(T)/233[b]		1.9862	1.0929	1.0961	10.26	181	2621	2082	

[a] The calculated harmonic vibrational frequencies for the $N{-}H^+$, $N{-}N$, and $Kr{-}H^+$ stretching modes as well as the red shift of the $N{-}H^+$ stretching vibrational frequencies are listed. (Units are in angstroms for bond distances, kcal/mol for dissociation energies, and cm^{-1} for vibrational frequencies). [b] Reference 11. CCSD(T) with the aug-cc-pVQZ basis set for Krypton atom and the cc-pVQZ basis set for N_2H^+ ion.

TABLE 5: Optimized Geometrical Parameters for the Equilibrium Structures for $N_2H^+{-}Xe$ and Their Dissociation Energies (D_e) at the B3LYP, MP2, MP4, CCD, CCSD, and CCSD(T) Levels of Theory[a]

$N_2H^+{-}Xe$	method	no. of basis functions	$X{-}H^+$	$H^+{-}N$	$N{-}N$	D_e	ω_{X-H^+}	ω_{H^+-N}	ω_{N-N}	$\Delta\omega_{H^+-N}$
	B3LYP/BS-I	88	2.0343	1.1779	1.0922	14.80	210.0	2513.2	1340.8	870
	MP2/BS-I	88	2.0750	1.1385	1.1170	13.05	189.7	2310.3	1639.0	1100
	MP4/BS-I	88	2.0943	1.1336	1.1172	12.68	182.9	2304.0	1674.5	1111
	CCD/BS-I	88	2.1631	1.1084	1.0965	11.05	162.5	2612.4	1963.9	852
	CCSD/BS-I	88	2.1568	1.0988	1.1118	11.18	164.2	2580.0	1926.8	868
	CCSD(T)/BS-I	88	2.1227	1.1248	1.1061	11.96	174.1	2475.6	1792.4	954
	B3LYP/BS-III	86	2.0596	1.1712	1.0921	15.26	180.3	2518.1	1354.2	865
	MP2/BS-III	86	2.0844	1.1408	1.1169	12.82	185.4	2302.9	1596.2	1108
	MP4/BS-III	86	2.0853	1.1421	1.1173	12.48	183.6	2280.0	1576.8	1135
	CCD/BS-III	86	2.1624	1.1129	1.0965	10.71	160.9	2594.3	1899.8	870
	CCSD(T)/BS-III	86	2.1146	1.1328	1.1062	11.76	173.1	2545.8	1688.1	884
	B3LYP/BS-II	104	2.0324	1.1787	1.0922	15.95	153.5	2526.4	1697.7	857
	MP2/BS-II	104	2.0913	1.1313	1.1168	13.45	190.7	2333.9	1721.2	1077
	MP4/BS-II	104	2.1170	1.1245	1.1170	12.48	183.3	2343.4	1777.5	1071
	CCD/BS-II	104	2.1768	1.1034	1.0964	10.88	166.0	2636.5	2028.9	828
	CCSD(T)/BS-II	104	2.1429	1.1165	1.1060	11.74	175.8	2505.5	1892.5	924
	MP2/BS-T	153	2.0174	1.1111	1.1594	16.83	213.1	2269.4	1396.5	1111
	MP2/BS-Q	244	1.9631	1.1822	1.1082	19.14	235.2	2260.8	1178.1	1131
	CCSD(T)/BS-T		2.0606	1.1440	1.1003	16.06				
	CCSD(T)/PP[b]		2.0606	1.1355	1.0967	13.81	196	2459	1631	

[a] The calculated harmonic vibrational frequencies for the $N{-}H^+$, $N{-}N$, and $Xe{-}H^+$ stretching modes as well as the red shift of the $N{-}H^+$ stretching vibrational frequencies are listed. (Units are in angstroms for bond distances, kcal/mol for dissociation energies, and cm^{-1} for vibrational frequencies). [b] Reference 11. CCSD(T)/PP-calculated result, with the scalar-relativistic energy-consistent pseudopotential basis set for Xenon atom and the cc-pVQZ basis set for N2H+ ion.

We noticed that there is still a 6% 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. Therefore larger basis sets were applied at MP2 level, such as the 6-311++G(3df,3pd), aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets, the $He{-}H^+$ distance indeed decreases to around 1.65 Å which is in excellent agreement with the experimental value.

The decreased bond strength of the $H^+{-}N$ fragment makes the $H^+{-}N$ stretching mode in the complex shift to a lower vibrational frequency. Experiments reported a red shift of 75.5 cm^{-1} on the ν_{H^+-N} in the $N_2H^+{-}He$ complexes with respect to that in free N_2H^+. The B3LYP/6-311+G(d,p)-level calculation predicted a red shift of 156 cm^{-1}, 105% larger than that in the experiment. This means that the DFT method cannot describe sufficiently the fairly weak interaction between He and N_2H^+. The DFT/6-311+G(d,p) level overestimates the interaction between the helium atom and H^+; therefore, a larger red shift of ω_{H^+-N} is obtained compared to the CCSD(T) result and the experimental values. With the same basis set, the MP2-, MP4-, and CCSD(T)-calculated ω_{H^+-N} value ranges from 3360 to 3410 cm^{-1} which amounts to a 6−8% deviation from the experiment.

The MP2/6-311++G(3df,3pd)-, MP2/aug-cc-pVTZ-, MP2/aug-cc-pVQZ-, and MP2/aug-cc-pV5Z-level calculated ω_{H^+-N} values are approximately 3300 cm^{-1}. The red shifts $\Delta\omega_{H^+-N}$ are 91, 93, and 94 cm^{-1}, respectively, slightly larger than the experimental values. The intramolecular stretching mode ω_{He-H^+} is also sensitive to both the basis set and the level of electron correlation. The MP2/6-311+G(d,p)-level calculations predicted ω_{He-H^+} value of 159 cm^{-1} (205.7 cm^{-1} at the MP2/aug-cc-pVTZ level, about 40 cm^{-1} larger than the experimental value). This difference may be reduced if the anharmonicity contribution is considered.

The dissociation energy D_e is also basis set dependent; the predicted D_e values obtained at the different levels are about 30% smaller than the experimental values. However, it increases to about 1.5 kcal/mol when the 6-311++G(3df,3pd) and aug-cc-pVXZ (X = Q or 5) basis sets are used, in excellent agreement with the experiment.

Therefore, for the N_2H^+-He complex, the deviation of geometrical parameters from the experiments obtained at the different levels by using the 6-311+G(d,p) basis set are about 7%. Such a difference decreases to around 1% when the aug-cc-pVQZ and aug-cc-pV5Z basis sets are used. Correspondingly, the ω_{H^+-N} values calculated at all levels agree with the experiment with an error of less than 8%. The basis set quality does not significantly improve the predicted ω_{H^+-N} values.

However, the D_e is much more sensitive to both the basis set and the level of electron correlation. The DFT method yields a larger D_e compared to the experiment, while all other methods predict smaller D_e values.

III.C. N_2H^+-Ne. Similarly to the N_2H^+-He complex, the DFT-, MP2-, and MP4-level-optimized H^+-Ne distance is shorter than the CCSD(T) result, while the CCD and CCSD methods yield longer H^+-Ne distances.

Interestingly, the DFT/6-311+G(d,p)-level-calculated H^+-Ne distance is very close to the reported experimental data (~1% error), while all the other methods predict H^+-Ne distances which are 6−8% 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 2 kcal/mol; the deviation from the experiments is as large as 30%. When a larger basis set is used, for instance the aug-cc-pVQZ basis set, D_e is predicted to be about 3.0 kcal/mol, the deviation is significantly decreased and amounts to 8%.

All level calculations using the 6-311+G(d,p) basis set yield ω_{H^+-N} values which are 10% larger than the experiment, while the difference decreases to 5% when the aug-cc-pVXZ (X=D, T, Q) basis sets are used. The basis set effect is significant for the red shift of the H^+-N stretch. The $\Delta\omega_{H^+-N}$ value calculated at the MP2/6-311+G(d,p) level is 97 cm^{-1}, a 46% deviation from experiment. The MP2/aug-cc-pVQZ predicted $\Delta\omega_{H^+-N}$ value amounts to 195 cm^{-1} which is much closer to the experimental value (181 cm^{-1}).

Similarly to the N_2H^+-He dimer, the intramolecular stretching frequency ω_{H^+-Ne} is also sensitive to the basis set effect, the MP2/6-311+G(d,p)-calculated ω_{H^+-Ne} is 111.5 cm^{-1}, while it amounts to 145 cm^{-1} when the aug-cc-pVTZ basis set is used, in good agreement with the experiment. Dopfer et al.[4a] reported the intramolecular stretching frequency of 160 cm^{-1} at the MP2 level using a modified aug-cc-pVTZ basis set. Their result is slightly larger than the experimental value.

The ω_{H^+-N} values calculated at all levels agree with experiment with an error of less than 11%. The application of the aug-cc-pVXZ (X = D, T, or Q) basis sets reduces this difference to less than 5%.

The differences between the predicted geometrical parameters and the experimental data are also reduced when a larger basis set is used. For instance, the deviations of the $Ne-H^+$ distance from the experiment obtained at different levels using the 6-311+G(d,p) basis set are about 8% and decrease to around 2% when the aug-cc-pVXZ (X = D, T, or Q) basis sets are used. The D_e and $\Delta\omega_{H^+-N}$ values are also rather sensitive to both the level of electronic correlation and especially the basis set effect. Both the Møller−Plesset (MP2 and MP4) methods and the coupled-cluster method (the 6-311+G(d,p) basis set) predict larger (30% and 60%) deviations of the D_e and $\Delta\omega_{H^+-N}$ values from the experiment. When the aug-cc-pVXZ (X = D, T, or Q) basis sets are used, the differences between the predicted and the experimental D_e and $\Delta\omega_{H^+-N}$ values drop to about 10% and 7%, respectively.

III.D. N_2H^+-Ar. For the N_2H^+-Ar complex, the $Ar-H^+$ and H^+-N distances predicted at the DFT/6-311+G(d,p) level are very close to the CCSD(T) value (0.006 Å difference). The $\Delta\omega_{H^+-N}$ value obtained at the DFT level amounts to 666 cm^{-1}, semiquantitatively reflecting the red shift effect of the $N-H^+$ stretching mode when an argon atom is attached to the proton of the N_2H^+ ion.

At the MP2, MP4, CCD, CCSD, and CCSD(T) levels, the predicted $\Delta\omega_{H^+-N}$ values are 774, 768, 608, 619, and 697 cm^{-1}, respectively. It is interesting that the MP2 and MP4 methods are sufficient to reproduce the experimental data, while the coupled-cluster methods tend to yield smaller $\Delta\omega_{H^+-N}$ values.

The size of the basis sets will not affect the calculated ω_{H^+-N} value as much as in the lighter complexes. The MP2/aug-cc-pVQZ-level-calculated ω_{H^+-N} is only 6% larger, while the MP2/6-311+G(d,p)-level ω_{H^+-N} is only 6% smaller than the experimental value.

A recent study[9] performed at the CCSD(T) level using modified cc-pv5z basis set revealed that vibrational frequencies for the H^+-N stretching, the $N-N$ stretching, and the $Ar-H^+$ stretching modes are 2783, 2195, and 191 cm^{-1}, respectively. Considering their calculated harmonic and the experimental anharmonic frequency values, anharmonicity contributions of 277 cm^{-1} was expected for ν_{H^+-N} mode in the N_2H^+-Ar dimer. In addition, the CCSD(T)/6-311+G(d,p) level predicted the harmonic stretching H^+-N vibrational frequency to be approximately 100 cm^{-1} larger than the MP2/6-311+G(d,p)-calculated result. If the difference retains, the anharmonic ν_{H^+-N} stretching vibrational frequency at the CCSD(T)/aug-cc-pVTZ level is expected to be around 2458 cm^{-1}, which is in excellent agreement with the experimental value.

The dissociation energy of N_2H^+-Ar is slightly less sensitive to the basis set used than in the cases of N_2H^+-He and N_2H^+-Ne complexes. One can see (Table 2) that the value of D_e increases from 7.23 to 8.98 kcal/mol when the basis set changes from 6-311+G(d,p) to aug-cc-pVQZ.

Recently Dopfer et al.[4a] studied the N_2H^+-Ne and N_2H^+-Ar dimers at the MP2 level with the modified aug-cc-pVTZ basis sets. They reported the $X-H^+$, $H-N$, and $N-N$ distances to be 1.7044, 1.0421, 1.1053 (N_2H^+-Ne) and 1.8363, 1.1070, 1.0838 Å (N_2H^+-Ar). The D_e value and the predicted ω_{H^+-N} for the N_2H^+-Ar dimer are 8.24 kcal/mol and 2603 cm^{-1}, respectively. Compared to our results (Tables 2 and 3), one can conclude that both standard and modified aug-cc-pVTZ basis sets yielded the similar results. In addition, the MP2/aug-cc-pVTZ predicted D_e value is in good agreement with the D_e value obtained by CCSD(T)/aug-cc-pVTZ method and the basis set limit extrapolation[25] using the CCSD(T)/aug-cc-pVnZ (n=3−6) calculations with the counterpoise (CP) procedure.[26] Therefore the triple-ζ basis set, such as the aug-cc-pVTZ basis set, is sufficient to study the interaction in the N_2H^+-X (X = He, Ne, and Ar) complexes. The results of the CCSD(T)/aug-cc-pVTZ calculations performed on the N_2H^+-X (X = He, Ne, and Ar) complexes are reported in the Tables 1−3. They yielded the similar optimized geometrical parameters and the dissociation energies as those obtained at the MP2/aug-cc-pVTZ level.

III.E. $N_2H^+-H_2$. In addition to the N_2H^+-X complexes, $N_2H^+-H_2$ was also investigated (see Table 3). The calculated values of the dissociation energy D_e by the DFT, MP2, and MP4 methods with the 6-311+G(d,p) basis set are 26%, 7%, and 5% larger than the CCSD(T) result, while the CCD and CCSD predict smaller, by around 4%, D_e values. The calculated H^+-N distance is less sensitive to the methods used, and the corresponding differences calculated at the MP2, MP4, CCD, and CCSD levels with respect to the CCSD(T) level results are 5%, 2%, 1%, and 3%, respectively.

One may conclude that the basis set effect is not as significant as those revealed for the N_2H^+-He and N_2H^+-Ne complexes. When we used the aug-cc-pVQZ basis set, the MP2-calculated H^+-H distance is 1.4443 Å, virtually the same as the result obtained at the MP2/6-311+G(d,p) level. Moreover, the differences in the D_e and ω_{H^+-N} values for these two basis sets are only 6% and 0.5%, respectively.

III.F. N_2H^+-Kr and N_2H^+-Xe. The investigated basis set and electron correlation effects on the predicted equilibrium geometries, harmonic vibrational frequencies, and the dissociation energies of the N_2H^+-X (X = He, Ne, and Ar) complexes allow one to conclude that the MP2 level in combination with aug-cc-pVTZ basis set yields quantitative results as discussed above. Up till now, only one complex involving the heavier krypton atom, $Kr-HCO^+$, has been studied by high-resolution spectroscopy,[27] and no experimental data is available for N_2H^+-Kr and N_2H^+-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 electron correction effects on the structures, vibrational frequencies, and the dissociation energies of complexes of the two heaviest rare gas elements. Even though MP2/aug-cc-pVTZ provides the quantitative results for their lighter analogues, it may not be suitable for N_2H^+-Kr and N_2H^+-Xe. Therefore, in the following section, we will discuss the effects of basis set and electron correlation on the equilibrium geometries, harmonic vibrational frequencies, and the dissociation energies of the N_2H^+-Kr and N_2H^+-Xe using B3LYP density functional, and MP2, MP4, CCD, CCSD, and CCSD(T) methods. To study the relativistic effect, the scalar-relativistic energy-consistent pseudopotentials (see section II) were also applied.

N_2H^+-Kr. For N_2H^+-Kr, we use basis set BS-I to study the differences among the different theoretical levels. The relativistic effects are considered using the quasirelativistic effective core basis set of the Stuttgart group with an eight-valence-electron pseudopotential. The calculated geometrical parameters, thermodynamic and vibrational properties of the N_2H^+-Kr dimer are shown in Table 4.

Similarly to complexes described above, the DFT method predicts a $Kr-H^+$ distance of 1.9321 Å, 0.07 Å shorter than the CCSD(T)-calculated value. This difference is smaller than in the cases of the N_2H^+-He and N_2H^+-Ne complexes but not as small as in the N_2H^+-Ar complex. The MP2 and MP4 methods also yield a longer $Kr-H^+$ distance compared to the CCSD(T) result, while the CCD and CCSD levels predict a $Kr-H^+$ distance which is approximately 0.03 Å longer than the CCSD(T) value. Correspondingly, the DFT-, MP2-, and MP4-predicted H^+-N and $N-N$ distances are slightly longer than the CCSD(T) value, while CCD and CCSD yield shorter values.

To study the relativistic effects for the N_2H^+-Kr complex, the 6-311+G(d,p) basis set was also used to calculate the geometrical parameters, thermodynamics, and vibrational properties of N_2H^+-Kr at the different theoretical levels. As one can see from Table 4, both the 6-311+G(d,p) and BS-I basis sets yield very close geometrical parameters, D_e, and ω_{H^+-N}, ω_{N-N}, ω_{H^+-Kr}, and $\Delta\omega_{H^+-N}$ values. This indicates that the relativistic effects are not significant in the N_2H^+-Kr complex.

The performance of different basis sets was also investigated at the MP2 level, the results are shown in Table 4. One can conclude that the results are sensitive to the basis set effect. The MP2/aug-cc-pVTZ-calculated $Kr-H^+$ distance amounts to 1.9112 Å, 0.0512 Å shorter than the MP2/BS-I value. The MP2/aug-cc-pVQZ calculation predicts an even shorter $Kr-H^+$ distance. The MP2/BS-Q calculations which use the quasirelativistic effective core basis set with an eight-valence-electron pseudopotential for Kr and the aug-cc-pVQZ basis set for the N and H atoms predict the $Kr-H^+$ distance to be 1.8765 Å which is very close to the MP2/aug-cc-pVQZ result. This further confirms that the relativistic effects are not significant in predicting the geometrical parameters for this system.

As for the vibrational property, the MP2/aug-cc-pVTZ level ω_{H^+-N}, ω_{N-N} values are by about 100, 82 cm^{-1} smaller than the MP2/BS-I results, while ω_{H^+-Kr} is by 19 larger. The MP2/aug-cc-pVQZ and MP2/BS-Q ω_{H^+-N}, ω_{N-N}, and ω_{H^+-Kr} values are only 19, 31, and 10 cm^{-1} difference; therefore, the difference could be negligible.

The dissociation energy is much more sensitive to the basis set and the relativistic effects than the geometrical parameters and vibrational frequency. The MP2/6-311+G(d,p)-level-calculated D_e amounts to 9.76 kcal/mol, similar to the MP2/BS-I result. However, the MP2/aug-cc-pVTZ-level-calculated D_e is about 13.04 kcal/mol, significantly higher than the MP2/BS-I result. The MP2/aug-cc-pVQZ and MP2/BS-Q-level-predicted D_e values are even larger, 12.98 and 14.09 kcal/mol, respectively. Even though there is no big difference between the MP2/aug-cc-pVQZ and MP2/BS-Q-level-predicted geometrical parameters and vibrational frequencies they differ by 1.11 kcal/mol in calculated dissociation energy. Therefore, the inclusion of the relativistic effect is crucial for obtaining an accurate prediction of the dissociation energy for the Kr-containing complex.

N_2H^+-Xe. For species involving the Xe atom, the $Xe-H^+$, H^+-N, and $N-N$ distances are notably dependent upon the levels of electron correlation. For instance, the DFT/BS-I-calculated $Xe-H^+$ distance is 2.0343 Å, 0.088 Å shorter than the CCSD(T) result, while the corresponding differences are 0.168, 0.097, 0.006, and 0.070 Å in the N_2H^+-He, N_2H^+-Ne, N_2H^+-Ar, and N_2H^+-Kr complexes, respectively. The MP2- and MP4-level $Xe-H^+$ distances are 0.049 and 0.028 Å shorter than the CCSD(T) result. The CCD and CCSD methods yield a $Xe-H^+$ distance which is 0.040 Å longer.

The SDB-cc-pVQZ Martin/Sundermann Stuttgart relativistic, large core VQZ ECP in conjunction with the 6-311+G(d,p) basis set for N and H atoms (**BS-II**) was also used for the N_2H^+-Xe ion. From Table 5, one can conclude that these two sets of results are in good agreement.

Another basis set (**BS-III**), which uses DZVP for Xe and the 6-311+G(d,p) basis set for H and N atoms without ECP, was used to study the relativistic effects for the N_2H^+-Xe complex. Besides the DFT/BS-III-level-calculated $Xe-H^+$ distance (0.02 Å longer than the DFT/BS-I-predicted value), the dissociation energy D_e and the ω_{H^+-N} and ω_{N-N} values are similar to each other.

Again, the basis set plays a very important role in obtaining accurate results. Within the MP2 scheme, the predicted Xe-

H^+ distance is 2.0750 Å using the BS−I basis set, and it decreased to 1.9631 Å using the BS-Q basis set. The MP2/BS-T and MP2/BS-Q-level D_e values are 16.98 and 19.14 kcal/mol, respectively, much larger than the MP2/BS-I result.

The dependence of vibrational frequencies is not as sensitive to the basis set quality as the dissociation energy. The MP2/BS-T and MP2/BS-Q-level ω_{H^+-N} values are 2269 and 2261 cm^{-1}, only 41 and 50 cm^{-1} larger than the MP2/BS-I-level frequency.

One may conclude that for clusters involving heavier atoms such as N_2H^+-Kr and N_2H^+-Xe, different core ECP basis sets provide similar results. The dissociation energy D_e is much more sensitive to the basis set quality and the relativistic effects than the vibrational properties.

The N_2H^+-Kr and N_2H^+-Xe dimers were also studied by Botschwina et al at the CCSD(T) level using cc-pVQZ basis set.[11] Their predicted $Kr-H^+$ and $Xe-H^+$ distances are 1.9862 and 2.0606 Å, respectively, slightly longer than the MP2/BS-Q-level values.

As one can see from Tables 4 and 5, that the MP2 method tends to predict smaller values of the harmonic vibrational frequencies ω_{H^+-N}, ω_{N-N}, and shorter $X-H^+$ distances than the CCSD(T) method. The differences between MP2 and CCSD(T)-calculated $X-H^+$ distances are approximately 0.05 and 0.03 Å for the N_2H^+-Kr and N_2H^+-Xe dimers, respectively. If these differences are retained, the CCSD(T)/aug-cc-pVTZ-predicted $X-H^+$ distances will be about 1.95 and 2.06 Å for the N_2H^+-Kr and N_2H^+-Xe dimers. This agrees well with the CCSD(T)/aug-cc-pVTZ-optimized values (1.9488 and 2.0606 Å, see Tables 4 and 5).

Using the different basis sets (see Tables 4 and 5), the differences between MP2 and CCSD(T)-level-predicted ω_{H^+-N} values fall in the range of 105−134 (N_2H^+-Kr) and 166−240 cm^{-1} (N_2H^+-Xe). When these differences applied to the BS-Q basis set, the CCSD(T)/BS-Q ω_{H^+-N} values are expected to be in the range of 2495−2524 and 2427−2503 cm^{-1} for the N_2H^+-Kr and N_2H^+-Xe dimers, respectively. This is in a good agreement with Botschwina's prediction.

IV. Conclusions

This study provides comprehensive investigation on the basis set and electron correlation dependence of the geometrical parameters, vibrational frequencies and dissociation energies for N_2H^+-X (X = He, Ne, Ar, Kr, Xe. and H_2). From the results of our study, we can draw the following conclusions:

In all the rare gas complexes, DFT, MP2, and MP4 methods tend to produces longer $X-H^+$ (X = He, Ne, Ar, Kr, Xe, and H_2) distance than the CCSD(T)-level value, while the CCD- and CCSD-calculated $X-H^+$ bond length are slightly shorter.

For the N_2H^+ 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 N_2H^+ ion geometrical structure.

DFT method is not reliable to study the weak interaction of N_2H^+-He and N_2H^+-Ne complexes. The accuracy of predicted geometrical parameters, dissociation energies, and red shift of H^+-N stretching mode ($\Delta\omega_{H^+-N}$) are highly depended upon the level of electron correlation and the size of basis set. The ω_{H^+-N} value is less sensitive to the level of electronic correlation and basis set. However, qualitative results can be obtained for N_2H^+-Ar and $N_2H^+-H_2$ complexes by using DFT method. The MP2 method in conjunction with aug-cc-pVTZ basis set can provide quantitative results in good agreement with the experiments. The basis set effect is not as significant as one in the N_2H^+-He and N_2H^+-Ne complexes. The basis set effect on the predicted interaction energy and vibrational property of $N_2H^+-H_2$ is very similar to one for the N_2H^+-Ar ion.

Recently we have investigated the structures and the thermodynamic and vibrational properties of $N_2H^+-(Ar)_n$ (n = 1−12) complexes using the MP2/6-311+G(d,p) method.[12] The dissociation energies of subsequent consecutive argon ligands around the N_2H^+ ion are around 2.0 kcal/mol. They increase with an increasing number of argon ligands, lying in the range of the same order of the dissociation energies as predicted for the N_2H^+-He and N_2H^+-Ne complexes. As described in sections II.B and III.C, the MP2/6-311+G(d,p) level is able to qualitatively describe such a weak (1.0−2.0 kcal/mol) interaction; thus, the application of the MP2/6-311+G(d,p) method makes a study of the size-dependent property for $N_2H^+-(Ar)_n$ complexes practical and conserves a large amount of CPU time when n is larger than 6. However, for $N_2H^+-(He)_n$, the D_e for the subsequent attachment of helium ligands ($n > 1$) are predicted to be less than 0.5 kcal/mol at the MP2/6-311+G(d,p) level; therefore, DFT and MP2 methods in conjunction with 6-311+G(d,p) might provide unreliable results.

The effects of basis set, electron correlation on the equilibrium geometries, harmonic vibrational frequencies, and the dissociation energies of the N_2H^+-Kr and N_2H^+-Xe complexes were systematically investigated. The scalar−relativistic energy-consistent pseudopotentials were also applied in order to study the relativistic effects. For the complexes involving the heavier atoms such as N_2H^+-Kr and N_2H^+-Xe, the relativistic effects have minor effect on the geometrical parameters, and the H^+-N stretching mode. However, the dissociation energy is highly depended on the relativistic effects. In addition, the dissociation energies and the geometrical parameters are sensitive to the basis set effect. The calculation using BS-Q basis set within MP2 scheme provide the reasonable results and might be extended to study the other complexes containing heavier rare gas atoms.

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