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Electronic state and potential energy function for UH^{2+}*

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Our theoretical study on UH^{2+}($X^4\Sigma$) using a density functional method shows that its potential energy curve has both minimum and maximum, which is the so-called "energy trapped" molecules. This sort of potential maximum is mainly caused by Coulomb repulsion. We have proposed the perturbation effect of ionic charges to explain the existence of the potential maximum for diatomic ions, and derived an analytic potential energy function has been derived, and the force constants and spectroscopic data are obtained. Finally, the vertical ionization potential for UH^{2+} has been calculated as well.

Keywords: UH^{2+}, potential energy function, electronic state, vertical ionization potential
PACC: 3110, 3120D, 3420

1. Introduction

Molecular ions have been widely studied because of their great practical importance and theoretical considerations. For almost all neutral or singly charged diatomic molecules, the ground state has only one stationary point at the minimum. The extended Rydberg function, i.e. the Murrell–Sorbie function, is the most satisfactory theoretical method for describing accurately the behaviour of these neutral or singly charged diatomic molecules in the equilibrium region.[1] However, the extended Rydberg function is unsatisfactory for describing the doubly or triply charged diatomic ions. Zhu *et al*[2] proposed an analytical potential energy function for doubly charged diatomic molecules, which is applied successfully to many doubly charged diatomic ions.[3]

As the simplest uranium hydrides, Krauss and Stevens[4] have reported *ab initio* studies of UH, UH^- and UH^+, applying Pitzer's relativistic effective core potentials (RECP) approach in self-consistent field (SCF) calculation. Energy curves were calculated, and the electronic bonding of these molecules was found to be similar to that of comparable alkaline-earth hydrides. However, they did not give the potential energy functions and are not concerned with UH^{2+} and UH^{3+}. As compared with neutral diatoms, highly charged diatomic ions have some new features. We can deduce their dissociation limits from the relation between their single- and double- ionization potentials, I.P.$^+$ and I.P.$^{++}$.[5] The first, second and third ionization potentials for uranium are 4.96,11.07 and 17.74 eV, respectively, and the first ionization potential for H is 13.598 eV, therefore, it is reasonable to assume that the possible optimum dissociation channels would be $UH^{2+} \rightarrow U^{2+}$+H, and $UH^{3+} \rightarrow U^{2+}$+$H^+$.

In this paper, we obtain the potential function for UH^{2+} ions, which has both potential minimum and maximum, and the force constants and spectroscopic data. The potential maximum is explained by the perturbation effect of ionic charges.

2.Potential energy function form

We derive the potential energy curves of the neutral or singly charged diatomic molecules as the extended Rydberg function form developed by Murrell and Sorbie[1]

$$V = -D_e(1 + a_1\rho + a_2\rho^3 + a_3\rho^3)\exp(-a_1\rho), \quad (1)$$

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where $\rho = r - r_e$, r being the interatomic distance and r_e its equilibrium value. However, for the doubly charged diatomic ions with both minimum and maximum values in potential, i.e. the "energy trapped molecules", there are two repulsive branches and one attractive branch. In order to describe the diatomic ions with the potential minimum and maximum or without any stationary point, Zhu *et al*[2] has proposed a new analytical potential energy function with four parameters (Wang *et al*[3] added the extra parameter a_4). The function form is

$$E = \frac{a_1}{\rho - a_2} - \frac{a_3}{(\rho + a_4)^2}, \tag{2}$$

where $\rho = R - R_{\min}$ is the displacement from the minimum for the diatomic ions with potential minimum and maximum, and $\rho = R$ only for the repulsive states. Equation (2) can be rewritten in the typically cubic form of ρ

$$\begin{aligned}&\rho^3 + \rho^2\left(2a_4 - a_2 - \frac{a_1}{E}\right)\\ &+ \rho\left(a_4^2 - 2a_2a_4 + \frac{a_3}{E} - \frac{2a_1a_4}{E}\right)\\ &- \left(a_2a_4^2 + \frac{a_2a_3}{E} + \frac{a_1a_4^2}{E}\right) = 0.\end{aligned} \tag{3}$$

If the potential energy E lies between the maximum and minimum, i.e. $E_{\min} < E < E_{\max}$, there will be three real roots; if $E > E_{\max}$ or $E < E_{\min}$, there will be one real root and a pair of imaginary roots. Equations (2) and (3) is of mathematically reasonable form, a_1–a_4 are the characteristic parameters of the particular molecule.

Based on the first derivatives at minimum and maximum, it is easy to obtain the following relations

$$\frac{a_1}{a_2^2} = \frac{2a_3}{a_4^3}, \tag{4}$$

where $\rho = R - R_{\min}$=0, and

$$\frac{a_1}{(\rho - a_2)^2} = \frac{2a_3}{(\rho + a_4)^3}, \tag{5}$$

where $\rho = R_{\max} - R_{\min}$. The quadratic, cubic, and quartic force constants have been derived from Eq. (2) at minimum, which is regarded as the equilibrium state

$$f_2 = \frac{2a_1}{(-a_2)^3} - \frac{6a_3}{a_4^4}, \tag{6}$$

$$f_3 = -\frac{6a_1}{(-a_2)^4} + \frac{24a_3}{a_4^5}, \tag{7}$$

$$f_4 = \frac{24a_1}{(-a_2)^5} - \frac{120a_3}{a_4^6}. \tag{8}$$

The expressions relating the force constants f_i with the spectroscopic constants ω_e, $\omega_e\chi_e$, B_e, α_e and R_e for diatomic molecules can be found[6,7]

$$f_2 = 4\pi^2\mu_a\omega_e^2c^2, \tag{9}$$

$$f_3 = -\frac{3f_2}{R_e}\left(1 + \frac{\alpha_e\omega_e}{6B_e^2}\right), \tag{10}$$

$$f_4 = \frac{f_2}{R_e^2}\left[15\left(1 + \frac{\alpha_e\omega_e}{6B_e^2}\right)^2 - \frac{8\omega_e\chi_e}{B_e}\right], \tag{11}$$

where c is the velocity of light, μ_a is the reduced mass of individual atoms, and the value of B_e is given by

$$B_e = \frac{h}{8\pi^2c\mu_aR_e^2} = \frac{h}{8\pi^2cI_e}. \tag{12}$$

3. Calculation and results

Calculations are carried out using the popular density functional, the "hybrid" B3LYP functional, which is a three-parameter mixture of a density functional and "exact" Hartree–Fock (HF) exchange. We use the RECP of Hay and Martin[8] to replace the 78 core electrons of the uranium atom $[Xe]4f^{14}5d^{10}$, in conjunction with a [3s3p2d2f] contracted Gaussian basis set to describe the 14 valence electrons ($6s^27s^26p^66d^15f^3$). And we use the 6-31G* basis set for H atom. The use of HF-based RECPs with the density-functional-based methods appears to be reasonable for obtaining results for actinide species, as has been so far found for main group and transition metals. We employ the Gaussian 98 program for the present calculation.

3.1. Dissociation limit and electronic states

For calculation and description of the full potential curves for diatomic molecules or ions, it is important to determine the reasonable dissociation limits at first. If U^{2+} and H are in their ground states ^5K and ^2S_g, based on the group theory and atomic and molecular reaction statics,[5] the representations ^6L and ^2S_g of the atomic group are resolved into those of $C_{\infty v}$ (UH^{2+}) as follows

$$^5K \to {}^5\Sigma \oplus {}^5\Pi \oplus {}^5\Delta \oplus {}^5\Phi \oplus {}^5\Gamma \oplus \cdots \tag{13}$$

$$^2S_g \to {}^2\Sigma_g^+. \tag{14}$$

Their direct product and its reduction are

$$\begin{aligned}&{}^2\Sigma_g^+ \otimes ({}^5\Sigma \oplus {}^5\Pi \oplus {}^5\Delta \oplus {}^5\Phi \oplus {}^5\Gamma \oplus \cdots) \to\\ &{}^{4,6}\Sigma \oplus {}^{4,6}\Pi \oplus {}^{4,6}\Delta \oplus {}^{4,6}\Phi \oplus {}^{4,6}\Gamma \oplus \cdots\end{aligned} \tag{15}$$

In order to determine the ground-state configuration of UH^{2+}, the sextet and quartet multiplicities for UH^{2+} molecules have been optimized by the density function theory (DFT/B3LYP) method. The optimized results are listed in Table 1.

Table 1. The optimized results.

Method		B3LYP
Quartet	R/nm	0.214361246
	E/a.u.	–51.4258211
Sextet	R/nm	0.275225215
	E/a.u.	–51.3338686

The present DFT calculations predict that the quartet state is the ground state and lies 2.502eV higher than the sextet state. According to the DFT calculation, the lowest energy level of the electron configuration and its corresponding electronic states of UH^{2+} are

α electrons: $\sigma\ \sigma\ \pi\ \pi\ \sigma\ \delta\ \delta\ \pi$

β electrons: $\sigma\ \sigma\ \pi\ \pi\ \sigma$

Thus the ground state of UH^{2+} is $X^4\Sigma$ and its dissociation limit is UH^{2+} $(X^4\Sigma) \rightarrow U^{2+}$ (^5K) $+H(^2S_g)$.

3.2. Potential energy function

The potential energy curve of *ab initio* calculated points is shown in Fig.1. For UH^{2+}, the minimum is at R_{min}=0.21436nm with E_{min}=–51.4258211a.u. (atomic units), and the maximum is at R_{max}=0.61436nm with E_{max}=–51.4128212a.u., $\Delta E = E_{max} - E_{min}$=0.3538eV. And the Zhu–Wang potential energy function is used to describe its potential curve. By iterating a system of normal equations based on a least-squares fit, the parameters a_1, a_2, a_3 and a_4 of Eq. (2) for UH^{2+} $(X^4\Sigma)$ have been worked out: a_1=0.63743eV·nm, a_2=–0.11773nm, a_3=0.29636eV·nm^2, a_4=0.23794nm; From these it is easy to derive f_2, f_3 and f_4, and then to calculate the spectroscopic data ω_e, $\omega_e\chi_e$, B_e, α_e using Eqs. (9)–(12) (see Table 2). The fitting curves coincide with those obtained by *ab initio* calculation. In order to explain the potential maximum, we consider the charge population of UH^{2+}, as shown in Fig.2. The trend of the charge population of U is in accord with the potential curve.

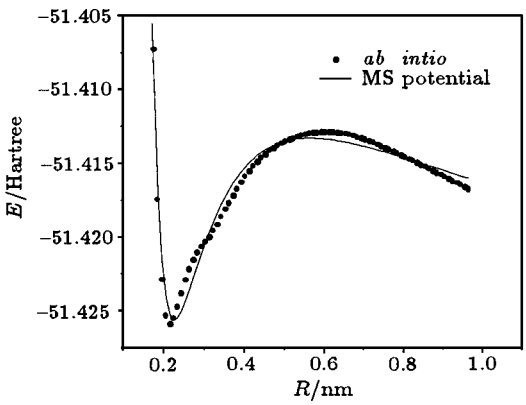


Fig.1. The potential curve of UH^{2+}.

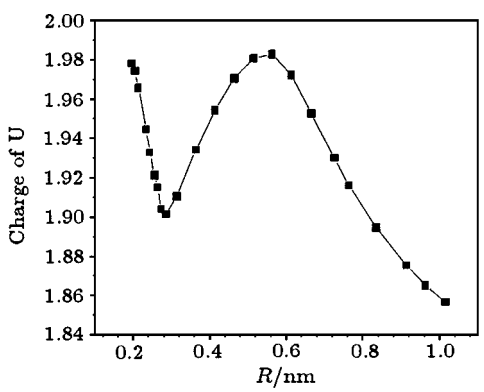


Fig.2. The charge population of UH^{2+}.

Table 2. Derived force constants and spectroscopic data.

Molecules	R_e/nm	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	f_2/aJnm^{-2}	f_3/aJnm^{-3}	f_4/aJnm^{-4}
$UH^{2+}(X^4\Sigma)$	0.21436	780.67	31.608	3.6292	0.23667	36.299	–1695.7	76982

Note: 1aJ=10^{-18}J.

3.3. Vertical ionization potential

The potential energy curves of UH and UH^+ can be derived using Murrell–Sorbie function (1), their parameters are listed in Table 3. According to the potential curves, the first and second vertical ionization potential for UH molecules can be calculated: I.P.$^+$=E(UH^+)–E_e(UH)–E_0(UH), I.P.$^{++}$=E(UH^{2+})–E_e(UH)–E_0(UH), where E_e(UH) is the equilibrium energy, E(UH^+) and E(UH^{2+}) are the energy of UH^+ and UH^{2+} at $R = R_e$(UH). E_0(UH) is the zero-point energy of UH, which can be obtained from the formula $E_0 = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e\chi_e$. For UH molecule, ω_e=1146.4cm^{-1}, $\omega_e\chi_e$=12.616cm^{-1}, E_0=

0.07067eV. Figure 3 shows that R_e(UH)=0.22857nm, E_e(UH)=–51.9980149a.u., $E(UH^+)$=–51.8233133a.u., $E(UH^{2+})$=–51.4259028a.u. Therefore, the first and second vertical ionization potential for UH molecule are I.P.$^+$=4.825eV, I.P.$^{++}$=15.64eV.

Table 3. Parameters of the analytical potential function.

Molecules	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	a_4/nm
UH($X^6\Sigma$)	24.010	176.57	576.17	0.22857
UH^+($X^5\Sigma$)	30.036	239.05	517.26	0.21627

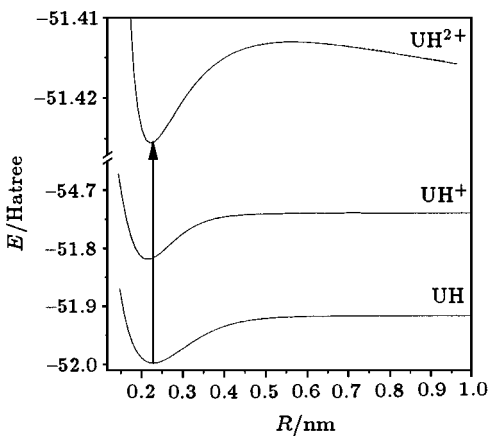


Fig.3. The potential energy curve for UH, UH^+, UH^{2+}.

4. Discussion

It is well known that there are three different types of potential maximum for diatomic molecules or ions, i.e. the potential maximum results from predissociation, or van der Waals interaction, or the noncrossing of potential curves of two states with the same irreducible representation for a given molecular group. The fourth is due to the Coulomb repulsion between the ionic pair with the same charges. For diatomic ions, the perturbation effect of ionic charges can be expressed as

$$E = E^0 + \langle\psi^0|\hat{H}'|\psi^0\rangle + \sum_{n\neq 0}\frac{|\langle\psi^0|\hat{H}'|\psi^0\rangle|^2}{E^0 - E^n} + \cdots, \quad (16)$$

where there are the zeroth-, first- and second- orders perturbation energies, etc. The perturbation operator is

$$\hat{H}' = \frac{q_1 q_2}{R}, \quad (17)$$

where R is the nuclear distance, and q_1 and q_2 are the electric charges. The Coulomb repulsive potential is closely related to the interionic distance and proportional to the product of ionic charges, therefore, the highly charged molecular ions would always be unstable.

This paper confirms that the potential maximum results from the Coulomb repulsion. Although the second ionization potential of uranium is less than the first ionization potential of H, the results of this paper indicate that during the dissociation process of UH^{2+}, neither of the ionic charges of U and H is zero, but positive. The trend of charge population shown in Fig.2 is consistent with that of the potential curve with both minimum and maximum points. At R_{max}=0.61436nm, the charge of U is 1.972211, and the charge of H is 0.027789, neither of q_1 and q_2 is zero. There will be perturbation effect of ionic charges. $\hat{H}'$ does not vanish, and hence the potential maximum occurs.

In summary, it could be concluded that: the larger the ionic charges, the more unstable the molecular ions, so the charges of molecular ions are not too large as the atomic ions are. UH^{3+} can be unstable, and its potential curve is repulsive, completely without minimum. For the singly and doubly charged diatomic ions, there is one minimum corresponding to the stable state on the potential energy curve, resulting from the equilibrium between the chemical bond force and the nuclear repulsive force. Specifically, the equilibrium between the chemical bond force and Coulomb repulsive force results in an energy maximum for doubly charged ions, such as UH^{2+}.

Our previous studies[9,10] indicate that the ions PuO^{2+} ($X^5\Sigma^-$), PuH^{2+} ($X^8\Sigma^-$), PuN^{2+} ($X^4\Sigma^+$) and PuC^{2+} ($X^9\Sigma^-$) have no potential maxima, since the dissociation channel is $PuX^{2+} \rightarrow Pu^{2+} + X$ (X=H, N, O and C), any Xs charge being zero. In this case, there will be no perturbation effect in ionic charges. In fact, the perturbation effect in ionic charges would still exist, because of the shorter nuclear distance concerned here. It is too small to be found during the calculation, and the potential maximum would appear at a suitable nuclear distance.

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