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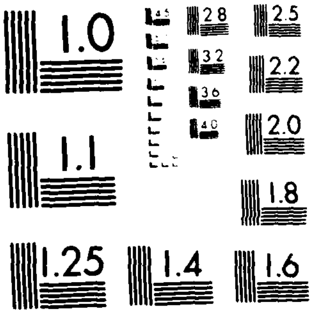

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→The broad goal of our research program was to study excited state chemistry, and electronic energy transfer and chemical energy redistribution processes, using the methods of ab initio electronic structure theory. As a prototypical system we chose reactions of the form

$$Me(Y) + N_2O(^1\Sigma^+) \rightarrow MeO(Z) + N_2(^1\Sigma_g^+)$$

where $Me(Y) = Mg(^1S, ^3P)$ and $Ca(^1S, ^3P)$.→Over the period of this grant we have studied the properties of several subspecies participating in this reaction including radiative decay of metastable atomic species, and the electronic

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20. structure, bonding and optical properties of the alkaline earth oxides. Ultimately we were able to characterize several regions of the lowest singlet and triplet potential energy surfaces of reaction 1 at the SCF/two configuration SCF(TCSCF)/CI level.

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FINAL REPORT

AFOSR-79-0073

THEORETICAL STUDIES OF EXCITED STATE ENERGY TRANSFER AND RADIATIVE PROPERTIES OF TRANSIENT SPECIES USING MCSCF/CI METHODS

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1 Apr 79 - 31 Dec 1982

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Abstract

The broad goal of our research program was to study excited state chemistry, and electronic energy transfer and chemical energy redistribution processes, using the methods of ab initio electronic structure theory. In the course of this research we have contributed to the rapid growth in multiconfiguration self-consistent field (MCSCF) methodology, initially, with the development of an MCSCF procedure based on the generalized Brillouins theorem and the approximate natural orbital method (GBT-NO MCSCF) and more recently with the extension of Lengsfield's density matrix driven quadratically convergent MCSCF procedure to treat state averaged wavefunctions (SA MCSCF). The later algorithm has significantly expanded the scope of problems in excited state chemistry amenable to treatment at the MCSCF/CI level.

As a prototypical system we chose reactions of the form

$$Me(Y) + N_2O(^1\Sigma^+) \rightarrow MeO(Z) + N_2(^1\Sigma_g^+) \qquad 1$$

where $Me(Y) = Mg(^1S, {}^3P)$ and $Ca(^1S, {}^3P)$. Although both the magnesium and calcium reactions are highly exoergic the reactivity and the distribution of product electronic states differs markedly for these two homologues.

Over the period of this grant we have studied the properties of several subspecies participating in this reaction including radiative decay of metastable atomic species, and the electronic structure, bonding and optical properties of the alkaline earth oxides. Ultimately we were able to characterize several regions of the lowest singlet and triplet potential energy surfaces of reaction 1 at the SCF/two configuration SCF(TCSCF)/CI level.

A. Radiative Properties of $Ca(^1D, {}^3P)$

Using GBT-NO MCSCF/CI methods the $1\,^1S$, $1\,^{3,1}P$ and $1\,^{3,1}D$ states of calcium atom were characterized. Using an orthogonal orbital transition moment method and atomic spectral data, line strengths for $^1D \rightarrow {}^3P$, $^1D \rightarrow {}^1S$, $^3P \rightarrow {}^1S$ and other transitions were estimated. It was shown that the principal decay channel of $Ca(^1D_2)$ is the spin forbidden dipole allowed path through the ^3P state to the ^1S state.

B. Electronic Structure of Alkaline Earth Oxides

MCSCF/CI wavefunctions were determined for BeO, MgO and CaO with particular attention focused on the $1,2\ ^1\Sigma^+$ states. It was shown that a viable starting point for the description of these states is necessarily multiconfigurational in character. In each case contributions from structures $Me^{+2}O^{-2}$ and $Me^{+}O^{-}$ must be considered simultaneously, and in the case of the $Me^{+}O^{-}$ structures alignment of the oxygen p-hole parallel and perpendicular to the axis must be included. Subsequently dipole allowed radiative transitions were studied for the $2\ ^1\Sigma^+$ and $1\ ^2\Pi$ states in MgO and CaO. Here the SA-MCSCF procedure proved to be essential.

C. The Reaction $Mg + N_2O = MgO + N_2$

The lowest $^{3,1}A'$ surfaces of this reaction were characterized using SCF/TCSCF/CI methods. These calculations, which were made economically feasible with the purchase (with funds from AFOSR and NSF) of a dedicated minicomputer system, have enabled us to characterize the mechanism for the production of $MgO(X\ ^1\Sigma^+$ and a $^3\Pi)$ and also explain the disparities between the magnesium and calcium reactions. The importance of curve crossings with open shell structures corresponding to excited atomic states in the ground state reaction was demonstrated. A clear phenomenological description of this reaction has emerged. The $^{3,1}A'$ surfaces can be qualitatively partitioned into three contiguous, nondisjoint regions characterized by distinct values of an approximate reaction coordinate, ζ; a reactant region in which $\zeta = \zeta_1 \simeq R(Mg\text{-}O)$, a bending reaction in which $\zeta = \zeta_2 \simeq \angle NNO$ and a product region in which $\zeta = \zeta_3 \simeq R(N\text{-}O)$. Following charge transfer increases in ζ_2 are driven by a Rener-Teller instability in $N_2O^-(^2\Pi)$.

Project Summary

Objectives and Accomplishments

The understanding of the properties and reactivity of transient electronically excited chemical species has important implications for the development of chemical laser systems, and energy storage and detection devices. Our approach to the study of excited state chemistry is theoretical using the methods of ab initio electronic structure theory, in particular stated averaged multiconfiguration self-consistent field (SA-MCSCF) and configuration interaction (CI) methods to characterize the relevant wavefunctions with the Born Oppenheimer approximation.

(A) Computational Methods

In the treatment of the reactive systems involving the interaction of several diabatic surfaces or excited electronic states the MCSCF approximation provides a valuable starting point. Unfortuneately the range of problems in excited state chemistry amenable to treatment at the MCSCF level is limited by variational collapse which precludes direct optimization of excited states of given electronic symmetry. Our studies of the SA-MCSCF procedure (bibliography references (BR) 7,8) have shown this approach to provide a generally useful method for circumventing this difficulty thereby extending the scope of MCSCF methodology.

To this point we have concentrated on the use of this procedure in the evaluation of interstate properties, total energies, spectroscopic constants and dipole moments and nonrelativistic interstate matrix elements, in particular transition dipole moments. The later have, in turn, been used to study optical properties of the alkaline eath oxides (BR 7-9). However a potentially significant application of this approach exists in the area of spin forbidden chemistry in which SA-MCSCF/CI methods could be applied to the determination of interstate matrix elements of the spin orbit operator. An application of this approach to the reactions

$$\begin{aligned} \mathrm{Mg}(^3P) + \mathrm{Ca}(^1S) &= \mathrm{Ca}(^1D) + \mathrm{Mg}(^1S) \\ &= \mathrm{Ca}(^3D) + \mathrm{Mg}(^1S) \end{aligned}$$

is discussed in a proposal recently submitted to AFOSR.

(B) Dedicated Minicomputer System

Ab initio electronic structure methods require large amounts of computer time. In the absence of a (subsidized) readily accessible mainframe computer system reserved for various forms of scientific computation a dedicated minicomputer system (i.e. a computer dedicated to a single class or limited number of related classes of problems) represents an economically viable approach to obtaining the requisite computational facilities. Here the economies result principally from reduced overhead associated a user run system and the increased operating efficiency resulting from improved scheduling.

During the course of this grant we have been fortunate to acquire (principally with funds from AFOSR and NSF) a Perkin Elmer 3200 series computer system, presently configured with a PE 3230, 1.5 megabyte (MB) central processing unit (CPU), 2-80 MB disc drives, 1600 bit/inch (BPI) tape drive and a line printer. Although as discussed in a University Research Equipment Proposal, additional hardware would significantly increase the scope of problems accessible to this system, this system despite its recent acquisition, has been indispensible in achieving the goals of our research program. In particular the characterization of the reaction (BR 10)

$$\mathrm{Mg}(^1S,{}^3P) + \mathrm{N_2O}(^1\Sigma^+) = \mathrm{MgO}(X^1\Sigma^+, a^3\Pi) + \mathrm{N_2}(^1\Sigma_g^+)$$

discussed below, would have been (economically) impossible without the PE system.

(C) Excited State Chemistry

The chemistry studied during the course of this grant falls naturally into three categories which are summarized below:

a. Radiative Decay of Metastable States of Ca Spin Forbidden and Spin Allowed Mechanisms

Several experimental investigations have uncovered apparent anamolies in radiative decay processes involving excited states of Ca, Sr and Ba. As a first attempt to understand these processes we used our Generalized Brilburns theorem (GBT) MCSCF/CI methodology, together with accurate atomic spectra data to determine branching ratios for radiative transitions out of the lowest ^3P, ^3D, ^1D and ^1P states of Ca (BR 3). Both spin-forbidden dipole-allowed (SFDA) and spin-allowed dipole-forbidden (SADF) mechanisms were considered in addition to the usual dipole- and spin-allowed channel. Relativistic effects were included in an approximate semi-empirical manner. The results of this investigation were quite encouraging. The decay of metastable Ca(^1D) was shown to proceed largely by a SFDA mechanism to the Ca(^3P) state rather then as might have been expected by direct quadrupolar decay (a SADF mechanism) to the ^1S ground state. In addition these results suggest a possible explanation for the weak lasting action of the (^1P-^1D) compared to the strong (^3D-^3P)-transition in Sr vapor.

b. Electronic Structure and Radiative Properties of Alkaline Earth Oxides

A series of studies of the low-lying states of BeO, MgO and CaO was performed with particular emphasis on the 1,2,3 $^1\Sigma^+$ states for which treatment at the (SA)-MCSCF/CI level appears to be essential. It has emerged that the electronic structure of these homologous states is qualitatively distinct. The differences were found to result from a combination of three factors, the stability of the states of Me^+, the relative contributions from $Me^{+2}O^{-2}$ and $Me^{+1}O^{-1}$ structures and the orientation of the oxygen p-hole, p_z or p_π, in the $Me^{+1}O^{-1}$ structure. Spectroscopic constants for the as yet unobserved b $^3\Sigma^+$ state of MgO were determined. In particular

(i) BeO (BR 1,4)

Using a Gaussian basis set of slightly better than double zeta plus polarization quality, MCSCF and CI calculations were performed for the ground and several low-lying singlet states of BeO. The computed separations for $X^1\Sigma^+$, $A^1\Pi$ and $B^1\Sigma^+$ states are in good agreement with experiment. The $^1\Sigma^-$ and $^1\Delta$ states, the likely upper states in the Bengtsson-Knave and Harvey-Bell systems, are predicted to lie $\sim$40,000 cm^{-1} above the X state, while the $2^1\Pi$ and $3^1\Sigma^+$ are predicted to lie 56,000 and 65,000 cm^{-1} above the X state, respectively.

(ii) MgO (BR 2,5,7,9)

Using a double zeta plus polarization basis set of Slater orbitals, full valence MCSCF (FVMCSCF) calculations were performed for the low-lying states of MgO. For each state FVMCSCF calculations were used to identify the important configurations which were then used in an MCSCF calculation and subsequently as references in a single and double excitation CI calculation. This approach was found to treat all states equivalently, with the maximum error in the computed T_e's and R_e's of 800 cm^{-1} and $\sim$0.03Å, respectively. The $b^3\Sigma^+$ state which has yet to be characterized experimentally was predicted to have a T_e of $\sim$8300 cm^{-1} and a bond length of 1.79 Å. A spectroscopic analysis of the potential curves indicates that their shapes are in quite reasonable agreement with the range of experimental results. Dipole and transition dipole moments were determined for the $X,B^1\Sigma^+$ and $A^1\Pi$ states at the MCSCF/CI level. Wavefunction determined at the SA-MCSCF/CI level were used to discuss radiative decay of the $B^1\Sigma^+$ and $A^1\Pi$ states, i.e. the $B^1\Sigma^+ \rightarrow A^1\Pi$, $B^1\Sigma^+ \rightarrow X^1\Sigma^+$ and $A^1\Pi \rightarrow X^1\Sigma^+$ radiative transitions.

(iii) CaO (BR 8)

State averaged multiconfiguration self-consistent field and configuration interaction methods were used to discuss the $1,2^1\Sigma^+$ states of CaO. Spectroscopic constants R_e, T_e, and ω_e were determined. In addition, radiative transitions between the $1,2^1\Sigma^+$ states, and the $1^1\Pi$ states were discussed. The spectroscopic constants are in reasonable agreement with experiment although the predicted bond lengths are uniformly long. The calculated lifetime for the v = 6 level of the $A^1\Sigma^+$ state of $130 \cdot 10^{-9}$ s is in good agreement with a preliminary experimental value. The lifetime of low-lying vibrational states in the $A'^1\Pi$ manifold are over an order of magnitude longer than their A state counterparts. The v = 0 level of the $A'^1\Pi$ state is predicted to have a lifetime of $25 \cdot 10^{-6}$ s.

c. The Reaction Me + $N_2O(^1\Sigma^+)$ = MeO + $N_2(^1\Sigma_g^+)$

The lowest singlet and triplet potential energy surfaces for this reaction have been investigated for Me = Mg(BR 10). Several regions of the C_s symmetry surfaces corresponding to $Mg(^1S)[1^1A']$ and $Mg(^3P)[1^3A']$ were considered. On the $1^3A'$ surface, which correlates diabatically with $MgO(a^3\Pi)$, the reaction occurs via charge transfer from magnesium to colinear N_2O, i.e.

$Mg^0 + N_2O^0$ becomes $N_2O^- - Mg^+$. Equivalently the highest singly occupied orbital changes from magnesium $3p_\pi$ to N_2O 3π in character. In the reactant channel π-type approach is downhill and favored over the alternative uphill σ-type approach. Charge transfer leads to distortion of N_2O from its equilibrium $C_{\infty v}$ geometry to a bent structure. Entrance into the product channel then corresponds largely to motion along the N-O coordinate and involves an orbital reorganization in the N_2O moiety. Equivalently this reorganization represents an avoided crossing of $^3A'$ surfaces correlating with $MgO(a^3\Pi)$ + $N_2(^1\Sigma_g^+)$ and $MgO(b^3\Sigma^+)$ + $N_2(^1\Sigma_g^+)$. In this region, which is stable with respect to the reactant asymptote R(N-N) is larger than in $N_2(^1\Sigma_g^+)$.

On the $1^1A'$ surface, there is a barrier to charge transfer. Approach of $Mg(^1S)$ to N_2O is uphill. The barrier to charge transfer is associated with the absence of accessible open shell configurations which correlate with excited singlet states in the isolated atom. For all nuclear configurations sampled the $1^1A'$ surface is lower than the $1^3A'$ surface. However following charge transfer the separation of the $1^1A'$ and $1^3A'$ surface decreases markedly.

In the Ca+ N_2O system, $Ca(^1S)$ is reactive. For calcium the excited singlet states have significantly lower excitation energies than their counterparts in magnesium. This suggests that the mechanism for the reaction of $Ca(^1S)$ involves a preliminary crossing with surfaces correlating with $Ca(^1D)$ or $Ca(^1P)$ followed by the charge transfer mechanism discussed above for $Mg(^3P)$. Single configuration (non variational) SCF calculations suggest that the electronic path leading to the MgO arc band states is uphill, a feature which may be attributable to large energy difference between $Mg^+(^2S)$ and $Mg^+(^2P)$. The Ca (^3P) + N_2O reaction is known to produce chemiluminescence attributable to arc band emission. In calcium, the $Ca^+(^2S)$ - $Ca^+(^2P)$ separation is significantly (~ 10000 cm^{-1}) smaller suggesting an additional direction for future theoretical investigation.

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Work (Partially) Supported by AFOSR Grant 79-0073

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