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Potential Function and Thermodynamic Property of UO

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(Dated: Received on November 23, 2012; Accepted on January 17, 2013)

Potential energy scan for uranium oxide (UO) was performed by *ab initio* configuration interaction (CI) method and density functional theory methods at the PBE1 and the B3LYP levels in combination with the (ECP80MWB_AVQZ+2f) basis set for uranium and 6-311+G* for oxygen. The dissociation energies of UO, after being corrected for the zero-point vibrational energy, are 2.38, 3.76, and 3.31 eV at the CI, PBE1, and B3LYP levels, respectively. The calculated energy was fitted to potential functions of Morse, Lennard-Jones, and Rydberg. Only the Morse function is eligible for the potential. The anharmonicity constant is 0.00425. The anharmonic frequency is 540.95 cm⁻¹ deduced from the PBE1 results. Thermodynamic properties of entropy and heat capacity at 298.2–1500 K were calculated using DFT-UPBE1 results and Morse parameters. The relationship between entropy and temperature was established.

Key words: Potential function, Uranium oxide, Density functional theory, Thermodynamic property

I. INTRODUCTION

In nature, uranium is generally found as an oxide. The properties of uranium are related to its oxidized surface [1]. First-principles calculations based on the projector augmented-wave technique have been applied to the prediction of materials properties of α -uranium and its (001) surface [2]. However, theoretical research on oxidized uranium is somewhat absent. Under condition of lacking experimental data, the electronic structure, stability, potential energy, and thermodynamic property *etc.* can be obtained by quantum chemical computing. In particular, the potential function is useful for optimizing the force field parameters, which in turn play an important role for the study of reaction mechanism, the binding energy of molecules and solid states. Among various theoretical methods, the first-principles and molecular dynamic simulation are very powerful theoretical techniques for computing the chemical and physical properties. However, to investigate dynamic behaviors and the time evolution processes, one should resort to the molecular dynamic simulations. The molecular dynamics does not care about the materials as whole but only deals with

the interatomic forces and the individual movement of each atom. Consequently, it is equally suitable for both crystalline and non-crystalline materials. Furthermore, molecular dynamics can fully account for the thermodynamical state by considering the total energy composed of all interatomic potential energies and kinetic energies of all individual atoms at any loading and temperature conditions. The key step in molecular dynamic simulations is the choice of interatomic potentials. For metals, Morse potential is the most popular one [3]. In this work, we calculated the potential energy surface of UO with configuration interaction (CI) and density functional theory (DFT) methods. Then, the Morse potential function was established. We also fit the Lennard-Jones (L-J) and Rydberg potentials. The thermodynamic properties were calculated by using the Morse potential parameters at temperature from 298.2 K to 1500 K. For comparison, the entropy and heat capacity were also obtained from the DFT-PBE1 results.

II. COMPUTATIONAL METHOD

Although high level computational methods usually produce more accuracy results, it is computationally too expensive or impractical to use methods like CASSCF to establish the potential energy surface of UO. So we used the less expensive *ab initio* CI method and the DFT methods to determine the potential energy surface. The calculations described in this work have

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been performed using the Gaussian 03 package with by *ab initio* CI method and DFT methods at the PBE1 and the B3LYP levels in combination with the (ECP80MWB_AVQZ+2f) basis set for uranium and 6-311+G* for oxygen [4, 5]. Both the CI and DFT methods are reliable for the investigation of transition metal compounds [6–8]. After the potential energies being obtained, a Morse function was fitted as follows,

$$U(r) = D_e \left[e^{-2\beta(r-r_0)} - 2e^{-\beta(r-r_0)} \right] \quad (1)$$

The eigenvalues of Morse potential is

$$E(n) = hc \left[(n + 0.5)\omega_e - (n + 0.5)^2 \chi_e \omega_e \right] \quad (2)$$

$$\omega_e = \beta \sqrt{\frac{2D_e}{\mu}} \frac{1}{2\pi c}, \quad \chi_e = \frac{\omega_e}{4D_e} \quad (3)$$

where ω_e is the harmonic vibrational frequency, D_e is the well depth of the Morse curve that corresponds to the dissociation energy of a diatomic system, β is a parameter in the Morse potential, which is related with the width of the Morse potential curve, μ is the reduced mass, r is the interatomic distance, h is Planck's constant, c is the speed of light in vacuum, n is the vibrational quantum number, and χ_e is the anharmonic constant. By neglecting the contribution of the electronic excitation state energy to its thermodynamic properties, the entropy and heat capacity were calculated. Thermodynamic properties of entropy and heat capacity were calculated by both the vibrational frequencies from DFT-B3LYP computing results and Morse parameters, respectively.

For comparison, we also fit the L-J and the Rydberg interatomic potential functions as the follows, respectively.

$$U(r) = \frac{A}{r^{12}} - \frac{B}{r^6} \quad (4)$$

$$U(r) = -D_e(1 + \beta r)e^{-\beta r} \quad (5)$$

III. RESULTS AND DISCUSSION

A. Potential energy

The calculated CI results in a dissociation energy of 2.41 eV for UO, and this value becomes into 2.38 eV after being corrected for the zero-point vibrational energy. DFT-UPBE1 results of dissociation energies for UO are 3.79 and 3.76 eV, before and after the ZPE correction, respectively. DFT-UB3LYP results are 3.34 and 3.31 eV, before and after the ZPE correction, respectively. The balance distance of UO is 2.199, 2.169, and 2.192 Å at CI, PBE1 and B3LYP levels, respectively. Figure 1 shows the relationship of potential energy from CI method and the diatomic distances of UO. As can be seen from Fig.1, the potential energy curve of UO splits

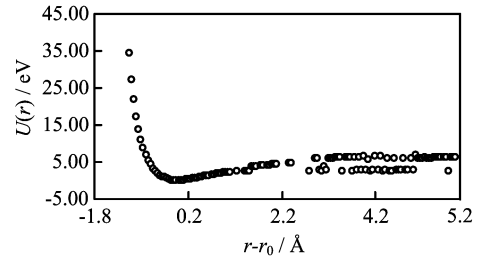


FIG. 1 Potential energy from CI method *vs.* diatomic distance.

TABLE I Parameters of potential functions of UO*.

	Methods	Parameters	R^2	RMSE
Morse	CI	$D_e=0.455, \beta=2.185$	0.898	1.924
	PBE1	$D_e=3.96, \beta=1.433$	0.993	0.584
	B3LYP	$D_e=3.37, \beta=1.406$	0.992	0.519
L-J	CI	$A=150.2, B=-52.12$	0.936	1.518
	PBE1	$A=144.0, B=-36.39$	0.896	2.251
	B3LYP	$A=223.2, B=-26.39$	0.880	2.047
Rydberg	CI	$D_e=-8759, \beta=6.455$	0.959	1.222
	PBE1	$D_e=-17060, \beta=7.182$	0.921	1.966
	B3LYP	$D_e=-19920, \beta=7.249$	0.905	1.821

* D_e and RMSE are in eV, β , A , and B are in Å⁻¹, eV·Å¹², and eV·Å⁶ respectively.

into two separated lines as the value of $r-r_0$ is about 2.8 Å or more. This phenomenon is due to the fact that the basis set is not a complete set of functions and not well-behaved for actinide elements, whose 5f orbital is much more diffused than its 4f orbital. Its configuration interaction is too sensitive and unsteady to atomic distance. To a common sense, the lower line was used to fit the Morse function of Eq.(1) since it acts in accordance with the lowest energy principle. The correlation coefficient R -square of the regression curve is 0.898, and root mean square error (RMSE) is as large as 1.924, indicating that the fit Morse function is not well related with the CI results. In contrast, as can be seen from Table I, the DFT results of both B3LYP and PBE1 can be fitted well to Morse functions (Fig.2). The values of D_e and β of the Morse function fitted from DFT-PBE1 results are 3.96 eV and 1.433 Å⁻¹ respectively, thus $\omega_e=543.26$ cm⁻¹ after substituting the β and D_e values into Eq.(3). Consequently, the anharmonicity constant $\chi_e=0.00425$ from Eq.(4), and $\chi_e\omega_e=2.31$ cm⁻¹. The anharmonic frequency is 540.95 cm⁻¹, which is slightly larger than the scaled frequency (523.98 cm⁻¹) obtained from DFT-PBE1 scaled by a factor of 0.96.

The correlation coefficients for the fitted L-J functions are 0.880 to 0.936, and RMSE are in range of 1.518 to 2.251, indicating the L-J is not a good model for UO potentials. Similarly, neither is the Rydberg. Especially, there is a lack of a potential well for the fit-

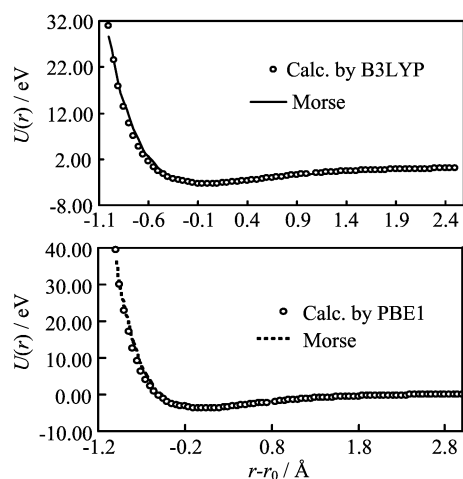


FIG. 2 Calculated potential energy and Morse function.

TABLE II Entropy and heat capacity of UO (in J/(mol K)).

T/K	DFT-PBE1		Morse	
	C_P	S	C_P	S
298.2	34.11	244.80	33.95	244.64
400.0	35.34	255.01	35.22	254.82
500.0	36.01	262.97	35.92	262.76
600.0	36.40	269.58	36.34	269.34
700.0	36.66	275.21	36.61	274.97
800.0	36.83	280.11	36.79	279.87
900.0	36.95	284.45	36.92	284.21
1000.0	37.03	288.35	37.01	288.10
1100.0	37.10	291.88	37.08	291.63
1200.0	37.15	295.11	37.13	294.86
1300.0	37.19	298.09	37.17	297.83
1400.0	37.22	300.84	37.21	300.58
1500.0	37.24	303.41	37.23	303.15

ted L-J and Rydberg functions as UO distance changes, *i.e.*, without minimum point of energy.

B. Thermodynamic properties

Table II lists the entropy C_P and heat capacity S of UO in temperature range of 298.2 K to 1500 K. The results from the Morse potential are almost identical to those of DFT-PBE1 calculation. The C_P values increase very slightly as the temperature increases. The entropies increase with temperature increasing. The relationship of entropy and temperature can be well fitted to the following: $S=272.63+0.02594T-10869.5T^{-1}$ and $S=272.32+0.02596T-10827.3T^{-1}$ from the DFT-PBE1 and Morse results, respectively. The correlation coefficients R^2 is 0.999, with RMSE of 0.69, for both the relationships.

IV. CONCLUSION

The first-principles investigation of actinide compounds is a challenge task. Many conventional and standard basis sets is unusable for UO. The anharmonicity constant of UO is small. The Morse function is suitable for the UO potential. The entropy and heat capacity of UO at temperature from 298.2 K to 1500 K from the Morse potential are close to those from the DFT-PBE1 results. The C_P values increase slightly, but the entropies increase greatly with temperature increasing.

V. ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No.21101070) and the Funding from the Laboratory of Science and Technology on Combustion and Explosion (No.9140C3501021101).

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