AD-A133 836 APPLICATION OF QUANTUM CHEMISTRY TO ATMOSPHERIC 1/1
CHEMISTRY(U) NATIONAL BUREAU OF STANDARDS WASHINGTON DC
QUANTUM CHEMISTRY GROUP M KRAUSS ET AL. 30 SEP 82
UNCLASSIFIED AFOSR-TR-83-0785 AFOSR-ISSA-82-0017 F/G 7/4 NL

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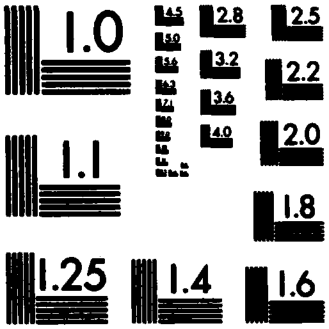

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER AFOSR-TR- 83-0785	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* APPLICATION OF QUANTUM CHEMISTRY TO ATMOSPHERIC CHEMISTRY		5. TYPE OF REPORT & PERIOD COVERED ANNUAL 1 Oct 81 - 30 Sep 82
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M Krauss W J Stevens		8. CONTRACT OR GRANT NUMBER(s) AFOSR-ISSA-82-0017
9. PERFORMING ORGANIZATION NAME AND ADDRESS Molecular Spectroscopy Division National Bureau of Standards Washington, DC		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2301/A4
11. CONTROLLING OFFICE NAME AND ADDRESS AFOSR/NP Building 410 Bolling AFB DC 20332		12. REPORT DATE 30 Sep 82
		13. NUMBER OF PAGES 31
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

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19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Relativistic effective potentials have been used to calculate the elctronic structure and spectroscopic properties of UO+. 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. These transitions are predominantly atomic-like f to d.

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AFOSR-TR- 83-0785

Annual Report: FY82
Application of Quantum Chemistry to Atmospheric Chemistry

Contract No. AFOSR-ISSA-82-0017

Submitted to:

Air Force of Scientific Research
Bolling Air Force Base
Washington, D.C. 20332

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INTRODUCTION

It is becoming increasing evident that the chemical and spectroscopic properties of molecules containing high Z atoms can be calculated using relativistic effective potentials (REP). The REP include the spin-orbit and are functions of the total orbital angular momentum, j. But for many problems in determining the electronic structure a more suitable approach is to decompose the REP into a non-relativistic potential (AREP), in which the spin-orbit interaction is averaged away, plus the spin-orbit interaction in the form of an ab-initio effective spin-orbit operator (2,3,4). Remarkably enough the uranium oxide systems described below are best treated by determining the electronic structure using the relativistic AREP operator and then introducing the spin-orbit interaction with the AESOP operator in a intermediate coupling calculation. This approach limits the number of states interacting through the spin-orbit since the present interest is in the behavior of the ground state and low-lying excited states.

The goals of this program are two-fold. The testing and development of the relativistic effective potentials necessarily forms the first goal. As we shall see below all of our tests to date have been successful. This allows the conconitant application of these techniques to the second goal which is to determine the spectra of the uranium oxide postive ions. A report of the spectra of UO^+ was reported at the DNA meeting on the Spectra of Uranium Oxide Species held at the Las Alamos National Laboratory in January 1983. A preliminary note was also prepared for distribution at that meeting and is included as Section 2 of this report. Both the infrared and visible spectra of UO^+ was predicted. Strong fluorescence pumping in the red part of the visible will pump excited vibrational levels of the ground complex of states. Under low-pressure excitation conditions, then, IR vibrational transitions are expected around 925 cm^{-1} as well as a weaker group of electronic transitions which can range from about 200 cm^{-1} to 1300 cm^{-1}. The intensities of the electronic transitions will depend on the extent of the pumping of the ground electronic states.

Section 3 will summarize the preliminary assignment of the FeO spectra. The assignments are still tentative since quantitative calculation of the differential correlation energy is still in progress. The present result do account for <u>all</u> of the observed levels below 1.5eV.

Section 4 summarizes the calculation of the spin-orbit interaction as a function of the internuclear distance for the ground state, $X^2\Pi$, of OH. This system was chosen as a test of the AESOP since very accurate experimental and theoretical data has just become available. In addition, this system is a prototype for the spin uncoupling that accompanies dissociation into two open-shell fragments. The present calculation accurately reproduces the shape of both the experimental and theoretical all-electron spin-orbit curves. The present calculation is a very simple one, though, compared to the all-electron result and is readily extended to heavier systems while the all-electron calculation can only be extended at great expense.

In the semi-annual report we noted that several of the test calculations on the effective potentials have been accepated for publication including references 3 and 4 on the AESOP operator and a paper entitled, "Electronic Structure of UH, UF, and Their Ions," which has been accepted by the Journal of Computational Chemistry [5]. We have also completed a manuscript on "Finite-Field SCF Calculations of the Dipole Polarizabilities of Heavy Atoms Using Relativistic Effective Potentials," which has been submitted to the Journal of Physics, London [6].

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SECTION 2

THE ELECTRONIC STRUCTURE AND SPECTRA OF UO^+

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Prepared for submission to
Chemical Physics Letters

ABSTRACT

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 $O^{-2}({}^1S)$. All of the quartet states from Σ^- to I, that arise from the coupling of these ionic fragments, are perturbatively mixed using an effective operator for the spin-orbit. The R_e and ω_e of the ground $\Omega=9/2$ state have been determined to be 3.48 bohr and 925 cm^{-1}. The vibrational and electronic states are interleaved with the lowest excited 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. These transitions are predominately atomic-like f to d.

INTRODUCTION

The study of the positive ions of uranium oxide dates from the observation of UO^+ and UO_2^+ from the interaction of U + O_2 in a molecular beam experiment [1,2]. Although the infrared spectra of matrix isolated neutral uranium oxide species from UO to UO_3 [3,4,5] and the spectra of UO_2^+ have been assigned [6], there is no reported spectrum of UO^+. In order to assist in the search for the IR and visible spectra of this ion, we have calculated the electronic structure and energies of the lowest ^4I and ^4H states of the ion and selected excited states which can couple radiatively with the ^4I ground state.

The use of relativistic effective potentials (REP) makes these calculations possible. Recent work on low-Z molecules with non-relativistic effective potentials has shown that the energy curves compare well with all-electron ab initio curves [7,8]. Lee, et al [9] have described the method for calculating the j-dependent REP based on pseudospinors. The $6s_{1/2}$, $6p_{1/2}$, $6p_{3/2}$, $5f_{5/2}$, $5f_{7/2}$, $6d_{3/2}$, and $6d_{5/2}$ spinors were obtained from a Dirac-Fock solution [10] of a degeneracy weighted energy average of the (core)$6s^2 6p^6 5f^3 6d$ open-shell configuration of U^{+2} and the 6g spinors were obtained from the (core)$6s^2 6p^6 6g$ ionic configurations. The spin-orbit interaction is very large for uranium, but the large components of the 6d and 5f spinors with different j values are not substantially different. The positions of the peaks of the outermost maxima of the $5f_{5/2}$ and $5f_{7/2}$ orbitals differ by 0.020 bohr and the $6d_{3/2}$ and $6d_{5/2}$ differ by 0.092 bohr. The calculation of the electronic structures of the ground states of these metal oxides are more readily done initially with neglect of the spin-orbit interaction using ℓ-dependent relativistic effective potentials, and subsequently introducing the spin-orbit interaction through configuration mixing.

The spin-orbit components, or j-dependence, of the REP is eliminated by taking a weighted average [11] of the $j=\ell+1/2$ and $j=\ell-1/2$ potentials:

$$U_{\ell}^{AREP} = \frac{\ell}{2\ell+1} U_{\ell,\ell-1/2}^{REP} + \frac{\ell+1}{2\ell+1} U_{\ell,\ell+1/2}^{REP}$$

The average potential has been designated AREP. Using the ALCHEMY system of codes [12], modified to use the AREP, we performed preliminary self-consistent-field (SCF) calculations which determined that the electronic structure of the lowest energy states is very ionic, and the molecular orbitals are substantially localized. All of the lowest energy states arise from the maximum projection of the angular momentum of the ionic fragments, $U^{+3}(f^3,{}^4I)$ $O^{-2}({}^1S)$, on the molecular axis. The lowest energy state at the SCF level is the ^4I. All of the SCF quartet states from Σ^- to I are found to be similar in electronic structure with the f orbitals being highly localized. Radiative transitions from the ^4I state will be assumed to be representative of the complex. An accurate calculation including correlation is very difficult because important correlating configurations are of different ionicity or orbital occupancy from the SCF configurations, and differential correlation effects for the ions embedded in the molecule complicate the calculation. A qualitative description of the electronic structure and spectroscopy is still possible because the $U^{+3}(f^3,{}^4I)$ state is energetically separate from the other atomic ion states. The f^3 doublets, for example, are nearly 2 eV higher in energy.

The spin-orbit mixing of the lowest energy $^4\Sigma^-$, $^4\Pi$, $^4\Delta$, $^4\Phi$, $^4\Gamma$, ^4H, and ^4I states has been studied perturbatively using the AESOP operator [13]. The lowest Ω states are still dominated by a single Λ function. The mixing coefficient of the ^4I function in the $\Omega=9/2$ ground state, for example, was calculated to be 0.94. Transitions from the dominant ^4I component will then provide a zero order description of absorption from the ground state. Small MC-SCF calculations were done to show that the SCF electronic description was adequate for a qualitative understanding of the ground state.

The excited state calculations were done by restriced valence configuration interaction (VCI) using several sets of localized molecular orbitals. Since we are only interested in those states which are dipole radiatively coupled to the ^4I ground state, we will describe in this note the electronic structure of the low-lying ^4I,^4H, and ^4K states. These data will be used to qualitatively describe the fluorescence pumping of cold UO^+. These calculations are presented to assist in the planning and interpretation of experiments designed to detect UO^+, and to present a preliminary analysis of the electronic structure of such heavy metal oxides.

DESCRIPTION OF THE CALCULATIONS

A double zeta Slater function atomic basis was energy optimized using the AREP on the U^{+2} ($6s^2 6p^6 6d5f^3$, ^5L), U^{+1}($6s^2 6p^6 7s6d5f^3$, ^6L), and U^{+1} ($6s^2 6p^6 7p6d5f^3$, ^6M) states. SCF calculations on the ^4I, ^4H, and ^6K molecular states provided a set of molecular orbitals primarily localized on the oxygen $p\sigma$ and $p\pi$ orbitals, and the uranium 6s,6p,$f\sigma$,$f\pi$,$f\delta$,$f\phi$,$d\pi$,$d\delta$, and $7s\sigma$ orbitals. In order to determine the spin-orbit coupling among the lowest energy $^4\Sigma^-$, $^4\Pi$, $^4\Delta$, $^4\phi$, $^4\Gamma$, ^4H, and ^4I states that arise from all f^3 couplings, it was necessary to calculate these states with a common orthogonal set. Using the SCF molecular orbitals from the ^4I and ^4H states, configuration interaction calculations were carried out using a base set of configurations for each state which arise from three-fold occupancy of the $f\sigma$,$f\Pi$,$f\delta$, or $f\phi$ orbitals and adding all configurations arising from a single excitation from all valence orbitals in the base configurations into the virtual space. The spin-orbit interaction was calculated using the AESOP operator. The energies of these Ω coupled states are given in Table 1 at one distance (3.625 a.u.) relative to the energy of the unperturbed ^4I state.

The lowest energy Ω states are still dominated by one Λ state. For example, the Ω=9/2 ground state is represented by

$$^4I_{9/2} = 0.94\ ^4I - 0.33\ ^4H - 0.10\ ^4\Gamma + 0.02\ ^4\Phi$$

and the $^4H_{7/2}$ first excited state is given by

$$^4H_{7/2} = 0.83\ ^4H - 0.48\ ^4\Gamma - 0.25\ ^4\Phi + 0.08\ ^4\Delta.$$

The energy splitting of the ^4I through $^4\Sigma^-$ states is about 0.3eV, but after considering the spin-orbit coupling, the complex of Ω states is spread over 1eV. Since spin-orbit coupling to states outside the quartet f^3 groups was neglected, only the description of the lowest energy states has any validity.

A Morse fit to the ^4I SCF curve yields an equilibrium internuclear distance of 3.46 bohr and a vibrational constant of 949 cm^{-1} for $U^{16}O^+$. The $^4I_{9/2}$ ground states energy curve is found to have the same R_e and a vibrational constant that is only 10 cm^{-1} smaller. A small multi-configuration SCF (MCSCF) calculation for the ^4I state that includes the dominant back transfer correlation yields an R_e of 3.48 bohr and an ω_e of 935 cm^{-1}. Assuming the spin-orbit correction to the ^4I CI function calculated above applies to the MC-SCF result, the vibrational constant for the spin-orbit perturbed MC-SCF energy curve is 935 cm^{-1}.

A restricted valence configuration interaction was performed on the ^4I, ^4H, and ^4K states to provide an estimate of the absorption spectrum. The U6s, U6p, and O2s orbitals were retained fully occupied and the $f\Pi$,$d\Pi$, and $d\delta$ orbitals were obtained in the ^6K SCF solution. This calculation does not allow for orbital relaxation, so the energy curves are not optimal. The R_e calculated for the ^4I state is about 3.6 a.u. in this calculation. This value is about 0.1 a.u. larger than that obtained in the MC-SCF calculation and is attributed to the use of orbitals that are intended to describe both the ground and excited states and are not optimal for either.

The excitation wavelengths in the visible region from the ^4I ground state are shown in Figure 1. All the curves are shifted so that the ^4I R_e agrees with the value calculated for the MC-SCF curve while retaining their relative positions. The VCI total correlation energy near R_e is about 1eV for both the ^4I and ^4H ground states and results from two types of configuration interaction. The first is the double excitation between the slightly bonding (αU7s + O2p)4σ valence orbital, which is doubly occupied in the SCF wavefunction and the slightly anti-bonding (U7s-αO2p)5σ correlating orbital (α<<1). The second type of correlation mixing results from back-bonding from the (O2p)2π valence orbital into π correlating orbitals. The dominant correlating orbital is primarily U6dπ in character for ^4I and a mixture of U5fπ and U6dπ for ^4H. The same correlating configurations were included in the MC-SCF calculation of the ^4I ground state.

Transition moments from the ground ^4I state to excited ^4I states and all the ^4H and ^4K states are given in Table 2 for R=3.625 bohr. The four strongest transitions which range from 0.75D to over 1D are all atomic f to d transitions. These electronic transitions range from the far red around 750 nm to the green at 455 nm. The electronic transition between the ground ^4I and ^4H states has a relatively weak transition moment of 0.07 D.

DISCUSSION

The ground state electronic structure and spectroscopic constants are based on SCF and MC-SCF calculations using the AREP with inclusion of the spin-orbit coupling as a perturbation. The MC-SCF calculation shows little change in the orbitals from the SCF results with only a modest shift in the dipole moment (∿0.2 a.u.) as a result of the π back-bonding. However, at least two major correlation effects have been neglected because of the inability to handle the calculation at this time. The differential atomic-like correlation between states of different ionicity and d or f occupancy and charge transfer plus polarization configurations must be considered at some future date. As a result it is impossible to gauge the accuracy of the calculations without recourse to comparison with experiment.

An estimate of the ground state vibrational frequency can be obtained by comparing the spectroscopic constants between the SCF curves for the ^4I state of UO^+ and the ^5I state of UO. The VCI curve is not sufficiently reliable because the correlation is not optimized as a function of the distance. The best Morse fits to the SCF curves yield an equilibrium internuclear distance of 3.46 bohr and a vibrational constant of 949 cm^{-1} for $U^{16}O^+$ compared to 3.56 bohr and 863 cm^{-1} for $U^{16}O$. A band at about 820 cm^{-1} has been assigned to $U^{16}O$ in the Ar matrix-isolated spectrum [5], but this value may be appreciably red-shifted from the gas phase value. For the Kr matrix the 820 cm^{-1} band is split and red-shifted to 819 and 815 cm^{-1}. These shifts are smaller than analogous shifts observed in the lithium halides [14]. Linevsky [14a] has shown that the dominant interaction causing the shift is the dipole induced-dipole coupling of nearest neighbors with the difference in the square of the dipole moments in the v=0 and 1 levels determining the magnitude of the shift. Both UO and the alkali halides have large dipole moment derivatives which we find are of comparable magnitudes. But the calculated value of the anharmonic constant for UO is about 2 cm^{-1} or about half the value for LiCℓ [15]. The variation of the dipole moment as a function of the vibrational state in UO is then much less than that in the alkali halides. However, it must be recognized that the $\omega_e x_e$ is obtained from a Morse fit to an energy curve that is not represented well by a Morse curve. The UO MC-SCF calculations yield an R_e of 3.57 bohr and an ω_e about 845 cm^{-1} or about 3% larger than the matrix isolation observed frequency. The spin-orbit coupling will be more complicated in UO than UO^+ but the additional states that mix would tend to lower the frequency. We thus feel that the accuracy is within the 3% range for the UO^+ ω_e of 925 cm^{-1} determined from the spin-orbit perturbed MC-SCF energy curve.

The vibrational infrared transition for the $^4I_{9/2}$ state is very strong with an oscillator strength of about 5.10^{-5} for the v=0 to v=1 transition. This compares with an electronic oscillator strength of about $2.2.10^{-5}$ for the $^4I_{9/2}$ - $^4H_{7/2}$ infrared transition. The vibrational and electronic infrared transitions will interleave. The present calculation predicts, for example, the lowest energy transition to be a vibrational transition at about 923 cm^{-1} followed by an electronic transition at about 1315 cm^{-1}.

The visible electronic transitions will be split by the spin-orbit interaction into a range over 1 eV wide roughly centered around the transitions given in Fig. 1. The spin-orbit interaction for the excited states is too complicated to be treated by the present methods, but the prediction of strong radiative transitions in the visible will not be affected. The quartet states that couple to the lowest $^4\Sigma$, $^4\pi$, $^4\Delta$, $^4\phi$, $^4\Gamma$, and ^4H states are also predominately f^2d systems and have the same transition moment behavior as the ^4H, ^4I, and ^4K excited states. Calculations on the sextet states indicate a dominant configuration with ionicity $U^{+2}O^{-1}$ that will not couple strongly to the radiatively important quartets with ionicity $U^{+3}O^{-2}$. The f^3 doublets are in this energy region but again the spin-orbit coupling is weak because the f and d orbitals, though polarized, do retain considerable atomic character.

Strong radiative transitions are expected in the red part of the visible. The fluorescence will pump the excited vibrational levels of the lower complex of states (which have similar vibrational structure) because the excited states are shifted in frequency and R_e. Under low-pressure excitation conditions the strong visible and IR transitions at about 925 cm^{-1} would be expected. Detailed modeling is not possible because of the true complexity of this system.

ACKNOWLEDGEMENT

Research supported in part by the Air Force Office of Scientific Research under Contract No. AFOSR ISSA-82-00017.

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TABLE I

Electronic Ω States at R=3.625 a.u.

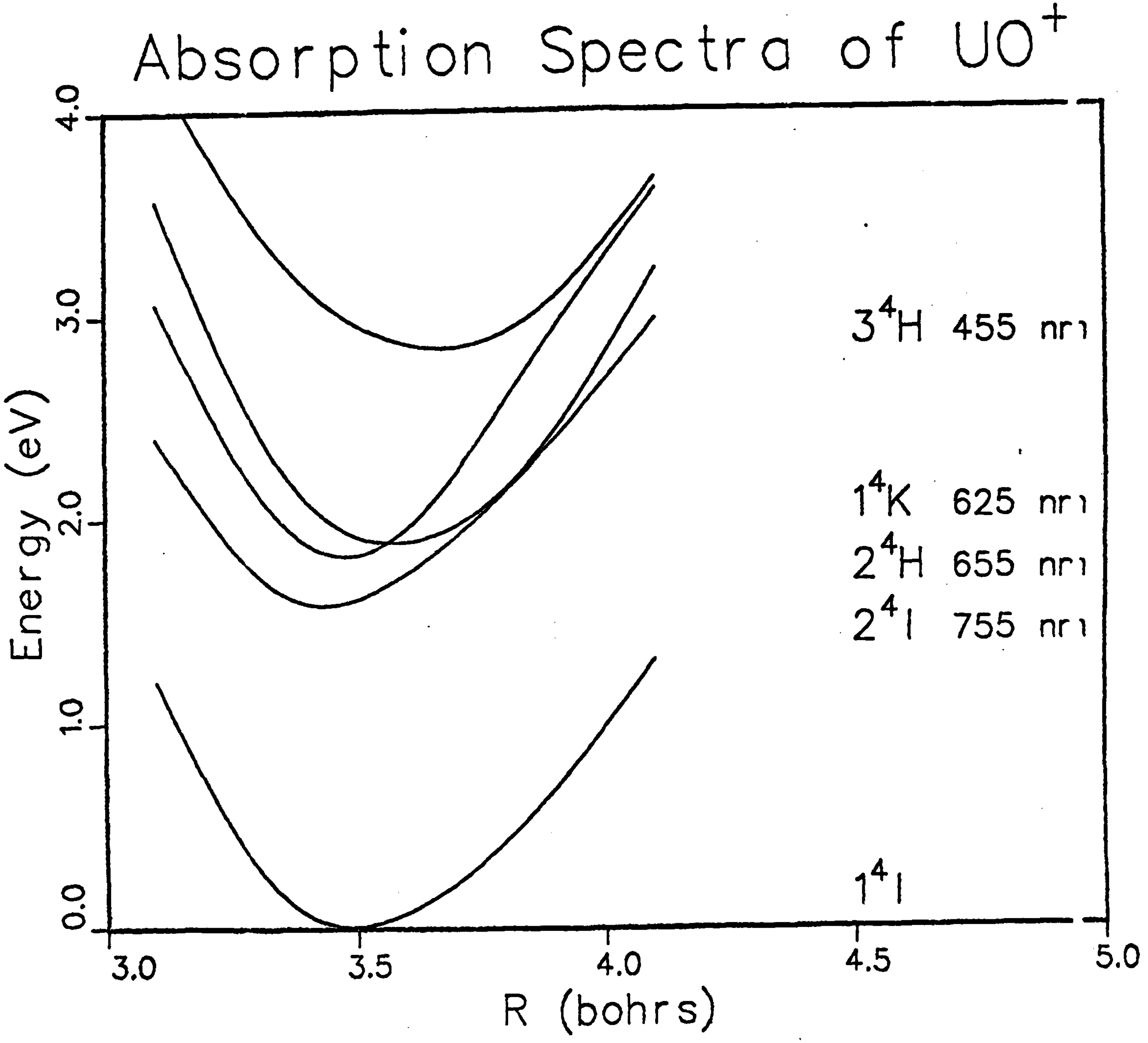
Ω	E (cm^{-1})
9/2	-4661
7/2	-3342
5/2	-2766
3/2	-2567
11/2	-2098
9/2	-1062
1/2	-1138
7/2	-616
3/2	-438
5/2	136
1/2	346
13/2	798
11/2	1827
9/2	2176
3/2	2553
5/2	2777
1/2	2788
7/2	2858
15/2	4128
1/2	4937
13/2	5027
11/2	5799
9/2	5831
7/2	5991
5/2	6285
3/2	6286

TABLE II

Transition Moments from the X ^4I State to the Excited I, H, and K States

Transition Moment (e - bohr)

		Roots	
State	1	2	3
^4I		0.31	0.092
^4H	0.028	0.31	0.61
^4K	0.30		


Absorption Spectra of UO^+
Energy (eV)
4.0
3.0
2.0
1.0
0.0
R (bohrs)
3.0
3.5
4.0
4.5
5.0
3^4H 455 nm
1^4K 625 nm
2^4H 655 nm
2^4I 755 nm
1^4I

3. Electronic Structure of FeO

A survey of the FeO calculations was given in the semi-annual report. The REP was shown to yield energy curves comparable to all-electron values at the SCF level where comparisions can be made. The configuration interaction calculations included all the valence bonding correlation energy but this is insufficient to determine accurate energy differences because of differential correlation energy effects. The valence states can have different ionicity or a different number of occupied d electrons and the "atomic" correlation of the dominant configurations is then required. Such calculations are presently underway but we will show that assignments of the spectra and an ordering of the states can still be made. Interplay between the ab initio results and experimental data permits the precise description of the electronic structure of the ground and excited states of FeO.

The lowest energy $X^5\Delta$, $^5\Sigma^+$, $^5\Phi$, $^5\Pi$, and $^7\Sigma^+$ states will be analyzed in this order. Experimental data exsits only for the first four states. The $^7\Sigma^+$ state provides a good example of the obstacles that differential correlation errors raise in the path of an accurate assignment. This state is actually calculated to be lowest in energy at the valence configuration interaction (VCI) level but it is evident from the orbital populations that the 'atomic' differential correlation will lead to this state being over 1eV above the ground state.

A. The $^5\Delta$ State

The ground state of FeO is now known to be the $^5\Delta$ from unequivacal experimental data [1,2]. Earlier calculations had also suggested a $^5\Delta$ ground state [3,4]. Cheung et al. report the spectroscopic parameters of the $^5\Delta$ state and, most important from our point of view, they determined the spin-orbit splitting.

Because the differential correlation errors result both in errors in calculated excitation energies and spectroscopic constants, we must look, at this stage of the calculation, for other properties to identify the calculated states with the observed ones. Cheung et al. report the spin-orbit coupling constant, $A=-94.9\ \mathrm{cm}^{-1}$. A complete active space multi-configuration self-consistent-field (CAS-MC-SCF) calculation was performed for the $^5\Delta$ state. The O2s and Fe3s and 3P atomic-like orbitals were kept doubly occupied and the three sigma, two pi, and one delta orbitals, that span the O2p and Fe4s and 3d orbitals, were populated with 12 electrons in all possible ways that yield $^5\Delta$. This calculation yields a variationally relaxed valence configuration interaction wave function and energy for the ground state of FeO. Using the CAS-MC-SCF wave function and the AESOF operators for Fe and O, we obtain an $A=-85\ \mathrm{cm}^{-1}$ for $R=3.2$ bohr. This includes a Breit correction of 0.895 for the Fe 3d spin-orbit operator. The error of about $10\ \mathrm{cm}^{-1}$ derives primarily from the neglect of the residual spin-other-orbit valence interactions among the open-shell d orbitals. These interactions arise from the Breit interaction and are not included in the Dirac-Fock atomic calculations from which the effective potentials are derived.

The agreement between experimental and calculated spin-orbit constants of around 10% supports the assignment of the $^5\Delta$ as the ground state. The electronic structure of the state can also be described in terms of the dominant configuration of the CI or the populations of the natural orbitals that represent the CI density matrix. A more complete description of these functions will be given in a subsequent report but the dominant configuration in this case is (core) $1\sigma^2 2\sigma^2 1\Pi^4 3\sigma^2 4\sigma^2 2\Pi^4 5\sigma 3\Pi^2 1\delta^3$, where the dominant atomic orbital contribution in the molecular orbitals are:

1σ - Fe3s, 2σ-Fe3p, 1Π-Fe3p, 3σ-O2s,

4σ-(Fe3d + O2p), 2Π-O2p, 5σ - Fe4s, 3Π - Fe3d, 1δ - Fe3d.

The most significant correlating configurations arise from excitation from the bonding 4σ orbital to the anti-bonding 6σ. Near R_e the population in the 6σ orbital is nearly 0.5.

The MC-SCF wavefuntion is remarkably different from the SCF wavefuntion. The 4σ orbital in the SCF function is almost purely O2p and the 5σ is composed primarily of Fe3d. The SCF function has the ionic character $Fe^{+2}O^{-2}$ but the back-transfer correlation allows the formation of a partial sigma bond. At the relatively short equilibrium internuclear distance, the stronger bond is formed with the Fe3d atomic function. As a result the open-shell 5σ orbital transforms from Fe3d in the SCF function to Fe4s in the MC-SCF function. This result points to the extreme caution required in accepting the result of configuration interaction calculations based on SCF molecular orbitals, e.g., the CI reported for MnO [5].

B. The $^5\Sigma^+$ State

Engelking and Lineberger [2] have found an excited state in the photodetachment spectrum of FeO^-. Using the theoretical calculations for both FeO and FeO^-, they assigned the state as a $^5\Sigma^+$. Our calculations support the assignment. A low-lying $^5\Sigma^+$ state is calculated with the dominant configuration (core) $1\sigma^2 2\sigma^2 1\Pi^4 3\sigma^2 4\sigma^2 2\Pi^4 5\sigma^2 1\Pi^2 1\delta^2$, but the molecular orbitals do not have the same atomic character as they do in the $^5\Delta$ state. The natural orbitals for the MC-VCI solution show that the $^5\Sigma^+$ state has far more s character than the $^5\Delta$ but both states are predominately $Fe^{+2}O^{-2}$. Because of the polarized character of the s containing orbital, the correlation energy is likely to be less for the VCI description of the $^5\Sigma^+$ state than for the $^5\Delta$. The MC-VCI calculations finds these two states within 0.1eV of each other. On the basis of the differental correlation energy, the $^5\Sigma^+$ state is a good assignment for the excited state at 0.5eV.

The ground state of FeO^- is calculated to be a $^4\Delta$. Both the ground $^5\Delta$ and the excited $^5\Sigma^+$ states can be obtained from this anion by removing a single electron from an orbital in the dominant configuration of this state. The orbitals of the anion are substantially different in their atomic structure from the neutral states but the overlap is still large enough to rationalize the spectra observed by Engelking and Lineberger.

C. The $^5\Pi$ and $^5\Phi$ States

These states are observed by Merer et al. to form a complex of levels that lie within 250 cm^{-1} of one another. The closeness of these levels is explained by the fact that the dominant configuration is the same for both states, (core) $1\sigma^2 2\sigma^2 1\Pi^4 3\sigma^2 4\sigma^2 2\Pi^3 5\sigma 1\Pi^2 1\delta^3 6\sigma$. The ionicity of these states is predominately Fe^+O^- with the O^- oriented Π and the Fe^+ in a predominately sd^6 $^6D\delta$ coupling. The 6σ is dominated by a very polarized Fe4s orbital. The $O^-\Pi$ and $Fe^+\delta$ 'atoms' are weakly coupled to produce the Π and Φ states.

The spin-orbit interaction will be used to confirm the electronic structure description. Merer has observed the spin-orbit splittings between the Ω states of the Π and Φ states. The data shows significant perturbations in both the Π and Φ states which is not quantitatively understood. Estimates of the spin-orbit coupling constant can be made from the data, though, for the purpose of comparing with the calculated vaules. For the $^5\Phi$ and $^5\Pi$ states the experimental coupling constants, A, are 47 and 200 cm^{-1}, respectively, for the $^5\Phi$ and $^5\Pi$ states. The calculated constants are 41.9 and 195 cm^{-1}, respectively, for the $^5\Phi$ and $^5\Pi$ states. The comparison is good enough to conclude that the overall electronic description of these states is understood. The energy curves of these states will be described in the next report.

D. The ${}^7\Sigma^+$ State

The MC-VCI energy of this state is about 0.25eV lower in energy than the ${}^5\Delta$ state. But the natural orbital analysis of the ${}^7\Sigma$ state shows that state is of $Fe^{+2}O^{-2}$ ionicity with the valence electrons of Fe in a sd^5 ${}^7S\Sigma$ coupling. The s orbital is highly polarized which will significantly reduce the correlation energy between the s and d electrons. The ${}^5\Delta$ and ${}^7\Sigma^+$ state energies must be corrected by the differential correlation energy between the d^6 and d^5 configuration. Calculations are now in progress to determine the magnitude of this energy which will probably exceed 1eV.

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4. Spin-Orbit Interaction in OH and SH, $X^2\Pi$

The spin-orbit coupling constant for OH, OD, and OT have been reported by Coxon et al. [1,2,3] as a function of internuclear distance. The curve was obtained by inverting data from the first 10 vibrational levels. The curve has a minimum around 1.5Å as seen in Fig. 1, and is found to then increase to larger distances. This was quite unexpected and prompted several theoretical calculations. An accurate all-electron calculation by Langhoff et al. [4] agreed accurately with the experimental data. We had already started a similar calculation using the effective potentials. This was reported in the 37th Symposium on Molecular Spectroscopy held at the Ohio State University in June 1982.

The abstract of the paper presented at that meeting is given below.

SPIN-ORBITAL COUPLING IN THE HYDROXYL RADICAL, OH

WALTER J. STEVENS AND M. KRAUSS

Ab initio effective spin-orbit operators (AESOP), derived from relativistic effective potentials based on Dirac-Fock atomic wavefunctions, have been used to calculate the spin-orbit coupling in the ground $^2\Pi_i$ state of OH as a function of internuclear distance. Spin-orbit interactions between the $^2\Pi_i$ state and the $^2\Sigma^-$ and $^4\Sigma^-$ states arising from the $O(^3P) + H(^2S)$ asymptote have been taken into account as well as interaction with the $A^2\Sigma^+$ state which correlates with the $O(^1D) + H(^2S)$ asymptote. The ground-state was represented by an 11 configuration MC-SCF wavefunction while the excited states were determined by full valence first-order CI calculations using the gound state molecular orbitals. Results near R_e are in excellent agreement with experimentally determined spin-orbit splittings. Spin recoupling is found to play an important role in the variation of the spin-orbit splitting with R. The coupling constant, A, does not decrease monotonically to the oxygen value as previously thought. Vibrational averaging of our calculated values gives excellent agreement with the experimentally determined values of Coxon and Foster [Can. J. Phys., to be published] through v=10.

The vibrational average for the OH, OD, and OT molecules are shown in Fig. 2. The shapes of the calculated and experimental curves are in excellent agreement but the experimental curve for OD is slightly lower than that for OH which does not agree with the calculation.

Using the effective potentials, it is straightforward to repeat these calculations for SH. The vibrationally averaged spin-orbit compling constants for SH, SD, and ST are shown in Fig. 3. The qualitative behavior of the OH and SH spin-orbit coupling is obviously very much the same. As in all calculations with the effective potentials, it is possible to range widely over valence iso-electronic molecules going down a column of the periodic table. The large amount of computer time required for the all-electron calculations precludes such excursions into the heavier systems.

The qualitative behavior of the spin-orbit curve is given by the spin-uncoupling inherent in the base wavefunction which will dissociate OH formally correctly into fragment Hartree-Fock atoms. The wavefunction is given in Fig. 4. Because of the open shell character of both of the atomic fragments, the base configuration has three components including the one with the $3\sigma 4\sigma$ orbitals triplet coupled. This leads to one of the asymptotic determinants to have a spin on the hydrogen atomic orbital opposite to that of the other two. As a result the asymptotic spin-orbit coupling constant for the $^2\Pi$ state is only two-thirds of the constant of the $O(^3P)$ atom. The proper atomic spin-orbit constant is recovered by coupling with the other states that arise from the $O(^3P) + H(^2S)$ interaction. However, this coupling does not become significant until the energy separation between the molecular states becomes comparable to the off-diagonal spin-orbit coupling. This occurs at distances of the order of 2.5Å which is well beyond the turning point for $v=10$. As a result the absolute value of the coupling constant will decrease as v increases until the molecule is excited close to the dissociation limit.

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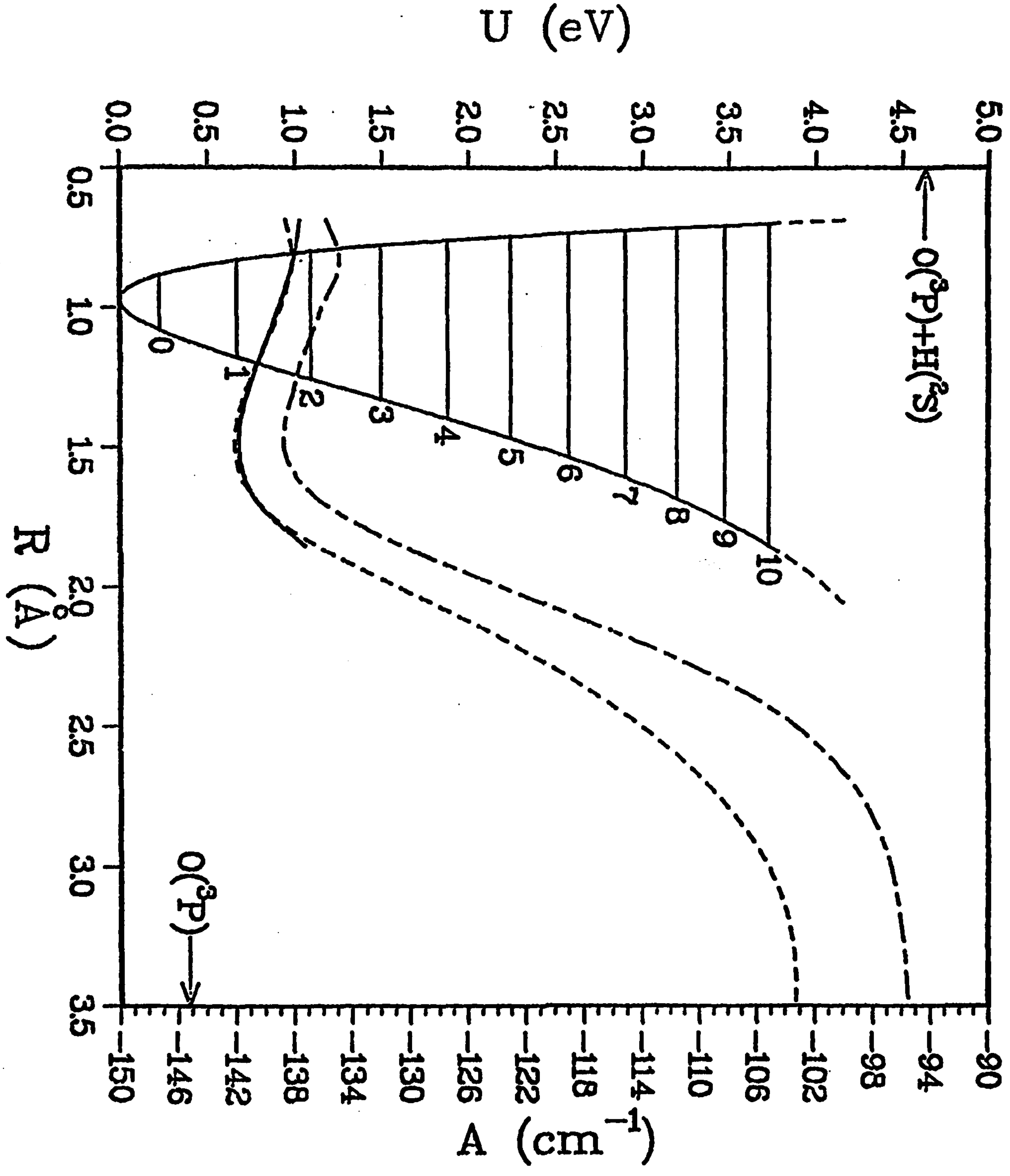
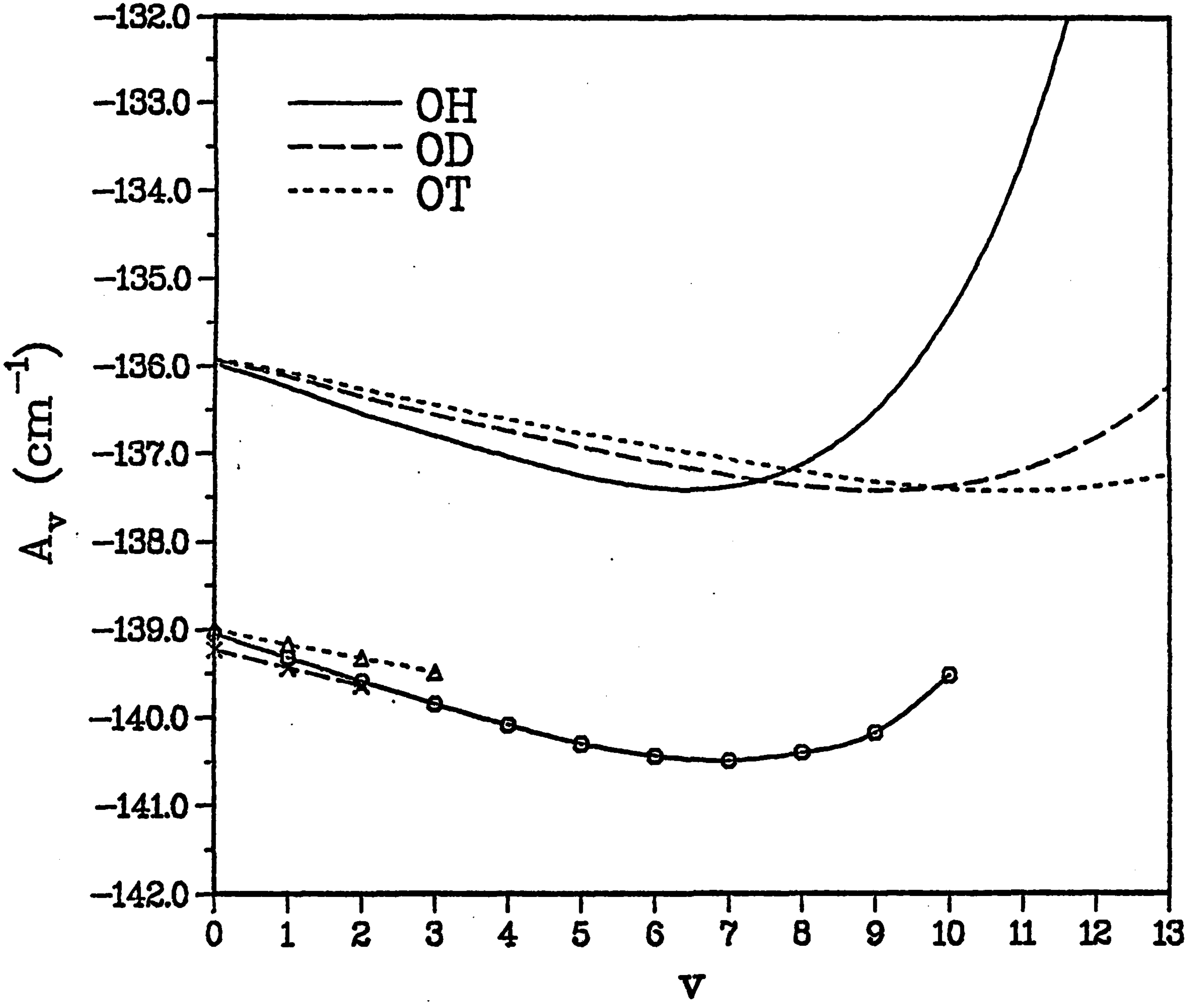
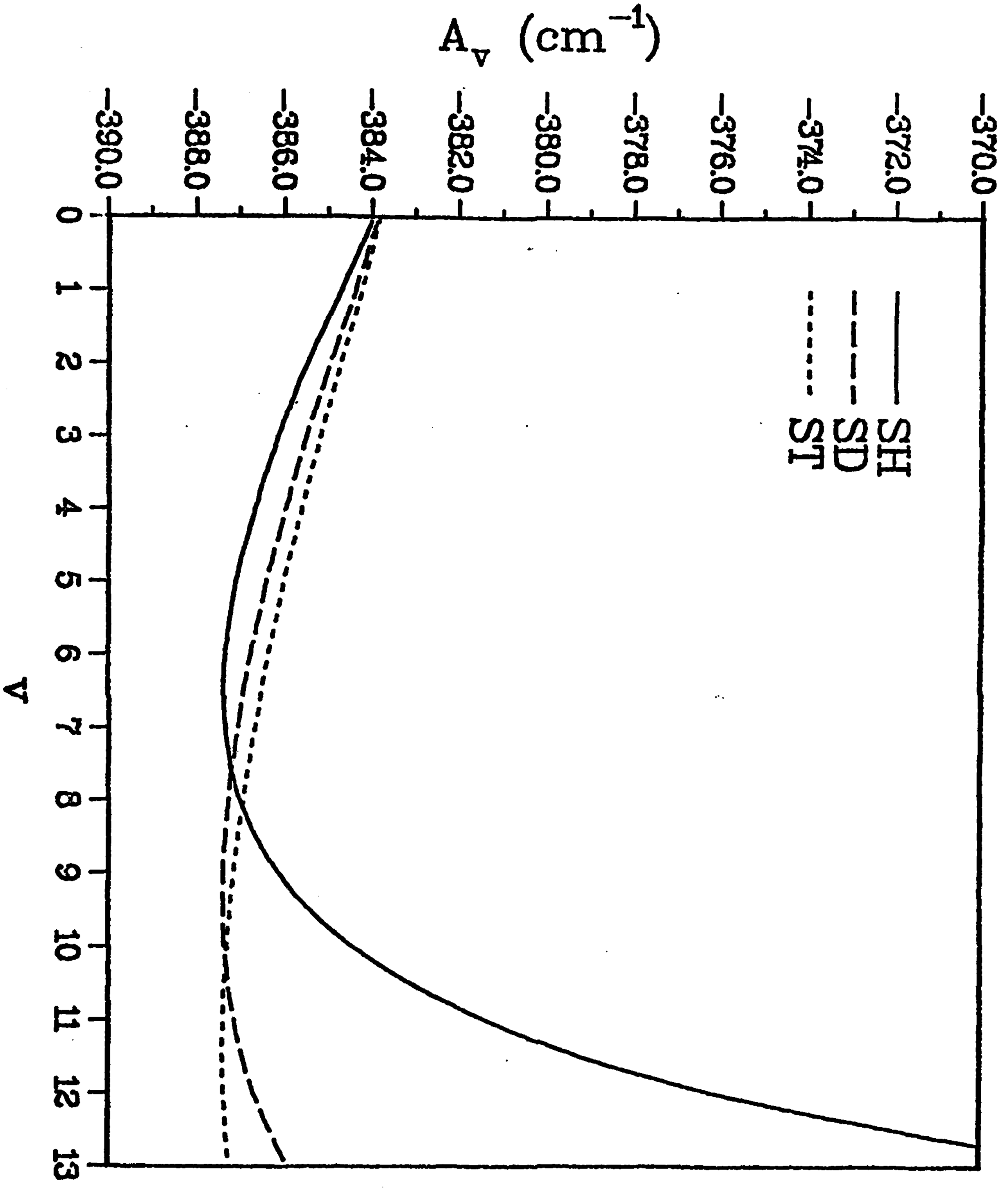


U (eV)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
O(^{3}P)+H(^{2}S)
O(^{3}P)
R (Å)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
1
2
3
4
5
6
7
8
9
10
A (cm^{-1})
-150
-146
-142
-138
-134
-130
-126
-122
-118
-114
-110
-106
-102
-98
-94
-90



A_v (cm^{-1})
-132.0
-133.0
-134.0
-135.0
-136.0
-137.0
-138.0
-139.0
-140.0
-141.0
-142.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
v
OH
OD
OT

2



A_v (cm^{-1})
-390.0
-388.0
-386.0
-384.0
-382.0
-380.0
-378.0
-376.0
-374.0
-372.0
-370.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
v
SH
SD
ST

OH $^2\Pi$ Base Wavefunction

$$\begin{array}{l|l}
C_1 \left[1\sigma^2\, 2\sigma^2\, 3\sigma^2\, 1\pi^3 \right] & \sqrt{\frac{3}{8}} \\
+\, C_2 \left[1\sigma^2\, 2\sigma^2\, 4\sigma^2\, 1\pi^3 \right] & -\sqrt{\frac{3}{8}} \\
+\, C_3 \left[1\sigma^2\, 2\sigma^2\, (3\sigma\, 4\sigma)_t\, 1\pi^3 \right] & \frac{1}{2}
\end{array}$$

Asymptotic ($R=\infty$) Determinants

$$\frac{2}{\sqrt{6}}\ (1s_H\beta)(2p\sigma_O\alpha)(2p\pi_O^-\alpha)$$

$$-\frac{1}{\sqrt{6}}\ (1s_H\alpha)(2p\sigma_O\beta)(2p\pi_O^-\alpha)$$

$$-\frac{1}{\sqrt{6}}\ (1s_H\alpha)(2p\sigma_O\alpha)(2p\pi_O^-\beta)$$

$$A(R=\infty) = \frac{2}{3}\, A(O\,^3P)$$

$$A(R) \sim \left(1.0 - \frac{4}{3} C_3^2\right) A(O\,^3P)$$