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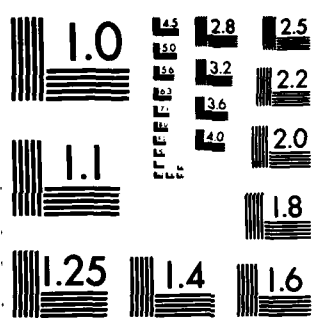
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Application of Quantum Chemistry of Atmospheric Chemistry

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I. INTRODUCTION

Information on the energetics and spectroscopy of metal oxides has long been required to model the potential radiation from disturbed atmospheres. Experimental determination of these properties has proved difficult for the transition metals and actinides. Theoretical calculation, however, has become possible with the development of relativistic effective potentials (REP) (1). The REP include spin-orbit interactions that act on the valence electrons as well as the core relativistic effects. REP have been generated for a number of relevant metals such as iron, neodymium, and uranium and applied to calculations of the oxide electronic states including intermediate coupling calculations of the spin-orbit interaction.

Uranium oxide cations are predicted to be present at long times in a disturbed atmosphere (2). These ions can be pumped by solar radiation to high vibrational temperatures. The electronic and infrared spectra of the ions have not been observed experimentally so the radiative possibilities have remained speculative. Since experimental observation has proved very difficult, ab initio calculations were attempted. Self-consistent-field (SCF) calculations were completed and the spin-orbit interaction included in an intermediate coupling calculations (3). The absorption spectra in the visible was found to be intense and the fundamental infrared frequency for the ground state was predicted. This work is described in the abstract given in Section 2.

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In order to assess the accuracy of these calculations on UO^+ , analogous calculations were completed for UO and NdO ground states and the spectroscopic constants were calculated. These values compare very well with the matrix isolation frequencies. For example, the most accurate calculation predicts a vibrational frequency of 845 cm^{-1} which is only 3% larger than the experimental values (4,5). The calculated data for NdO agrees with the matrix isolation frequency (6) with similar accuracy. Since the calculations for the neutral and cationic oxides are quite analogous, this agreement with experiment supports the accuracy of the predicted UO^+ frequency.

Field (7) has recently presented an analysis of the spectra and electronic structure of the lanthanide oxides based on an accurate ligand field theory (LFT). He has noted that the centro-symmetric term in the ligand field due to the anion leads to a differential destabilization of the d (or f) electrons relative to the valence s electrons. From his analysis the electronic structure of the lanthanide oxides are readily predicted. The actinide oxide structures, however, can be different since it is known from atomic energies that the d and f electrons are now much closer in energy. Calculations of NdO and UO have determined interesting differences in the relative energies of sf^3 compared to df^3 configurations. These results are described in a note on "The Electronic Structure of NdO and UO ". The abstract for this note is given in Section 3. The calculated energy curves are given in Tables I and II together with the spectroscopic constants obtained with a fit to a Morse curve.

The data on the NdO^+ ground state was used to generate all the Ω states arising in the ground state in an intermediate coupling calculation analogous to that done for UO^+ . These energies are given in Table III and provide data for evaluating LET parameters for NdO interactions. The ab initio effective spin-orbit operator (AESOP) (8) was used to calculate the spin-orbit interaction for NdO^+ .

The semi-annual report (1983) described the calculations on the electronic structure and spin-orbit constants of FeO . Although a paper was prepared on these calculations, further work was decided on the analogous RuO systems to clarify problems in analyzing the electronic structure. This will be reported in the FY84 report. The binding in FeO and spin-orbit properties are described in the abstract given in Section 4.

Effective potentials (REP) have been generated for a number of other lanthanides and actinides but calculations of the molecular oxide electronic states were not completed due to two factors. The first was an unexpected increase in computer charges due to a change in DOE policy in recovering costs at the Argonne National Laboratory computer facility which results in a considerable reduction in available computer time. The second factor were convergence difficulties for electronic states involving several open shell orbitals of the same symmetry. Quadratic convergence codes are becoming available which may solve this problem.

II. ELECTRONIC STRUCTURE AND SPECTRA OF UO^+

Relativistic effective potentials are used to calculate the electronic structure and spectroscopic properties of UO^+ . The lowest-energy states are very ionic and the molecular orbitals substantially localized so that

the molecule is described by the ionic fragments, U^{3+} (f^3 , 4I) and $(O^{2-})^1S$. The R_e and ω_e of the ground state, $\Omega=9/2$, have been determined to be 3.48 bohr and 925 cm^{-1} . The vibrational and electronic states are interleaved with the lowest electronic state, $\Omega=7/2$, at 1315 cm^{-1} . The excitation energies of the excited states of UO^+ were calculated using a restricted valence configuration interaction. Strong radiative transitions are predicted in the red part of the visible.

III. ELECTRONIC STRUCTURE OF NdO AND UO

The electronic structure of NdO and UO were compared using relativistic effective potentials (REP) in self-consistent-field (SCF) calculations of electronic states arising from sf^3 , df^3 , and sdf^2 electron configurations. The ground state of NdO is calculated to be a 5I (sf^3) state. The SCF energy curve and spectroscopic constants are given in Table I. About 0.4eV higher in energy, there is the SCF 5A state which is the state with maximum multiplicity that arises from the df^3 configuration. As can be seen from the spectroscopic constants, these states have essentially different curve shapes.

The analogous states for UO are seen to be separated by about 1.0eV and the 5I and 5A spectroscopic constants differ for UO in an analogous manner to the differences for NdO. Examination of the wave functions reveals that the molecular orbitals are substantially localized and the bonding is predominantly ionic. This accounts for the similarity in the R_e among the different for the same metal. The s orbital on the metal is polarized away from anion in a manner reminiscent of the s orbital in UF (9). This polarization yields energy curves with slightly shorter R_e and larger ω_e than is the case for the df^3 system of states.

The electronic structure of the 5I state was confirmed to be ionic in a multi-configuration-self-consistent-field (MCSCF) calculation which correlated the putative σ bonding orbital. The energy curve is found to shift downward (as seen in Table II) by about 0.6eV but the spectroscopic constants are only slightly altered. The correlation of the orbital does not alter the ionic character and the correlation is primarily a little piece of the oxygen atomic correlation. The frequency diminishes slightly due to the slight anti-bonding behavior of the correlating orbital. This decrease in the frequency produces better agreement with the experimental value.

The spin-orbit coupling in these molecules is only large between those states that arise from the same atomic configuration. The 2I state is calculated to be about 2 eV higher in energy than the 4I state so the manifold of doublet states weakly perturb the quartet states. The manifold of Ω states arising from the f^3 electrons in the molecular field were calculated by considering only the 4I , 4H , 4F , $^4\Phi$, $^4\Delta$, $^4\Pi$, and $^4\Sigma^-$ states and their spin-orbit couplings. The results for NdO^+ are reported in Table III.

The analogous quintet sf^3 states are found to be energetically split from one another by energies comparable to that found in the quartet states. The s electron couples to the f^3 quartet states to yield a set of triplet states as well as the quintets. For NdO the splitting between the quintet and triplet states is quite small. The energy difference between the 5I and 3I states is only 0.1eV at 3.50 bohr. But for UO , the difference is nearly 0.7eV reflecting the larger overlap of the s and f

electrons. However, the laborious task of computing the coupling is not needed for qualitative understanding since the energy curve for the 5I and 3I states are so similar.

IV. FeO: BONDING AND SPIN-ORBIT COUPLING

A detailed description of the FeO calculation was given in the semi-annual report. Calculations on RuO which will be reported next year prompted a reassessment of the bonding in this molecule. The bonding is now determined to be covalent but between ionic fragments for the ground state of FeO. The sigma bond forms between the $Fed\sigma$ and $Op\sigma$ orbitals. There is also significant amounts of π electron transfer into open π orbitals. This can occur in both directions but in the case of the $^5\Delta$ ground state, it is $Op\pi$ back transfer into the $Fed\pi$ orbital. The process is masked by the strong bonding and antibonding character of the valence π orbitals. To the extent that the occupancy of the antibonding 3π orbital can be kept small, the dissociation energy of the molecule will be high. The precipitous drop in dissociation energy from VO to CrO, for example, can be explained by noting that the 3π orbital is first occupied in the ground state of CrO.

The non-bonded σ orbitals that is derived primarily from the metal s orbital is polarized as much as possible away from the bonding region. The s contribution to the non-bonding orbitals is enhanced relative to the d contribution by the ligand field of the anion.

The electronic structure of the 5Δ , $5\Sigma^+$, 5Π , 5Φ , 5Γ , $7\Sigma^+$, 7Π , 7Φ , 3Π , and 3Φ states have been studied. The spin-orbit interaction coupling constants have been calculated for the Δ , Π , and Φ states. Comparison of the coupling constants to the experimental values of Merer et al (10), for the 5Δ , 5Π , and 5Φ states is good and confirms the assignments of these states.

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TABLE 1a. Energy Curves of NdO

$-E(71.(a.u.)+)$		
R	5_I	5_A
3.125	0.132793	0.108696
3.25	0.145250	0.123991
3.375	0.149455	0.131389
3.50	0.147270	0.132665
3.625	0.140159	0.129180
3.75	0.129295	0.122024
$R_e(a.u.)$	3.39	3.47
$\omega_e(cm^{-1})$	836	769
$\omega_e x_e(cm^{-1})$	1.9	1.4

TABLE 1b. Energy Curves of UO

$-E(66.(a.u.)+)$			
R	5_I	5_A	5_K
3.25	0.350157	0.305795	0.355852
3.375	0.366864	0.325158	0.369828
3.50	0.374068	0.335137	0.374177
3.625	0.373846	0.337800	0.371085
3.75	0.367866	0.334791	0.362319
4.00	0.343853	0.316860	0.333209
$R_e(a.u.)$	3.56	3.61	3.50
$\omega_e(cm^{-1})$	862	806	909
$\omega_e x_e(cm^{-1})$	1.9	2.0	2.0

TABLE 2. Correlated Energy Curves of UO.

$-E(66.(a.u.)+)$

R	5_I	3_I
3.25	0.3686229	0.3455277
3.375	0.3861980	0.3621616
3.50	0.3942241	0.3693034
3.625	0.3947669	0.3690605
3.75	0.3895035	0.3631138
4.00	0.3668792	

R_e	3.57	3.56
ω_e	845	860
$\omega_e x_e$	2.4	1.9

TABLE 2. Correlated Energy Curves of UO.

$-E(66.(a.u.)+)$

R	5_I	3_I
3.25	0.3686229	0.3455277
3.375	0.3861980	0.3621616
3.50	0.3942241	0.3693034
3.625	0.3947669	0.3690605
3.75	0.3895035	0.3631138
4.00	0.3668792	
R_e	3.57	3.56
ω_e	845	860
$\omega_e x_e$	2.4	1.9

TABLE 3. Electronic Ω States of NdO^+ ($f^3 \ ^4I$) at $R=3.50$ a.u.

Ω	$E(\text{cm}^{-1})^*$
9/2	-2300
7/2	-1670
5/2	-1617
3/2	-1520
1/2	-1396
11/2	-1009
9/2	-497
7/2	-426
3/2	-343
5/2	-174
1/2	-108
13/2	433
11/2	965
9/2	998
3/2	1159
7/2	1238
5/2	1241
1/2	1429
15/2	2066
9/2	2771
13/2	2603
7/2	2841
11/2	2843
5/2	3029
1/2	3050
3/2	3087

*Relative to energy of $\ ^4I$ state