slower than the dynamics of photoinduced bond cleavage. The instantaneous change in the CD signal following photolysis reflects the expected electronic state change of the heme group that accompanies dissociation.[10]

Several possible models can be invoked to account for the dynamic changes in the CD signal that is observed on the 100-ps time scale. Three molecular mechanisms that are consistent with the observed data include vibrational relaxation in the vicinity of the heme, a time-dependent splitting of the degeneracy of the heme transitions, and relaxation of the surrounding protein matrix. Recent picosecond Raman studies by Ondrias and co-workers[11] reveal that vibrational relaxation in the vicinity of the heme is complete within 30 ps, significantly faster than the relaxation process revealed by the CD data. This conclusion is also consistent with recent transient grating studies reported by Miller and co-workers.[12] In order to address the possibility of a time-dependent splitting in the degeneracy of the heme transitions, the following experiments were conducted: (1) picosecond linear dichroism studies on the Soret absorption bands, (2) transient picosecond magnetic circular dichroism of the Q-band absorption, and (3) detailed time-resolved absorption studies of the Q band. These studies, which will be reported in detail at a later date,[13] reveal no evidence for a time-dependent splitting of the degeneracy of the heme transitions and confirm that the spin state of the iron changes within 20 ps of photolysis.

From these observations we are able to conclude that transient CD kinetics provide information on the relaxation dynamics of the protein structure following photodissociation. Calculations reported by Hsu and Woody[14] suggest that the CD of the N band of Mb is primarily due to coupled oscillator interactions between the N_x and N_y transitions on the heme and the $\pi \rightarrow \pi^*$ transitions on the surrounding aromatic amino acids. These calculations also show that aromatic residues as far away as 12 Å from the heme can significantly contribute to the CD spectrum, suggesting that this new form of spectroscopy can be useful in probing the dynamics of protein structural changes that occur outside the immediate environment of the heme group.

One particular local molecular motion that could account for the evolution of the CD signal involves the tilting of the proximal histidine. This can be independently addressed by examining the near-infrared absorption band of Mb at 760 nm as this transition arises from a porphyrin to iron charge transfer and has been shown to be sensitive to the conformation of the proximal histidine with respect to the heme ring.[15] Detailed dynamical studies of this absorption band reveal no change in band shape or band position from 20 ps (the instrument response) to 10 ns following photodissociation.[13] This result suggests that the tilting of the proximal histidine, as well as other structural changes that contribute to the shape and maximum of this absorption band, is not responsible for the observed CD kinetics. Further studies on mutant proteins are planned in order to determine the origin of this relaxation process.

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Ab Initio Studies of the Electronic Structure of the Diuranium Molecule

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Although bonding between two transition-metal atoms is commonly observed, no discrete molecules showing direct actinide–actinide bonding have been isolated. Efforts to synthesize uranium analogues of metal–metal-bonded Mo and W clusters have failed; the propensity for forming U–ligand bonds is apparently much greater than that for forming U–U bonds.[1,2]

The simplest systems in which one could find direct actinide–actinide bonds are the ligand-free actinide diatomics, such as U_2, which has 12 valence electrons that could participate in the formation of U–U bonds. U_2 has been detected in the gas phase,[3] and significant $f\sigma$, $f\pi$, $f\delta$, and $f\phi$ diatomic interactions were predicted by our approximate nonrelativistic molecular orbital calculations at short bond lengths.[4] These theoretical studies provided no information on the bond length, binding energy, or detailed electronic structure of U_2. In addition, the inclusion of relativistic effects is essential for the proper description of heavy-metal systems. We therefore have undertaken the first ab initio study, including correlation and relativistic effects, of the bonding in an actinide diatomic molecule, U_2. The results reported here are decidedly different from those reported earlier[4] and indicate that the U_2 potential surface is quite complex, with two groups of states exhibiting energy minima at two different bond lengths.

SCF, CAS-SCF, and single-reference CI (SRCI) calculations have been performed on a Cray Y-MP (60 CPU h) using the COLUMBUS programs.[5] A relativistic core potential[6] replaced the 156 core electrons (1s–5d), while the 28 semicore (6sp) and valence (5f, 6d, 7s) electrons were described by a (5s6p5d4f) → [3s4p3d2f] Gaussian basis.[7] Relativistic effects give 7s, 6d, and 5f AOs of similar energy and spatial extent. The resultant MOs are closely spaced in energy, allowing many open-shell configurations. As with Cr_2,[8] both long-bond-length (LBL) and short-bond-length (SBL) energy minima are found.

In the SBL states of U_2, the 12 valence electrons occupy MOs formed from 5f, 6d, and 7s AOs, yielding low-spin states such as ^5A_g and $^3B_{1g}$ (D_{2h} symmetry). In the CAS-SCF approach, the lowest valence σ_g and π_u MOs were filled, and the remaining six electrons were distributed among two σ_g, one π_u, two δ_g, and one ϕ_u active MOs. The CAS-SCF calculations involved up to 1749 configuration functions (cf), and the ^5A_g SRCI expansion contained 75 329 cf. For the LBL states, six electrons occupy essentially atomic f orbitals. All possible states with six electrons in the $7s\sigma_g$, $7s\sigma_u^*$, $6d\sigma_g$, $6d\pi_u$, and $6d\delta_g$ MOs were investigated by CAS-SCF (up to 700 cf) and SRCI (up to 313 770 cf). SCF, CAS-SCF, and SRCI energies were evaluated at a range of bond lengths. The energies of the separated atoms were calculated by using a supermolecule of two U atoms at 200 au, ^9A_u state, to avoid size-consistency errors.

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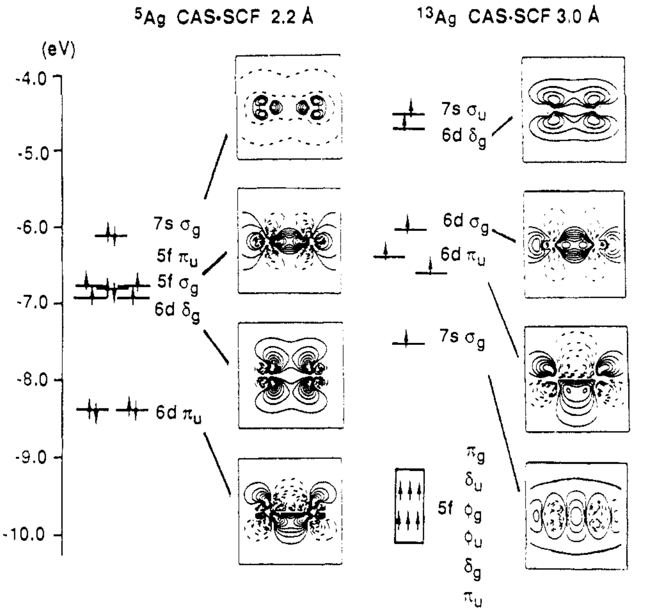

Figure 1. CAS-SCF occupied orbital energy diagrams and contour plots for ^{5}Ag and ^{13}Ag states of U_2. MOs are plotted on a 12 au × 12 au grid, with contour lines at levels of −0.34 to 0.34 au in steps of 0.02 au.

The lowest energy SBL state for U_2 is ^5A_g ($^5\Sigma_g^+$), corresponding to the $7s\sigma_g^2 d\pi_u^4 f\sigma_g^2 d\delta_g^2(t) f\pi_u^2(t)$ configuration. CAS-SCF orbital energies for this state are shown in Figure 1. The MO contour diagrams reveal significant overlaps for $7s\sigma_g$, $f\sigma_g$, and $d\pi_u$, giving an approximate quadruple bond. The energy minimum for these states is at 2.2 Å, 0.6 Å shorter than in the bulk metal.[9] However, this state is not bound with respect to the separated atoms. SCF calculations place the ^5A_g state 740 kJ/mol above the separated atoms; at the SRCI level it is still unbound by 340 kJ/mol.

In contrast to the apparently unbound SBL states, a set of 22 high-spin states with shallow potential minima at 3.0–3.8 Å and approximate harmonic frequencies of 85–105 cm^{-1} were found to lie below the separated atoms in energy. Surprisingly, the lowest energy configuration, $^{13}A_g$ ($^{13}\Delta_g$), has 12 unpaired electrons: $(5f)^6 7s\sigma_g^1 7s\sigma_u^{*1} d\sigma_g^1 d\pi_u^2 d\delta_g^1$. The orbital energies for this state, which has a minimum energy at 3.0 Å, are given in Figure 1. The MO contours for the $7s\sigma_g$, $d\sigma_g$, $d\pi_u$, and $d\delta_g$ MOs show strong overlaps, yielding an approximate double bond. At the SCF level, this state lies 400 kJ/mol below the separated atoms. With SRCI the difference is reduced to 160 kJ/mol.

The improved correlation treatment from SCF to CAS-SCF to SRCI calculations leads to a decrease in the ^5A_g (SBL) energy relative to those of the $^{13}A_g$ (LBL) and atomic states. Although additional correlation effects should lower the ^5A_g energy further, the state may remain unbound even at the highest level of theory. On the other hand, the LBL states may become approximately isoenergetic with the separated atoms when additional correlation effects are considered.

The picture emerging for U_2 is not unlike the complex and controversial one for its analogous 12-valence-electron transition-metal dimers, Cr_2 and Mo_2.[8,10] The simple f-orbital overlap model[4] is an inadequate description of the bonding in U_2: the relatively poor overlap of the U 5f orbitals does not foster U-U bond formation, especially at the sacrifice of electron exchange. Nevertheless, the SBL states show steep potential curves and may indicate the existence of bound metastable species. The LBL states exhibit flat potential curves. Although it is possible that these bound states are artifacts of an incomplete correlation treatment, the diffuse 6d and 7s orbitals of the uranium atom should have optimal overlap at long bond lengths, and these states may remain bound at even higher computational accuracy. Calculations with improved correlation treatment and spin-orbit CI are in progress.

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Spectroscopic Studies on Charge-Transfer Photooxygenation of Disiliranes

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Much attention has been drawn to the reaction of organosilicon compounds with molecular oxygen in recent years. It is well-known that strained silicon–silicon σ-bonds are oxidized exothermically with molecular oxygen to afford disiloxanes as monooxygenated products.[1,2] In spite of the significance of aerobic oxygenation of organosilicon compounds, few mechanistic investigations were carried out.[1,2] Recently we have reported the results on singlet oxygenation of disilirane[3] and oxadisilirane[4] to give 1,2,3,5-dioxadisilolane and 1,2,4,3,5-trioxadisilolane, demonstrating that the silicon–silicon σ-bond is a good electron donor toward singlet oxygen.[3] Our interest in photochemical oxygenation[5] has led us to investigate the direct charge-transfer (CT) photochemical reaction of a silicon–silicon σ-bond with molecular oxygen.[6] We report here the charge-transfer photooxygenation of disilirane and oxadisilirane on the basis of the IR spectroscopic observation of a disilirane–oxygen adduct in a cryogenic oxygen matrix together with ab initio calculations.

The UV absorption spectrum of 1,1,2,2-tetramesityl-1,2-disilirane (**1a**)[3,7] in an oxygen-saturated solvent such as methylene chloride or acetonitrile reveals a weak broad contact CT band with a maximum at 300 nm. The main continuum is seen up to ca.

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