On the reaction of a uranium atom with a nitrogen molecule: a theoretical attempt

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An attempt has been made to study the reaction between a uranium atom and a nitrogen molecule theoretically using multiconfigurational wave functions. The \( C_2 \) part of the reaction surface has been computed for several electronic states of various spin multiplicities. The system proceeds from a neutral uranium atom in its \( (5f)^3(6d)(7s)^2 \), \( ^5L \) ground state to the linear molecule NUN, which has a \( ^1\Sigma_g^+ \) ground state and uranium in a formal U( VI) oxidation state. The effect of spin–orbit coupling has been estimated at crucial points along the reaction. These preliminary results shows that the system proceeds from a quintet state for \( U + N_2 \), via a triplet transition state to the final closed shell molecule. An eventual energy barrier for the insertion reaction is caused by the spin–orbit coupling energy.

1 Introduction

There is a current interest in the chemistry of uranium with atmospheric components like carbon, nitrogen and oxygen in relation with the development of gas-phase separations involving atomic uranium.1–5 The vibrational frequencies of the linear triatomics OUO, OUO+, OUO2+, NUN, and CUO have recently been measured in solid neon and argon matrices using infrared spectroscopy, using laser ablation techniques to prepare the species. 6

From the theoretical point of view, the pioneer in this area was Pyykkö,7 who already in 1994, presented, together with Runeberg, a Hartree–Fock study on the trends of geometries and vibrational frequencies of several uranyl iso-electronic species like NUN, CUO, CUN–, and NUO+.8 More recently, theoretical studies, using the density functional approach (DFT/B3LYP), have been performed.5,6,9 We have previously reported equilibrium geometries and vibrational frequencies for a number of U(vi) and U(vi) triatomic molecules and their positive ions XUY (X = C,N,O).10 The computed frequencies were in agreement with experiment provided that extended basis sets were used. These calculations were performed using multiconfigurational (CAS) SCF theory11 with dynamic correlation effects added using second order perturbation theory (CASPT2).12–14 Relativistic effective core potentials (ECP) were used and no spin–orbit effects were included. The equilibrium structure of the OUO molecule was later determined15 using the same approach together with a new method (CASSI-SO) to treat spin–orbit coupling.16 The molecule was found to have a \( (5f\phi)(7s) \), \( ^3\Phi_a \), \( \Omega = 2 \) ground state. This study also included a number of the low lying excited states. A high density of states was found already at low energies.

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spin–orbit coupling there were 21 states with excitation energies lower than 2.5 eV. The electronic structure of these states corresponds to excitations from the highest occupied σ- and π-orbitals to the 5fδ and 5fϕ orbitals of uranium.

All these earlier studies have been performed on systems with uranium in a formally high oxidation state (IV, V, or VI), even if the U–X (X = C, N, O) bonds have a large covalent character. They have been performed around the equilibrium geometry, where the electronic structure is well defined and not so complicated to describe. We refer to the quoted papers for details. A much more complicated situation is obtained, if one wants to describe the formation of these molecules. Experimentally, laser-ablated uranium atoms react with the diatomic XY during condensation and the reaction products include the insertion product XUY. It seems that this reaction occurs rather easily indicating a low barrier. One would conclude that uranium atoms can easily break the strong XY bond, for example in the N₂ molecule.

We thought it might be of interest to see if current theoretical methods can describe such a reaction. The U + N₂ reaction is quite complicated, since the uranium atom has a high spin ground state ((5f)³(6d)(7s)², 5L), while NUN is a closed shell molecule. The connection between this state and the dissociation channel must therefore occur via spin–orbit coupling, including also triplet states and intermediates. The computational procedure used here includes spin–orbit coupling a posteriori. Thus, a number of electronic states have to be computed, which form the basic states for the spin–orbit Hamiltonian.

In this paper we report the preliminary results of such a study where the formation of the NUN molecule, from a uranium atom and N₂, occurs on a reaction path of C₂v symmetry. A number of electronic states have been computed along this reaction path. The CASSCF/CASPT2 method has been used with spin–orbit coupling added using the CASSI-SO mentioned above.

2 Method and details of the calculations

All calculations were carried out with the software MOLCAS-5.2. The complete active space (CAS) SCF method was used to generate molecular orbitals and reference functions for subsequent multiconfigurational second order perturbation calculations of the dynamic correlation energy (MS-CASPT2). The multistate option (MS) of the CASPT2 method was used. This is a new feature of MOLCAS-5.2 that allows CASPT2 calculations to be performed for a number of the selected roots from a state average CASSCF calculation. An effective Hamiltonian, constructed using second order perturbation theory, is diagonalized to obtain the final MS-CASPT2 energies.

Scalar relativistic effects were included using a Douglas–Kroll (DK) Hamiltonian. The effects of spin–orbit (SO) coupling were introduced using a newly developed method based on the CASSCF State Interaction approach (CASSI). Here, the CASSCF wave function generated for a number of electronic states are allowed to mix under the influence of a spin–orbit Hamiltonian. The method has recently been described, and we refer to this article for details.

ANO type basis sets were used for U and N. The U exponents were optimized using the DK Hamiltonian. The primitive set 26s23p17d13f was contracted to 9s8p7d5f, and this was combined with the ANO-L basis of the MOLCAS library for N, contracted to 4s3p2d.

In our recent study of the U(vi) and U(vi) systems XUY (X,Y = C,N,O), we found that it was important to include in the active space the nitrogen 2p orbitals and the corresponding UN antibonding orbitals of σ and π type. They will be hybrid orbitals mixing 5f, 6d, and 7s. This gives an active space of twelve electrons in twelve orbitals (12/12).

It would be desirable to include also the four 5fδ and 5fϕ orbitals, but this yields an active space of 14 electrons in 16 (14/16) orbitals. CASSCF/CASPT2 calculations of this size would be very time consuming and it would not be practical when computing an energy surface, where many points are needed. Therefore test calculations were performed by reducing the 14/16 active space to 14 electrons in 14 orbitals (14/14). These calculations indicated that the 12/12 choice was already reasonable and the surface has been investigated with such an active space. However, this means that some of the lower excited states are not included in the calculations near the linear geometry because they correspond to excitation to the 5fδ and 5fϕ orbitals (³Φ and ³Δ states). However, when the symmetry is lowered to C₂v these states will be included in the manifold generated by the 12/12 active space.
The energy surface was investigated by imposing \( C_{2v} \) symmetry, where the uranium atom moves on a perpendicular line bisecting the N–N distance. Thus, two degrees of freedom were varied on the surface, the N–N bond distance and the distance from the uranium atom to the midpoint of the N–N bond. This distance was used as the reaction coordinate and the energy was optimized with respect to the N–N distance. Two singlet, two triplet and two quintet states in each irreducible representation of \( C_{2v} \) were computed for each grid point. This gives eight singlets, eight triplets and eight quintets in all. At the most significant geometries, the dissociation limit, the NUN equilibrium and in the transition state region, these states were coupled through the spin–orbit Hamiltonian, generating 72 spin–orbit states. This procedure is not optimal, however. At the dissociation limit the ground state of uranium (\(^5\)L) is 17-fold degenerate and all these components were not included in the calculation. A separate calculation was therefore performed on the free uranium atom in order to estimate the effect of spin–orbit coupling at the lowest level of theory (including only the components of the \(^5\)L state).

3 Results

Fig. 1 shows a preliminary scan of the potential energy surface without spin–orbit coupling, for the lowest twelve states: four singlets, four triplets and four quintets. The main purpose of this picture is to indicate the complexity of the problem. Most of the electronic states become very close in energy when the U–N bond starts to break. We can also see that some excited states change their energies rather drastically when the uranium atom has reached a distance of about 3 au from the N–N midpoint. This is due to a change in character of the states with larger occupation of 5f\(\delta \) and 5f\(\phi \) orbitals. This behavior is thus an artifact of the calculation. It will, however, not affect the ground state energy surface near the NUN equilibrium geometry, not even after inclusion of spin–orbit coupling, because the \(^3\)\(\Delta \) and \(^3\)\(\Phi \) states do not interact directly with the \(^1\)\(\Sigma_g^+ \) ground state of NUN.

The equilibrium structure of NUN has been investigated in a previous study.

The molecule turned out to be linear and, with the largest basis set, the \( R_{\text{NU}} \) bond distance was estimated to be 1.734 Å (3.277 au). In the present study we have used this value for the bond distance (what we call the equilibrium NUN geometry) to recalculate both the ground state and the excited states.

![Fig. 1](image_url)
At the equilibrium geometry of NUN, the $^1\Sigma_g^+$ ground state is well separated from the higher states included in the calculation. The first $^3\Sigma_u$ excited state lies 2.09 eV (48.2 kcal mol$^{-1}$) higher in energy than the ground state. As a result of this separation, the inclusion of spin–orbit coupling will not have any sizable effect on the ground state energy. Along the reaction path the multiplicity of the lowest state changes. While in the vicinity of equilibrium NUN, the $^1\Sigma_g^+$ is the lowest state, in the vicinity of the transition state, TS, a triplet state becomes the lowest in energy, and at dissociation a quintet state is the lowest.

In Fig. 2 the ground state potential energy surface, without spin–orbit coupling, along the reaction is reported. Spin changes of the ground state are indicated in the plot. The energetics of the reaction is reported in Table 1. At the MS-CASPT2 level without spin–orbit coupling, the NUN molecule lies about 84 kcal mol$^{-1}$ below U and N$_2$ at dissociation, and the TS is found to lie about 86 kcal mol$^{-1}$ above NUN. The insertion reaction of U into N$_2$ seems thus to proceed with only a small barrier of 2 kcal mol$^{-1}$.

As has already been said, spin–orbit coupling does not affect the ground state of NUN. However it might have a larger effect on dissociated U and N$_2$ and on the TS. In order to evaluate spin–orbit coupling at dissociation, we decided to investigate the uranium atom alone. The $^5\Sigma$ ground state has $2 \times 8 + 1 = 17$ degenerate components. A spin–orbit calculation including only the components of the $^5\Sigma$ state resulted in a lowering of the lowest state ($^5\Sigma_a$) energy of about 25 kcal mol$^{-1}$ below the energy without the inclusion of spin–orbit coupling. This is certainly not a complete spin–orbit treatment for uranium atom. More states should ideally be included in the SO Hamiltonian. The first excited electronic configuration of U is, however, (5f)$^2$(6d)$^2$(7s)$^2$, which is even and will not interact with the ground electronic state. We thus expect the higher order effects of spin–orbit coupling to be small and the computed value of 25 kcal mol$^{-1}$ should give a reasonable estimate of the spin–orbit effect on the uranium atom.

In the TS state region spin–orbit coupling was estimated in the same way as for NUN equilibrium structure and it turned out to have a very small effect of only a few kcal mol$^{-1}$. In Table 1 the spin–orbit energy differences are also reported. The isolated U and N$_2$ species lie 58.9 kcal mol$^{-1}$ above NUN and the TS lies 84.6 kcal mol$^{-1}$ above NUN. The inclusion of spin–orbit coupling seems to have a relevant effect only on the uranium atom. This gives a different shape to the

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**Fig. 2** The potential energy surface of the lowest energy state without spin–orbit coupling. On the x- and y-axes, the x- and y-coordinates (atomic units) of the nitrogen atom in the $C_{2v}$ calculations are reported. The U atom was placed in the 0,0,0 position in all calculations.
reaction path, namely that the formation of NUN has an activation barrier of about 25 kcal mol$^{-1}$, which could not be detected without the inclusion of spin–orbit coupling.

It is somewhat surprising that the effect of spin–orbit coupling is so small in the TS region. However, the geometry of the molecule is here: $R(\text{NN}) = 1.48$ Å, $R(\text{UN}) = 1.93$ Å, which should be compared to the UN distance at the NUN equilibrium: 1.73 Å. The charge on the uranium atom is very similar to that in NUN. Thus we still maintain the NU bonds and the large atomic spin–orbit splitting is not yet in effect.

**Conclusions**

We have presented results of a theoretical study of the reaction between uranium atom and nitrogen molecule which form the linear NUN molecule. The reaction surface has been computed for several electronic states of various spin multiplicities. spin–orbit coupling has also been estimated along the reaction path, and it turns out to be important only at the dissociation limit, while in the minimum and transition state regions, it has virtually no effects on the energetics. When spin–orbit coupling is not included, the NUN formation reaction turns out to be almost barrierless, while, with the lowering of the energy of the U atom due to spin–orbit coupling, an activation barrier of about 25 kcal mol$^{-1}$ has been found.

This calculation may not give the final answer to the question of the barrier for the U + N$_2$ insertion reaction. First of all, only a symmetric reaction path has been studied. Further, only a limited number of electronic state have been included in the study, which is especially problematic close to the dissociation limit where the density of states is very large. The approach used here is not ideal, but the best that can be done at present. It would, in such a degenerate system as this, be preferable if spin–orbit coupling could be included already in the wave function calculation, such that it could be limited to the ground state energy surface. We do not know of such a method, however, that has this property and at the same time is able to treat a reaction path. It is certainly not possible to use a method based on single configuration reference functions, like for example coupled cluster methods or density functional theory. A more advanced multiconfigurational approach, which includes spin–orbit coupling from the start, is needed.

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