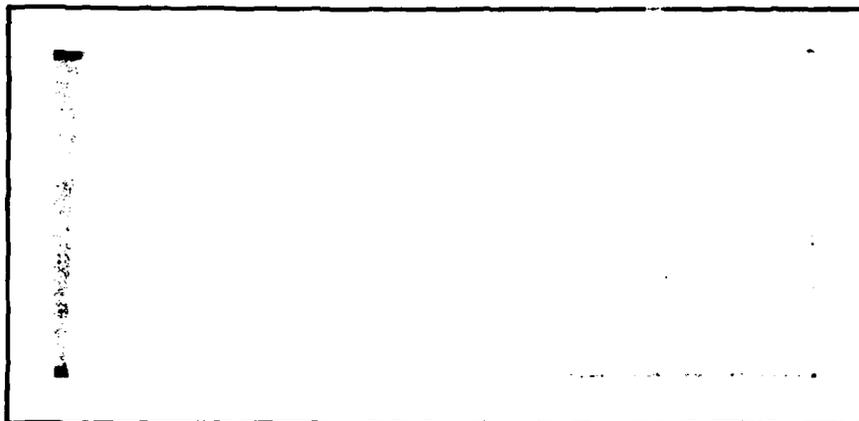


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FINAL REPORT ON
AFOSR CONTRACT F49620-78-C0050
ATMOSPHERIC TRIATOMIC MOLECULAR STUDIES
NOVEMBER 17, 1980

Report Prepared by:

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number): A systematic study at the SCF and MCSCFCI level has been made of several of the fifteen triatomic atmospheric molecules which have formed the focus on this and previous work. In addition a powerful new (MCSCF) method has been developed and partially implemented. Also, in order to achieve accurate electron affinities and ionization potentials, a new scheme for configuration selection has been developed called the differential correlation energy method. This method has been tested on the processes, CH-CH and CO₂+CO₂.

TABLE OF CONTENTS

	Page
I. Introduction and Objectives.	2
II. Overall Status of Molecular Triatomic Project.	3
III. The Differential Correlation Energy Method.	9
IV. MCSCF Method Development: Multidimensional Newton-Raphson Method.	17
V. Molecule by Molecule Summary.	19
VI. Publications Planned, in Preparation and Published.	29
VII. Interactions and Attendance at Meetings.	31
VIII. Project Personnel.	33
IX. Concluding Remarks	34
X. References	35
Appendix I: Publications Resulting from Atmospheric Project. (1974-1980)	36

I. Introduction and Objectives

The purpose of this report is to present work performed under this AFOSR contract. As has been repeatedly discussed elsewhere (Ref. 1-5) the thrust of this project is triple pronged: 1) to calculate on a consistent and comprehensive basis basic energy quantities for the triatomic molecules H_2O , CO_2 , NO_2 , N_2O , and O_3 and their positive and negative ions. These quantities include the vertical spectra, the ionization potentials and the electron affinities of these systems. As part of this effort portions of potential energy surfaces are computed and used to predict vibrational spectra and to interpret the mechanisms of chemical reactions of interest. 2) second the development of two new methods for treating electronic structures will be discussed. 3) the third topical area of this research involves the study of specific atmospheric problems involving these molecular systems as they are brought to our attention through the literature or directly by experimentalists. In this section a molecule by molecule summary will be given.

This report will follow the above structure. First, overall status will be given, then progress on two new method development projects (MCSCF and Differential Correlation Energy (DCE) will be summarized, next a molecule by molecule summary summary will be given.

II. Overall Status of Molecular Project

The overall status of the triatomic project is summarized in Table I. This is a cumulative table with results obtained during the current contract period (March 1, 1978 - May 30, 1980), given in parenthesis.

Reference to papers published covering work in Table I are given in Appendix I.

TABLE I
ELECTRONIC STATES TO WHICH ATTENTION HAS BEEN THUS FAR GIVEN
IN THE THEORETICAL AIR TRIATOMICS PROJECT AND ASSOCIATED THEORETICAL PROJECTS^{a,b}

System	Vertical Electronic Spectrum ^c		Surface Scans	Comments ^d Surface-Cuts	Vibrational Spectra
	SCF	Correlated			
H ₂ O ⁺	2B ₁ (2), A ₁ (2), B ₂ (2), A ₂ 4B ₁ , A ₂ , B ₂ (2)	2B ₁ , B ₂ , A ₁ , A ₂ 4B ₁ , A ₁	X ² B ₁ , B ₂	R ₁ , R ₂ ; θ	X ² B ₁ , B ₂
H ₂ O	1, 3A ₁ , B ₁ , A ₂ , B ₂	1A ₁ , 3B ₁	X ¹ A ₁ 3B ₁	R ₁ , R ₂ R ₁ , R ₂ ; θ	
H ₂ O ⁻					
N ₂ O ⁺	2Π(4), Σ [±] (2), Δ(2), Φ 4Π(3), Σ [±] (2), Δ(2) 1A'(2), 1A''(2), 4A', 4A''	2Π(2), Σ [±] , Δ 4Π, Σ [±] , Δ	[X ² Π, Σ ⁺ , A''] 1 ⁴ Σ ⁻ , 2 ⁴ Σ ⁻ , a ⁴ A''	R ₁ , R ₂ , θ R ₁ , R ₂ , θ	1 ⁴ Σ ⁻ X ² Π ⁺ A ² Σ ⁺ a ⁴ A''
N ₂ O	1Σ ⁺ (3), Σ ⁻ , Π(2), Δ 3Σ ⁺ (2), Σ ⁻ , Π(2), Δ 5Σ ⁺ , 5Π 1A'(2), 1A'', 3A', 3A''	1Σ ⁺ (2), Σ ⁻ , Π(2), Δ 3Σ ⁺ , Σ ⁻ , Π(2), Δ 5Σ ⁺	1Σ ⁺ , Σ ⁻ , Π, Δ 3Σ ⁺ , Σ ⁻ , Π, Δ 1A', A'' 3A', A''	R ₁ , R ₂ ; θ R ₁ , R ₂ ; θ	X ¹ Σ ⁺

TABLE I (con't.)

System	Vertical Electronic Spectrum ^c		Surface Scans	Comments Surface-Cuts	Vibrational Spectra
	SCF	Correlated			
N_2O^+	$2\Pi(2), \Sigma^+(3), \Sigma^-(2), \Delta(2), \Phi$ $4\Pi(2), \Sigma^+, \Sigma^-(2), \Delta$ $6\Sigma^+$	$2\Pi, \Sigma^+$ $4\Sigma^+, \Sigma^-, \Delta$	X^2A'	R_1, R_2, θ	X^2A'
CO_2^+	$2\Pi_g, \Pi_u(2), \Sigma_g^+, \Sigma_u^+$ $4\Pi_u$ $2B_2(2), A_2, B_1(2), A_1(3)$ $4B_1, A_1$	$2\Pi_g, \Pi_u(2), \Sigma_u^+, \Sigma_g^+$ $4\Pi_u$			
CO_2	$[1\Sigma_g^+(5), 3\Sigma_g^+(4)]$ $1, 3\Sigma_g^-(2), \Sigma_u^-(4), [\Sigma_u^-(2), 3\Sigma_u^+]$ $1, 3\Pi_g(5), \Pi_u(5), \Delta_g(3), \Delta_u(3)]$ $1, 3\Phi_g, \Phi_u$ $1A_1, A_2(2), B_2(2)$ $3B_2(2), A_2(2)$	$1\Sigma_g^+, \Sigma_u^-, \Delta_u$ $3\Sigma_u^+, \Delta_u$	$[X^1\Sigma_g^+(^1A_1)]$	R, θ	

TABLE I (con't.)

System	Vertical Electronic Spectrum ^c		Surface Scans	Comments Surface-Cuts	Vibrational Spectra
	SCF	Correlated			
CO ₂ ⁻	$2\Pi_u, \Sigma_g^+, \Sigma_u^+, \Pi_g, \Phi, g$ $4\Pi_g$ $[2A_1(2), B_1, B_2(3), A_2(2)]$	$2\Pi_u, \Sigma_g^+, \Sigma_u^+, \Phi, \Pi_g, g$ $4\Pi_g [X^2A_1]$	$[X^2A_1]$	R, θ	
NO ₂ ⁺	$1A_1, A_2, B_2, B_1$ $3B_2, A_2, A_1, B_1$ $1\Sigma_g^+, \Sigma_u^+(2), \Pi_u, \Pi_g(2), \Delta_u, \Delta_g$ $3\Sigma_g^+, \Sigma_u^+(2), \Pi_u, \Pi_g(2), \Delta_u, \Delta_g$	$1A_1, A_2, B_2, B_1$ $3A_1, A_2, B_2, B_1$ $X^1\Sigma_g^+, \Delta_g, \Sigma_g^-, \Pi_g(2)$ $1\Sigma_u^+, \Delta_u, \Pi_u(2)$ $3\Sigma_g^+, \Delta_g, \Pi_g(2)$ $3\Sigma_u^+, \Delta_u, \Pi_u$	$X^1\Sigma_g^+, 1A'$	R ₁ , R ₂ , θ	$X^1\Sigma_g^+(A')$
NO ₂	$[2A_1(2), B_1, A_2(4), B_2(4)]$ $4B_2, A_2$	$2A_1, B_1, B_2, A_2$ $4B_2, A_2$ $2\Sigma_g^+$	X^2A_1, B_2, B_1, A_2 $4A_2, B_2$ $2\Sigma_g^+$	R, θ R ₁ , R ₂	
NO ₂ ⁻	$[1A_1, B_1, A_2, B_2]$ $3B_1, B_2, A_2, A_1$		$[X^1A_1]$ $[1A']$	R, θ R ₁ , R ₂ , θ	

TABLE I (con't.)

System	Vertical Electronic Spectrum ^c		Surface Scans	Comments Surface-Cuts	Vibrational Spectra
	SCF	Correlated			
0_3^+	$^2A_2(2), A_1(2), B_2(2), B_1(2)$ $^4A_2, B_2; A_1, B_1$	$^2A_1, A_2, B_1, B_2$ $^4A_1, A_2, B_1, B_2$	X^2A_1	θ	
0_3	$^1A_1(2), A_2(2), B_2(2), B_1$ $^3B_2(2), B_1(2), A_2(2), A_1$	$^1A_1, A_2, B_2, B_1$ $^3B_2, B_1, A_2, A_1$ $^1A_1^u$	X^1A_1 a^3B_1	R_1, R_2, θ R_1, R_2, θ	X^1A_1 a^3B_1
0_3^-	$^2B_1, A_1, B_2, A_2$ $^4B_2(2), A_2(2), B_1(2), A_1(2)$	$^2B_1, A_1, A_2, B_2$ $^4B_1, A_1, A_2, B_2$	X^2B_1	θ	

^aThese calculations have been performed with a double-zeta or better quality basis set. Most of the correlated vertical excitations have now also been performed with basis sets augmented with polarization and, where needed, diffuse functions. Correlation is at the MCSCF/CI optimized valence level.

^bProperties such as the dipole moment are available for most SCF and all correlated wavefunctions of each molecule-state reported in this table. The dipole moment function is available for the correlated geometry scans.

^cSome adiabatic excitation energies have been obtained for H_2O^+ , H_2O , N_2O^+ , N_2O , N_2O^- , NO_2^+ , NO_2^- , and O_3 .

TABLE I FOOTNOTES (CONT'D)

- d. R_1, R_2, θ Indicates portions of the energy surface in which all three geometry parameters have been varied have been done.
- R_1, R_2 Indicates only bond lengths have been varied at fixed angle.
- R, θ Symmetric bond variation and angular variation.
- θ Only angle variation explored.

III. The Differential Correlation Energy Method

a. Introduction

Although potential curves of chemical accuracy can now be computed routinely, the calculation of electron affinities and ionization potentials still presents a considerable challenge. Methods which have been used to calculate electron affinities and ionization potentials are extensive configuration interaction, equations of motion, pair energy schemes, Hess cycles, perturbation theory, Koopmans theorem and Hartree Fock methods.

The Hartree-Fock model (and Koopman's theorem) usually yield electron affinities and ionization potentials which are in error by several eV, however through fortuitous cancelation of basis set and correlation errors, good agreement with experiment is sometimes obtained. The errors in other methods are usually smaller however only extensive configuration interaction or Hess cycle calculations have yielded quantitative results.

In this section we present a configuration selection scheme designed to only include those excitations which directly contribute to the correlation energy difference between the neutral and ionic system. The orbitals for each configuration are evaluated via the MCSCF method. We call this scheme the Differential Correlation Energy (DCE) method.

b. The Differential Correlation Energy Method

We are currently developing a new method for choosing configurations in a MCSCF/CI calculation to give accurate (within 0.1 eV) electron affinities and ionization potentials using the smallest number of configurations possible. The key to this method is the determination of the configurations which contribute to the differential correlation energy (DCE) associated with the addition or removal of an electron. It is our aim to develop a prescription for the choice DCE configurations analogous to the OVC prescription⁶ for the choice of configurations to give accurate ($\pm .1$ eV) bond dissociation energies. THE OVC method concentrates only on the changes in correlation energy associated with bond formation.

The DCE method takes advantage of some simple properties of correlation energy,

- 1) Correlation energy is very sensitive to electron occupations, i.e., new pairs, orbital occupations.
- 2) Correlation energy is relatively insensitive to details of orbital shapes.
- 3) Pair energy schemes work.

In light of the above.

- 1) It is reasonable to evaluate only the correlation energy difference between neutrals and ions or different states.
- 2) Major differences come from new pairs formed and cross shell correlation of extra electrons with remaining ones. (Active orbital contribution).
- 3) Minor differences some from pair correlation energy contribution due to availability of open orbital. (Excluded space effect.)

c. Formal Development for Electron Affinities and Ionization Potentials

Below we give specifically the formulation of ideas proposed for the calculation of electron affinities by the DCE method.

In order to discuss electron affinity or ionization potential, it is convenient to use a second-quantized treatment. Thus we introduce the usual electron annihilation and creation operators a_i and a_i^+ , respectively. The index i serves to distinguish among different spin-orbitals in our ordered base. The operators satisfy the anticommutation relations

$$\{a_i, a_j\} = \{a_i^+, a_j^+\} = 0 \quad ,$$

$$\{a_j^+, a_j\} = \delta_{ij} \quad .$$

Now if ϕ denotes an electronic state function (in Fock space), $a_i^+ \phi$ will describe the same state function with an additional electron in the i -th orbital. This assumes that the i -th orbital is unoccupied in ϕ . For simplicity, we shall assume that ϕ , and consequently $a_i^+ \phi$, represent single-configuration state functions.

The Hamiltonian can be written

$$H = \sum_{ij} a_i^\dagger h_{ij} a_j + \frac{1}{2} \sum_{ij} \sum_{kl} a_i^\dagger a_k^\dagger g_{ij,kl} a_l a_j$$

This can be partitioned according to

$$H = H_0 + H',$$

where

$$H_0 = \sum_{ij} a_i^\dagger h_{ij}^0 a_j,$$

$$H' = \sum_{ij} a_i^\dagger (h_{ij} - h_{ij}^0) a_j + \frac{1}{2} \sum_{ij} \sum_{kl} a_i^\dagger a_k^\dagger g_{ij,kl} a_l a_j.$$

We have not specified our orbital base in detail, so we are free to assume that it is chosen so that

$$h_{ij}^0 = \delta_{ij} \epsilon_i.$$

Then ϕ and $a_i^\dagger \phi$ are eigenvectors of H_0 ; that is,

$$H_0 \phi = E_0 \phi,$$

$$H_0 a_i^\dagger \phi = (E_0 + \epsilon_i) \phi,$$

where

$$E_0 = \sum_{i \in \phi} \epsilon_i.$$

We have some freedom in the choice of h^0 ; for example, we can choose h^0 so as to give Hartree-Fock orbitals (for the state ϕ) as its eigenfunctions. Note that in this case E_0 is not the Hartree-Fock energy for the state; the Hartree-Fock energy is given by $\langle \phi | H | \phi \rangle$.

No matter what the choice of h^0 we use, ϕ will not be an eigenvector of H because of electron correlation effects, and the same observation applies also to $a_i^\dagger \phi$. We can compute these correlation effects approximately by application of Rayleigh-Schrodinger perturbation theory, with H_0 as the unperturbed Hamiltonian and H' as the perturbation.

This yields to first order,

$$\Psi = \phi + R\phi ,$$

$$\Psi_e = a_i^+ \phi + R a_i^+ \phi ,$$

where

$$R = \sum_{ij, i \neq j} a_i^+ (h_{ij} - h_{ij}^0) a_j / (\epsilon_j - \epsilon_i)$$

$$+ \frac{1}{2} \sum_{ij, \sum_{kl, \epsilon_i + \epsilon_k \neq \epsilon_j + \epsilon_l} a_i^+ a_k^+ g_{ij,kl} a_l a_j / (\epsilon_l + \epsilon_j - \epsilon_i - \epsilon_k) .$$

To second order the energies are given by

$$E = \langle \phi | H | \phi \rangle + \langle \phi | H' R | \phi \rangle ,$$

$$E_e = \langle \phi | a_i H a_i^+ | \phi \rangle + \langle \phi | a_i H' R a_i^+ | \phi \rangle .$$

Since we have $a_i a_i^+ \phi = \phi$, the electron affinity is given to second order by

$$E_e - E = \epsilon_i + \langle \phi | [a_i, H'] a_i^+ | \phi \rangle$$

$$+ \langle \phi | [a_i, H'] R a_i^+ + H' [a_i, R] a_i^+ | \phi \rangle .$$

From this expression we see that the computed electron affinity remains unaltered to this order if we modify H' by adding to it any Hermitian operator that commutes with a_i . Hence we can use in place of H' the expression

$$H'' = a_i^+ H'_+ + H'_- a_i$$

where

$$H'_+ = \sum_j [h_{ij} - h_{ij}^0 + \sum_k a_k^+ a_l g_{ij,kl}] a_j ,$$

$$H'_- = \sum_j a_j^+ [h_{ji} - h_{ji}^0 + \sum_{kl} a_k^+ a_l g_{ji,kl}] .$$

In other words, any part of H'' that does not reference the orbital i does not contribute to the computation of the electron affinity.

It is not advisable to take the above argument too literally. For example, it does not indicate that many-body perturbation theory will give a good result for the electron affinity if carried to second order only. Higher order effects are likely to prove important. Many of these effects are automatically included in a SCF or MCSCF treatment, so we shall not pursue such questions further. What remains is a guide in attempting to answer the question: What configurations are needed to handle electron correlation effects that directly affect the calculation of electron affinity? From the above discussion, the configuration lists

$$\Phi, a_i^+ a_j^+ a_k a_l \Phi, \text{ any } j, k, l, \neq, i,$$

$$a_i^+ \Phi, a_j^+ a_k^+ a_l \Phi, \text{ any } j, k, l, \neq, i,$$

appear as the answer to this question. In essence, this tells us that for the state without the added electron we should include the dominant (i.e., Hartree-Fock) configuration and all single and double replacements which contain the orbital of the electron to be added. For double replacements, we note that in addition to the spin orbital i , the configuration may also contain another orbital from this shell. For the state with the added electron, we should again include the dominant configuration and any single and double replacements that are generated by eliminating the spin orbital of the added electron in the dominant configuration.

Some obvious refinements can be added to this scheme: single replacements from the dominant configuration are unlikely to be important, since Brillouin's theorem applies to an SCF approach, and replacements which involve excitation of a core orbital are probably negligible because a large excitation energy is involved (the core orbitals can be defined as those orbitals to which such an argument applies). We also must be concerned with the need for a multiconfiguration reference state.

A similar analysis is being performed for the calculation of vertical spectra.

d. Applications

Using the DCE configuration selection rules MCSCF calculations have been performed on $\text{CN} \rightarrow \text{CN}^-$ and $\text{CO}_2^- \rightarrow \text{CO}_2$.

For CN^- we must include all correlation within the $5\sigma^2$ orbital and all cross shell correlation of $5\sigma^2$ with $3\sigma^2$, $4\sigma^2$, and 1π . Using 3 new MCSCF correlating orbitals, 6σ , 7σ , 2π this yields 25 configurations.

For CN the DCE prescription tells us to include all cross shell correlation involving the 5σ orbital and all excitations into the half filled 5σ orbital. This yields 41 configurations. Results of these calculations are presented in Table II.

For CO_2 we must include all valence excitations into the $6a_1$ orbital, this yields 67 configurations. For CO_2^- we must include all cross shell correlation of $6a_1$ electron with valence shell and valence excitations into $6a_1$ orbital. Results on $\text{CO}_2^- \rightarrow \text{CO}_2$ are presented in Table III.

These results indicate that the DCE rules may provide a reasonable starting point for the MCSCF procedure which can then be followed by a larger CI for truly quantitative results.

TABLE II
DCE METHOD APPLIED TO CN CN⁻

<u>State/Energy</u>	<u>MCSCF/CI 15/26</u>	<u>Single/Conf.</u>	<u>SCF</u>	<u>ΔE</u>
CN ⁻ R=2.117	-92.3724551	-92.321633	-92.3221717	.0508
" 2.217	-92.3812117	-92.326182	-92.3267819	.0550
" 2.317	-92.3780383	-92.318317	-92.3189866	.0597
CN(19MC)2.117	not converged		-92.2045157	
" 2.217	" "		-92.2027169	
" 2.317	-92.2510795	-92.172356	-92.1890972	.0787
CN(fromCN ⁻) 2.117	-91.9523405	-91.905750	-92.2045157	.0466
2.217	-91.9451404	-91.897083	-92.2027169	.0491
2.317	-91.9445647	-91.895993	-92.2090972	.0486
CN (17MC)2.117	-92.2317141	-92.203380	-92.203380	.0312
2.217	-92.2402757	-92.201029	-92.2027169	.0392
2.317	-92.2358326	-92.186712	-92.1890972	.0491

TABLE III

DCE

METHOD

APPLICATION TO $\text{CO}_2^- \rightarrow \text{CO}_2$ $(\theta_{\text{OCO}} = 135.77^\circ, R_{\text{CO}} = 2.3734 \text{ bohrs})$ Configurations for CO_2^-

Orbitals

1a ₁	1b ₂	2a ₁	3a ₁	4b ₂	4a ₁	2b ₂	5a ₁	3b ₂	6a ₁	7a ₁	5b ₂	1b ₁	1a ₂	2b ₁
2	2	2	2	2	2	2	2	2	1	0	0	2	2	0

- 1) Include all cross shell correlation of 6a₁ electron with valence electrons.
- 2) Include all valence excitations into 6a₁ orbital.

E = -187.56976 a.u. 19MCSCF/70CI

Configurations for CO_2

2	2	2	2	2	2	2	2	2	0	0	0	2	2	0
---	---	---	---	---	---	---	---	---	---	---	---	---	---	---

- 1) Include all valence excitations into 6a₁ orbital

E = -187.52993 a.u. 19MCSCF/67CI

$\Delta E = 1.08\text{ev}$

$\Delta E = .3\text{ev}$ (basis set error in CO_2^-)

Vertical Ionization Potential of $\text{CO}_2^- \sim 1.4\text{ev}$

Experimental* IP of CO_2^- $1.4 \pm .3\text{ev}$

IV. A Multidimensional Newton-Raphson MCSCF Method

The merits of the MCSCF approach to the calculation of electronic wave functions for atoms or molecules are well documented⁶ and, in fact, the method has become the standard starting point for most researchers. The principal limitation of this approach has been the frequent difficulty in obtaining converged solutions for the MCSCF wave function. A new MCSCF method⁷ under development by J. Detrich and C.C.J. Roothaan* is expected to eliminate this difficulty.

This method applies whenever the spin-orbitals (SO) are put forward as finite expansions in terms of a basis set. In the MCSCF approach one also constructs term state functions (TSF) as linear combinations of configuration state functions (CSF); the latter are defined as symmetry-adapted linear combinations of Slater determinants arising from a single configuration of orbital assignments. A complete set of trial SO's can be put forward, which spans the same linear space as the one-electron basis functions, and, analogously a set of trial TSF's spanning the same linear space as the set of CSF's can be developed.

The method deals in terms of the unitary transformations of the reference SO's and TSF's which will give optimized SO's and TSF's. These unitary transformations are expressed as exponentials of anti-Hermitian operators. In terms of the reference SO's and TSF's, the variational energy expression is of the form

$$E' = E + \sum_i E_i x_i + \frac{1}{2} \sum_{ij} E_{ij} x_i x_j + \dots,$$

where the x_i 's are the independent matrix elements of the anti-Hermitian operators. The quantities E , E_i and E_{ij} are evaluated by rather elaborate contractions involving integrals over basis functions, occupation numbers and coupling constants, and the expansion coefficients representing the set of reference SO's and TSF's.

Approximating this expression by dropping all terms of third and higher order, the extremum of E' with respect to all the variables x_i occurs when they satisfy

$$\sum_j E_{ij} x_j = -E_i$$

Once the solution of this equation has been obtained, new reference SO's and TSF's are easily computed, thus completing an iterative MCSCF cycle.

This method is seen to be a multidimensional generalization of the Newton-Raphson iterative process, and it converges quadratically in the general case. The availability of such a method will substantially enhance the range of problems where the advantages of the MCSCF approach can be exploited. Even in cases where other MCSCF methods suffice, the availability of a method that virtually guarantees convergence in a few iterations is expected to significantly reduce the man-hours required to perform a given series of calculations. These advantages indicate that the new method will become the standard vehicle for molecular orbital calculations in the basis-set expansion regime.

A preliminary implementation of this method has been coded for atoms under the auspices of the National Resource for Computation in Chemistry by Prof. Roothaan. A comprehensive description of the formalism and analysis for the method is currently in preparation.

*Professor C. C. J. Roothaan is a technical consultant on self consistent field techniques to SAI.

V. Molecule by Molecule Summary

CO₂ and its Ions

Work on CO₂ and its ions during the contract period consisted primarily of trial calculations intended to help establish an efficient and reliable approach to the calculation of electron affinities and ionization potentials. As discussed in Section III above, this goal has motivated development of the Differential Correlation Energy (DCE) method. The calculations for CO₂ and CO₂⁻ summarized here serve as a test for the method.

For both CO₂ and CO₂⁻ the (3s,2p) contracted Cartesian Gaussian basis of Dunning⁸ was adopted. This choice permits trial calculations to be economically performed, but involves some sacrifice in accuracy of the orbital description. As an aid in assessing such effects, SCF vertical spectra for CO₂ were computed with the (3s, 2p) basis and compared with previous results using a more flexible basis⁹ at the experimental linear equilibrium geometry (Table IV) and a bent geometry (Table V). In general, the SCF vertical spectra for CO₂ are in good agreement, the only exception being in the case of the $1\Sigma_u^+$ state, which is predominantly Rydberg rather than valence in character,¹⁰ and hence not well described by a basis set which does not contain diffuse functions. This indicates that the correlation effects of interest are reasonably well described in terms of the (3s, 2p) basis. Another indication of the utility of the (3s, 2p) basis comes from the results of an SCF geometry scan for the ground state of CO₂⁻. The equilibrium geometry is found to be $\theta_{OCO} = 136^\circ$, $R_{CO} = 2.37$ bohr, in good agreement with the determination $\theta_{OCO} = 135^\circ$, $R_{CO} = 2.35$ bohr by Pacansky, Wahlgren and Bagus¹¹ using a considerably larger basis.

The DCE method was applied to compute the vertical ionization potential of CO₂⁻ at the SCF equilibrium geometry $\theta_{OCO} = 135.77^\circ$, $R_{CO} = 2.3734$ bohrs. In addition to the orbitals occupied in the dominant ground state CO₂⁻ configuration, three correlation orbitals, $7a_1, 5b_2, 2b_1$, were introduced. The list of configurations developed according to the DCE method contained

70 for CO_2^- and 67 for CO_2 . The orbitals were taken from an MCSCF calculation for CO_2^- involving the 19 most significant configurations from the list of 70 DCE configurations for CO_2^- . Note that the orbitals from CO_2^- calculation were used in the CO_2 as well; this was the only obvious way to preserve the character of the $6a_1$ orbital in the CO_2 calculation.

The energy computed from the 67-configuration interaction calculation for CO_2 was $E = 187.52993$ hartrees; from the 70-configuration interaction calculation for CO_2^- the energy $E = -187.56976$ was obtained. This implies a vertical ionization potential for CO_2^- $\Delta E = 1.08$ eV.

As noted above, the basis set adopted affects the accuracy of this result. Since the effect is not expected to depend strongly on correlation, one can obtain a quantitative estimate by comparing the SCF result for the CO_2 adiabatic electron affinity computed with the (3s,2p) basis, $-.65$ eV, with the corresponding SCF result from Pacansky, *et.al.*,¹¹ $-.38$ eV. This indicates a basis set error of about $.3$ eV. Revising our computed result accordingly gives 1.4 eV for the vertical ionization potential of CO_2^- .

Strictly speaking, there is no corresponding experimental determination, but a close analogue can be constructed as follows. When CO_2 is distorted from its experimental equilibrium geometry to the theoretical CO_2^- equilibrium geometry adopted in these calculations, the CO_2 potential constructed by Suzuki¹² from spectroscopic data gives a distortion energy of 2.0 eV.

Adding this to the experimentally derived CO_2 electron affinity of $-.6 \pm .2$ eV reported by Compton, Reinhardt and Cooper¹³ yields 1.4 ± 0.3 eV for the CO_2^- vertical ionization potential.

This result is in good agreement with the result based on the DCE method.

More refined computations are necessary to confirm our estimate of basis set error, but our present results already establish the DCE method as a promising new approach.

TABLE IV
LINEAR CO₂ VERTICAL SPECTRUM

$$r_1=r_2 = 2.1944 \text{ bohrs } \theta = 180^\circ$$

State	Configuration(s) ^a						Energy		4s,3p Energy ^c
	1 π_{ux}	1 π_{gx}	2 π_{ux}	1 π_{gy}	1 π_{uy}	2 π_{gy}	a.u.	eV ^b	eV ^b
$X^1\Sigma_g^+$	2	2	0	2	2	0	-187.553005	0.00	0.00
$3^3\Sigma_u^+$	{ 2 2	{ 2 1	{ 0 1	{ 2 2	{ 1 2	{ 1 0	-187.292459	7.09	7.07
$3^3\Sigma_u^-$	{ 2 2	{ 2 1	{ 0 1	{ 2 2	{ 1 2	{ 1 0	-187.270395	7.69	7.66
	{ 2 2	{ 2 1	{ 1 0	{ 2 2	{ 1 2	{ 0 1	-187.270654	7.68	—
$3^3\Sigma_u^-$	{ 2 2	{ 2 1	{ 1 0	{ 2 2	{ 1 2	{ 0 1	-187.249106	8.27	8.26
$1^1\Sigma_u^-$	{ 2 2	{ 2 1	{ 1 0	{ 2 2	{ 1 2	{ 0 1	-187.249361	8.26	8.26
$1^1\Delta_u$	{ 2 2	{ 2 1	{ 1 0	{ 2 2	{ 1 2	{ 0 1	-187.238979	8.54	—
	{ 2 2	{ 2 1	{ 0 1	{ 2 2	{ 1 2	{ 1 0	-187.279319	7.45	8.52
$1^1\Sigma_u^+$	{ 2 2	{ 2 1	{ 0 1	{ 2 2	{ 1 2	{ 1 0	-186.901777	17.72	14.15

$$^a \text{Core} = 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 3\sigma_u^2$$

$$^b 1 \text{ a.u.} = 27.21070 \text{ eV}$$

^cFrom reference 9.

TABLE V
BENT CO₂ VERTICAL SPECTRUM

[3s,2p] Basis, SCF

$r_1=r_2= 2.1944$ bohrs $\theta=130^\circ$

State	Configuration ^a						Energy		4s/3p Energy ^c eV ^b
	5a ₁	4b ₂	6a ₁	1b ₁	1a ₂	2b ₁	a.u.	eV ^b	
1 ¹ A ₁	2	2	0	2	2	0	-187.462871	0.00	0.00
1 ³ B ₂	2	1	1	2	2	0	-187.394377	1.86	2.30
1 ³ A ₂	2	2	1	2	1	0	-187.363691	2.70	2.76
1 ¹ A ₂	2	2	1	2	1	0	-187.352623	3.00	3.07
1 ¹ B ₂	2	1	1	2	2	0	-187.316653	3.98	4.05
2 ³ B ₂	2	2	0	2	1	1	-187.239182	6.09	6.13
2 ³ A ₂	2	1	0	2	2	1	-187.220412	6.60	6.70
2 ¹ A ₂	2	1	0	2	2	1	-187.208979	6.91	7.01
2 ¹ B ₂	2	2	0	2	1	1	-187.080537	10.40	10.39

^a Core = 1a₁² 1b₂² 2a₁² 3a₁² 2b₂² 4a₁² 4b₂²

^b 1a.u. = 27.21070

^c Reference 9

$N_2O^+ X^2_{II}$ MCSCF/CI Calculation

A geometry scan for the equilibrium bond lengths of the linear $N_2O^+ X^2_{II}$ state was performed. The wave functions were constructed from orbitals expanded in terms of a basis set consisting of a 4s,3p 1d Gaussian basis on each center. The MCSCF calculations consist of 20 configurations, and the supplementary CI calculations consist of 99 configurations.

The results for the linear NNO geometry indicate equilibrium bond lengths $R_{NN} = 2.126$ a.u., $R_{NO} = 2.367$ a.u. A preliminary fit to a molecular potential function of the form

$$v = \frac{1}{2} K_{NN} (\Delta R_{NN})^2 + \frac{1}{2} K_{NO} (\Delta R_{NO})^2$$

$$\text{yields } K_{NN} = 19.563 \text{ md/\AA}^2, K_{NO} = 5.144 \text{ md/\AA}^2$$

A more elaborate characterization of the potential surface is needed in order to extract spectroscopic characteristics such as vibrational behavior.

NO_2^- Ground State Geometry Scan

A preliminary SCF-level geometry scan of the NO_2^- ground electronic state has been performed. They include the normal $X^1A_1 C_{2v}$ state of equilibrium geometry, the peroxy well, and the energy-minimum pathway between the two geometries. As indicated in Table VI, the geometries of the C_{2v} and peroxy C_s minima are in good agreement with the earlier results of Pearson, et. al.¹⁴ Hence the delineation of the potential surface between these two geometries is useful, although somewhat crude. It would appear that the indicated saddle point between the two geometries (Table VI) is above the molecular dissociation threshold, so that isomerization cannot be expected to take place. Evidently this is consistent with the experimental observations that bear on the existence of a NO_2^- peroxy well. On the other hand, a preliminary calculation cannot be relied upon with regard to such questions, and a more elaborate set of calculations utilizing multiple configurations and a larger basis set is planned.

TABLE VI
PRELIMINARY SURVEY OF THE $\text{NO}_2 \times {}^1\text{A}_1 ({}^1\text{A}')$ HYPERSURFACE

SCF, (9s5p)/ [3s2p]^a

Critical Geometry	$E_T + 203$ (a.u.)	V (eV)	R_{NO} (A)	R_{OO} (A)	A_{ONO} (deg.)	A_{OON} (deg.)
C_{2V}	-1.0247 (-1.0336)	0.0 (0.0)	1.27 (1.26)	2.17	116.8 (117.0)	31.
S.P. Ring	-0.83 (-0.8736)	5.3 (4.4)	2.28 (1.50)	2.06	63.8 (58.5)	82.6
C_s	-0.9067 (-0.9161)	3.2 (3.2)	1.25 (1.25)	1.51 (1.49)	34.	118.2 (118.5)
D(ON-O ⁻)		4.0				

^aThe values in parenthesis are (9s5p)/ [5s3p] results from reference 14.

The wave functions utilized in this set of calculations are based on the (3s,2p) contracted gaussian basis sets of Dunning.⁸ In support of these calculations, the X^2A_1 , 1^2A_1 , 1^2B_1 , 1^2B_2 , 1^4B_2 , and 1^4A_2 states of NO_2 were computed using the same basis set. In Table VII these results are compared with earlier results⁹ using the more elaborate 4s,3p basis set.

Similar calculations were performed for the 1^3B_2 , 1^1B_2 and 1^3A_1 states of NO_2^- , as well as the X^1A_1 ground state. These are of some interest in their own right, since they use the computed ground state NO_2^- equilibrium geometry, rather than the NO_2 equilibrium geometry used previously,¹⁰ or the experimental geometry adopted by Benioff¹⁵. Our results for the computed excitation energies are given in Table VIII. Our $X^1A_1 \rightarrow 1^1B_2$ excitation energy appears to be in better agreement with experiment than obtained in previous work,^{8,13} but more elaborate calculations are required to clarify whether this agreement is fortuitous.

TABLE VII
COMPUTED SCF ENERGIES FOR NO₂

State ^a	Configuration ^b	Excitation Energy (eV) ^c	
		<u>3s2p</u>	<u>4s3p</u>
X ² A ₁	4b ₂ ² ba ₁ 1b ₁ ² 1a ₂ ²	0.00	0.00
1 ⁴ A ₂	4b ₂ ² ba ₁ 1b ₁ ² 1a ₂ ² 2b ₁	2.05	2.13
1 ⁴ B ₂	4b ₂ ² 6a ₁ 1b ₁ ² 1a ₂ 2b ₁	2.10	2.14
1 ² B ₁	4b ₂ ² 1b ₁ ² 1a ₂ 2b ₁	2.50	2.50
1 ² A ₂	4b ₂ ² 6a ₁ ² 1b ₁ ² 1a ₂	2.80	2.83
1 ² B ₂	4b ₂ 6a ₁ ² 1b ₁ ² 1a ₂ ²	3.82	3.84

^a All states at bond length of 2.25 a.u. and bond angle of 134°

^b The omitted orbitals 1a₁, 1b₂, 2a₁, 3a₁, 2b₂, 4a₁, 3b₂, 5a₁ are doubly occupied in each configuration.

^c The SCF total energy of the X ²A₁ state is -203.95597 a.u. for the 4s3p basis set and -203.94646 a.u. for the 3s2p basis set. The difference in eV is 0.26.

TABLE VIII
EXCITATION ENERGIES FOR NO₂

State ^a	Configuration ^b	Excitation Energy (eV)	
		This Work ^c	Experiment ^d
X ¹ A ₁	4b ₂ ² 6a ₁ ² 1b ₁ ² 1a ₂ ²	0.0	0.0
1 ³ B ₂	4b ₂ ² 6a ₁ ² 1b ₁ ² 1a ₂ 2b ₁	2.30	-
1 ¹ B ₂	4b ₂ ² 6a ₁ ² 1b ₁ ² 1a ₂ 2b ₁	6.08	-6 ^e
1 ³ A ₁	4b ₂ ² 6a ₁ ² 1b ₁ 1a ₂ ² 2b ₁	7.43	-

a) All states at bond length 2.40 bohr and bond angle of 116.8°

b) The omitted orbitals 1a₁ 1b₂ 2a₁ 3a₁ 2b₂ 4a₁ 3b₂ 5a₁ are doubly occupied in each configuration.

c) Vertical

d) Adiabatic

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Via PUBLICATIONS PLANNED AND IN PREPARATION

1. Vertical Spectra for CO_2^- and Electron Affinity of CO_2 . E. Sachs.
2. Application of the Differential Correlation Energy Method to the Calculation of the Electron Affinity of CN and CO_2 . A. C. Wahl, E. Sachs, and J. Detrich.
3. A Review of Ab Initio Calculations on H_2O , CO_2 , N_2O , N_2O , O_3 and their Positive and Negative Ions. J. Detrich, E. Sachs, and A. C. Wahl.
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VIB RECENT PUBLICATIONS IN TECHNICAL JOURNALS
FROM THIS PROJECT

1. Theoretical Studies of Atmospheric Molecules: SCF and Correlated Energy Levels for the NO_2 , NO_2^+ , and NO_2^- Systems
P. J. Fortune, B. J. Rosenberg, W. B. England, and A. C. Wahl
Theoret. Chem. Acta 46, 185(1977)
2. Ab Initio Calculations of the Minimum Energy Path in the Doublet Surface for the Reaction $\text{N}(^4\text{S}) + \text{O}_2(^3\Sigma_g^-) \rightleftharpoons \text{NO}(^2\Pi_u) + \text{O}(^3\text{P})$
P. Benioff, G. Das, and A. C. Wahl
J. Chem. Phys. 67, 2449(1977).
3. Mechanisms of the Reaction of Ground State Positive Atomic Oxygen Ions with Nitrogen
D. G. Hopper
J. Amer. Chem. Soc. 100, 1019(1978).
4. Ab Initio Calculations of the Vertical Electronic Spectra of NO_2 , NO_2^+ and NO_2^-
P. A. Benioff
J. Chem. Phys. 68, 3405(1978).
5. Ab Initio Calculations on NO_2 and NO_2^- : Optimization of Diffuse Gaussian Exponents
P. A. Benioff, Theoret. Chem. Acta 00, 000(1978).
6. Theoretical Studies of Atmospheric Triatomic Molecules: New Ab Initio Results for the $^1\Pi_g - ^1\Delta_u$ Vertical State Ordering in CO_2
W. B. England and W. C. Ermler,
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7. An Improved MCSCF Method
C. C. J. Roothaan, J. Detrich, and D. G. Hopper
Int. J. Quantum Chem. 13 S(1979).
8. The Differential Correlation Energy Method for the Calculation of Electron Affinities, Ionization Potentials, and Electronic Spectra
A. C. Wahl, E. S. Sachs, and J. H. Detrich
Int. J. Quantum Chem. 14 S, 0000 (1980).
9. Theoretical Studies of Atmospheric Molecules
J. H. Detrich, E. S. Sachs, and A. C. Wahl
Int. J. Quantum Chem. 14 S, 0000 (1980).
10. A Practical Guide to Application of the MCSCF Method
J. H. Detrich and A. C. Wahl
NRCC-MCSCF Workshop Proceedings.
National Resource for Computation in Chemistry, July, 1980.
11. General Quadratically Convergent MCSCF Theory in Terms of Reduced Matrix Elements
C. C. J. Roothaan and J. H. Detrich
Reviews of Modern Physics

VII INTERACTIONS AND ATTENDANCE AT MEETINGS

- October 1978 - J. Detrich, Trip to Washington to discuss NBS contract and Wisconsin contract
- November 28 - December 1, 1979 - J. Detrich, APS Meeting, Division of Electron and Atomic Physics
- May 3 - 5, 1979 - J. Detrich, Midwest Theoretical Chemistry Conference (Poster Presentation)
- July 11 - 15, 1979 - J. Detrich, OSU Spectroscopy Conference 34th Symposium on Molecular Spectroscopy (2 talks)
- August 13 - 18, 1979 - J. Detrich, Gordon Conference on Few Body Interactions
- Summer 1979 - J. Detrich, Numerous discussions of new MCSCF method with scientists at NBS, NRCC, and the Gordon Conference
- September 17 & 18, 1979 - J. Detrich, DOD Physics Review - NAS Washington, D.C.
- March 9 - 15, 1980 - J. Detrich, Sanibel Symposium - Palmcoast, Florida
- May 10 & 11, 1980 - J. Detrich, Midwest Theoretical Chemistry Conference, Minneapolis Minnesota
- July 14 - 16, 1980 - J. Detrich, NRCC - MCSCF Workshop - College Station, Texas
- May 3 - 5, 1979 - A. C. Wahl, Midwest Theoretical Chemistry Conference, Chairman Session I
- June 1, 1979 - A. C. Wahl, Discussion of current and future status of AFOSR contract with R. Kelley, Physics Directorate AFOSR, Washington, D.C.
- September 17 & 18, 1979 - A. C. Wahl, DOD Physics Review, NAS Washington, D.C.
- November 5 & 6, 1979 - A. C. Wahl, DOD Chemistry Review, NAS Washington, D.C.
- March 9 - 15, 1980 - A. C. Wahl, Sanibel Symposium - Palmcoast, Florida
- May 10 & 11, 1980 - A. C. Wahl, Midwest Theoretical Chemistry Conference, Minneapolis, Minnesota
- June 20 - 25, 1980 - A. C. Wahl, Spectroscopy Conference - Columbus, Ohio
- July 14 - 16, 1980 - A. C. Wahl, NRCC - MCSCF Workshop - College Station, Texas
- July 21 - 25, 1980 - A. C. Wahl, Gordon Conference - Wolfeboro, New Hampshire

May 3 - 5, 1979 - E. Sachs, Midwest Theoretical Chemistry Conference,
La Fayette, Indiana

July 25 - 27, 1979 - E. Sachs, Workshop on Software Standards and Computational
Chemistry, Salt Lake City, Utah.

March 13 - 18, 1978 - D. Hopper, Sanibel Symporium - Palmcoast, Florida

March 18 - 20, 1978 - D. Hopper, Eleventh Midwest Theoretical Chemistry
Conference, Columbus, Ohio

May 28 - June 2, 1978 - D. Hopper, Twenty-Sixth Annual Conference on Mass
Spectrometry and Allied Topics, St. Louis, Missouri

June 12 - 16, 1978 - D. Hopper, Thirty-Third Annual Symposium on Molecular
Spectrometry, Columbus, Ohio

March 11 - 17, 1979 - D. Hopper, Sanibel Symporium, Palmcoast, Florida

June 3 - 8, 1979 - D. Hopper, Twenty-Seventh Annual Conference on Mass
Spectrometry and Allied Topics.

July 11 - 15, 1979 - D. Hopper, Thirty-Fourth Symporium on Molecular
Spectroscopy, Columbus, Ohio.

Sept. 17 - 18, 1979 - D. Hopper, DOD Physics Review, Washington, D.C.

Oct. 29 - Nov. 3, 1979 - D. Hopper, Third International Conference of
Quantum Chemistry, Kyoto, Japan.

Over the past year, A. C. Wahl has interacted by telephone and letter with
a number of atmospheric scientists whose experimental work relates to this
AFOSR contract (NBS, NOAA, JILA, SRI).

VIII PROJECT PERSONNEL

Below the names and durations of association with project of personnel is given:

J. Detrich joined the project in September 1978 and is presently associated with the project as project scientist.

D. G. Hopper joined the project in March 1978. His association with the project ended in November 1979.

Ed Sachs joined the project in June 1978 and left to accept a permanent position at Bell Labs in September 1979.

Frank Tobin joined the project in October 1978, left in June of 1979 and accepted a position at Johns Hopkins University.

Chris Wahl brought the project to SAI from Argonne beginning March of 1978, was on a leave of absence due to illness July 1978 through June 1979, and is currently principal investigator.

IX Concluding Remarks

We believe that this comprehensive systematic project has enhanced our knowledge and understanding of the atmospheric triatomic systems under study. In many cases, particularly for excited states and ions, new information has been generated which was not and continues not to be available experimentally. In addition, during the course of this work several powerful methods for investigating molecular structure were developed.

It is our hope that the Air Force will continue to support this exciting work which can form the basis for improved modelling and for new insights into our understanding of the chemistry and physics of the earth's atmosphere.

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APPENDIX I
PUBLICATIONS RESULTING FROM
THE ATMOSPHERIC PROJECT

These publications report atmospheric related research performed with the support of the Air Force Office of Scientific Research, the Advanced Research Projects Agency, the Aerospace Research Laboratories, the Atomic Energy Commission, the Energy Research and Development Administration and the Department of Energy over the period 1972 - 1980.

The work represented by these papers involved a number of individual contracts involving A. C. Wahl and his collaborators, P. Benioff, G. Das, J. Detrich, W. England, P. Fortune, D. Hopper, R. Hosteny, B. Rosenberg, E. Sachs, W. Stevens, and C. W. Wilson.

TECHNIQUE PAPERS

Application of Perturbation Theory in Large Configuration Interaction Calculations

P. J. Fortune and B. J. Rosenberg
Chem. Phys. Lett. 37, 110-114 (1977)

A Modified Pseudopotential Approach to the Heavy-Atomic Molecular Systems: Application to the $X^2\Sigma_{1/2}^+$, $A^2\Pi_{1/2}$, and the $A^3\Pi_{3/2}$ States of the HgH Molecule

G. Das and A. C. Wahl
J. Chem. Phys. 64, 4672-4679 (1976)

BISON-MC: A FORTRAN Computing System for MCSCF Calculation on Atoms, Diatoms and Polyatoms. This polyatomic MCSCF-CI capability was developed out of this project. This has been widely used in polyatomic MCSCF calculations by many researchers.

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C. C. J. Roothaan, J. Detrich, and D. G. Hopper, I.J.Q.C. S13, 93 (1979):
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The Differential Correlation Energy Method for Electron Affinities, Ionization Potentials and Vertical Spectra

A. C. Wahl, E. Sachs, and J. H. Detrich, International Journal of Quantum Chemistry S14, 0000 (1980).

Theoretical Studies of Atmospheric Triatomic Molecules

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BOOK CHAPTERS

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WATER AND ITS IONS

MCSCF Calculations on the Lowest Triplet State of H₂O

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Chem Phys. Lett. 23, 9-12 (1973)

Theoretical Studies of Atmospheric Molecules: SCF and Correlated Potential
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P. J. Fortune, B. J. Rosenberg, and A. C. Wahl
J. Chem. Phys. 65, 2201-2205 (1976)

OZONE AND ITS IONS

Recent applications of the Multiconfiguration Self-Consistent Field Method
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CARBON DIOXIDE AND ITS IONS

Ab Initio Vertical Spectra and Linear Bent Correlation Diagrams for the
Valence States of CO₂ and its Singly Charged Ions

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Vertical Spectrum for Valence, Mixed Character, and Rydberg States of
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W. B. England, W. C. Ermler, and A. C. Wahl
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Theoretical Studies of Atmospheric Triatomic Molecules: Ab Initio Equations-
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