NUO^+, a New Species Isoelectronic to the Uranyl Dication UO_2^{2+}

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Abstract: The nitridooxouranium cation NUO^+ has been prepared as a new isoelectronic homologue to the uranyl dication UO_2^{2+} by a sequence of ion–molecule reactions starting from the atomic uranium cation U^+. Collision-induced dissociation experiments and ligand-exchange reactions serve to unambiguously identify the ion as a species in which the uranium cation is formally inserted in the NO molecule. New thermochemical data for NUO^+ and UN^+ are given, and the stability of NUO^+ with respect to UO_2^{2+} is investigated by means of quasi-relativistic density-functional calculations.

Keywords: density-functional calculations · ion–molecule reactions · relativistic effects · thermochemistry · uranium compounds

Introduction

The uranyl dication UO_2^{2+} is one of the most prominent molecules for the study of relativistic effects on bonding in heavy transition-metal complexes.[1, 2] The semi-corelike behavior of the uranium 6p orbitals and the involvement of the 5f orbitals in covalent bonding have been recognized as particularly important aspects of the electronic structure of UO_2^{2+} with respect to relativistic influences. Recently, Pyykkö et al. theoretically investigated all species formally isoelectronic to UO_2^{2+} that can be formulated by substituting one or two of its oxygen atoms by a boron, carbon, nitrogen, or fluorine atom and adjusting the molecular charge to yield the required closed-shell $^1\Sigma^+$ term.[3] Of these compounds, the neutral molecules CUO[4] and NUN[5] have been prepared in rare-gas matrices and characterized as linear species by vibrational spectroscopy. However, no experimental evidence has so far been reported for the cationic uranyl homologue NUO^+, even though a theoretical estimate based on Hartree–Fock calculations predicted that NUO^+ is thermodynamically more stable than CUO and NUN.[3] Here, we communicate the first experimental observation of NUO^+, which was generated in the gas phase by ion–molecule reactions involving the atomic uranium cation U^+. In addition, density-functional calculations are used to evaluate the role of relativistic effects in determining the electronic structures of NUO^+ and the parent uranyl dication UO_2^{2+}.

Experimental and Theoretical Procedures

The experiments were performed in a Spectrospin-CMS-47X Fourier-transform ion-cyclotron resonance mass spectrometer equipped with an external ion source [6]. Briefly, U^+ ions were generated by laser desorption/laser ionization by focusing the beam of a Nd:YAG laser (Spectron Systems, $\lambda = 1064$ nm) onto a pure uranium metal piece. The ions were extracted from the source and transferred to the analyzer cell by a system of electrostatic potentials and lenses. After deceleration, the ions were trapped in the field of a superconducting magnet (Oxford Instruments, maximum field: 7.05 T). The $^{238}U^+$ isotope (no $^{235}U^+$ was present in the instrument) was isolated from $^{238}UO^+$ and $^{238}UO_2^+$ ions by using FERETS [7]. Thermalization and removal of excess energy was afforded by collisions with pulsed-in argon (maximum pressure ca. 5×10^{-5} mbar), and special care was taken to ensure that the ions undergoing ion–molecule reactions were not kinetically and/or electronically excited. The reactants were admitted to the cell through a leak valve at a stationary pressure of $1-5 \times 10^{-8}$ mbar (as measured by a Balzers IMG070 ion gauge). The elemental composition of reaction products was identified with high-resolution mass spectrometry, and the reaction pathways were elucidated by MS/MS and double-resonance techniques. Rate constants k derived from the pseudo first-order decay of the reacting ion are reported as a percentage of the theoretical collision rate k_{ADO} [8] and have an estimated accuracy of ±30%. Collision-induced dissociation (CID) experiments were carried out by 1) isolation of the desired ion by using FERETS, 2) kinetic excitation of this ion by a radio frequency pulse, and 3) trapping it for 1 s in argon at a static pressure of 2×10^{-8} mbar. All functions of the mass spectrometer were controlled by a Bruker Aspect 3000 minicomputer.

For the density-functional calculations, the Amsterdam Density-Functional code (ADF, version 1.1.2 [9]) was employed, which is characterized by an efficient numerical integration scheme for the one-electron Hamiltonian matrix elements (an integration parameter of 4 was employed for the present purpose). Slater-type basis functions were used in the LCAO–MO expansion (double-ζ quality basis sets for O, N, and 7s and 6p of U; triple-ζ for 5f and 6d of U with one d-type polarization function for N and O and one p-type for U as suggested by van Wezenbeek et al. [1i]), and Slater-type fit-functions for the evaluation of the Coulomb potential. A frozen-core approximation was used [10] (2s and 2p electrons explicitly considered for N, O; 6s, 6p, 5f, 6d, and 7s for U). The functional employed was the local-density approximation in the Vosko–Wilk–Nusair parametrization on the homogeneous electron gas with Becke and Perdew's gradient corrections to exchange and correlation [11]. Relativistic effects were treated in a quasi-relativistic one-component manner by employing indirect potentials for the description of the relativistic effects in the core shells, adding the Darwin and mass-velocity operators to the Hamiltonian ("Pauli approximation"), and diagonalizing this operator in the space of the zero-order (i.e., nonrelativistic) solutions [12]. All geometries were optimized stepwise by calculating several points in the proximity of the minima on the potential energy surfaces. The chosen treatment of relativistic effects is a computationally feasible approximation to a more accurate fully relativistic four-component calculation [2], which would itself be a highly demanding task for the present system.

Results and Discussion

Experimental Results: As evident from the mass spectrum displayed in Figure 1, the NUO^+ cation can be generated by the

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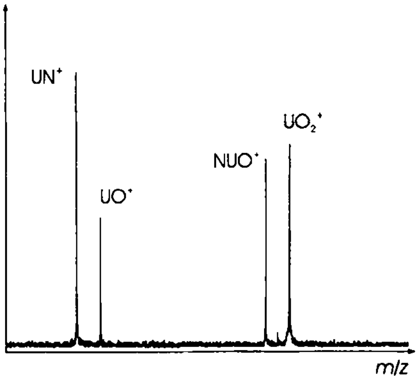
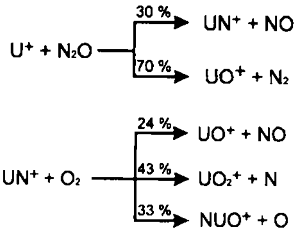
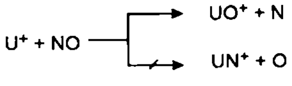


Fig. 1. FT-ICR mass spectrum monitoring the reaction of UN^+ with O_2 ($p \approx 1.9 \times 10^{-8}$ mbar) after a reaction time of 3 s.

sequence of ion–molecule reactions depicted in Scheme 1. The uranium cation U^+ was first allowed to react with nitrous oxide; this resulted in the efficient formation ($k = 8.5 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}, 125% of the theoretical collision rate k_{ADO}) of the cationic uranium oxide (70%) and uranium nitride (30%) species. The exothermic formation of UN^+ in this process provides a lower limit of 115.2 kcal mol^{-1} for the bond dissociation energy BDE(U^+–N) or, in other words, an upper limit of 267.6 kcal mol^{-1} for $\Delta H_f^\circ(UN^+)$.[13] In a less efficient subsequent reaction of UN^+ with molecular oxygen ($k = 4.8 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}, 87% of k_{ADO}), three reaction pathways were observed: 1) ligand exchange with formation of UO^+ and neutral NO (24%), 2) oxidation to UO_2^+ and loss of a nitrogen atom (43%), and 3) formation of NUO^+ and loss of an oxygen atom (33%). By using the known heats of formation of cationic uranium oxide ($\Delta H_f^\circ = 135.1$ kcal mol^{-1}[13]) and cationic uranium dioxide ($\Delta H_f^\circ = 13.5$ kcal mol^{-1}[13]), an upper limit of 225.9 kcal mol^{-1} for BDE(U^+–N) can be derived from processes 1) and 2). A comparison of the resulting range of $115.2 \leq$ BDE(U^+–N) ≤ 225.9 kcal mol^{-1} with the value obtained in an early ion-beam study[14] (108 ± 5 kcal mol^{-1}) suggests that the true bond energy in the cationic uranium nitride is around 120 kcal mol^{-1} rather than 200 kcal mol^{-1}. This conclusion is corroborated by the data available for the neutral UN molecule:[15] Based on the heats of formation of UN(s) (-70.8 kcal mol^{-1}), its enthalpy of sublimation (171.1 ± 5.0 kcal mol^{-1}[16]), and the fact that the ionization energy (IE) of UN is about 1 eV higher[17] than that of the neutral uranium atom (IE = 6.2 eV[13]), the bond energy for UN^+ can be estimated to be 116.6 ± 5 kcal mol^{-1} from a thermochemical cycle. Accordingly, in the reaction of U^+ with NO (Scheme 2), exclusive formation of UO^+ was observed ($k = 12 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}, 200% of k_{ADO}). Formation of UN^+ from this substrate would require BDE(U^+-N) > 150.8 kcal mol^{-1}. A value of 120 ± 10 kcal mol^{-1} for BDE (U^+-N), corresponding to $\Delta H_f^\circ(UN^+) = 262.8 \pm 10$ kcal mol^{-1}, is used below.

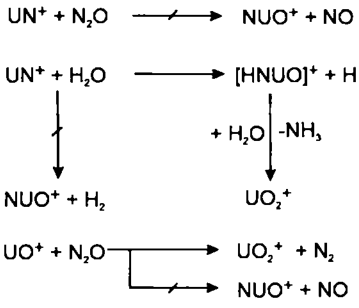


Scheme 1. All rate constants k in cm^{3}molecule^{-1}s^{-1}. Top: $k = 8.5 \times 10^{-10}$, bottom: $k = 4.8 \times 10^{-10}$.



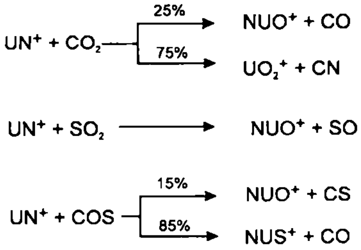
Scheme 2. $k = 12 \times 10^{-10}$.

The exothermic formation of NUO^+ from UN^+ and O_2 (Scheme 1) indicates that the bond energy of the oxygen atom to UN^+ (BDE(NU^+–O)) exceeds 119.2 kcal mol^{-1}. Attempts to generate NUO^+ from UN^+ and H_2O, UN^+ and N_2O, or UO^+ and N_2O were, although thermochemically possible,[13] not successful (Scheme 3). While UN^+ was unreactive with N_2O, the reaction with H_2O occurred with formal transfer of a hydroxyl group to UN^+ (loss of H˙ from H_2O) and subsequent generation of UO_2^+ in a secondary reaction. Thermochemical considerations[13] strongly suggest that an NH_3 molecule is lost as a neutral species in the second step of the complicated ion–molecule reaction sequence. However, it cannot be decided from the mass-spectrometric experiments whether the intermediate UNOH$^+$ ion is a mixed imido–oxo complex $HNUO^+$ or a nitrido–hydroxo species $NUOH^+$. In the reaction of UO^+ with N_2O, UO_2^+ was the only observed product; this is due to the atwo very strong uranium–oxygen bonds (BDE(U^+–O) = 194.3 kcal mol^{-1}; BDE(OU^+–O) = 181.1 kcal mol^{-1}[13]) in the cationic uranium dioxide.



Scheme 3.

Surprisingly, NUO^+ could be generated exothermically by reaction of UN^+ with CO_2 (Scheme 4): Reaction between these two species occured with $k = 1.6 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1} (24% of k_{ADO}) with transfer of one (25%) and two (75%) oxygen atoms to UN^+ and simultaneous loss of CO and a CN˙ radical, respectively. Further studies on the remarkable ability of "bare" and ligated uranium cations to activate the unpolar and highly unreactive carbon dioxide molecule,[18, 19] with special emphasis on the role of relativistic effects in these processes, are in progress in this laboratory. SO_2 and COS also transfer an oxygen atom to UN^+. These reactions provide a final lower limit of 157.6 kcal mol^{-1} for the strength of the NU^+–O bond, which is equivalent to an upper limit of 174.8 kcal mol^{-1} for $\Delta H_f^\circ(NUO^+)$. The reaction of NUO^+ with H_2O (Scheme 5), in which UO_2^+ is formed at 6% of the theoretical collision rate, provides a lower limit of 116.4 kcal mol^{-1} for $\Delta H_f^\circ(NUO^+)$, assuming that NH_2 is lost as the neutral species.[13] On the basis of $\Delta H_f^\circ(UN^+) = 262.8 \pm 10$ kcal mol^{-1} (see above) and the upper limit for $\Delta H_f^\circ(NUO^+)$, available from the oxygen tranfer to UN^+ from COS (174.8 kcal mol^{-1},



Scheme 4. Top: $k = 1.6 \times 10^{-10}$, middle: $k = 10 \times 10^{-10}$, bottom: $k = 2.3 \times 10^{-10}$.

$$NUO^+ + H_2O \longrightarrow UO_2^+ + NH_2$$

Scheme 5. $k = 1 \times 10^{-10}$

see above), we finally reach the following themochemical data for the new species NUO^+: $\Delta H_f^\circ(NUO^+) = 145.6 \pm 29.2\ \mathrm{kcal\,mol^{-1}}$; $\mathrm{BDE(OU^+-N)} = 102.5 \pm 29.2\ \mathrm{kcal\,mol^{-1}}$; $\mathrm{BDE(NU^+-O)} = 176.6 \pm 39.2\ \mathrm{kcal\,mol^{-1}}$.

To probe the structure of NUO^+ (nitrosyl complex $U^+(NO)$ versus the uranyl-like structure with the uranium cation inserted in NO) we performed ligand-exchange as well as CID experiments. In the CID process (Fig. 2), loss of a single nitrogen atom clearly predominates over loss of a single oxygen atom; this reflects the relative strengths of the NU^+-O and OU^+-N bonds (see discussion above). The absence of a U^+ signal in the low-to-modest energy region indicates that the nitrogen and oxygen ligands are in fact separately bonded to the uranium cation and that no nitrosyl complexes $U-NO^+$ are among the observed species. This conclusion is corroborated by the observation that $NU^{18}O^+$ did not exchange NO in the presence of $N^{16}O$ (Scheme 6). Furthermore, NUO^+ was unreactive with O_2. Reaction via the oxophilic U^+ cation would be expected to be favorable if NO were bound as an intact ligand. These experiments give a clear indication that an isoelectronic homologue to the uranyl dication UO_2^{2+} has been prepared, as predicted by theory.[3]

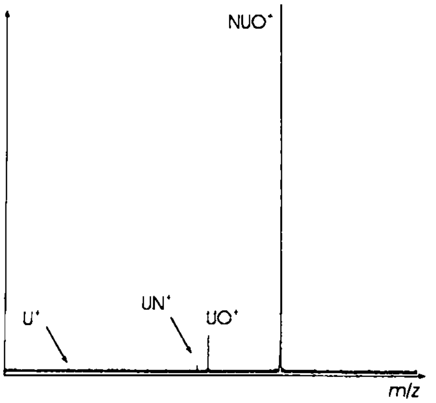


Fig. 2. Typical CID spectrum of NUO^+ at a center-of-mass energy of 35 eV using argon ($p \approx 2 \times 10^{-8}$ mbar) as collision gas.

$$NU^{18}O^+ + N^{16}O \not\longrightarrow NU^{16}O^+ + N^{18}O$$

$$NUO^+ + O_2 \not\longrightarrow UO_2^+ + NO$$

Scheme 6.

Theoretical Results: A remarkable aspect of the electronic structure of the uranyl dication UO_2^{2+} is the relativistic bond lengthening, which has been investigated in a number of detailed theoretical studies.[1,2] Here, we present a brief comparison of NUO^+ with the parent uranyl species, focusing on relativistic effects on the structures and relative stabilities of these species. Both linear molecules have no unpaired electrons, and their ground states correspond to a $^1\Sigma^+$ term ($^1\Sigma_g^+$ in the case of UO_2^{2+}, which has an additional center of inversion). The energies of the frontier molecular orbitals calculated by the quasi-relativistic method (see Theoretical Procedure) are displayed in Figure 3. The arrangements of the one-electron levels in UO_2^{2+} and NUO^+ are similar: the occupied and the virtual spaces are well separated in both cases. The one-electron levels of "gerade" and "ungerade" symmetry in UO_2^{2+} become symmetry-equivalent in NUO^+ and are thus allowed to interact. This causes some energetic reordering of the MOs as compared to those of the UO_2^{2+} ion. As the highest occupied molecular orbital (HOMO) we find an orbital of σ symmetry ($3\sigma_u$ in UO_2^{2+}, which becomes 6σ in the $C_{\infty v}$ point group of NUO^+), which is characterized as a bonding MO with the main contributions from the uranium $5f_{z^3}$ (UO_2^{2+}: 53%; NUO^+: 41%), oxygen $2p_z$ (UO_2^{2+}: 36%; NUO^+: 1%), and nitrogen $2p_z$ (NUO^+: 35%) atomic orbitals.[20] The lowest unoccupied molecular orbital (LUMO) corresponds to a pure uranium 5f orbital of ϕ symmetry. Interestingly, the HOMO–LUMO gap in NUO^+ is 1.3 eV smaller than in UO_2^{2+}. The absorption energies in the optical spectra of compounds containing the uranyl dication and the NUO^+ molecule should therefore be quite different.

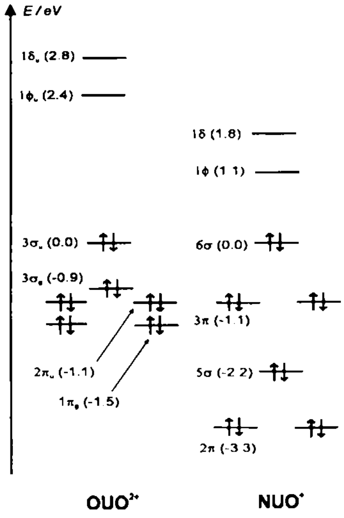


Fig. 3. Frontier molecular orbital schemes for UO_2^{2+} and NUO^+ from quasi-relativistic calculations (orbitals energies ε given in eV relative to the highest molecular orbital; ε_{HOMO} was set to zero in each case).

The equilibrium internuclear bond lengths for NUO^+ and UO_2^{2+} from nonrelativistic and quasi-relativistic geometry optimizations are given in Table 1. The results agree with the Hartree–Fock calculations by Pyykkö et al.[3] in that the U–N bond in NUO^+ is both shorter than the U–O bond in NUO^+ (by 0.055 Å on the quasi-relativistic level) and that in UO_2^{2+} (by 0.011 Å). Furthermore, NUO^+ is also subject to a relativistic lengthening of both bonds of the same order of magnitude (0.03–0.04 Å) as in UO_2^{2+}. This rare effect (most chemical bonds tend to become shorter due to the influence of relativistic effects[2,25]) is characteristic of the electronic structure of UO_2^{2+} and has been shown to arise from a subtle interplay of different factors. Here, we simply take the relativistic bond lengthening in NUO^+ as a further indication that this new cationic species is, also from the point of view of the structural influence of relativistic effects, a new homologue of the uranyl dication UO_2^{2+}. Interestingly, the relationship between the bond lengths and bond energies in the NUO^+ cation is not a simple one: the uranium–nitrogen bond, although 0.055 Å shorter than the uranium–oxygen bond, is $74.1 \pm 68.4\ \mathrm{kcal\,mol^{-1}}$ *weaker* than the latter (see thermochemical data in Experimental Results).

Table 1. Nonrelativistic (nr) and quasi-relativistic (qr) bond lengths r for UO_2^{2+} and NUO^+ (in Å).

	UO_2^{2+}			NUO^+		
	nr	qr	Δ	nr	qr	Δ
r(U–O)	1.690	1.723	+0.033	1.733	1.767	+0.034
r(U–N)	–	–	–	1.675	1.712	+0.037

An estimate of the relative stabilities of NUO^+ and UO_2^{2+} can be derived from the calculated reaction energies for the hypothetical ligand exchange reaction shown in Scheme 7. The nonrelativistic energy for this process is $-5.5\ \mathrm{kcal\,mol^{-1}}$.[21] When the scalar relativistic effects are included, the reaction becomes endothermic with an

$$OUO^{2+} + N \longrightarrow NUO^+ + O^+$$

Scheme 7.

overall energy difference of +40.1 kcal mol^{-1}. Obviously, the energetic stabilization[22] of UO_2^{2+} by relativistic effects is nearly 50 kcal mol^{-1} greater than that of NUO^+. The origins of this difference can be analyzed in terms of the relativistic effects on the total atomization energies[23] of NUO^+ and UO_2^{2+} (Scheme 8). Overall, the strengths of the two bonds in both NUO^+ and UO_2^{2+} are reduced by relativistic effects. The effect is, however, more pronounced in NUO^+ (−56.1 kcal mol^{-1} for the total atomization energy) than in UO_2^{2+} (−10.3 kcal mol^{-1}). The energy partitioning analysis of the relativistic bond weakening as proposed by the groups of Morokuma and Ziegler[24, 25] (Table 2) shows that changes in the orbital interactions of σ and π symmetry are much more important than electrostatic or Pauli repulsion terms. The large relativistic effects on the energies and spatial extent of the uranium atomic orbitals (stabilization and contraction of 6s and 7s, destabilization and extension of 6d and 5f, intermediate situation for 6p[26]) disfavor bonding in NUO^+ much more than in the uranyl prototype species UO_2^{2+}. We conclude that the isoelectronic analogy, which has proven a useful concept in the prediction and gas-phase synthesis of NUO^+ and in the analysis of some electronic and structural aspects common to the two uranyl species, should not be expected to give information on thermodynamic stability, in particular when considerable relativistic effects come into play.

$$NUO^+ \longrightarrow N + U^+ + O \qquad UO_2^+ \longrightarrow O^+ + U^+ + O$$

$$\Delta E = 437.7\ \text{kcal/mol (nr)} \qquad \Delta E = 432.1\ \text{kcal/mol (nr)}$$
$$381.6\ \text{kcal/mol (qr)} \qquad 421.8\ \text{kcal/mol (qr)}$$

Scheme 8. Nonrelativistic (nr) and quasi-relativistic (qr) total atomization energies for UO_2^{2+} and NUO^+.

Table 2. Energy partitioning analysis [a] of the relativistic effects [b] on the total atomization energies of UO_2^{2+} and NUO^+ (all energies in eV).

	NUO^+	UO_2^{2+}
Δ Pauli repulsion	+8.28	+6.85
Δ electrostatic interaction	−2.30	−0.55
Δ steric energy	+5.98	+6.30
orbital interactions		
Δσ	−11.10	−10.75
Δπ	−5.47	−4.71
Δδ/ϕ	+8.31	+8.85
Δ orbital interactions	−8.26	−6.61
relativistic effect	−2.28	−0.31

[a] Atomization energy = steric energy + orbital interactions = (Pauli repulsion + electrostatic interaction) + orbital contributions from all occupied orbitals [24, 27]. [b] The Table gives the changes Δ in each energy term when the quasi-relativistic terms are included, e.g., Δ Pauli repulsion = Pauli repulsion (nonrelativistic) − Pauli repulsion (quasi-relativistic).

Summary

The theoretically postulated nitrido–oxo uranium cation NUO^+ has been successfully generated and characterized by ion–molecule reactions in the gas phase. The heat of formation of this molecule is within the range $\Delta H_f^\circ(NUO^+) = 145.6 \pm 29.2$ kcal mol^{-1}. Theoretical calculations indicate the similarities between NUO^+ and UO_2^{2+} from the point of view of their electronic states and the relativistic effects on the U–O and U–N bond lengths. However, from an energetic point of view, the NUO^+ species benefits from a smaller relativistic stabilization than UO_2^{2+}.

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[20] The molecular orbitals are expanded in basis functions, which have no direct physical significance (R. Mulliken, *J. Chem. Phys.* **1962**, *36*, 3428.). Identification of basis functions with atomic orbitals is an interpretation that has to be treated with caution. Bader has stressed that instead of the common term LCAO–MO (Linear Combination of Atomic Orbitals to Molecular Orbitals) one should rather speak of LCBF-MO (Linear Combination of Basis Functions to Molecular Orbitals): R. F. W. Bader, P. A. L. Popelier, T. A. Keith, *Angew. Chem.* **1994**, *106*, 647; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 620.

[21] Uncorrected for zero-point vibrational energies, which differ by only 30 cm^{-1} (Hartree–Fock results, see ref. [3]) for NUO^+ and UO_2^{2+}. N and O^+ were treated in unrestricted calculations.

[22] We employ the term "stabilization" since the total energies are lowered by inclusion of the relativistic effects.

[23] The ground state configurations (A. A. Radzig, B. M. Smirnov, *Springer Ser. Chem. Phys.* **1985**, vol. 31, Reference Data on Atoms, Molecules and Ions) for the computation of the total atomization energies from unrestricted calculations are: $U^+(6s^27s^25f^3)$, $N(2s^22p^3)$, $O^+(2s^22p^3)$, and $O(2s^22p^4)$. As we have recently demonstrated (ref. [25]), the LDA + B + P functional, employed in the present study tends to overestimate bond energies significantly. Using only the LDA + B part of this functional (i.e., neglecting Perdew's gradient correction to the correlation functional, ref. [11 b]) leads to theoretical nonrelativistic and quasi-relativistic total atomization energies for NUO^+ of 403.3 kcal mol^{-1} and 349.1 kcal mol^{-1}, respectively. The quasi-relativistic result, which does not include spin orbit corrections, compares much better with our experimental value of 296.9 ± 29.2 kcal mol^{-1}. Moreover, this comparison reveals that the absolute magnitude of the relativistic effect on bond energies is relatively insensitive to the choice of "the" functional.

[24] a) K. Kiaura, K. Morokuma, *Int. J. Quantum Chem.* **1976**, *10*, 325. b) T. Ziegler, A. Rauk, *Theor. Chim. Acta* **1977**, *46*, 1.

[25] For a recent, quasi-relativistic application of this scheme to heavy transition-metal systems, see: C. Heinemann, R. H. Hertwig, R. Wesendrup, W. Koch, H. Schwarz, *J. Am. Chem. Soc.*, **1995**, *117*, 495.

[26] For a recent calculation of relativistic effects on the atomic orbital energies of uranium, see: R. van Leeuwen, E. van Lenthe, E. J. Baerends, J. G. Snijders *J. Chem. Phys.* **1994**, *101*, 1272.

[27] The total atomization energies were calculated with respect to the "unrestricted" (F. M. Bickelhaupt, N. N. Nibbering, E. M. van Wezenbeeck, E. J. Baerends, *J. Phys. Chem.* **1992**, *96*, 4864) atomic fragments $U^+(6s^27s^25f^3)$, $N(2s^22p^3)$, $O^+(2s^22p^3)$, and $O(2s^22p^4)$. The ϕ/δ contributions to the bond energy are not due to occupied δ or ϕ MOs (these are part of the virtual spaces, see Fig. 3), but rather reflect the relaxation of 4 out of the 7 5f orbitals due to the change from the K_h (atomic U^+) to the $D_{\infty h}$ and $C_{\infty v}$ (UO_2^{2+}, NUO^+) point groups. The relativistic effects on the total atomization energies from the energy partitioning analysis are somewhat different (3–4 kcal mol^{-1}) from those given in Scheme 8, because the orbitals for the "unrestricted fragments" have to originate from a restricted calculation (see ADF manual, version 1.1.2).