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QUANTUM CHEMICAL STUDY OF METHANE OXIDATION SPECIES

Final Project Report

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Report for Period: June 1981 - December 1993

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I. INTRODUCTION

Cooperative Agreement No. NCC1-55 has been in effect between NASA Langely Research Center and Wake Forest University throughout the period June 1981 - December 1993. During that entire period, Dr. Charles F. Jackels of Wake Forest University served as Principal Investigator, and Dr. Donald H. Phillips of NASA Langley Research Center served as Technical Officer.

The research funded by this project has focused on quantum chemical investigations of melecular species thought to be important in the chemistry of the Earth's upper and lower atmospheres. The body of this report contains brief discussions of the results of the several phases of this investigation. In many instances these results have been presented at scientific meetings and/or published in refereed journals. Those bibliographic references are also given below.

In addition to the study of specific chemical systems, there were several phases during the course of this investigation where much of the effort went into the development and modification of computer codes necessary to carry out these calculations on the wide range of computer equipment used during this study. This type of code maintenance and development work did not generally result in publications and presentations, but a brief review is given below.

II. CHEMICAL SYSTEMS

The Methoxy Radical

The methoxy radical CH_3O is an important intermediate in atmospheric oxidation of methane. A careful characterization of its ground and excited state electronic structure was an early target of this research. In the first phase of this study, first-order CI wavefunctions were used to characterize the ^2E ground state potential surface. Large scale CI wavefunctions were then used to characterize the vertical excitation energy of the $^2A_1$ - ^2E system. These results were reported in Ref. 1 of the bibliography given below.

In subsequent work, the $^2A_1$ excited state potential surface was characterized in detail, and the harmonic vibrational frequencies were determined for both the ground and first excited states, allowing detailed comparison to the available experimental data. We carried out extensive potential surface calculations to determine the energies and conformations of intersections between the $^2A_1$ first excited state and the three nearby dissociative states. This information is useful in predicting the importance of predissociation of the methoxy radical in the atmosphere. The results of this phase of the methoxy radical study were described in detail in Ref. 2 below.

Intermediates in the Reaction of the Hydroxyl and Hydroperoxyl Radicals

The reaction of OH• and HO_2• to form water and molecular oxygen is a key chain-terminating step in atmospheric free radical oxidation mechanisms. There had been a great deal of uncertainty and controversy concerning which mechanism governed this reaction: 1) A direct hydrogen abstraction mechanism, in which OH• removed a hydrogen from HO_2• *via* a concerted attack; or 2) An indirect mechanism in which a stabilizable intermediate would be formed, followed by a dissociation that would yield water and oxygen.

The first target of our investigation was the possible covalently bonded intermediate, HOOOH. Our calculations characterized the ground state minimum energy conformation and determined that this intermediate is stable with respect to the free radical reactants by about 26 kcal/mol. We also characterized a hydrogen bonded intermediate, HO---HOO, that was predicted to have a stability of about 5 kcal/mol. After extension of this work to some nearby excited states of the intermediates, this study was published in full in Ref. 3 of the bibliography.

Work on this chemical system was suspended for a considerable time to allow more efficient computer programs to be implemented on the PI's machines and to allow our limited personnel resources to concentrate on problems judged to be more important. The system was revisited, however, with the goal of obtaining a prediction of the vibrational spectrum of both the covalent- and hydrogen-bonded H_2O_3 intermediates. This work was completed using high quality configuration interaction and perturbation theory approaches and was fully described in Ref. 4. This information should be

invaluable to any experimental attempt to identify the intermediates by FTIR techniques in high pressure flow systems.

The Complex of the Hydroxyl Radical and Carbon Dioxide

A study of the $HOCO_2$ system was undertaken with the goal of determining its stability relative to the $HO + CO_2$ fragments. If the complex were stable enough (approximately 10-15 kcal/mol) relative to the fragments, its lifetime might be sufficient for it to be an important species in atmospheric OH chemistry. If a significant amount of HO were tied up as the $HOCO_2$ complex, that fact would help explain discrepancies between observed and measured OH concentrations in the atmosphere. Considerable progress was made on this problem. However, in our judgement it was more important to devote our full effort to characterization of chlorine oxide species that might be important in the Antarctic ozone depletion phenomenon. Accordingly, work on this project was suspended before formal publication, and we give full details of our preliminary results here. It is expected that work on this problem will be resumed sometime during the next year and that full publication will follow at that time.

SCF calculations on the hydrogen bonded OH---OCO form of the complex showed that it would be only about 2 kcal/mol more stable than the fragments. This result indicates a hydrogen bond strength in the normal range and too small to be important in the present context.

The covalently-bonded form of the complex, $HOCO_2$, was studied using both SCF and large scale CASSCF (MCSCF) wave functions. The minimum energy geometry for this species was found to be planar, or nearly so, with bond angles and lengths not at all unusual. The $C=O$ double bond was localized on the same side of the planar molecule as the hydrogen atom. On the opposite side was the singly bonded terminal oxygen bearing the in plane unpaired electron. The structure was optimized using calculations that correlated either the entire pi or sigma active space at one time. We were unable to carry out the geometry optimization with CAS wave functions that correlated both spaces at once.

Our present results indicate that the complex may be unstable with respect to dissociation to OH and CO_2 by about 1-2 kcal/mol at the SCF level, but is stable by about 9 kcal/mol at the CASSCF level. This estimate is based upon CASSCF calculations using DZP quality basis sets with active spaces of about 55,000 configuration spin functions. These results have not taken into account any differential energy effect that arises from dynamic electron correlation. Upon resumption of work on this project, the PI plans on obtaining estimates of the dynamic correlation energy for this system using conventional selected-CI and GUGA-CI techniques.

Water Dimer

As a background and calibration study preliminary to the vibrational spectrum study described above for H_2O_3, we carried out calculations of the shifts in vibrational

frequencies of the water molecule upon dimerization. We found that the shifts for both the proton donor and acceptor molecule in this hydrogen bonded dimer were reasonably well predicted by RHF or UHF calculations. However, while the absolute value of the frequencies were much improved at the MCSCF level, the *shifts* in frequency were badly reproduced. In fact they were scattered about the experimental values in an almost random fashion. These results were never published in full, but were reported at the Fifth National Conference on Undergraduate Research in 1991. They have also been used to guide our approach to predicting the shifts in vibrational frequency upon formation of the hydrogen bonded HO--HOO species, described above.

Cholrine Oxide Species

In January of 1992, Dr. Quelch joined this research project and our main effort was directed toward the study of chlorine containing species that might be important to an understanding of the stratospheric ozone depletion phenomenon. Some of this work has been submitted for publication and another aspect of it is about to be put into manuscript form. The main conclusions of this study are outlined below.

The Cl_2O_2 System. The photolysis of the ClOOCl species to yield ClOO + Cl has been generally postulated as a key mechanistic step in the stratospheric Antarctic ozone depletion event observed each spring. Since any significant photolysis to form ClO + ClO would lessen the importance of this species to the overall depletion, we have begun a theoretical investigation of the vis-UV absorption spectrum of ClOOCl to determine its excitation energies, absorption intensities, and nature of the excited state(s). This first investigation of the excited states is expected to either confirm that ClO---OCl cleavage is unlikely, or suggest that further studies be undertaken to determine branching ratios between the possible photolytic channels.

In the first phase of this study, we carried out work on ClOOCl using DZP, DZP + diffuse, and ANO basis sets. At the experimental geometry we have calculated excitation energies at the RHF and selected CISD(Q) levels. These results indicate the following SCF vertical excitation energies: $^1B <-- {}^1A$ (6.21 eV); $^3A <-- {}^1A$ (5.90 eV); $^3B <-- {}^1A$ (4.63 eV) ; and $2^1A <-- {}^1A$ (6.36 eV). At the single-reference, extrapolated selected CISD + quadruples corrected level, the following excitation energies are obtained: $^1B <-- {}^1A$ (5.14 eV); $2^1A <-- {}^1A$ (6.02 eV). This places both of the allowed excitations in the 210-250 nm wavelength range. Examination of the excited state natural orbitals shows that the orbital occupied by the excitation has significant antibonding character in both the O-O and Cl-O bonding regions.

We have extended these results to the CASSCF level. A series of ever increasing CASSCF expansions was explored until the results appeared to be stable with respect to further expansions of the active space. These calculations include all valence shell oribitals and electrons [26/16] for this problem. Work is still in progress, but results are available for several of the low lying states:

ClOOCl Excitation Energies (in eV) from the Ground State at the CASSCF[26/16] Level.

State	Energy	State	Energy
A^1A	4.33	D^1B	5.37
B^1B	4.34	E^1A	in progress
C^1A	5.32	F^1B	in progress

Examination of the molecular orbitals for these wave functions shows that each of the excitations into these states arises from excitation of a $3p$ lone pair electron on chlorine into an orbital that is largely Cl-O antibonding, with the excited states having various degrees of O-O antibonding character.

Work is continuing on this system, with the focus being the convergence of the E and F energies, inclusion of external correlation effects *via* large scale selected configuration interaction calculations, and determination of transition moments. A paper reporting these results will be prepared during the next six months.

The ClOOOCl system. Besides the chlorine oxide dimer, heavier chlorine oxide molecules may form in the Antarctic climate and their photolysis should be understood in order to dermine their importance to the models of ozone depletion. Dr. Quelch of this laboratory has carried out calculations that are aimed at characterizing the conformation and stability of the open-chain ClOOOCl molecule. This work is part of a collaborative effort with Dr. Donald H. Phillips of NASA Langley Research Center that focuses on the general class of compounds ClO_nX, with n=2,3 and X=H,Cl. The minimum energy conformation of the ClOOOCl system has been determined for the C_2 and C_s forms:

ClOOOCl Calculated Minimum-Energy Conformations ($\mathring{A}$,deg).

Symmetry	R_{OO}	$R_{Cl\text{-}O}$	Θ_{OOO}	Θ_{ClOO}	ϕ_{ClOOO}	Energy(au)
C_s	1.4563	1.7636	105.01	107.87	102.76	-1143.49050
C_2	1.4525	1.7602	105.69	107.34	84.36	-1143.49281

This work has been submitted for publication and is presently undergoing referee review. See Ref. 5 of the bibliography below.

III. COMPUTER CODE DEVELOPMENT.

At various times during the course of the cooperative agreement, considerable effort was put into the development of computer codes for use in the PI's laboratory and at NASA Langley Research Center. While these efforts have not resulted

in formal publication and mostly have been peripheral to the scientific work reported above, one of them consumed enough of our time that it was reported at a scientific meeting and is briefly described below.

During the early stages of this program considerable effort was devoted to implementation of gradient-search MCSCF programs and large scale CI programs on the CDC VPS-32 vector computer then being used at NASA Langley. The architecture of this machine provided very good performance for codes that carried out their calculations using data structures of very long vectors. However, for the shorter vectors more often encountered in electronic structure calculations, this machine performed very inefficiently and often required more time for completion of the task at hand than would have been required by conventional, scalar, main-frame computers. Working with the HYDRA and MELD programs we heavily modified the loop structures in order to make effective use of the KAP-205 precompiler, which in turn allowed efficient use of the VPS-32 itself. This work consumed a great deal of time and resulted in a report at one scientific meeting. However, due to the extreme problems associated with this particular architecture, the HYDRA and MELD codes never performed dependably and efficiently on the VPS-32. We concluded that electronic structure codes were much better suited for execution on supercomputers with shorter natural vector lengths (e.g. the Cray series) or on superscalar workstations (e.g. HP 735 and Sun Sparc 10).

IV. BIBLIOGRAPHY

The following list contains those publications that report in detail the completed phases of the work supported by the cooperative agreement:

1.   "A Theoretical Potential-Energy Surface Study of Several States of the Methoxy Radical", Charles F. Jackels, J.Chem. Phys. **76**, 505 (1982).

2.   "A Potential-Energy Surface Study of the $^2A_1$ and Low-lying Dissociative States of the Methoxy Radical", Charles F. Jackels, J. Chem. Phys. **82**, 311 (1985).

3.   "An ab initio Investigation of Possible Intermediates in the Reaction of the Hydroxyl and Hydroperoxyl Radicals", Charles F. Jackels and Donald H. Phillips, J. Chem. Phys. **84**, 5013 (1986).

4.   "The Vibrational Spectrum of H_2O_3: An *ab initio* Investigation", Charles F. Jackels, J. Chem. Phys. **99**, 5768 (1993).

5.   "Normal-valent ClO_nX compounds for $n = 2,3$ and $X = Cl,H$: An MCSCF investigation", Donald H. Phillips and *Geoffrey E. Quelch*, J. Chem. Phys., submitted for publication, August 1993.

The following publication wase published by Dr. Quelch reporting work he completed in the PI's laboratory during the period he was supported by the cooperative agreement:

6.   "Octahedral and Prismatic Isomers of CrF_6: Energies and Vibrational Frequencies", Colin J. Marsden, David Moncrieff and *Geoffrey E. Quelch*, J. Phys. Chem. **98**, 2038 (1994).

One or two publications will be submitted during the next year reporting work done during the final phases of the cooperative agreement.

V. PRESENTATIONS
The following list contains presentations given by the PI and associates during the course of the cooperative agreement that acknowledged NASA's support:

Invited Seminars:

1.   "Quantum Chemical Calculations on Small Molecules", given at the Department of Chemistry, East Carolina University, Greenville, NC, Jan. 28, 1983.
2.   "Quantum Chemical Calculations on Small Molecules", given at the Department of Chemistry, Virginia Polytechnic and State University, Blacksburg, VA, Feb. 24, 1983.
3.   "Intermediates in the Reaction of the OH and HO_2 Radicals", given at the Center for Astrophysics, Harvard College Observatory, Cambridge, MA, January 27, 1986.
4.   "Intermediates in the Reaction of the OH and HO_2 Radicals", given at the Department of Chemistry, Harvard University, Cambridge, MA, April 23, 1986.
5.   "Computational Investigations of Atmospheric Species", given at the Department of Chemistry, University of Notre Dame, South Bend, IN, January 30, 1990.
6.   "*Ab initio* Studies of Atmospheric Species: Cl_2O_2 and H_2O_3", given at Pacific Northwest Laboratories, Richland, Washington, January 21, 1993.
7.   "From the Fermi Hole to the Ozone Hole: Quantum Chemistry of Cl-O-O-Cl", given at the Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia, February 18, 1993.

Invited presentation at a National ACS Meeting:

8.   "Quantum Chemical Investigation of Short-Lived Species Arising from Hydroxyl Radical Reactions", given at the 203d National American Chemical Society Meeting, San Francisco, April 7, 1992.

Contributed presentations at Scientific Meetings:

9.   "A Quantum Chemical Investigation of the $^2A_1$ Excited State of the Methoxy Radical" 185th National American Chemical Society Meeting, Seattle, Washington, March 1983.

10.   "Intermediates in the Reaction of the Hydroxyl and Hydroperoxyl Radicals"; C. F. Jackels and D. H. Phillips, 5th International Congress on Quantum Chemistry, Montreal, Quebec, August, 1985.

11.   "A Potential-Energy Surface Study of Intermediates and Transition States in the Reaction of Hydroxyl and Hydroperoxyl Radicals", C. F. Jackels and D. H. Phillips, 192nd National American Chemical Society Meeting, Anaheim, California, September, 1986.

12.   "The Performance of an Advanced Vectorizing Preprocessor on Some Typical Quantum Chemistry Codes", Charles F. Jackels, Paul V. Gregory and Donald H. Phillips, 1987 American Conference on Theoretical Chemistry, Gull Lake, Minnesota, July, 1987.

13.   "Vibrational Frequencies and Intensities of the H_2O_3 Species", Charles F. Jackels, Seventh American Conference on Theoretical Chemistry, San Diego, California, August, 1990.

14.   "Calculated Vibrational Frequency Shifts of the Water Dimer", presented by Dereck M. Haskins at the Fifth National Conference on Undergraduate Research, Pasadena, California, March, 1991.

15.   "Photodissociation of Cl_2O_2: Implications for Ozone Depletion", G. E. Quelch and C. F. Jackels, the 21st Southeastern Theoretical Chemistry Association Conference, Huntsville, Alabama, May 28-30, 1992. Presented by G. E. Quelch.

16.   "Photodissociation of Cl_2O_2: Implications for Ozone Depletion", G. E. Quelch and C. F. Jackels, 11th Canadian Symposium on Theoretical Chemistry, Montreal, Quebec, August 2-7, 1992. Presented by G. E. Quelch.

17.   "Excited States of Cl_2O_2: Implications for Ozone Depletion", G. E. Quelch and C. F. Jackels, the 22nd Southeastern Theoretical Chemistry Association Conference, Raleigh, North Carolina, May 20-22, 1993. Presented by G. E. Quelch.

VI. PERSONNEL

Dr. Charles F. Jackels, Professor of Chemistry at Wake Forest University, served as Principal Investigator throughout the term of this cooperative agreement.

Dr. Geoffrey E. Quelch, Postdoctoral Research Associate, devoted his full effort to the work supported by this agreement from January 1992 - September 1993.

The following undergraduates made significant contributions to the work:

Mr. V. Paul Gregory, undergraduate research student, worked on the code optimization problem for execution on the VPS-32 computer.

Mr. Dereck Haskins, undergraduate research student, carried out the calculations on the water dimer outlined above.

Ms. Stephanie Parker, summer NSF-REU undergraduate research student, developed the interactive graphics tools used by us to realize 3D visualizations of molecular orbitals on our Sun workstation.

The following undergraduates carried out their research projects in the PI's laboratory during the course of the cooperative agreement and made minor contributions to the supported work:

Mr. Walter Slomiany, "Computer Graphics for the Tektronix Terminal", 1982.
Mr. Wolfgang Bergmann, "Analytical Fit to Potential Energy Surfaces", 1982.
Mr. Buck Cochran, "Cartesian Coordinates of CH_3O at Low Symmetry", 1982.
Mr. John Williams, Summer 1984, "MO Plotting Program for *Ab Initio* Calculations".