Theoretical study of the neutral and ionic states of hypermetalated potassium compounds K_2OH and K_2NH_2 and potassium complexes KH_2O and KNH_3

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Ab initio molecular orbital calculations are reported for potassium-containing hypermetalated compounds of K_2OH and K_2NH_2 , and potassium–Lewis-base complexes of KH_2O and KNH_3 , the corresponding positive ions were also studied. The optimized equilibrium geometries, the harmonic vibrational frequencies, the bond dissociation energies, and the adiabatic ionization potentials are reported for these compounds. The similarities and the differences of these physical and chemical properties of the neutral and its positive ionic states are discussed. These theoretical findings were also compared with the theoretical and experimental results reported in the literature. The unique bonding properties of the hypermetalated compounds were specifically investigated by electron density deformation maps.

1. Introduction

The hypermetalated compounds of alkali atoms and the molecular complexes formed between alkali atom and Lewis base molecule, such as the water or ammonia molecules, have attracted attention of both theoretical and experimental researchers in the past decade. On the theoretical side, the predictions of the moderate interaction between alkali atom and Lewis base molecule have been reported by quite a few groups [1–9]. The energetic stability and the nature of bonding of some hypermetalated compounds of lithium and sodium were also studied [10–13]. On the experimental side, clusters formed between the sodium atom and water clusters or ammonia clusters have been generated by pickup source and studied by photoionization mass spectrometer [14,15]. Hypermetallic oxide compounds of sodium, potassium and cesium have been investigated by the same technique [16–18]. More recently, some hypermetallic hy-

droxyl compounds of potassium were also been reported [19,20]. These gas-phase studies gave us information on the ionization potentials and sometimes bond energies of these compounds. However, none of these gas-phase studies have yielded further spectroscopic information, such as the vibrational or rotational data of neutral species. Up to date the only vibrational information available was from the IR studies on the matrix-isolated alkali-atom–water/ammonia complexes [21–24]. Nevertheless, these vibrational data are still far from complete. In these experiments the major experimental difficulty is to generate a high enough concentration of these complexes either in the gas phase or being trapped in a low temperature matrix for good spectroscopic measurements.

Restricting ourselves to the potassium-containing species, there was only one report on the electrostatic calculation of KH_2O complexes and an equilibrium bond dissociation energy of 5.0 kcal/mol was pre-

dicted [6]. No *ab initio* calculations were reported on the bond energies and the vibrational frequencies of KH_2O and KNH_3 . For the hypermetalated hydroxyl compounds, the sodium species has been studied and the nature of the chemical bonding also has been elucidated theoretically [12]. There were no reports on the corresponding potassium compounds. The simplest hypermetalated amide K_2NH_2 was not studied theoretically either.

As for the potassium-containing ionic species, in experiments, the best-studied physical quantities are their enthalpies of complex formation. These include $\text{K}^+\text{H}_2\text{O}$ [25,26], K^+NH_3 [26,27], and K_2^+OH [28]. The other physical properties were not yet reported. On the theoretical side, there were only one Hartree-Fock calculation on $\text{K}^+\text{H}_2\text{O}$ [29] and some electrostatic calculations on both $\text{K}^+\text{H}_2\text{O}$ and K^+NH_3 [26,30]. In these studies the bonding energies and the vibrational frequencies were calculated at somewhat lower levels of sophistication. Further studies on the physical pictures of these ions are needed.

In light of the recent experimental progress on the potassium-containing hypermetalated compounds and the potassium-atom- $\text{H}_2\text{O}/\text{NH}_3$ molecular complexes, which have been carried out in the gas phase and also in the matrix-isolated form, we embarked upon the present theoretical study. The reported molecules are KH_2O , $\text{K}^+\text{H}_2\text{O}$, KNH_3 , K^+NH_3 , K_2OH , K_2^+OH , K_2NH_2 , and K_2^+NH_2 . This study serves as a theoretical check of the present available experimental results and also as a guide for further experimental studies.

2. Computational methods

All *ab initio* molecular orbital calculations were carried out with either restricted or unrestricted Hartree-Fock theory using the GAUSSIAN 90 package of computer codes [31]. Electron correlation was calculated by Møller-Plesset perturbation theory up to the second order (MP2).

For the hydrogen atom, the contracted [2s] basis of Salez and Veillard [32] from the Huzinaga (6s) basis set [33] was used. For the nitrogen and oxygen atoms, the contracted [5s, 3p] basis sets of Gianolio et al. [34] from van Duijneveldt's (13s, 8p) basis sets [35] were used. A p-type polarization function

set was added to the H basis set and a d-type polarization function set was added to the N and O basis sets, respectively, in the same way as the standard 6-311G** [31]. The potassium basis set was adapted from the Wachters' contracted [8s, 4p] set of the (14s, 9p) basis set [36]. For the potassium atom, polarization functions were not added in the calculations of geometries and vibrational frequencies. In the final calculations of the bond dissociation energies and ionization energies, the (2d) set of polarization functions of Klein et al. [37] was also included in the potassium basis set.

With these basis sets, KOH , H_2O and NH_3 were first calculated up to the MP2 level. The equilibrium geometries of KOH agree with the best available theoretical results to within 2.6% [38]. The electric dipole moment agrees with each other to within 8%. These previous theoretical results have an estimated accuracy of 2% [38]. The harmonic vibrational frequencies of H_2O and NH_3 agree with the experimental harmonic vibrational frequencies to within 2.5% [39,40]. The equilibrium geometries of NH_3 and H_2O agree with the experimental results to within 0.6%.

In the present report, KH_2O , KNH_3 , K_2OH and K_2NH_2 and their ionic states are studied. The equilibrium geometries, the harmonic vibrational frequencies, the bond dissociation energies, and the adiabatic and vertical ionization potentials were calculated. All the calculations were done up to MP2 level and the geometries were also optimized at MP2 level. For completeness, the bond dissociation energies and the ionization potentials were then calculated at these optimized geometries with the potassium basis set augmented with the d-type polarization functions. In the course of the calculations of KNH_3 and K^+NH_3 , the symmetries of the highest occupied doubly degenerate molecular orbitals, the e symmetry of C_{3v} , were undetermined by the available program. In these cases the symmetries were determined directly by the inspection of the molecular orbital maps. The energies of these molecular orbitals and the other physical quantities converge normally.

3. Results and discussion

3.1. KH_2O , KNH_3 , $\text{K}^+\text{H}_2\text{O}$, and K^+NH_3 molecular complexes

The physical and chemical properties of the potassium complexes are listed in the upper halves of tables 1, 2, 3, 6, and 7 and the whole of tables 4 and 5. They are discussed in the following categories.

3.1.1. Structures and bonding

The upper part of table 2 lists the equilibrium geometries of these potassium complexes obtained at MP2 level. Comparing the equilibrium geometries of free H_2O and NH_3 with those of the corresponding potassium molecular complexes and ions, one finds that these ligands only undergo minor changes during the formation of these potassium neutral or ionic complexes. This is a direct consequence of the comparatively weak interactions between K or K^+ with the water or ammonia molecules. In the case of H_2O , there is only a slight decrease of the HOH angle and a little increase of the OH distance in the formation of the potassium complexes. The ammonia molecule behaves similarly. The changes of the internuclear equilibrium distance between K and O or K and N as one goes from the neutral to the positive ionic state are minor too. This result also ensures that in the photoionization studies of these simple systems, the

adiabatic ionization potential would be close to the threshold ionization potential one usually measured in the experiments.

The LiH_2O complex has been reported to be non-planar with a bending angle of 40.1° between the Li–O and the H_2O plane [8]. The NaH_2O complex also has a bending angle of 46.2° . The present study, with the K basis augmented with d-type polarization functions and calculated up to MP2 level, yields a planar structure for KH_2O . In the paper of Broughton and Bagus [7], RbH_2O has been assumed to be in the planar form. The optimized geometry of RbH_2O has not been reported yet. For these alkali-atom–water molecule systems, the interaction potential along the bending angle is rather flat. A conclusive resolution of the correctness of this trend of the bending angles may eventually require some spectroscopic experiments in the gas phase. As for the ammonia complexes, a geometry of C_{3v} was always obtained.

There have been quite a few theoretical discussions on the nature of the bonding between an alkali atom and a H_2O or NH_3 molecule [1–9]. The stabilities of these complexes have been attributed to several factors: the electron correlation effect in the complexes, the charge polarization on the metal atom, the charge transfer from the Lewis base to the metal atom and the electrostatic interaction of the unperturbed molecular charge distributions. According to the result of the latest theoretical studies, the re-

Table 1
Total energies (au) of potassium-containing compounds

Species	State	Symmetry	Energy	
			HF	MP2
K	^2S		–599.1428761	–599.2645937
K^+	^1S		–598.9960480	–599.1177747
H_2O	$^1\text{A}_1$	C_{2v}	–76.0563505	–76.2910626
NH_3	$^1\text{A}_1$	C_{3v}	–56.2160117	–56.4306848
KH_2O	$^2\text{A}_1$	C_{2v}	–675.2061796	–675.5641528
$\text{K}^+\text{H}_2\text{O}$	$^1\text{A}_1$	C_{2v}	–675.0801899	–675.4361878
KNH_3	$^2\text{A}_1$	C_{3v}	–655.3657902	–655.7041878
K^+NH_3	$^1\text{A}_1$	C_{3v}	–655.2402027	–655.5768208
K_2OH	$^2\text{A}_1$	C_{2v}	–1273.7838178	–1274.2706513
K_2^+OH	$^1\text{A}_1$	C_{2v}	–1273.6872233	–1274.1719717
KOH	$^1\Sigma^+$	$\text{C}_{\infty v}$	–674.6157197	–674.9798304
K_2NH_2	$^2\text{A}_1$	C_{2v}	–1253.9088100	–1254.3787257
K_2^+NH_2	$^1\text{A}_1$	C_{2v}	–1253.8103360	–1254.2769801
KNH_2	$^1\text{A}_1$	C_{2v}	–654.7414354	–655.0872440

Table 2

Geometry index (results of MP2)

Species	Bond length (Å)		Interatomic angle	
	KO or KN	OH or NH		
H ₂ O (C _{2v})		0.964	∠ (HOH) = 104.2°	
NH ₃ (C _{3v})		1.015	∠ (HNN) = 107.1°	
KH ₂ O (C _{2v})	2.770	0.966	∠ (KOH) = 127.8°	
K ⁺ H ₂ O (C _{2v})	2.725	0.966	∠ (KOH) = 128.4°	
KNH ₃ (C _{3v})	2.977	1.018	∠ (KNH) = 112.8°	
K ⁺ NH ₃ (C _{3v})	2.916	1.019	∠ (KNH) = 114.1°	
KOH (C _{∞v})	2.346	0.961	∠ (KOH) = 180.0°	
K ₂ OH (C _{2v})	2.524	0.966	∠ (KOH) = 121.9°	∠ (KOK) = 116.2°
K ₂ ⁺ OH (C _{2v})	2.562	0.967	∠ (KOH) = 108.1°	∠ (KOK) = 143.8°
KNH ₂ (C _{2v})	2.535	1.023	∠ (KNH) = 129.2°	
K ₂ NH ₂ (C _{2v})	2.710	1.027	∠ (KNK) = 107.3°	∠ (HNN) = 101.5°
K ₂ ⁺ NH ₂ (C _{2v})	2.720	1.027	∠ (KNK) = 137.4°	∠ (HNN) = 101.1°

ported Mulliken populations of LiH₂O, NaH₂O, and RbH₂O indicate that the charge transfer from H₂O to the metal atoms are 0.079e, 0.062e, and <0.05e [7,9], respectively. The present study obtains a charge transfer of 0.025e for KH₂O and 0.029e for KNH₃. The reported theoretical dipole moment enhancements (in debye), the electric dipole moment difference between the complexes and the base molecules, are: 3.7 [6] or 3.0 [8] (LiH₂O), 3.3 (NaH₂O) [6], 4.1 (LiNH₃) [2], and 3.3 (NaNH₃) [2]. In the present study the dipole moment enhancements are 1.0 and 1.4 for KH₂O and KNH₃, respectively. The theoretical equilibrium bonding energies (kcal/mol) of these complexes are 13.8 (LiH₂O) [8], 7.4 (NaH₂O) [9], 5 (RbH₂O) [7], 14.5 (LiNH₃) [2], and 6.0 (NaNH₃) [2]. As shown in table 6, the present study yields 7.2 for KH₂O and 7.5 for KNH₃.

Some of the classifications of the above interaction forces have their origin in the classical electromagnetic theory. However, by ab initio molecular orbital methods, for instance, one can not unambiguously distinguish the charge-density shift due to the charge-transfer factor from the shift due to the dipole-induced-dipole factor. In this study we shall use the charge transfer obtained by Mulliken population analysis as a measure of the charge-transfer factor and the classical dipole-induced-dipole interaction between the dipole moment of the Lewis base molecule and the alkali atom as a measure of the dipole-induced-dipole factor [9]. Here the general trend of the

interaction strengths instead of their absolute values is emphasized.

Following the procedure of ref. [9], the dipole-induced-dipole interaction energy is [41]

$$E(r) = -\mu_{\text{LB}}^2 \alpha_{\text{M}} (1 + 3 \cos^2 \theta) / 2r^6, \quad (1)$$

in which μ_{LB} is the dipole moment of the Lewis base molecule, α_{M} is the polarizability of the alkali atom, θ is the angle between the dipole moment and the alkali metal atom, and r is the distance between the alkali atom and the center of the dipole. The dipole moments of H₂O and NH₃ are 1.85 and 1.47 D, respectively. The polarizabilities of the alkali atoms are 24.3, 23.6, 43.4 and 47.3 Å³ for Li, Na, K, and Rb, respectively [42]. Adapting the experimental geometries of H₂O and NH₃ and the theoretical bonding distances between the alkali atom and H₂O or NH₃, one obtains the dipole-induced-dipole interaction energies (kcal/mol): Li-H₂O (−14.8), Na-H₂O (−4.3), K-H₂O (−5.2), Rb-H₂O (−4.3), Li-NH₃ (−11.3), Na-NH₃ (−2.3), and K-NH₃ (−2.7). The general trend of the above data suggests that the charge polarization of the alkali atom by a Lewis base molecule, electron correlation effect, and electrostatic interactions are all playing important roles in the stabilization of the potassium complexes. The charge-transfer process, an important stability factor in the Li and Na complexes, becomes less important in the K and Rb cases. As for the ionic species, the major bonding force is electrostatic interaction be-

tween the alkali ion and the Lewis base molecule.

3.1.2. Harmonic vibrational frequencies

The upper part of table 3 lists the normal mode harmonic vibrational frequencies of KH_2O , KNH_3 , $\text{K}^+\text{H}_2\text{O}$ and K^+NH_3 . The vibrational frequency shifts of water and ammonia in both K and K^+ complexes are tabulated in tables 4 and 5. The experimental harmonic vibrational frequencies of the isolated water and ammonia are also listed in tables 4 and 5. The only reported experimental vibrational spectra were those of matrix-isolated KH_2O and KNH_3 measured by the IR spectroscopy [23,24]. Up to date there have been no reports on the experimental vibrational frequencies of the ionic species yet. As indicated in tables 4 and 5, the theoretical and experimental harmonic vibrational frequencies of NH_3 and H_2O agree with each other to within 2.3%. A direct comparison of the present harmonic vibrational frequencies of free-form molecular complexes with the observed vibrational frequencies of the matrix-isolated complexes would not tell one the goodness of the agreements between these two sets of results. A comparison of the H_2O and NH_3 vibrational frequency shifts in KH_2O or KNH_3 between the theoretical and the experimental results could offer better insight. Except for the bending mode of H_2O in which the experiment shows a -5 cm^{-1} shift (but the theory predicts a 14 cm^{-1} shift), the results agree very well. The reasons for the disagreement, although comparatively small in the absolute magnitude, may come from the theoretical inaccuracy in correctly predicting the minimum position of the bending angle between the plane of H_2O and the $\text{K}-\text{O}$ bond, because of the flatness of the potential along this coordinate, or it may just come from the change of the equilibrium geometry of the complex due to the presence of the rare-

gas matrix in the matrix experiments. Further works, especially some experiments of the gas-phase vibrational analysis, are needed to clarify these disagreements.

Generally speaking, the tables show that, in the case of H_2O , there is an increase in the frequency of the bending mode and a decrease in the frequencies of both symmetric and antisymmetric stretching modes in the formation of both the neutral and ionic potassium complexes. For the NH_3 molecule, however, the frequency shifts are somewhat more complicated. For the KNH_3 complexes, there is an increase in the $a_1(\nu_2)$ mode, and a decrease for the other normal modes. For the K^+NH_3 ion, both the $a_1(\nu_2)$ and $e(\nu_4)$ normal modes show blue frequency shifts and the rest two modes have red frequency shifts. The vibrational frequencies of $\text{K}^+\text{H}_2\text{O}$ have been calculated before through simplified Hartree-Fock potential by Kistenmacher et al. [29]. The six vibrational frequen-

Table 4
Harmonic vibrational frequency shifts of $\text{K}-\text{H}_2\text{O}$ and $\text{K}^+-\text{H}_2\text{O}$ (cm^{-1})

Symmetry		$a_1(\nu_2)$	$a_1(\nu_1)$	$b_1(\nu_3)$
H_2O	HF	1732	4131	4238
	MP2	1623	3841	3975
	exp. ^{a)}	1648	3832	3943
KH_2O	HF	1751	4102	4204
	MP2	1637	3798	3928
	$\Delta\nu$	HF	19	-29
$\Delta\nu$	MP2	14	-43	-47
	exp. ^{b)}	-5	-39	
$\text{K}^+\text{H}_2\text{O}$	HF	1789	4104	4185
	MP2	1682	3827	3929
	$\Delta\nu$	HF	57	-27
$\Delta\nu$	MP2	59	-14	-46

^{a)} Ref. [39]. ^{b)} Ref. [24].

Table 3
Harmonic vibrational frequencies (MP2) (cm^{-1})

KH_2O	170 (a_1)	238 (b_2)	265 (b_1)	1637 (a_1)	3798 (a_1)	3928 (b_1)			
$\text{K}^+\text{H}_2\text{O}$	200 (a_1)	375 (b_1)	427 (b_2)	1682 (a_1)	3827 (a_1)	3929 (b_1)			
KNH_3	157 (a_1)	293 (e)	1156 (a_1)	1659 (e)	3461 (a_1)	3613 (e)			
K^+NH_3	189 (a_1)	399 (e)	1262 (a_1)	1673 (e)	3481 (a_1)	3607 (e)			
K_2OH	72 (a_1)	228 (b_1)	275 (a_1)	336 (b_2)	473 (b_1)	3869 (a_1)			
K_2^+OH	87 (a_1)	221 (a_1)	336 (b_2)	352 (b_1)	582 (b_1)	3843 (a_1)			
K_2NH_2	70 (a_1)	252 (b_2)	258 (a_1)	299 (b_1)	362 (a_2)	485 (b_2)	1541 (a_1)	3410 (a_1)	3501 (b_1)
K_2^+NH_2	77 (a_1)	206 (a_1)	296 (b_1)	313 (b_2)	471 (a_2)	554 (b_2)	1543 (a_1)	3412 (a_1)	3499 (b_1)

Table 5
Harmonic vibrational frequency shifts of K–NH₃ and K⁺–NH₃ (cm^{−1})

Symmetry		a ₁ (ν ₂)	e(ν ₄)	a ₁ (ν ₁)	e(ν ₃)
NH ₃	HF	1083	1785	3686	3821
	MP2	1043	1665	3502	3660
	exp. ^{a)}	1022	1691	3506	3577
KNH ₃	HF	1202	1785	3660	3786
	MP2	1156	1659	3461	3613
Δν	HF	119	0	−26	−35
	MP2	113	−6	−41	−47
	exp. ^{b)}	90		−54	
K ⁺ NH ₃	HF	1323	1795	3666	3770
	MP2	1262	1673	3481	3607
Δν	HF	240	10	−20	−51
	MP2	219	8	−21	−53

^{a)} Ref. [40]. ^{b)} Ref. [23].

cies in their report were (in cm^{−1}): ν₁=3714.2, ν₂=1631.8, ν₃=176.1, ν₄=3769.0, ν₅=398.2 and ν₆=444.3. For these ionic species Kibarle and co-workers also developed an electrostatic model for the calculations of the vibrational frequencies [26,30]. Following their general procedure in determining the interaction potential between the potassium ion and a ligand, and assuming that the vibrational force constants and the geometry of the ligand remain unchanged in the formation of the complex, one can obtain the vibrational frequencies of K⁺H₂O to be: ν₁=3698, ν₂=1612, ν₃=211, ν₄=3792, ν₅=490 and ν₆=407 cm^{−1} and the vibrational frequencies of K⁺NH₃ to be: ν₁=3351, ν₂=1159, ν₃=2.16, ν₄=3440, ν₅=1547 and ν₆=263 cm^{−1}. Here the force constants of the H₂O molecule are set at the fundamental vibrational frequencies of ν₁=3652, ν₂=1595, and ν₃=3756 cm^{−1} and those of the NH₃ molecule are set at ν₁=3337, ν₂=950, ν₃=3414, and ν₄=1628 cm^{−1} [40]. Additionally, in all these electrostatic calculation the intramolecular potential functions were assumed to be in the form of valence forces [43]. Comparing these theoretical results with those of the present study, one finds that, for the K⁺H₂O ion, the results of Kistenmacher et al. has a better agreement with the present values than those obtained by electrostatic model. Similarly, for the case of K⁺NH₃, the agreement between the results of electrostatic model and the present values is at best only fair. If one looks further into the vibrational frequency shifts of H₂O and NH₃ in the formation of the ionic complexes, ex-

cept for the ν₂ mode of H₂O and the ν₂ mode of NH₃, the electrostatic model even predicts opposite shift directions for the rest of the vibrational modes, let along the shift magnitudes. In short, the electrostatic model, if considered at the present level of sophistication, is not adequate in doing the vibrational normal mode analysis.

3.1.3. Bond dissociation energies and ionization potentials

There are three commonly used measures for the bond strength of a molecule: equilibrium bond dissociation energy (*D_e*), bond dissociation energy (*D₀*) and the enthalpy of bond dissociation (*ΔH_T⁰*, *T*=absolute temperature). In the case that a molecular complex dissociates into an atomic species and a molecule, to a good approximation, these three quantities are related with each other through statistical mechanics by the following relations:

$$\begin{aligned} \Delta H_T^0 = & D_c + \frac{5}{2}RT \\ & + \sum_{\text{products}} \sum_i^n \frac{1}{2}N h \nu_i - \sum_{\text{reactants}} \sum_i^m \frac{1}{2}N h \nu_i \\ & + RT^2 \left(\sum_{\text{products}} \sum_i^n \frac{\partial \ln Q_{\nu_i}}{\partial T} - \sum_{\text{reactants}} \sum_i^m \frac{\partial \ln Q_{\nu_i}}{\partial T} \right), \end{aligned} \quad (2)$$

with *N*=Avogadro number, *R*=gas constant, and

$$Q_v = \prod_i^n [1 - \exp(-h\nu_i/kT)]^{-1},$$

the vibrational partition function. D_0 and D_e are related by

$$D_0 = D_e + \sum_{\text{products}} \sum_i^n \frac{1}{2} N h \nu_i - \sum_{\text{reactants}} \sum_i^m \frac{1}{2} N h \nu_i. \quad (3)$$

In thermodynamic measurements, one usually obtained ΔH_f^0 over a certain range of temperature. In the experiments of photoionization, photodissociation, or spectroscopic measurements, the directly related energy quantity is D_0 . However, for theoretical studies, the first obtained energy quantity is D_e . In this report all the data are adjusted to D_0 with the help of the above equations and the theoretical harmonic vibrational frequencies. These results are listed in the upper part of table 6. The agreement between the theoretical values and the experimental results is

within the experimental uncertainties. The theoretical vertical and adiabatic ionization energies of these complexes are listed in table 7. The agreement between the theoretical values and the experimental results is only fair. We shall come back to this point in the end of this section.

3.2. K_2OH , K_2NH_2 , K_2^+OH , and $K_2^+NH_2$ hypermetalated potassium compounds

The physical and chemical properties of the bi-potassium systems are listed in the lower parts of tables 1, 2, 3, 6 and 7. They are discussed in the following categories:

3.2.1. Structures and bonding

Comparing the equilibrium geometries of the neutral species and their positive ionic states, one finds

Table 6
Theoretical and experimental dissociation energies (kcal/mol)

Reactions	Theoretical						Experimental D_0 ^{b)}
	D_e (HF)	D_e (HF*) ^{a)}	D_e (MP2)	D_e (MP2*) ^{a)}	D_0 (HF*) ^{a)}	D_0 (MP2*) ^{a)}	
$KH_2O \rightarrow K + H_2O$	4.36	4.70	5.33	7.18	3.75	6.33	5.8 ^{c)}
$K^+H_2O \rightarrow K^+ + H_2O$	17.44	17.95	17.16	18.73	16.48	17.30	18.4 ^{d)} , 17.4 ^{e)}
$KNH_3 \rightarrow K + NH_3$	4.33	4.71	5.59	7.48	3.59	6.47	7.6 ^{c)}
$K^+NH_3 \rightarrow K^+ + NH_3$	17.66	18.23	17.80	19.55	16.58	17.98	20.7 ^{f)} , 18.5 ^{e)}
$K_2OH \rightarrow K + KOH$	15.83	16.16	16.46	18.60	16.17	18.47	19.9 ^{c)}
$K_2^+OH \rightarrow K^+ + KOH$	47.35	46.77	46.67	47.07	46.45	46.70	38.0 ^{g)}
$K_2NH_2 \rightarrow K + KNH_2$	15.37	15.25	16.87	19.22	14.48	18.31	
$K_2^+NH_2 \rightarrow K^+ + KNH_2$	45.72	45.17	45.16	46.12	44.03	44.93	

^{a)} d-type polarization functions were augmented in the K basis set.

^{b)} See text for the recalculations of some experimental data.

^{c)} Ref. [19]. ^{d)} Ref. [25]. ^{e)} Ref. [26]. ^{f)} Ref. [27]. ^{g)} Ref. [28].

Table 7
Theoretical and experimental ionization energies (eV)

Reactions	Vertical (MP2)	Adiabatic (MP2)	Adiabatic (MP2*) ^{a)}	Experimental
$K \rightarrow K^+$		4.00	4.04	4.339 ^{b)}
$K_2 \rightarrow K_2^+$		3.56	3.67	4.0637 ^{c)}
$KH_2O \rightarrow K^+H_2O$	3.48	3.48	3.54	3.92 ^{d)}
$KNH_3 \rightarrow K^+NH_3$	3.47	3.47	3.51	3.87 ^{d)}
$K_2OH \rightarrow K_2^+OH$	2.83	2.69	2.80	3.55 ^{d)}
$K_2NH_2 \rightarrow K_2^+NH_2$	2.95	2.77	2.87	3.94 ^{d)}

^{a)} d-type polarization functions were augmented in the K basis set.

^{b)} Ref. [44]. ^{c)} Ref. [45]. ^{d)} Ref. [19].

that the bonding distances between the center atom and the surrounding atoms only make small changes in going from the neutral species to ionic species. However, the angles between the alkali atoms undergo quite an appreciable change between these two states. These structure changes are just the geometrical manifestation of the nature of the chemical bonding in the molecules. According to the concept of hypermetallic bonding proposed by Pople and co-workers, the extra valence electrons, after the completion of the filling of the molecular valence shell in accordance to the octet rule, go to the bonding between the metal atoms [10–12]. In this study the bi-potassium compounds have one extra valence electron for the hypermetallic bonding. Their positive ionic states become closed-shell systems. Apparently, the interaction strength between the potassium atoms determines their relative distance. Qualitatively speaking, the increase of the positive charge on the potassium atoms and the absence of the extra bonding electron between the potassium atoms as one goes from the neutral to the ionic state induce the large change of the potassium bonding angle.

One can look into the nature of the hypermetallic bonding in a more quantitative way. One good measure for the interaction is the overlap population between potassium atoms. They are: 0.53 (K_2), 0.35 (K_2OH), 0.0 (K_2^+OH), 0.30 (K_2NH_2), and 0.0 ($K_2^+NH_2$) at the MP2 level. These values suggest the large extent of the sharing of the extra valence electron between the two potassium atoms in the neutral species. There is no such kind of electron-sharing in the ionic states. Another measure is the electron density deformation in the formation of the molecule. Figs. 1 and 2 show the total electron density deformation maps of K_2OH and K_2NH_2 on the xz and yz molecular planes, respectively, at the MP2 level. The deformation density is obtained by taking the difference between the molecular density and the density of the sphericalized atoms [46]. There are two general features emerging from Figs. 1 and 2. One is that from the map of the xz molecular plane, there is a minor density deformation between the two potassium atoms. This indicates that a chemical bonding, although not a strong one, exists between these two potassium atoms. The second observation is that, comparing the density deformation around the oxygen atom or nitrogen atom of the present compounds

with those of H_2O obtained by Mensching et al. [46], one finds that a semi-quantitative similarity in the deformation contours between these three molecular systems centering around the oxygen or nitrogen atom. To be more specific, if one disregards the magnitude of the net electron charges on the center atom, one finds that the electron density deformation of the two lone-paired electrons of H_2O closely resemble the electron density deformation of the two potassium-oxygen bonds of K_2OH and also that of the two potassium-nitrogen bonds of K_2NH_2 . The electron density deformation of the two OH bonds of H_2O appears to be similar to the single OH bond of K_2OH and, not unexpectedly, even is much closer to the two NH bonds of K_2NH_2 . In the H_2O and K_2OH molecules, because of the different orientation of the hydrogen atoms with respect to the oxygen atom, the density deformations around the hydrogen atoms between these two systems show some minor difference in space. Nevertheless, the general features of the electron-density deformation around the oxygen atom are similar to each other. Figs. 1 and 2 suggest that the bonding between the potassium and oxygen or nitrogen in K_2OH or K_2NH_2 molecule has strong ionic character and is formed between two negatively-charged lone-paired electrons of the oxygen or nitrogen atom and the positively-charged potassium atoms. The OH bond of K_2OH and the NH bond of K_2NH_2 have the same bonding character as the OH bond of H_2O .

3.2.2. Harmonic vibrational frequencies

The lower part of table 3 lists the harmonic vibrational frequencies and the associated symmetries of the bi-potassium molecular systems. To the best of the authors' knowledge, the experimental vibrational spectra of these molecular systems have not yet been reported.

Figs. 3 and 4 show the normal mode motions of K_2OH and K_2NH_2 , respectively. The corresponding ionic state has the identical normal mode motions. As one changes from the neutral species to their positive ionic states, most of the normal modes do not change their vibrational frequencies much. For the K_2OH and K_2^+OH systems, the $b_2(\nu_6)$ vibrational mode almost preserves its vibrational frequency between these two states. The $b_2(\nu_6)$ mode is an umbrella motion between the H, K, K atoms and the O

Fig. 1. Electron density deformation map of K_2OH along the yz and xz planes: long dashed line $0.00 \text{ e}/\text{\AA}^3$, short dashed line $-0.008n \text{ e}/\text{\AA}^3$, solid line $+0.008n \text{ e}/\text{\AA}^3$ ($n=1, 2, 3, \dots$).

Fig. 2. Electron density deformation map of K_2NH_2 along the yz and xz planes: long dashed line $0.00 e/\text{\AA}^3$, short dashed line $-0.008n e/\text{\AA}^3$, solid line $+0.008n e/\text{\AA}^3$ ($n=1, 2, 3, \dots$).

Fig. 3. Vibrational normal modes of K_2OH . The lengths and directions of the arrows indicate the relative vibrational magnitudes and their directions, respectively.

atom. Apparently, the ionization of the potassium electron does not alter the interaction force constant perpendicular to the C_2 axis of the molecule. The same phenomenon happens to the $b_1(\nu_7)$ mode of the K_2NH_2 and $K_2^+NH_2$ pair. This suggests the electrostatic nature of the interaction between the molecular parts of K_2 and OH in K_2OH or the molecular parts of K_2 and NH_2 in K_2NH_2 . This observation is also consistent with the results of the electron density

deformation discussed in section 3.2.3. The largest vibrational frequency shifts are in the modes of $b_1(\nu_4)$ and $b_1(\nu_5)$ for K_2OH and $a_2(\nu_5)$ for K_2NH_2 . These modes are mainly involved in the stretching motion of KO in the K_2OH molecule or the twisting motion between NH_2 and NK_2 in the K_2NH_2 molecule. The increase of these normal mode frequencies as one goes from neutral to positive ionic state is a direct result of the increase of the interaction strength between

Fig. 4. Vibrational normal modes of K_2NH_2 . The lengths and directions of the arrows indicate the relative vibrational magnitudes and their directions, respectively.

these bonds. The lowest vibrational frequency modes are the $a_1(\nu_3)$ mode of the K_2OH/K_2^+OH pair and the $a_1(\nu_4)$ mode of the $K_2NH_2/K_2^+NH_2$ pair. These are all bending motions for the K atom pair and are close to the vibrational frequency of the gaseous K_2 , 92.0 cm^{-1} . This also implies the weak interaction of K_2 with the rest part of the molecular complexes in these species.

3.2.3. Bond dissociation energies and ionization potentials

The lower halves of tables 6 and 7 show the bond dissociation energies and ionization potentials of the bi-potassium molecular systems. For the hydroxyl systems, the agreement of the dissociation energies between the theoretical results and the experimental values is very good. There are no reports on the ex-

perimental measurements of the amide molecules yet. The bond dissociation energies of the neutral species are always much lower than the corresponding ionic states. This reflects that the ion–electrical dipole interaction is much stronger than the hypermetallic bonding in these species. Note that the bonding energy of the pure covalent bond of K_2 is only 11.9 kcal/mol. For the adiabatic ionization potentials, the agreement between the theoretical values and experimental data is poor. In an attempt to calculate the ionization potentials of some hypermetalated compounds of Na and Li, Wurthwei et al. also encountered the same poor agreement between the results of theory and experiments [12]. Further work is needed to clarify these situations.

4. Conclusions

The following conclusions can be drawn from the results of the present study of the neutral and ionic states of the potassium-containing hypermetalated compounds and molecular complexes.

(i) Evidences suggest that electron correlation effect, electrostatic interaction and charge polarization of the alkali atom are all play a part in stabilizing the KH_2O and KNH_3 complexes. The charge-transfer process is comparatively less important in these cases.

(ii) In the cases of K_2OH and K_2NH_2 , the two potassium atoms that are responsible for the so-called hypermetallic bonding are spatially oriented to the two lone-paired electrons of the center oxygen or nitrogen atom. A weak bonding feature is developed between the two potassium atoms.

(iii) The majority of the geometrical and vibrational quantities of the neutral species is close to those of their ionic species studied in this report. Due to the different nature of the bonding as one changes from the neutral to ionic state, only those quantities directly related with this local change of the bonding undergo major changes.

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