J. Phys. Chem. A **2002,** *106,* 11637−11643

Density Functional Theory Study of Alkali Metal−Noble Metal Diatomic Molecules

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Received: July 17, 2002; In Final Form: September 30, 2002

Molecular properties, equilibrium bond lengths, dissociation energies, and vibrational frequencies of the ground state, of diatomic molecules formed from alkali metal (Li, Na, K) and noble transition metal (Cu, Ag, Au) have been calculated using density functional theory (DFT) with eight different density functionals. In addition, ab initio wave function based Hartree−Fock (HF) and coupled cluster singles doubles with triple excitations added perturbatively (CCSD(T)) methods are also included for comparisons. The pure density functionals PW91 and BP86 predict well the dissociation energies and harmonic vibrational frequencies but underestimate the bond lengths. CCSD(T) predicts the geometry well but underestimates the dissociation energies and vibrational frequencies. The hybrid HF/DFT B3P86 and B3LYP provide reasonable estimates for all the spectroscopic parameters. From the discrepancy between the computed and experimental bond length of KAg and the vibrational frequency of LiCu, we suggest a reanalysis or reexamination of the experimental spectrum of these two molecules. With only medium sized basis sets and small core relativistic effective core potentials, calculations using DFT functionals often give comparable or even superior results to ab initio wave function based methods in this mixed metal system.

I. Introduction

In recent years, a considerable amount of effort has been focused on understanding the chemical and physical properties of molecules and solids that are formed from dissimilar metals. In part, this interest has been motivated by the extensive technological applications that mixed-metal systems have in areas of metallurgy, electrochemistry, microelectronics, catalysis, and structural material science. For instance, bimetallic surfaces are known to have catalytic activity that is significantly different from monometallic surfaces.[1] Hence, an understanding of the heteronuclear metal−metal bond is crucial to design and master new bimetallic molecules. Research work has recently been performed to understand the microscopic details of metal−metal bonding in bimetallic surfaces,[2] in particular those including alkali metal atoms preadsorbed on transition metal surfaces,[3] which show enhanced catalytic activities. The alkali metals serve as promoters, donating their valence electrons to the transition metal substrate, rendering the metal−metal bond partially ionic. This has been shown to dramatically reduce the work function of the catalyst and substantially increase the rate of dissociative chemisorption of molecules such as CO, N_2, and NO.[3] Study of the mixed metal diatomic molecules is useful because these molecules are simple systems that can be easily modeled and tracked by both theoreticians and experimentalists.

Due to the limited number of valence electrons in alkali and noble metals, spectroscopic study and theoretical computations are successful and yield results that agree with each other. Recent experimental work included photoionization spectroscopy of LiCu,[4,5] LiAg[4,6] NaAg,[7] KAg,[8] NaAu,[9] and KAu[9] and theoretical studies of LiCu,[10−12] NaCu,[12] and KCu.[12] It is expected (and confirmed by theory and experiments) that the combination of a noble-metal (NM) atom ($n\mathrm{d}^{10}\,(n+1)\mathrm{s}^1$) and an alkali-metal (AM) atom (s^1) will result in a simple, polarized s−s σ bond, thus giving a $^1\Sigma^+$ ground state for these heteronuclear diatomic molecules.

Density functional theory (DFT) has drawn the attention of theoretical chemists in the past decade, because it can accurately estimate the chemical properties of a wide variety of molecular systems with much less computational effort when compared to conventional ab initio wave function based methods. Even though there are many different DFT functionals available presently, and a large number of DFT studies and comparisons of performance of different DFT functionals on transition metal containing systems, the applicability of DFT to the metallic bonds of transition metal containing systems is far from definite. In addition, no comprehensive study of the chemical bonds of simple systems such as the AM−NM diatomic molecules using DFT has been performed so far.

In this paper, we compared the performance of eight different DFT functionals against both standard wave function based methods and, more importantly, against experimental measurements.[4−13] To achieve this, calculations of equilibrium bond lengths, r_e, harmonic vibrational frequencies, ω_e, and dissociation energies D_e were carried out on nine AM−NM diatomic molecules. The accuracy of these results was then used as the criterion for assessing the different methods. The chemical bonding of these mixed metal diatomic molecules has also been examined.

II. Computational Details

The basis sets used for the alkali metal atoms (Li, Na, K) are of triple-ζ quality with polarization and diffuse functions added: 6-311++G(2d,2p).[14] For the noble transition metals (Cu, Ag, Au), the Stuttgart small core relativistic effective core potentials (RECP) and the accompanied basis sets[14] are employed for the present calculations. This is due to the large number of electrons present in the group IB atoms and the importance of relativistic effects as one proceeds down the group. Gold is known to have extremely large scalar relativistic

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10.1021/jp026550w CCC: \$22.00

effects, which has been parametrized in the RECP, but the spin−orbit interaction in the electronic ground state is so small that it can be safely neglected.[15,16] It is also important to choose a suitable size of the core for the RECP approximations. For instance, even though the core orbitals are not included in the bonding, they may have spatial extents similar to those in the valence space and their inclusion in the valence space is thus necessary. In view of that, the small core RECP was chosen, which also has the *n*s and *n*p, in addition to the $(n + 1)$s, $(n + 1)$p, and *n*d orbitals included in the valence space.

The following *eight* density functionals were employed to perform our calculations:

(1) the Becke 1988 exchange (B88) only[17]

(2) the B88 exchange + Perdew 1986 (P86)[18] correlation (BP86)

(3) the B88 exchange + Lee−Yang−Parr (LYP)[19] correlation (BLYP)

(4) the half-and-half HF/DFT hybrid exchange (BH)[20] + LYP correlation (BHLYP)[21]

(5) the Becke three-parameter HF/DFT exchange (B3) + LYP correlation (B3LYP)[22]

(6) the B3 exchange + P86 correlation (B3P86)[23,24]

(7) the B3 exchange + Perdew−Wang 1991 (PW91) correlation (B3PW91)[23,25]

(8) the Perdew−Wang 1991 exchange-correlation (PW91)[25]

These eight functionals are commonly used in DFT calculations, and each has various degrees of success and merit as documented in the literature. In addition, calculations of two wave function based methods are included for comparison. They are Hartree−Fock (HF) and CCSD(T) calculations. HF is useful in initiating calculations, but the main comparative interest will be the results of CCSD(T) because it has electron correlation incorporated. In the CCSD(T) calculations, all electrons in the valence space of the noble metals are correlated (*n*spd and $(n + 1)$s) and all orbitals are retained in the post-SCF calculations. Core-valence correlation[26] is known to be important in the alkali atoms, and we have correlated all the electrons for Li (1s and 2s) and nine electrons for Na (2sp and 3s) and K (3sp and 4s). Only the core orbitals of Na (1s) and K (1s, 2s, and 2p) are kept frozen during the post-SCF calculations.

All calculations were performed using the GAUSSIAN 98 suite of programs.[27] A HF/(6-311++G (2d,2p), Stuttgart RECP) calculation was first obtained to set up an initial guess of orbitals. Geometry optimizations were then carried out using the different calculation methods mentioned earlier. For each of the nine molecules, the equilibrium bond length, r_e, and the vibrational frequency, ω_e, were calculated analytically. In the CCSD(T) calculations, the equilibrium bond lengths were calculated by a quadratic fit of 11 points at exactly $r = r_e$ and $r = r_e \pm m \times 0.005$ Å ($m = 1-5$) to the form

$$E = E_0 + \frac{1}{2}k(r - r_e)^2$$

where E is the electronic energy at a bond distance r, E_0 is the electronic energy at the equilibrium bond length at r_e, and k is the force constant. The vibrational frequencies, ω_e, were obtained from the formula

$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where μ is the reduced mass of the diatomic molecule. The dissociation energy, D_e, was computed by taking the difference between the total energy of the molecule at its equilibrium geometry and the energy of the ground state of separated atoms (^{2}S (alkali metal) + ^{2}S (noble metal)). D_0 was obtained by subtracting one-half of the predicted ω_e from the calculated D_e.

III. Results and Discussion

The calculated bond lengths, dissociation energies, and vibrational frequencies are given in Tables 1−3, respectively. Experimental results and previous theoretical calculations are also shown in these tables for easy references.

To compare the various methods, percentage errors in the calculated spectroscopic parameters−bond lengths, dissociation energies, and vibrational frequencies−were found by comparison with the experimental data. For each calculated parameter (x), we define the percentage error, ϵ, as

$$\epsilon = \left(\frac{x_{\text{expt}} - x_{\text{calc}}}{x_{\text{expt}}}\right) \times 100\%$$

The root-mean-square (RMS) % error, ξ_x is then calculated from the percentage errors of each parameter x for each method,

$$\xi_x = \sqrt{\frac{{\epsilon_1}^2 + {\epsilon_2}^2 + ... + {\epsilon_n}^2}{n}}$$

where n is the number of experimental data for each spectroscopic parameter.

A. Comparisons between ab Initio Wave Function Based Calculations and Various DFT Functionals. The results listed in Table 1 indicate that the HF calculation predicts the longest bond length among all the methods studied. Upon inclusion of correlations (as in the cases of CCSD(T) and DFT with exchange-correlation functionals), the calculated bond lengths decrease. Even without the correlation functional (as in the case of B88, where there is only exchange functional), it predicts shorter bond lengths when compared with the HF result. The effects of a different exchange operator in HF and B88 are somewhat quenched in the M−Au series (M = Li, Na, K). Among the DFT functionals, we noticed that B88 predicts the longest bond lengths. Inclusion of the correlation functional decreases the calculated bond lengths (when B88 is compared with BLYP or BP86). When the HF exchange energy is included in the calculations (comparing BLYP with the HF/DFT hybrids, BHLYP with B3LYP, and BP86 with B3P86), the predicted bond lengths increase. The PW91 exchange functional also predicts shorter bond lengths than the B3 exchange functional (as in the comparisons between B3PW91 and PW91 results). The difference among different correlation functionals used is smaller than 0.035 Å (when B3LYP, B3P86, and B3PW91 or BLYP and BP86 are compared) whereas it is smaller than 0.074 Å among different exchange functionals (when BLYP, BHLYP, and B3LYP or B3PW91 and PW91 are compared). Hence, the bond lengths calculated are more sensitive to the exchange functional than the correlation functional. All the bond lengths obtained using the CCSD(T) method fall within the range of the DFT functionals studied in the present work.

Previous ab initio calculations have predicted a bond length for LiCu of (i) 2.645 Å by Beckmann et al.[10] using a nonempirical pseudopotential (PP) MRD-CI method, (ii) 2.295 Å by Bauschlicher et. al.[11] using a coupled pair functional (CPF) method, and (iii) 2.444 Å by Lawson et al.[12] using an ACPF method. Russon et al. obtained a bond length r_0 of 2.2625 Å[5] from resonant two-photon ionization spectroscopy (R2PI). It is seen that the HF/DFT hybrid methods B3P86, B3LYP, and B3PW91 give the best agreements with experimental results.

TABLE 1: Theoretical Bond Lengths r_e (Å) of the Ground State AM−NM Diatomic Molecules Using HF, CCSD(T), and DFT Methods[a]

	expt	HF	CCSD(T)	B88	BP86	BLYP	BHLYP	B3LYP	B3P86	B3PW91	PW91	previous calc
LiCu	2.2618(3) [5]	2.450	2.272	2.315	2.250	2.240	2.296	2.257	2.259	2.273	2.243	2.645 [10]
		(0.187)	(0.009)	(0.052)	(−0.013)	(−0.023)	(0.033)	(−0.006)	(−0.004)	(0.011)	(−0.02)	(0.383)
												2.295 [11]
												(0.033)
												2.444 [12]
												(0.182)
NaCu		2.710	2.576	2.648	2.551	2.551	2.567	2.550	2.550	2.566	2.547	2.569 [11]
KCu		3.158	2.960	3.010	2.849	2.875	2.948	2.898	2.871	2.897	2.847	2.915 [11]
LiAg	2.41 ± 0.02 [4,6]	2.560	2.406	2.451	2.371	2.369	2.414	2.382	2.377	2.394	2.368	
		(0.150)	(−0.004)	(0.041)	(−0.039)	(−0.041)	(0.004)	(−0.028)	(−0.033)	(−0.016)	(−0.042)	
NaAg		2.825	2.696	2.779	2.671	2.679	2.688	2.675	2.664	2.684	2.669	
KAg	2.40 [8]	3.266	3.086	3.161	2.989	3.021	3.069	3.031	2.999	3.026	2.989	
		(0.866)	(0.686)	(0.761)	(0.589)	(0.621)	(0.669)	(0.631)	(0.599)	(0.626)	(0.589)	
LiAu		2.378	2.270	2.342	2.285	2.283	2.295	2.284	2.281	2.288	2.275	
NaAu		2.692	2.607	2.696	2.610	2.618	2.612	2.610	2.600	2.613	2.604	
KAu		3.089	2.969	3.030	2.887	2.9210	2.953	2.927	2.895	2.913	2.884	
ξ_x[b]		7.32	0.33	2.02	1.21	1.40	1.05	0.84	0.97	0.58	1.38	

[a] Relevant experimental and previous theoretical values are also given. The differences between the theoretical and experimental values are included in parentheses. [b] We have not included the RMS % error of KAg.

TABLE 2: Theoretical Dissociation Energies D_e (eV) for the Ground State AM−NM Diatomic Molecules Using HF, CCSD(T), and DFT Methods[a]

	expt	HF	CCSD(T)	B88	BP86	BLYP	BHLYP	B3LYP	B3P86	B3PW91	PW91	previous calc
LiCu	1.95 ± 0.002 [4]	0.50	1.81	1.32	2.07	2.09	1.58	1.92	1.88	1.73	2.07	1.30 [10]
		(−1.45)	(−0.14)	(−0.63)	(0.12)	(0.14)	(−0.37)	(−0.03)	(−0.07)	(−0.22)	(0.12)	(−0.65)
												1.75 [11]
												(−0.20)
												1.45 [12]
												(−0.50)
NaCu	1.79 [13]	0.32	1.48	1.04	1.72	1.74	1.31	1.57	1.56	1.42	1.76	1.43 [11]
		(−1.47)	(−0.31)	(−0.75)	(−0.07)	(−0.05)	(−0.48)	(−0.22)	(−0.23)	(−0.37)	(−0.03)	(−0.36)
KCu		0.30	1.42	1.08	1.77	1.76	1.27	1.56	1.64	1.46	1.81	1.35 [11]
LiAg	1.89 ± 0.004 [6]	0.51	1.69	1.20	1.96	1.96	1.55	1.85	1.83	1.67	1.96	
		(−1.38)	(−0.20)	(−0.69)	(0.07)	(0.07)	(−0.34)	(−0.04)	(−0.05)	(−0.22)	(0.07)	
NaAg	≥1.59 [7]	0.34	1.40	0.98	1.66	1.66	1.29	1.52	1.54	1.40	1.69	
		(−1.25)	(−0.19)	(−0.61)	(0.07)	(0.07)	(−0.30)	(−0.07)	(−0.05)	(−0.19)	(0.10)	
KAg		0.34	1.34	1.01	1.70	1.67	1.28	1.53	1.63	1.44	1.75	
LiAu	2.92 [13]	1.23	2.75	2.13	3.00	2.94	2.45	2.82	2.85	2.68	2.99	
		(−1.69)	(−0.17)	(−0.79)	(0.08)	(0.02)	(−0.47)	(−0.10)	(−0.07)	(−0.24)	(0.07)	
NaAu	2.64 ± 0.2 [9]	0.93	2.27	1.73	2.52	2.45	2.03	2.31	2.40	2.25	2.55	
		(−1.71)	(−0.37)	(−0.91)	(−0.12)	(−0.19)	(−0.59)	(−0.33)	(−0.24)	(−0.39)	(−0.09)	
KAu	2.75 ± 0.2 [9]	1.01	2.24	1.85	2.69	2.58	2.12	2.43	2.62	2.42	2.72	
		(−1.74)	(−0.51)	(−0.90)	(−0.06)	(−0.17)	(−0.63)	(−0.32)	(−0.13)	(−0.33)	(−0.03)	
ξ_x		71.1	13.1	35.0	4.07	5.17	21.0	8.33	6.73	13.4	4.03	

[a] Relevant experimental (D_0) and previous theoretical values are also given. The differences between the theoretical and experimental values are included in parentheses.

CCSD(T) also predicts a bond length that is very close to the experimental measurement. Except for B88 and marginally for BHLYP, all the DFT functionals give better agreements with experimental results than previous ab initio calculations for LiCu. For LiAg, Brock et. al.[4] obtained a bond length of 2.41 Å by R2PI. Our DFT calculations give bond lengths in the 2.368−2.451 Å, with the best agreement being BHLYP. CCSD(T) actually predicts the closest agreement with the experimental value. For KAg, all calculations (DFT and CCSD(T)) predict a bond length in the range 2.989−3.161 Å, which is much longer than the experimental measurement of 2.40 Å by more than 0.6 Å. Yeh et al.[8] analyzed the rotational spectrum of the (0, 0) band of the more intense electronic transition to obtain the ground state bond length. However, as noted by the authors, the rotational transitions are heavily overlapped, and a trial-and-error method was used to obtain the best match between the experimental spectrum and the simulation of the contour and the few isolated peaks that were observed there. A refitting of the parameters is thus prompted using the present calculated bond lengths (and other spectroscopic constants obtained here) to see if these calculated parameters could shed some light on the analysis.

From the results listed in Table 2, we quickly notice that the dissociation energy obtained from HF calculation is the smallest among all the methods studied in this work. Upon inclusion of correlations, the calculated dissociation energies increase considerably. As in the case of bond lengths, the B88 exchange-only functional also gives dissociation energies almost 3 times larger than the HF results for the M−Cu and M−Ag series (M = Li, Na, K). The difference is less pronounced in the M−Au series, but still more than 1.5 times larger than the HF values. Among the DFT functionals, the B88 gives the smallest dissociation energy. When correlation is added to the calculations (BLYP and BP86 compared with B88), the dissociation energies increase by about 0.7 eV. When HF exchange is included in the calculation in the HF/DFT hybrid method (comparisons of BLYP, BHLYP, and B3LYP; or BP86 and B3P86), the dissociation energies decrease. The PW91 exchange

TABLE 3: Theoretical Vibrational Frequency ω_e (cm^{-1}) for the Ground State AM−NM Diatomic Molecules Using HF, CCSD(T), and DFT Methods[a]

	expt	HF	CCSD(T)	B88	BP86	BLYP	BHLYP	B3LYP	B3P86	B3PW91	PW91	previous calc
LiCu	465.9 [4]	328.8 (−137.1)	384.3 (−81.6)	364.0 (−101.9)	406.4 (−59.5)	409.4 (−56.5)	375 (−90.9)	397.5 (−68.4)	399.5 (−66.4)	389.5 (−76.4)	408.5 (−57.4)	379 [11] (−86.9) 350 [12] (−115.9)
NaCu		181	210	199	217	215	211	215	217	214	217	205 [11]
KCu		126	148	136	157	154	148	153	157	153	157	173 [11]
LiAg	389.0 [6]	315 (−74)	364 (−25)	350 (−39)	376 (−13)	373 (−16)	360 (−29)	369 (−20)	375 (−14)	367 (−22)	375 (−14)	
NaAg	210 [7]	172 (−38)	199 (−11)	178 (−32)	209 (−1)	206 (−4)	202 (−8)	207 (−3)	210 (0)	206 (−4)	209 (−1)	
KAg		117	135	123	146	140	136	140	146	141	145	
LiAu		408	464	434	469	468	455	465	469	465	473	
NaAu		211	242	217	236	234	234	235	238	235	237	
KAu		140	158	145	162	159	158	160	163	160	162	
ξ_x[b]		18.5	5.80	12.8	2.32	3.15	5.99	3.85	2.52	4.23	2.47	

[a] Relevant experimental and previous theoretical values are also given. The differences between the theoretical and experimental values are included in parentheses. [b] We have not included the RMS % error of LiCu.

functional also gives larger dissociation energies, compared with the B3 exchange functional (as comparisons between B3PW91 and PW91). From the results, we can see that the calculated dissociation energies are again more sensitive to the exchange functional than the correlation functional, just as in the case with bond length calculations. Again, CCSD(T) results fall in the range of the various DFT functionals.

Brock et. al.[4] obtained a dissociation energy D_0 of 1.95 eV for LiCu using photoionization spectroscopy. Most of our DFT calculations fall close to the experimental measurements. Previous ab initio calculations obtained values of 1.30,[10] 1.75,[11] and 1.45 eV,[12] which are much smaller than the experimental measurements. NaCu has a dissociation energy of 1.79 eV [13] and our DFT calculated dissociation energy is in the range 1.04−1.76 eV, with PW91 being the closest. Bauschlicher et al.[11] using CPF calculation obtained a dissociation energy of 1.43 eV for NaCu, which is much smaller than our DFT results with both exchange and correlation added (except B3PW91 and BHLYP). The theoretical dissociation energies of LiAg calculated using DFT functionals are in the range 1.20−1.96 eV, which is in reasonably good agreement with experimental measurement.[6] Among them, the B3LYP gives the best agreement. For NaAg, the experimental dissociation energy was found to be 1.59 eV by photoionization spectroscopy.[7] Our DFT results give dissociation energies in the range 0.98−1.69 eV. Except for B88, all the DFT values are satisfactory with the best agreements from the B3P86. In the M−Au series (M = Li, Na, K), LiAu has an experimental dissociation energy of 2.92 eV.[13] The present DFT calculations give dissociation energies in the range of 2.13−3.00 eV. The BLYP gives the best agreement with the experimental value. For NaAu and KAu, the dissociation energies were determined to be 2.64 and 2.75 eV, respectively, using R2PI.[9] Our DFT results give dissociation energies in the range 1.73−2.55 and 1.85−2.72 eV for NaAu and KAu, respectively. For both molecules, the PW91 results give the best agreement.

Theoretical vibrational frequencies of the AM−NM diatomic molecules are listed in Table 3. HF calculations give the smallest harmonic vibrational frequencies among all methods studied. Comparing the different DFT functionals shows that the B88 exchange-only functional gives the smallest vibrational frequencies. Introducing correlations in the DFT calculation increases the vibrational frequencies calculated, no matter what correlation functional was used (when B88 is compared with BLYP and BP86). As in the cases of bond lengths and dissociation energies, the HF/DFT methods adjust the pure DFT calculations in the direction as HF calculations affect the corresponding quantity. Hence, the vibrational frequencies are smaller when BLYP is compared with BHLYP and B3LYP, or BP86 and B3P86. The PW91 exchange functional gives higher vibrational frequencies than the B3 exchange functional. The calculated vibrational frequencies are again more sensitive to the change of exchange functionals than the change in correlation functional, which is just similar to the case of dissociation energy calculations. CCSD(T) results are again within the range of the various DFT calculations.

The experimental vibrational frequency of LiCu was obtained from analyzing transitions from hot bands, which was determined to be 465.9 cm^{-1}.[4] This value is larger than all the DFT results and previous ab initio values of 379 [11] and 350 cm^{-1} [12] by a considerable amount. Judging from the accuracy of our calculations, we suggest a reanalysis of the data obtained. The vibrational frequency determined for LiAg is 389 cm^{-1}.[6] Our DFT results are all smaller than this experimental value with the BP86 giving the best agreement and PW91 being the second best. NaAg had a vibrational frequency of 210 cm^{-1} from photoionization spectroscopy.[7] As in LiCu and LiAg, the DFT results of NaAg are all smaller than the experimental value. The B3P86 gives the best agreement with experiment, with PW91 again the next best one.

In summary, HF gives the longest bond length but the smallest dissociation energy and vibrational frequency. With the inclusion of correlation effects, the calculated bond lengths decrease and the dissociation energy and vibrational frequency increase. The B88 exchange-only functional gives the longest bond length and smallest dissociation energy and harmonic vibrational frequency among all DFT functionals studied in this work. Furthermore, all the calculated molecular properties are more sensitive to the change in the exchange functional than the correlation functional. The results of CCSD(T) calculations always fall in the range of the DFT functionals studied in the present work. From the RMS % errors, it can be seen that CCSD(T) gives the best agreement of equilibrium bond lengths with experimental values, whereas PW91 gives closest agreements with the experimental dissociation energies and vibrational frequencies. When the overall performances are compared, PW91 and BP86 have the smallest RMS % errors, following by BLYP, B3P86, and B3LYP. Though the pure DFT methods PW91 and BP86 give good estimates of the dissociation energies and vibrational frequencies with experimental values, they underestimate the bond lengths. CCSD(T) gives good agreement on the bond lengths but underestimates the dissociation energies and vibra-

TABLE 4: Effective Nuclear Charge Z_{eff}[a] on the Alkali Metal Atom for the Ground State AM−NM Diatomic Molecules Using HF, CCSD(T), and DFT Methods

	HF	CCSD(T)	B88	BP86	BLYP	BHLYP	B3LYP	B3P86	B3PW91	PW91
LiCu	0.30	0.31	0.44	0.47	0.46	0.40	0.42	0.46	0.44	0.45
NaCu	0.33	0.34	0.42	0.46	0.43	0.39	0.42	0.45	0.44	0.44
KCu	0.51	0.52	0.53	0.58	0.54	0.54	0.55	0.58	0.57	0.55
LiAg	0.27	0.28	0.41	0.45	0.44	0.38	0.42	0.44	0.42	0.43
NaAg	0.31	0.31	0.39	0.44	0.41	0.38	0.40	0.43	0.42	0.42
KAg	0.49	0.50	0.51	0.56	0.53	0.53	0.54	0.57	0.56	0.54
LiAu	0.48	0.48	0.55	0.58	0.56	0.53	0.56	0.57	0.56	0.56
NaAu	0.52	0.52	0.56	0.60	0.57	0.55	0.57	0.60	0.60	0.58
KAu	0.66	0.66	0.65	0.69	0.66	0.67	0.67	0.69	0.69	0.66

[a] Z_{eff} = dipole moment divided by bond length, μ_e/r_e.

TABLE 5: Calculated Dipole Moments (Debye) for the Ground State AM−NM Diatomic Molecules Using HF, CCSD(T), and DFT Methods

	HF	CCSD(T)	B88	BP86	BLYP	BHLYP	B3LYP	B3P86	B3PW91	PW91
LiCu	3.51	3.37	4.83	5.03	4.87	4.39	4.48	4.90	4.79	4.81
NaCu	4.23	4.13	5.26	5.55	5.20	4.79	5.10	5.42	5.38	5.36
KCu	7.70	7.32	7.58	7.83	7.41	7.56	7.56	7.94	7.93	7.51
LiAg	3.33	3.22	4.83	5.12	4.95	4.37	4.79	4.94	4.80	4.90
NaAg	4.17	4.01	5.15	5.55	5.18	4.80	5.11	5.45	5.38	5.37
KAg	7.69	7.35	7.63	8.02	7.57	7.71	7.72	8.13	8.09	7.69
LiAu	5.43	5.19	6.15	6.26	6.08	5.84	6.03	6.18	6.13	6.06
NaAu	6.69	6.48	7.16	7.50	7.05	6.90	7.07	7.46	7.42	7.21
KAu	9.74	9.36	9.43	9.43	9.15	9.43	9.33	9.56	9.55	9.05

tional frequencies. Thus, to obtain reasonable results of the spectroscopic parameters of the AM−NM diatomics, the HF/DFT hybrid functionals B3P86 and B3LYP seem to be the better choices.

B. Chemical Bonding in These Mixed Metal Diatomic Molecules. From our results in Table 1, we notice that the bond lengths increase down the alkali metal group and the bond lengths increase from Cu to Ag but decrease from Ag to Au. Such a pattern follows from the atomic radii of the metals. As one goes down the alkali metal group, the atomic radius increases, and thus the bond length is expected to increase down the alkali metal group. One might initially be surprised by the longer bond lengths of the AM−Ag as compared to the AM−Au, this is precisely what should be expected on the basis of the radial expectation values of *n*s as one moves down the noble metal group: 4s < 5s > 6s. Such a result is due to the strong relativistic effects in Au such that the 6s orbital contracts.

Concomitant to the increase in bond length down the alkali metal group, the vibrational frequencies decrease, as can be seen in Table 3. Because ω_e is inversely proportional to the square root of the reduced mass μ, as one goes down the alkali metal group, the reduced mass increases and, hence, the vibrational frequency decreases down the group. If we follow the same reasoning, we would expect also a decrease in vibrational frequency down the group IB. However, this is actually not the case, but it is in the order AM−Au > AM−Cu > AM−Ag. This is because ω_e is also proportional to the square root of the force constant, *k*. Due to the large relativistic effects and poor screening of the *f* electrons in Au, the 6s orbital experiences a larger effective nuclear charge and becomes more compact. To form a strong chemical bond, a significant accumulation of electron density must occur between the constituent atoms as they are brought together. Such an accumulation of electron density is favored by compact bonding orbitals (as in the cases of Cu and Au) but is disfavored when more diffuse orbitals are involved (as in the case of Ag). Moreover, as the electronegativity is much larger in Au (2.54) than Cu and Ag (1.90 and 1.93, respectively), the AM−Au diatomics have a much stronger ionic character than the Cu and Ag analogues, further strengthening the chemical bond. Hence, the bond strength is in the order AM−Au > AM−Cu > AM−Ag (AM = Li, Na, K). As the reduced mass changes slightly down the noble metal group, the force constant factor outweighs the reduced mass effect.

For the dissociation energies, the trend is Li−NM > K−NM > Na−NM and AM−Au > AM−Cu > AM−Ag. The trend observed down the NM group can be explained by the increase in bond strength as discussed above. However, the anomalous trend in the AM series is best explained by the much lower ionization potential (IP) of the alkali metals, which places the lowest separated ion asymptote much closer to the ground state atoms. (IP: Li, 5.40; Na, 5.15; K, 4.35 eV) As a result, there is a considerable contribution coming from ionic configurations for the K−NM diatomics. This ion-pair character makes the ground state bound much more deeply and hence a stronger bond resulted. Thus, besides the spatial extent that affects the bond strength, the ion-pair effects also contribute to the bond strength, and hence the trend in dissociation energies is in the above order. Such a trend is not observed in the vibrational frequencies because the reduced mass effect outweighs the bond strength one.

The alkali metal forms a very polarized s−s bond with the noble metal, as can be seen from the large effective nuclear charges Z_{eff} and large dipole moments of the AM^+NM^- shown in Tables 4 and 5, respectively. In general, the wave function based methods predict a smaller effective nuclear charge than the DFT methods. For the K−NM, the difference is actually marginally small. All the methods considered here give a similar qualitative description of the bond. The Li−NM and Na−NM have similar Z_{eff}, whereas K−NM has a much larger Z_{eff}. It may be due to the similar electronegativity values of Li (0.98) and Na (0.93), but it is much smaller for K (0.82) such that K−NM's are the most ionic for the three alkali metals considered in the present study. Similarly, AM−Cu and AM−Ag have similar Z_{eff}, but AM−Au have much larger Z_{eff} due to the larger electronegativity of Au (2.54) than both Ag (1.93) and Cu (1.90), which are close, and hence, the AM−Au have the highest ionic character.

Table 6 summarizes the calculated ionization potential energies (IP) of the alkali metals and the electron affinities (EA) of the noble metals, together with the experimental data.[28] An

TABLE 6: Calculated Ionization Potential Energies (IP) of the Neutral Ground State Alkali Metal Atoms and the Electron Affinities (EA) of the Neutral Ground State Noble Metal Atoms Using HF, CCSD(T), and DFT Methods.[a]

	expt[b]	HF	CCSD(T)	B88	BP86	BLYP	BHLYP	B3LYP	B3P86	B3PW91	PW91
IP(Li)	5.40	5.32	5.34	5.33	5.53	5.50	5.49	5.56	5.96	5.54	5.58
IP(Na)	5.15	4.93	5.04	5.07	5.31	5.33	5.25	5.40	5.71	5.26	5.36
IP(K)	4.35	3.99	4.31	4.16	4.46	4.41	4.32	4.48	4.78	4.35	4.45
ξ_x		5.39	1.48	2.73	2.80	2.53	1.59	3.82	10.5	1.95	3.39
EA(Cu)	1.23	0.02	1.08	0.75	1.48	1.38	0.93	1.30	1.69	1.13	1.37
EA(Ag)	1.30	0.10	1.10	0.78	1.54	1.42	1.02	1.38	1.79	1.21	1.42
EA(Au)	2.31	0.62	1.81	1.55	2.42	2.26	1.76	2.19	2.66	2.08	2.33
ξ_x		88.5	17.0	37.7	16.1	8.99	23.4	5.63	31.8	8.68	8.70

[a] Experimental values are given for reference.[28] The units are in eV. [b] Reference 28.

TABLE 7: Theoretical IP(AM) − EA(NM) Gap (eV) for the Ground State AM−NM Diatomic Molecules Using HF, CCSD(T), and DFT Methods

	IP(AM) − EA(NM)[a]	HF	CCSD(T)	B88	BP86	BLYP	BHLYP	B3LYP	B3P86	B3PW91	PW91
LiCu	4.17	5.30	4.26	4.59	4.05	4.12	4.56	4.26	4.26	4.41	4.21
NaCu	3.92	4.91	3.95	4.32	3.83	3.95	4.32	4.10	4.02	4.13	3.98
KCu	3.12	3.97	3.23	3.41	2.97	3.03	3.39	3.18	3.09	3.22	3.07
LiAg	4.10	5.22	4.24	4.55	3.99	4.08	4.47	4.18	4.17	4.33	4.16
NaAg	3.84	4.82	3.94	4.29	3.78	3.91	4.23	4.03	3.93	4.05	3.93
KAg	3.04	3.89	3.21	3.38	2.92	2.99	3.30	3.10	2.99	3.15	3.03
LiAu	3.09	4.70	3.53	3.79	3.12	3.24	3.73	3.37	3.37	3.30	3.46
NaAu	2.83	4.31	3.23	3.52	2.90	3.08	3.49	3.21	3.06	3.18	3.03
KAu	2.03	3.37	2.50	2.61	2.04	2.16	2.56	2.29	2.12	2.28	2.12
ξ_x		44.9	11.9	19.3	3.07	4.66	17.6	8.32	4.69	9.15	4.01

[a] The experimental IP(AM) and EA(NM) from ref 28 have been used to evaluate these differences.

analysis involving the IP and EA may be useful to judge whether the calculated results exaggerated the ionic character of the AM−NM chemical bond. All the methods give quite good estimates of the IPs of the AM's (within ~5% error) except B3P86 and HF, which have errors of more than 10% and 8%, respectively. CCSD(T) gives the best estimation of IP and the BHLYP is the second best. On the other hand, both wave function based and DFT methods employed here with the present basis sets do not have as good agreements of NM EAs as that of AM IPs with experimental values. At best, it has 5% error (B3LYP), but the worst can be as much as 98% (HF). Even correlated methods such as CCSD(T) may have errors up to 12%. The performance of B3P86 is again the poorest among all the correlated methods discussed here (more than 37% error).

The ionic contribution to the chemical bond will be the greatest with small AM IP and large NM EA.[9] Hence, it should be useful to look at the IP(AM) − EA(NM) gap (the energy separation between the ion pair asymptote and the neutral ground state atoms asymptote) instead of individual IPs and EAs: the smaller the IP(AM) − EA(NM) gap, the higher the ionic character of the chemical bond. The IP(AM) − EA(NM) gaps of the AM−NM diatomic molecules are shown in Table 7. Though B3P86 gives a poor estimation of both IP(AM) and EA(NM), it has good agreement with the experimentally derived gaps. This is also the case for BP86, which gives only fair agreement with individual IP(AM) and EA(NM) but the best agreements of the measured gap. Such agreements could result from a cancellation of errors in the IP(AM) and EA(NM). On the contrary, CCSD(T) and B3LYP give the best estimates of IP(AM) and EA(NM), respectively; they give only fair agreement with the gaps as the former underestimates EA(NM) and the latter overestimates IP(AM) too much.

IV. Conclusions

We have shown that, in this study, many of the DFT methods with only medium sized basis sets and small core RECPs give comparable or even superior results than ab initio methods (MRD-CI PP, SDCI, CPF, MRCI-SD, and ACPF) for the AM−NM diatomic molecules. Although CCSD(T) is the most accurate in predicting the bond lengths of this class of molecules, it is computationally expensive and time-consuming. DFT is less computationally demanding, which makes it a suitable tool for computing molecular properties of mixed metal systems. The best functional choice among all the eight density functionals studied is the hybrid B3P86, followed by B3LYP. The pure functionals PW91 and BP86 actually give a better prediction of the dissociation energies and vibrational frequencies. This is in contrast with the previous DFT calculations for transition metal (TM) dimers,[29,30] where it was found that the hybrid density functionals were less accurate than the pure functionals in predicting the bond lengths. In TM dimers, B3LYP generally gives accurate dissociation energies than those of the pure density functionals. We suggest a detailed theoretical study to examine the TM containing molecules with different density functionals to find out which of them is the most appropriate for these molecules. Moreover, the agreement between DFT calculations and experimental measurements of TM containing molecules is still behind that for diatomic molecules formed from first or second row main group elements in the periodic table. It seems that a parametrization with TM may be necessary to achieve the same success.

Acknowledgment. We thank Dr. G. H. Jeung for critically reading the manuscript. The work described here was supported by grants from the Committee on Research and Conference Grants of the University of Hong Kong.

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