

A very short uranium–uranium bond: The predicted metastable U_2^{2+}

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Quantum chemical calculations, based on multiconfigurational wave functions and including relativistic effects, show that the U_2^{2+} system has a large number of low-lying electronic states with S of 0 to 2 and A ranging from zero to ten. These states share a very small bond length of about 2.30 Å, compared to 2.43 Å in neutral U_2 . The Coulomb explosion to $2 U^+$ lowers the energy by only 1.6 eV and is separated by a broad barrier.

1. Introduction

Uranium metal has a high atomization energy of 533(8) kJ mol⁻¹,¹ and an experimental dissociation energy of 218(21) kJ mol⁻¹ has been reported for the neutral diatomic U_2 molecule from mass-spectrometric measurements.² A recent quantum chemical calculation on U_2 yielded a bond length of 2.43 Å and revealed a very complicated fivefold chemical bond with a total spin S of 3 and a total orbital angular momentum A of 11.³ This study took into account electron correlation using a multiconfigurational wave function and relativistic effects. (Earlier, more approximate calculations on neutral U_2 are quoted there.) This analysis is interesting, given the virtual absence of well-defined uranium–uranium, or more generally, actinide–actinide bonds, especially multiple bonds, in molecular inorganic or organometallic chemistry.

If two of the twelve valence electrons of U_2 are removed, some simplification of the electronic structure could be expected. Indeed, preliminary DFT or CAS calculations⁴ suggested for U_2^{2+} a singlet, predominantly $(\sigma_g)^2(\pi_u)^4(\delta_g)^4$ state with bond lengths, as short as 2.15 Å.

On the experimental side it is interesting to note that a mass-spectroscopic study using an Au–U liquid-alloy ion source for uranium with 20% ²³⁵U and 80% ²³⁸U showed no fingerprint for the mixed diatomic dication, while the mixed-isotope U_2^+ was seen.⁵ The authors point out, however, that the strong electric field in the experiment might destabilize the heteronuclear species.

We report here the results of a study on the U_2^{2+} species, at a comparable level as that used for U_2 .³ No other earlier work seems to exist on U_2^{2+} .

2. Results and discussion

The spin-free potential energy curves around equilibrium for the lowest electronic states of U_2^{2+} are reported in Fig. 1. The region near equilibrium has been enlarged (Fig. 2) in order to explore the various electronic states. The most stable spin-free electronic state was found to be a singlet state and to have a total orbital angular momentum, A , equal to 10 atomic units, (a ¹N_g state). The equilibrium bond distance is 2.30 Å without

the inclusion of spin–orbit coupling and the harmonic vibrational frequency is 300 cm⁻¹. A triple-bond covalent radius of 1.18 Å has recently been proposed for uranium.⁶ For a triple U–U bond this would give 2.36 Å, close enough to the calculated 2.30 Å.

Inspection of the wave function for the lowest electronic states reveals a triple bond, corresponding to the electron configuration $(\sigma_g)^2(\pi_u)^4$. The molecular orbitals are reported in Fig. 3. The σ orbital is a hybrid comprising 7s, 6d σ , and 5f σ atomic orbitals and the π_u orbital is mainly 6d in character. The next four electrons, which were active in the calculations, occupy the 5f δ and 5f ϕ orbitals. They are essentially non-bonding in all the low-lying electronic states. Thus, the electronic structure corresponds to a triple bond plus two localized 5f electrons on each of the uranium ions. This is different from the neutral molecule U_2 , where the 6d orbitals take a more active part in the formation of the chemical bond.³ Ionization will stabilize 5f more than 6d and the weaker bond in U_2^{2+} will favor the electronic configuration of the U^+ ion, which is 5f³7s², ⁴I. This explains the high angular momentum preferred by the non-bonding 5f electrons.

The total spin of the four unpaired electrons in the molecule can be 0, 1, or 2. With an angular momentum on each atom of 5, one obtains $A = 0, 5, \text{ or } 10$ in the molecule. Which of these

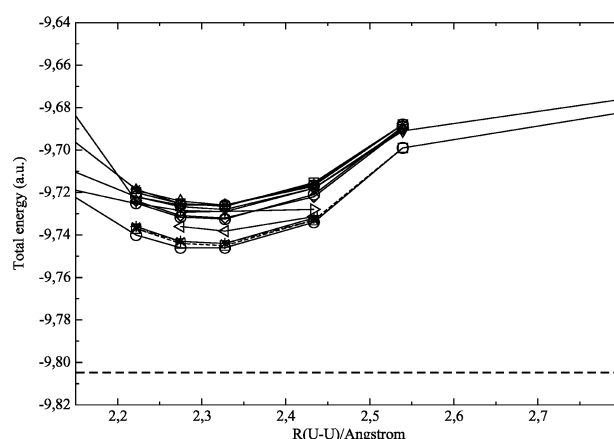


Fig. 1 Spin-free potential energy curves for the lowest electronic states of U_2^{2+} around the equilibrium distance. Calculations have been made at the geometries indicated with the symbols. The lines have been drawn simply to connect the points. The lowest curve (solid line, circle) is the ground state ¹N_g⁺ ($A = 10$). The dashed curve with square is a ¹Σ_g state and it is almost degenerate with two triplet curves (dotted line and cross) and (solid line and star). The solid curve with triangle left is a quintet state. The upper curves are of various spin multiplicities (singlet, triplet and quintet). The horizontal line (dashed) at the bottom is the energy of two U^+ ions at infinite distance.

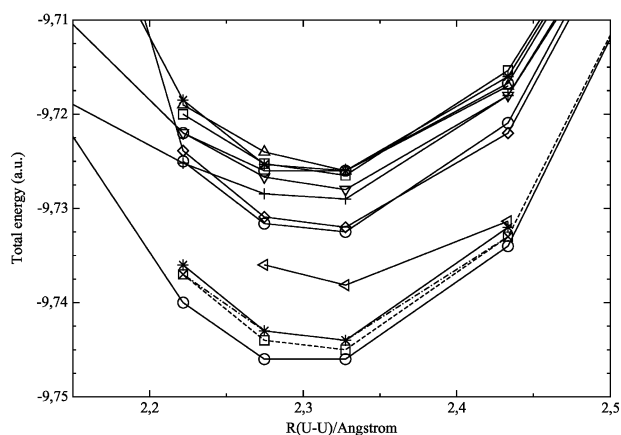


Fig. 2 An enlarged version of Fig. 1 for bond distances near equilibrium.

combinations will give the lowest energy, is difficult to predict and the calculations show that all combinations have low energy. The predicted ground state has $S = 0$ and $A = 10$. Thus the two atomic open shells add their local angular momenta, while the coupling between them is antiferromagnetic. In the neutral molecule on the other hand, a ferromagnetic coupling occurs between the open-shell electrons. This is due to the formation of two 6d one-electron bonds. Exchange stabilization then favors parallel spin for all the six open shell electrons. This mechanism does not work here, because all four open-shell electrons are localized, with one triplet-coupled pair of electrons on each atom. Antiferromagnetic coupling between the two atoms will then be favored because it leads to some additional, but weak binding.

In our previous study on neutral U_2 ,³ the inclusion of spin-orbit coupling did not have any effect on the equilibrium bond distance. We have thus not recalculated the equilibrium bond distance including spin-orbit coupling, but only estimated spin-orbit effects at the 2.328 Å interatomic distance. Inspection of Fig. 2 shows that at this bond distance the first spin-free excited state of $^1\Sigma_g^+$ type lies 279 cm^{-1} above the ground state 1N and it is degenerate with the first triplet excited state. The first quintet state (triangle left in Fig. 2) lies 1682 cm^{-1} above the ground state. A triplet and a singlet state follow lying about 2920 cm^{-1} above the ground state. All the higher states that we have included in our calculation lie within a range of at most 4350

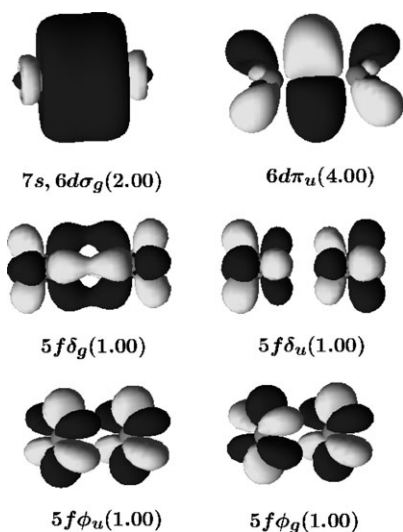


Fig. 3 The valence molecular orbitals forming the chemical bond in U_2^{2+} . The orbital label is given below each orbital together with the number of electrons occupying this orbital or pair of orbitals in the case of degeneracy.

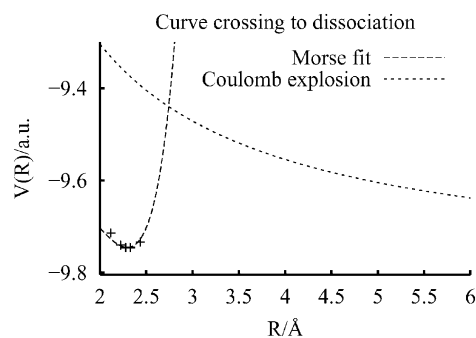


Fig. 4 A Morse-potential fit to the calculated ground-state potential curve and its crossing with an $1/R$ estimate for the Coulomb explosion to two U^+ ions. The dissociation limit is the abscissa.

cm^{-1} above the ground state. The inclusion of spin-orbit coupling gives a ground state $\Omega = 0_g^+$, arising from the combination of a triplet, singlet and quintet state, all with $A = 0$.

The U_2^{2+} system is metastable and lies 1.59 eV higher in energy than two U^+ ions. Calculations for larger distances need an active space which is outside the limits of present technology because all valence electrons have to be active (see Method section for details). Studies of the curve-crossing region, including SO splitting are therefore not possible. A rough estimate for the curve-crossing from the bound ground-state singlet curve to the point-charge-like long-distance Coulomb explosion is shown in Fig. 4. It is high enough and far enough, not to form a likely danger for the metastability of the predicted U_2^{2+} species.

A potential future problem is the study of neutral molecules with a similar bonding system, a possible candidate being FUUF.

3. Method and details of the calculations

The quantum chemical calculations were performed using the software MOLCAS-6.0.⁷ The complete active space (CAS) SCF method⁸ was used to generate molecular orbitals and reference functions for subsequent multiconfigurational second order perturbation calculations of the dynamic correlation energy (CASPT2).^{9–11}

The choice of the active space is crucial for the method. The valence electronic configuration of the uranium atom is $(5f)^3(6d)^1(7s)^2$. In the U_2 case there are thus twelve valence electrons available for bonding. It was shown³ that three normal electron pair bonds, involving six of the twelve valence electrons are formed by hybrid atomic orbitals dominated by 7s and 6d character. They were thus kept doubly occupied in the CASSCF calculations. The remaining six electrons were allowed to freely occupy the remaining 5f and 6d orbitals. Four electrons were allowed to occupy the same orbitals in U_2^{2+} . Electronic states of singlet, triplet and quintet type were then calculated.

Relativistic all electron atomic basis sets of atomic natural orbital (ANO) type were used. A primitive set of 27s24p18d14f6g3h functions was contracted to 9s8p6d5f2g1h.

The relativistic effects which need to be included in the treatment of an atom as heavy as uranium were taken into account using the second-order Douglas-Kroll-Hess Hamiltonian. The scalar part of this Hamiltonian was used in the generation of the CASSCF wavefunction. Spin-orbit (SO) coupling was included by allowing the CASSCF wavefunctions to mix under the influence of the SO Hamiltonian. The method has been described in detail in a recent article.¹²

Calculations were performed for a number of points around the equilibrium bond distance. The binding energy was estimated by a calculation on the uranium monocation, U^+ , which was performed with the same basis set used for U_2^{2+} and with the valence orbitals active.

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