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DETERMINATION OF ENERGETICS AND SPECTRA OF
SIMPLE MOLECULAR SYSTEMS USING THEORETICAL METHODS

G.P. Raine
(Ph.D. Thesis)

October 1983

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Determination of Energetics and Spectra of Simple Molecular
Systems using Theoretical Methods

By

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Abstract

Ab initio molecular orbital theory has been used to evaluate several chemical systems. The applicability of the current standard models has been explored. Within the Hartree-Fock self-consistent-field (SCF) and configuration interaction (CI) approaches, the non-relativistic Schroedinger equation was used to determine energetic stability of the dimers of carbon monoxide and carbon monosulfide. For these systems the harmonic vibrational frequencies were predicted and the nature of the chemical bond in the dimers was explored.

Application of the Breit-Pauli Hamiltonian, including only those terms important to small systems, within an SCF and CI treatment was used to explore relativistic effects. A prediction for the importance of these effects on the methylene molecule is given, with particular focus on the singlet-triplet excitation energy.

Focusing on vibrational frequencies, anharmonic effects

were included using the Darling-Dennison-Watson Hamiltonian. Using a variational treatment, frequencies were predicted for the molecular ion, O H^+ , at the SCF and CI levels of theory using double zeta (DZ) and double zeta plus polarization (DZP) basis set.

TO MY PARENTS

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Special thanks to Fritz Schaefer who has been both an academic and spiritual guide. I have appreciated his friendship, tolerance and good will. Professor Nick Handy has been a great source of incentive and advice, and Dr. Paul Saxe initiated me into the programs at Berkeley, without them this research might not have progressed. I especially want to thank the now Dr. Doug Fox for his friendship and willingness to jump into any problem, and the entire Schaefer research group for providing a stimulating work environment.

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I. INTRODUCTION

In the past few decades theoretical chemistry has moved to the forefront of science as an investigative tool for probing chemical systems. In particular, the development of theoretical methods, which require virtually no experimental data, has allowed the study of chemical systems that have not yet been looked at using more conventional techniques. The fundamental basis for this theory lies in the Schroedinger equation, which provides a description of the motion of electrons and nuclei for an atom or molecule. In principle the complete solution of this equation provides all energetic information about the system via the calculated energy hypersurface. In practice, an analytic solution of this equation is possible only for one electron systems of atoms and molecules, and without the application of models and approximations it is of limited use.

In the study of molecules, one of the first simplifications is the application of the Born-Oppenheimer approximation, which amounts to neglect of the motion of the nuclei. The justification for this lies with the relative mass of the electron and proton, where the lower mass of the former leads to higher electron velocities. In this picture, electrons may be viewed as instantaneously rearranging to accommodate the motion of the nuclei. This approximation allows separation of the Schroedinger equation into two parts, a nuclear part and an electronic part. The electronic Schroedinger equation is then solved for a particular set of

nuclear parameters yielding a potential energy hypersurface dependent on these parameters.

When studying a system of more than one electron, the coulomb interaction between electrons must be included in the Hamiltonian. In the Hartree-Fock scheme, the instantaneous interaction of electrons is approximated using an average electron field, the electron-electron interaction represented by each electron seeing an average field of all the other electrons. Within this scheme, the wavefunction is taken to be an antisymmetrized product of one-electron orbitals. This neglect of electron correlation can lead to qualitative as well as quantitative errors. The Hartree-Fock wavefunction frequently does not dissociate properly and may produce unreliable results for problems such as barrier heights and reaction pathways. This level of theory may even produce erroneous predictions for energetic stability, where the classic example is the F_2 system.¹ Hartree-Fock predicts this to be an unbound system relative to the dissociated atoms. These problems may be remedied in part by inclusion of electron correlation, which in this research has been treated using configuration interaction (CI) techniques.

Within the Hartree-Fock scheme an infinite set of one electron orbital functions represents an exact solution, the "Hartree-Fock limit." In practice it is necessary to truncate the set of expansion functions and chose a limited basis set. The size of basis set needed depends on the

basis set. The size of basis set needed depends on the particular system under study, but many studies have been done and several standard basis sets are available and the quality of their results well understood.² Even with the above approximations the Hartree-Fock equations are not easily solved and for the many-electron system cannot be solved analytically. The solution method of choice, the self-consistent-field, is an iterative method. A guess is made for the wavefunction and the equations iterated upon until self consistency is achieved. In spite of the inherent difficulties, the HF-SCF model is the simplest ab initio approach for chemical information and may be safely applied to a wide variety of systems.³

For studying chemical formation and dissociation, as well as for more accurate predictions for certain properties, electron correlation may be included using configuration interaction (CI) techniques.⁴ Within the CI scheme the Schroedinger equation is solved exactly by expanding the wavefunction in a set of electron configurations representing excitations of electrons from the Hartree-Fock reference configuration. A particularly elegant way of dealing with the generation of configurations is the Graphical Unitary Group Approach⁵ and the calculations here have been carried out using the set of programs developed at Berkeley using this approach.⁶ Within a given basis set, all possible excitations of electrons can lead to a lengthy configuration list and multiply the cost of calculation enormously. Fre-

quently, this list of configurations is limited to such excitations that correspond to single or double excitations from the reference state. This is referred to as a singles and doubles configuration interaction (SD CI) calculation and typically yields adequate results, recovering a good portion ($\sim 95\%$ for systems on the order of 20 electrons) of the correlation energy. Since the Hamiltonian includes only one and two body terms, configurations of more than double excitations will not interact with the reference configuration and hence are not expected to be of great importance.⁷

An exact solution to the Schrodinger equation may be obtained if all possible configuration states are included in the CI calculation (a full CI) and the SCF basis set is complete. This is of course not practical, but full-CI calculations are now possible for a small number of chemical systems when the basis set size is limited.⁸ This type of calculation represents an exact solution within a given basis set. Both the Hartree-Fock and CI schemes are variational, so the lowest energy obtained represents the best approximation to the true energy of the system.

A major thrust of the research using these techniques involves determining equilibrium structures and obtaining harmonic vibrational frequencies. This information is obtained from a search along the potential energy hypersurface determining a minimum point, which defines an equilibrium geometrical structure. Further information is required to

determine if this point is a true minimum or simply a saddle point on the surface. This search may be carried out by a pointwise study or using the more sophisticated derivative techniques developed in the past few years.⁹ The use of gradient information, as well as, second derivative information greatly simplifies the minimum search and prediction of quadratic force constants. The force constants can then be subjected to a standard analysis¹⁰ to yield harmonic vibrational frequencies. These frequencies provide the information as to the nature of the stationary point, all real frequencies indicate a true minimum point, whereas, a single imaginary frequency indicates a transition state. All of the above have been applied to study the energetics of the carbon monoxide and carbon monosulfide dimers. The vibrational spectra and energetic stability of these species has been predicted.

The research presented in the following chapters uses the above techniques but also explores the consequences of some of the above described approximations. For most theoretical studies the non-relativistic Schroedinger equation presents the starting point for calculations. In systems comprised of light atoms such as carbon and hydrogen, this is considered a perfectly valid approximation. The neglect of these relativistic effects has been explored in the present research and applied in a study of the methylene molecule, CH_2 . Most questions one is likely to consider about a particular chemical system will not be affected

considerably by relativistic effects, but there has been speculation that exact values of excitation energy gaps provide a possible area for importance. Here due to the change in electronic states, one or the other, ground or excited state, may be affected more by relativistic corrections. The methylene system provides a good study for this, as currently theoretical and experimental estimates of the excitation energy for $B_{31} - A_{11}$ are not in precise agreement, and possibly this is affected by previously ignored relativistic effects. Other studies have been conducted using perturbation techniques to include the major contributions. For a system like methylene, the Breit-Pauli Hamiltonian describes the system adequately and was used in this research in a SCF formalism. These relativistic effects can be included in a configuration interaction scheme also to yield a calculation described as a relativistic SCF, relativistic CI.

Further comparison between theory and experiments require calculation beyond simply energies of chemical systems. Experimentally determined properties such as vibrational frequencies provide a good comparison for testing the predictive quality of theoretical calculations. Typically the vibrational motion of a molecule is treated as a simple harmonic oscillator and the frequencies obtained neglect all higher order effects. These frequencies are in error by 8-12%,¹¹ and unless an ansatz correction is applied to them,

they do not compare directly to experimental frequencies. In an attempt to make direct comparison possible these higher order effects have been included in a direct quantum mechanical treatment for the HO^+ system. Methods such as this have been fairly successful in predicting frequencies previous to their actual observation.

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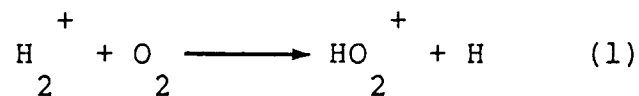
II. THE HO₂⁺ MOLECULAR ION

Gas phase polyatomic molecular ions are usually difficult to study via high resolution spectroscopy, in large part due to the problem of obtaining a satisfactory concentration of the desired ion.¹ It is certainly true that less than 1% of even the most common polyatomic molecular ions have been studied by high resolution spectroscopic techniques. However, the challenge presented by this essential void in the knowledge of the structures and energetics of simple molecular ions has recently attracted the attention²⁻⁸ of some of the most capable spectroscopists.

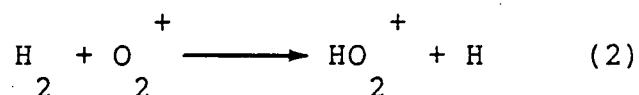
A significant fraction of those molecular ions observed at high spectroscopic resolution are the protonated counterparts of highly abundant neutral diatomic molecules. Thus the HCO⁺ and HN₂⁺ molecules have been studied by microwave spectroscopy⁶ and in fact have succumbed to complete structural determination.^{9,10} In the same vein one is tempted to say that protonated molecular oxygen, HO₂⁺, should be observed at high resolution. The fact that this species has a triplet electronic ground state is not helpful from the perspective of microwave spectroscopy,¹¹ but does allow at least one more recent technique, laser magnetic resonance (LMR)¹² to be applied. The intuition that HO₂⁺ probably has a significant abundance in dense interstellar clouds¹³ adds another element of interest.

There is a considerable amount of gas phase spectro-

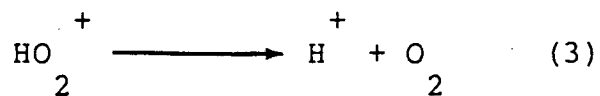
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 scopic data available for the neutral HO₂ radical and its ionization potential was determined as long ago as 1962 to be 11.5 ± 0.1 eV. Moreover, the existence of HO₂⁺ has long been established from kinetic studies of the well-known reaction



The companion reaction



has now been studied with both conventional kinetic³⁰⁻³² and molecular beam techniques,³³⁻³⁵ the latter yielding more information concerning the dynamics³⁶ of (2). Finally, the proton affinity of O₂, i.e., ΔH for the reaction



has been determined experimentally to be 101 kcal by Bohme.³⁷

Three previous theoretical studies of the HO₂⁺ molecular ion have been reported in the literature.³⁸⁻⁴⁰ Unfortunately the most reliable (i.e., highest level of theory) study, that of Shih, Peyerimhoff, and Buenker,³⁸ is concerned primarily with the neutral HO₂ and only coincidentally with the cation HO₂⁺. Buenker and Peyerimhoff considered only the vertical ionization potentials of HO₂, using extensive configuration interaction (CI) in conjunction with a basis set of better than double zeta plus polari-

zation (DZ+P) caliber. Their predicted lowest vertical IP was 11.65 eV, in very good agreement with the observed value 11.5 ± 0.1 eV of Foner and Hudson.²⁸ The second theoretical study, that of van Lenthe and Ruttink,³⁹ was carried out at a lower level of theory but spanned a much broader range of HO^+ properties. Van Lenthe and Ruttink used the single configuration self-consistent-field (SCF) method in conjunction with a DZ+P basis set to study the lowest A_1 , A_2 , and A_1 states of HO^+ . The equilibrium geometry of each electronic state was determined to within 0.01 Å in bond distances via a grid of total energies. Finally, Hiraoka, Saluja, and Kebarle⁴⁰ have used minimum basis set SCF theory to provide a qualitative discussion of the electronic structure of HO^+ in the context of their measurements of the thermochemistry of $(\text{O})^+ \text{H}^n$ species ($n=1$ to 7). The first direct spectroscopic study of HO^+ was reported in late 1981 by Dyke, Jonathan, Morris and Winter.⁴¹ Using vacuum ultraviolet photoelectron spectroscopy (PES), the adiabatic IP of HO^+ was determined to be 11.35 ± 0.01 eV, resulting in improved values for the heat of formation of HO^+ and the proton affinity of O^+ . Moreover Jonathan's PES showed vibrational structure which was analyzed in terms of the O-O stretching mode of HO^+ being $\omega_e = 1560 \pm 50$ cm^{-1} . Examination of the comparable DO^+ PES yielded $\omega_e = 1595 \pm 50$ cm^{-1} for the O-O stretching vibration. The increase in O-O stretching frequency with deuteration has also been observed for the neutral $\text{HO}^+ - \text{DO}^+$ pair by matrix isolation.⁴² Dyke

et al.,⁴¹ also theoretically predicted the vertical IP's of HO₂⁺ with a DZ+P SCF method and analyzed the HO₂⁺ and DO₂⁺ vibrational frequencies using the earlier reported force constants of van Lenthe and Ruttink.³⁹ The resulting harmonic vibrational frequencies are $\omega = 3577 \text{ cm}^{-1}$, $\omega = 1576 \text{ cm}^{-1}$, $\omega = 1346 \text{ cm}^{-1}$ for HO₂⁺ and 2610, 1558, and 1023 for the comparable frequencies of DO₂⁺. It may be noted that the predicted vibrational analysis does not give the observed result that deuteration increases the O-O stretching frequencies.

In this paper are reported a series of systematic theoretical predictions of the structure and vibrational frequencies of HO₂⁺ and DO₂⁺. At the highest levels of theory, this research goes significantly beyond that of van Lenthe and Ruttink.³⁹ In addition, the vibrational frequencies have been obtained both within the harmonic approximation and by direct quantum mechanical treatment⁴³ of the vibration-rotation energy levels. Thus we hope to provide a framework in which to understand the (yet to be observed) high resolution molecular spectroscopy of HO₂⁺.

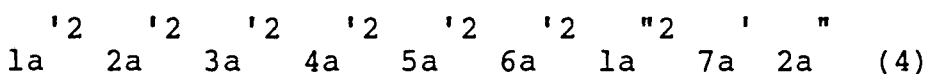
A. Theoretical Approach - Electronic Structure

Standard double zeta (DZ) and double zeta plus polarization (DZ+P) basis sets of contracted gaussian functions were used in this research. Specifically, the Huzinaga primitive (9s 5p) set for oxygen and (4s) set for hydrogen were contracted following Dunning to (4s 2p) and (2s), respectively. Thus the DZ basis may be designated O(9s 5p/4s 2p), H(4s/2s). To this DZ basis were added a set of six d-like functions to each of the two oxygen atoms and a set of p functions (p_x, p_y, p_z) to the hydrogen atom. Polarization function orbital exponents took on standard values $\alpha_d(O) = 0.8, \alpha_p(H) = 1.0$.

Although the size and character of the basis set required for the prediction of properties for neutral, normal "organic-type" molecules has long been established, studies on charged species have been less definitive. These standard basis sets are optimized for neutral atoms and may not have sufficient flexibility or contain the correct character to describe molecular ions. To allow more flexibility the DZ+P basis set was contracted less tightly, specifically O(9s 5p 1d/5s 3p 1d), H(4s 1p/3s 1p), and has been labeled EXT I. The effectiveness of these HO basis sets was further explored by adding a second set of polarization functions, allowing both diffuse and tight functions to be included. Exponents for both sets of polarization functions were those recommended by van Duijneveldt,

namely $\alpha_d(O) = 0.35, 1.5,$ and $\alpha_p(H) = 0.25, 1.4.$ These polarization functions augment the EXT I basis and form what has been labeled the EXT II basis set. A large set of primitive gaussian functions, essentially a TZ type basis set (Ext III), was also used to test the description of this charged system. For the oxygen atom EXT III is the standard Huzinaga primitive (10s 6p) contracted to (6s 4p),⁵⁰ and for the hydrogen atom the van Duijneveldt⁴⁹ primitive (6s) contracted to (4s) was used. In this EXT III basis each atom has one set of polarization functions as described for the DZ+P basis set. The different basis sets are collected in Table I.

The equilibrium geometry of the A^3 electronic ground state of HO^+ is bent,^{39,40} arising from the electron configuration



Restricted self-consistent-field (SCF) theory⁵¹ was applied to the A^3 state using the DZ, DZ+P, EXT I, EXT II, and Ext III basis sets, and second derivative techniques⁵² were used to determine both equilibrium geometries and force constants from which harmonic vibrational frequencies were determined. Explicitly correlated wave functions were obtained via configuration interaction including the Hartree-Fock interacting⁵³ single and double excitations. The two core or oxygen 1s-like orbitals were kept doubly-occupied in all configurations, and the two highest virtual orbitals (also

core-like for a DZ or DZ+P basis set) were deleted from the CI. With these restrictions, all remaining A^3 single and double excitations amounted to 1961 configurations for the DZ basis set and 9156 configurations for the DZ+P basis set.

B. Theoretical Approach - The Vibrational Problem

The direct quantum mechanical treatment of the vibrational-rotational levels begins with the Darling-Dennison Hamiltonian as simplified by Watson.⁵⁴ For a bent triatomic the Hamiltonian takes the form:

$$H = 1/2 \sum_{\alpha\beta} \mu_{\alpha\beta} (\Pi_{\alpha} - \pi_{\alpha}) (\Pi_{\beta} - \pi_{\beta}) \\ + 1/2 \sum_k P_k^2 - 1/8 \hbar \sum_{\alpha} \mu_{\alpha\alpha} + V.$$

P_k is the momentum conjugate to the normal coordinate Q_k , Π_{α} is the component of the total angular momentum, $\mu_{\alpha\beta}$ is the reciprocal effective inertia tensor and the component of the vibrational angular momentum is given by:

$$\pi_{\alpha} = \sum_{kl} \zeta_{kl}^{\alpha} Q_k P_l.$$

Where ζ_{kl}^{α} is the Coriolis coupling coefficient.

The energies are then obtained variationally as described by Whitehead and Handy.⁴³ An appropriate basis set for such studies is the product of Hermite polynomials and spherical harmonics, where the spherical harmonic functions may be integrated analytically and the Hermite polynomials integrated numerically using Gaussian quadrature formulas. Perhaps the most difficult problem to be addressed is the form of the potential in this Hamiltonian. With an adequately dense description of the energy hypersurface, the

potential function may be characterized by a polynomial expansion about the equilibrium geometry. As noted above, the geometry of HO_2^+ at an equilibrium structure was obtained using analytic second derivative techniques at the Hartree-Fock level and using analytic gradient techniques at the CI level.⁵⁵ The details of the anharmonic vibrational problem were then explored using four surfaces, DZ SCF, DZ+P SCF, DZ CI, and DZ+P CI. Obtaining a balanced *ab initio* surface description adequate for the study of vibrational properties, has been discussed in detail for the water molecule by Shavitt, *et al.*⁵⁶ Using their work as a guide, the HO_2^+ surface is characterized using a regular grid of points, determined by changing internal coordinates by multiples of fixed displacements away from the equilibrium geometry. To adequately describe the HO_2^+ surface a set of 77 geometrical displacements is necessary as opposed to the set of 35 points used for the more symmetric water surface.

These 77 points were chosen such that all points $(\pm l, \pm m, \pm n)$ with $|l| + |m| + |n| \leq 4$ are included, except those of the form $(\pm 2, \pm 1, \pm 1)$ and $(\pm 1, \pm 2, \pm 1)$. The notation $(\pm l, \pm m, \pm n)$ has been used to describe the geometrical grid displacements, where l, m, n are integer multiples of $\delta R_1, \delta R_2, \delta \theta$. Here $\delta R_1, \delta R_2, \delta \theta$ have been chosen as 0.05 bohr, 0.03 bohr, and 3° respectively, corresponding to $\sim 1/3$ of the root-mean-square zero-point vibrational amplitudes of the molecule. This set of 77 points has been tested to be sufficient: using the DZ basis, calcu-

lations with all points such that $|l| + |m| + |n| \leq 4$ (93 points) gave frequencies of 3331, 958, and 1327. Addition of further points such that $|l| + |m| + |n| \leq 5$ (116 points) changed these to 3340, 957, and 1326. This evidence justifies our statement that we think the error in our frequencies, because of this difficulty, is no more than 10^{-1} cm.

In order to obtain force constants, this surface is least squares fit to a potential expressed in terms of Simons-Parr-Finlan⁵⁷ variables through quartic, where

$$V = \sum_{abc} d_{abc} \left(\frac{\Delta r}{r} \right)_1^a \left(\frac{\Delta r}{r} \right)_2^b \Delta \theta^c$$

In all cases the surface is fit with a standard deviation no worse than 10^{-5} hartree. A qualitative test for this surface was achieved by a simple calculation of the harmonic frequencies. The diagonal quadratic force constants are extracted from the potential expansion and used in a standard harmonic analysis. Although these are not completely equivalent to harmonic force constants they yield frequencies within 1% of those obtained in the standard harmonic manner, supporting the reliability of this description of the potential energy surface. Using this form of the potential and the described vibrational basis functions the integrations are carried out and vibrational energies predicted. The convergence of the numerical integration to within 10^{-1} cm has been guaranteed using polynomial expansions to $\sum_i n_i =$

7, where n_i are the exponents of the polynomial. Within this expansion, 12 gaussian quadrature points are needed to converge the integration.

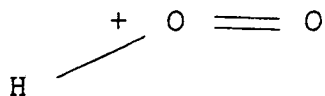
C. Geometrical Structures

The structures predicted at seven distinct levels of theory are shown in Figure 1. Both the SCF and CI equilibrium geometries have been determined for the DZ and DZ+P basis sets. In general, the DZ SCF level of theory yields good qualitative structures,⁴⁷ but it is evident that for HO⁺₂ the DZ SCF method does not correctly describe the oxygen-oxygen bond length and the inclusion of polarization functions is necessary. With the addition of polarization functions this structure (DZ+P SCF) is in good agreement with the previous work of van Lenthe³⁹ who determined the equilibrium geometry from an extrapolated pointwise search. Further extension of the basis set beyond the DZ+P level shows relatively little effect on the structure of the ion. Uncontracting the basis set slightly, allowing for more flexibility as in the EXT I calculation, moves the bond distance 0.002 Å for O-O and only 0.001 Å for O-H, with the angle similarly affected a small amount, 0.2°. Adding another set of polarization functions (the EXT II basis set) produces a larger geometrical change, ~ 0.01 Å for the O-O distance, but this does not qualitatively change the structure. The largest sp basis set, EXT III, again shows very good agreement with the DZ+P structure, bond lengths within 0.001 Å and the angle within 0.4°. The conclusion from this comparison is that the DZ+P basis set does yield reliable geometrical structures and allows sufficient flexibility for

the ion. The most serious deficiency of the DZ+P basis set is seen to be the absence of a second set of polarization functions on each atom. With the inclusion of electron correlation the theoretical prediction should agree well with the yet to be determined experimental structure. Comparison of the DZ+P SCF and CI results shows the expected trends, lengthening of both bonds and little change in the bond angle.

To put these structures in perspective, the experimentally known neutral HO_2 , has an O-O bond length of 1.334 Å, an O-H bond length of 0.977 Å and an O-O-H bond angle of 104.2°. The present research shows then that ionization of HO_2 weakens the O-H bonding, as indicated by the bond lengthening, and in addition opens up the angle. In contrast, the O-O bond shortens, a consequence of removing an electron from a partially antibonding orbital. Characterizing these bond lengths can be facilitated by comparison with two possible parent molecules, hydrogen peroxide, H_2O_2 , and molecular oxygen, O_2 . The O-O bond length in the HO_2^+ ion is predicted to be ~ 0.02 Å longer than that in molecular oxygen, an increase one might expect when removing electron density to allow for a hydrogen-oxygen bond. Comparing with hydrogen peroxide, with $R_{\text{OO}} = 1.475$ Å, $R_{\text{OH}} = 0.959$ Å, and an O-O-H angle of 94.8°, the HO_2^+ structure has an O-O bond length much more like the stronger oxygen-oxygen bond of O_2 . The O-H bond length in HO_2^+ is ~ 0.035 Å longer than the hydrogen peroxide O-H bond length, indicating a

weaker O-H bond. The predicted HO_2^+ structure may thus be considered as a double bond between the two oxygen atoms, as indicated by the simple valence structure:



D. Vibrational Frequencies

The prediction of vibrational transitions has been the major thrust of this work. For the five different basis sets, the SCF harmonic vibrational frequencies are listed in Table II. In comparing the frequencies predicted with different basis sets and levels of theory, one generally expects an increase in predicted bond length to be accompanied by a decrease in the stretching vibrational frequency for that particular bond. A glance at Table II shows that in most cases this is true. The DZ+P SCF structure changes dramatically from the DZ SCF, all bonds shortening and the angle decreasing, and these changes are reflected in the frequencies. This comparison shows the deficiencies in the DZ basis set, in the sense that it misses the ν_3 vibration by $\sim 200 \text{ cm}^{-1}$ and the ν_1 vibration by $\sim 100 \text{ cm}^{-1}$. There are some slight exceptions to the geometrical trend rule in the extended basis treatments, but these deviations are small and have been noted in other calculations with related extended basis sets.⁶⁰ Comparison of extended basis frequencies with the DZ+P frequencies shows again that the DZ+P set yields good qualitative predictions, and should be a sufficient basis set for use in the more exacting anharmonic vibrational studies.

Also included in Table II are the DZ and DZ+P configuration interaction (CI) frequencies. The addition of electron correlation affects the frequencies in a manner that is

basically consistent with the changes in geometrical parameters. One exception is notable, the ν_3 frequency increases from DZ+P SCF to DZ+P CI, even though the O-O bond length increases. This vibrational mode, in spite of being characterized as an O-O stretch, has some O-O-H bending character. The correlation between bending frequency and bond distances is not as clearcut as that between stretching frequency and the analogous bond distance. Given the mixed character of the ν_3 mode the increase in this frequency should not be too disturbing.

The effect of anharmonicity on the vibrational frequencies is summarized in Table III, corresponding harmonic frequencies being listed in parenthesis for easy comparison. As a rough rule of thumb the anharmonic predictions are 5-8% smaller than the strictly harmonic ones, but the degree to which each of the frequencies is lowered is seen to depend on the particular vibrational mode and potential energy surface. On the basis of these calculations and the previous analysis our best prediction of experimental frequencies would be the DZ+P CI frequencies with anharmonicity included, i.e., 3200, 1150, and 1570 cm^{-1} . However the basis set deficiency must be recognized, and one would expect these effects to be of the order of 50 cm^{-1} .

The above errors bars should be treated with some caution in light of the theoretical paper of Langhoff and Jaffe⁶¹ on the neutral HO₂ molecule. Using what appears to be roughly comparable CI methods, Langhoff and Jaffe predict the har-

monic O-H stretching frequency of HO₂ to be 469 cm⁻¹ above the observed fundamental. Table III shows for HO₂ the prediction for the anharmonic correction is only 244 cm⁻¹. Applying this order correction to the prediction of Langhoff and Jaffe does not entirely resolve the discrepancy with experiment.

This prediction for ν₃ mode is in good agreement with the experimental assignment of Dyke and co-workers⁴¹ of ω_e = 1560 ± 50 cm⁻¹ and ω_x_e = 15 ± 20 cm⁻¹. The experimental error bars are large but it is encouraging to get both the harmonic frequency (ω_e = 1607 cm⁻¹) and the anharmonic correction (ω_x_e = 35 cm⁻¹) in agreement with the observation. Another set of comparisons can be made using the deuterium substituted species. The most reliable prediction for DO₂, again DZ+P CI with anharmonicity, yields ν₂ = 2360 cm⁻¹, ν₁ = 1560 cm⁻¹ and ν₃ = 870 cm⁻¹. Although this result for the ν₂ mode is also well within the experimental error bars, ω_e = 1595 ± 50 cm⁻¹ and ω_x_e = 25 ± 10 cm⁻¹, we see the opposite trend with deuteration. Theory predicts a decrease in frequencies but the experimental observation is an increase in frequencies. Dyke and co-workers note that this observation is also seen for the HO₂ radical in matrix isolation.⁴²

As with the geometrical analysis, the vibrational frequencies can be compared with molecular oxygen. The ν₃ mode (1570) is very close to the experimental O₂ fundamental, ω_e = 1580.2 cm⁻¹ and ω_x_e = 1.0 cm⁻¹. This and the predicted

O-O bond distance would lead one to believe that the HO⁺₂ system has significant O character, with protonation causing little change in the oxygen-oxygen bonding.

E. Comparison with Neutral HO

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Since the properties of neutral HO are now well-established,²⁴ it is of interest to compare with the present theoretical predictions for the positive ion. Barnes, Brown, and Radford have given the r structure for HO as $r(\text{H-O}) = 0.977 \text{ \AA}$, $r(\text{O-O}) = 1.334 \text{ \AA}$, and $\theta(\text{HOO}) = 104.2^\circ$. The H-O separation for the neutral is 0.028 Å shorter than our prediction for HO⁺, consistent with the observation that the H-O separation for the latter is rather long, compared for example to the 0.957 Å known⁶² for water. However, a much larger difference between HO and HO⁺ is found for the O-O distance, which is 0.095 Å longer² for the neutral. This is nevertheless consistent with our conclusion that the oxygen-oxygen bond in HO⁺ is a true double bond, while that for neutral HO is something less.

These significant differences in bonding are borne out in the vibrational frequencies for each species. Yamada, Endo and Hirota⁶³ have observed the ν_1 (O-H stretch) fundamental at 3436 cm⁻¹ for the HO radical using difference-frequency laser spectroscopy. The ν_1 frequency for the ion HO⁺ is predicted to be 3204 cm⁻¹, in keeping with the observation that this ion has a rather long O-H bond distance. Using diode laser spectroscopy, Nagai, Endo and Hirota²⁵ place the ν_2 (O-O-H bend) vibration of HO at 1392 cm⁻¹, ~ 250 cm⁻¹ higher than the corresponding ν_2 vibration in HO⁺. Work by McKellar²⁷ using laser magnetic spectro-

2

scopy identifies the ν (O-O stretch) vibration for the neutral HO_2 at 1098 cm^{-1} . Theoretical predictions for HO_2^+ reverse the order of these two frequencies, $\nu = 1144 \text{ cm}^{-1}$, $\nu = 1572 \text{ cm}^{-1}$. This ν ($\sim 500 \text{ cm}^{-1}$ higher than the neutral frequency) is again reflective of the O-O bond distance closer to O than the neutral HO_2 . These frequency predictions as well as the geometrical structures support the description of the molecular ion HO_2^+ , as protonated oxygen, not simply ionized HO_2 radical.

F. Concluding Remarks

We have presented a detailed vibrational analysis and predicted the equilibrium structure for the molecular ion HO^+ . Theoretical studies of this type are not in great abundance and experimental confirmation of the predictions even rarer. We are encouraged by recent experimental results of Saykally and co-workers^{64,65} on the molecular ions HN^+ and HCO^+ . They have obtained high resolution infrared spectra of these ions, using the theoretical predictions of Dierckson, et.al.,⁶⁶ as a frequency guide to begin their experimental search for these molecular ions. The final assignment of the fundamental frequencies under study agreed with theory to within 12 cm^{-1} for HN^+ and within 30 cm^{-1} for HCO^+ . The methods of calculation used by Dierckson⁶⁵ were similar to those used here and would lead us to hope that experimental findings will confirm the present results as well.

In fact, the present theoretical predictions have already been of some value to Saykally's research group. In their initial search for the infrared spectrum of HO^+ , a prominent feature at $\sim 3500 \text{ cm}^{-1}$ was thought to be a candidate for the OH stretching frequency. However, our research established that at $\nu_1 = 3200 \text{ cm}^{-1}$ the OH stretch in HO^+ is in fact one of the lowest OH stretching frequencies in existence. A later collaboration between theory⁶⁷ and experiment⁶⁸ showed Saykally's prominent feature near 3500 cm^{-1} to be the e vibration of the H_2O^+ molecular ion.

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Table I. Basis sets of contracted gaussian functions used in this research. Polarization function orbitals exponents are given in the text.

Designation	Description	
DZ	O(9s 5p/4s 2p)	H(4s/2s) ^a
DZ+P	O(9s 5p 1d/4s 2p 1d)	H(4s 1p/2s 1p) ^a
EXT I	O(9s 5p 1d/5s 3p 1d)	H(4s 1p/3s 1p) ^a
EXT II	O(9s 5p 2d/5s 3p 2d)	H(4s 2p/3s 2p) ^a
EXT III	O(10s 6p 1d/6s 4p 1d)	H(6s 1p/4s 1p)

^a
Hydrogen basis set scaled by 1.2.

Table II. Predicted harmonic vibrational frequencies for
 HO_2^{a}

Level of Theory	ν_1	ν_2	ν_3
DZ SCF	3547	1059	1397
DZ+P SCF	3642	1335	1590
EXT I SCF	3606	1331	1567
EXT II SCF	3579	1348	1574
EXT III SCF	3598	1335	1552
DZ CI	3249	1065	1332
DZ+P CI	3430	1182	1607

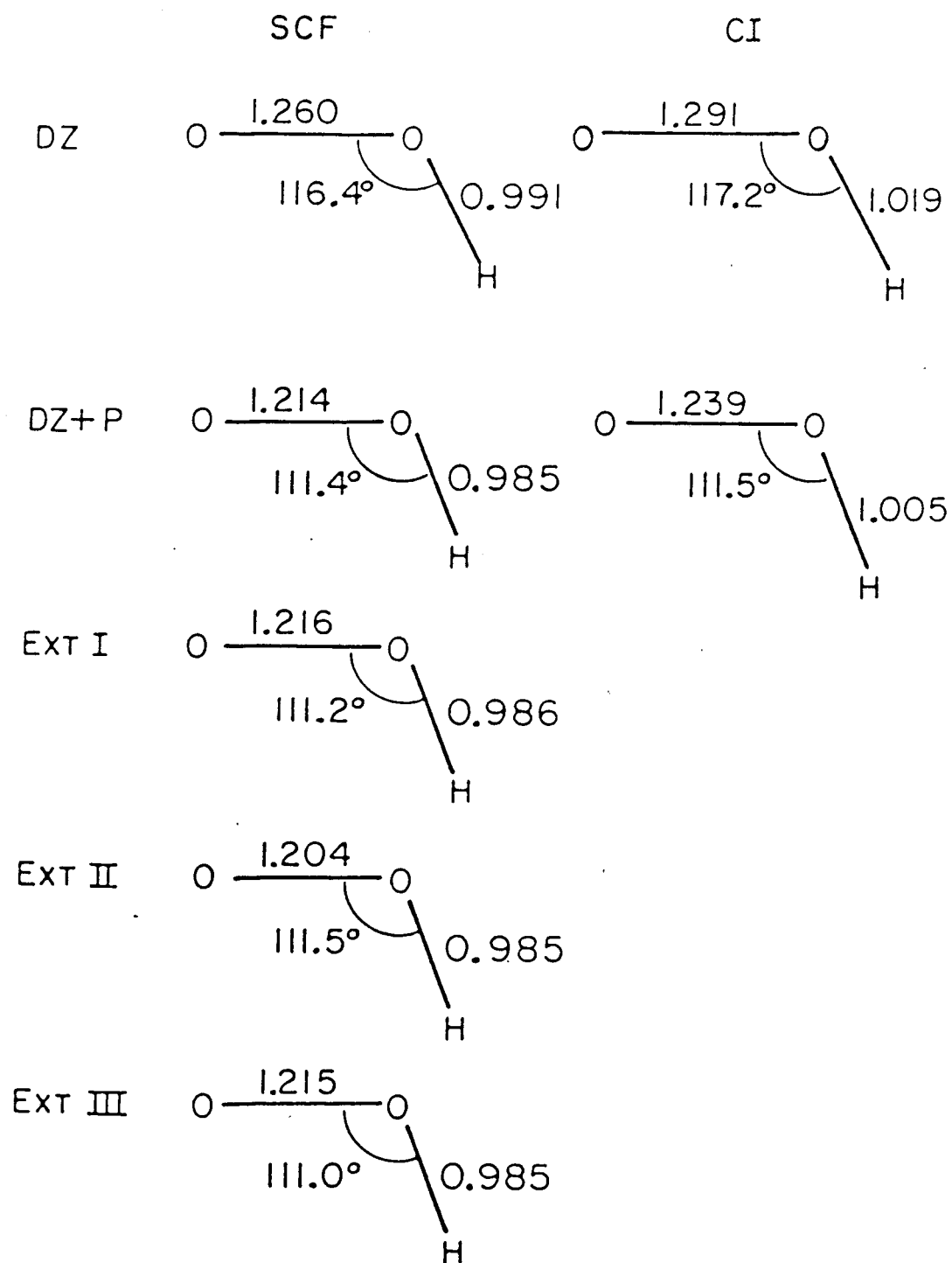
^a All frequencies are in cm^{-1} .

Table III. Predicted anharmonic vibrational frequencies for
 $\text{HO}_2^{\text{+ a}}$

Level of Theory	ν_1	ν_2	ν_3
DZ SCF	3335 (3547) ^b	953 (1059)	1325 (1397)
DZ+P SCF	3398 (3642)	1283 (1335)	1527 (1590)
DZ CI	3142 (3249)	1054 (1065)	1282 (1332)
DZ+P CI	3194 (3430)	1145 (1182)	1572 (1607)

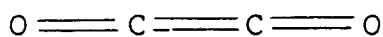
^a All frequencies are in cm^{-1} .

^b Frequencies in parentheses are harmonic frequencies.

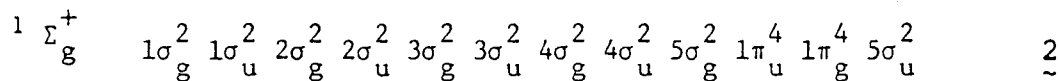


III. THE DIMERS OF CARBON MONOXIDE AND CARBON MONOSULFIDE

It has long been appreciated¹ that it is possible to write down a plausible valence structure for the carbon monoxide dimer (CO)₂. The chemical name ethylenedione is readily seen to be applicable to structure 1. The existence of valence structure 1 suggests a

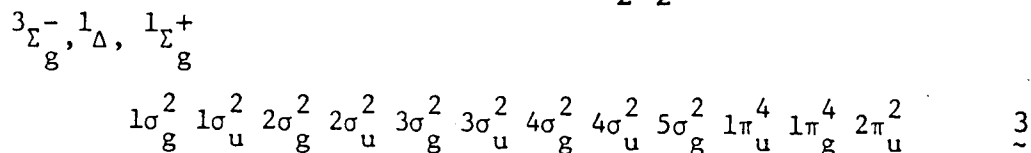


1
closed-shell singlet electronic ground state, and this arises from the electronic configuration



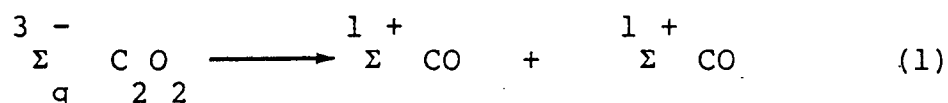
Nevertheless, all efforts, beginning as early as 1913, to prepare a chemically bound C O species have proven unsuccessful.²⁻⁷ (CO)₂ does of course exist as a van der Waals molecule, but its dissociation energy appears to be less than 1 kcal/mol.⁸ The cation (CO)₂⁺ is reasonably well characterized experimentally and has a dissociation energy D₀ (OC-CO⁺) = 22 ± 1 kcal,⁹ indicative of considerably less than a true carbon-carbon single bond.

Theoretical studies have shown^{1,10-14} that the ground-state electron configuration of C O is not 2 but rather

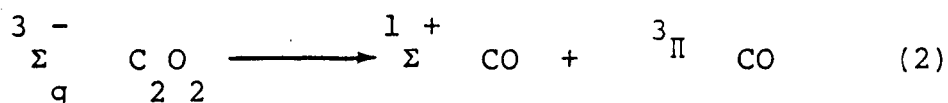


Hund's rules then require the lowest electronic state of the

open-shell configuration 3 to be the Σ_g^3 state. Moreover, a triplet ground state of $C O$ might be more difficult to detect experimentally than an ordinary closed-shell singlet (note of course that ESR experiments would be more suitable for a triplet ground state). However, a point that does not appear to have been given proper emphasis is the fact that $C O$ is a genuine chemically bound system. In the absence of spin-orbit coupling (which should be small for a molecule as light as ethylenedione), the ground triplet state is forbidden by spin conservation to dissociate to two ground-state carbon monoxide molecules:



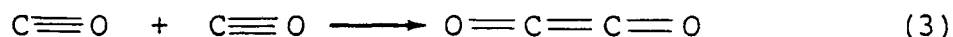
The lowest energy dissociation limit available for C-C bond rupture involves the lowest triplet state of CO, and inspection of (2) shows that this dissociative channel is symmetrically allowed



only for nonlinear pathways. Since the Π^3 state of CO lies $48,687 \text{ cm}^{-1} = 139 \text{ kcal}$ above the Σ^1 ground state, it is implicit in earlier theoretical studies that the Σ_g^3 ground state of $C O$ could be quite stable with respect to C-C dissociation. One can, however, envision a predissociative mechanism that might yield a relatively short lifetime for $\Sigma_g^3 C O$. The spin-orbit coupling might be large enough if a potential curve crossing occurs

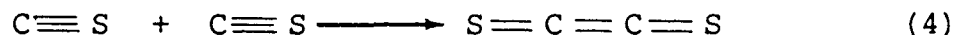
not too far from the minimum in the Σ state (e.g., by a $1 +$ Σ_g state repulsive with respect to carbon-carbon stretch).

The failure of ethylenedione to display a ground electronic state significantly bound compared to two ground-state carbon monoxide molecules may reasonably be attributed to the exceptional stability of the isolated CO molecule. With a dissociation energy of 11.1 eV = 256 kcal, $C \equiv O$ incorporates the strongest known chemical bond.¹⁵ In the formation of $C O$,
 $2 \quad 2$



one loses the second π bond in each CO molecule and gains the double bond between the two carbon atoms. If we ascribe the standard values¹⁶ of 77 kcal to the third bond in CO and 146 kcal for the C=C double bond in ethylenedione, it is readily seen that reaction (3) is endothermic by 8 kcal. Although this crude estimate is certainly reliable to no better than ± 10 kcal, one nevertheless concludes that breaking the third bond in $C \equiv O$ is sufficiently costly in energetic terms that $C O$ cannot be a terribly stable molecule.
 $2 \quad 2$

Several years ago it occurred to us that the analogous carbon monosulfide dimerization



might be more favorable energetically. Specifically, the $C \equiv S$ bond energy (170 kcal)¹⁵ is much weaker than that in

carbon monoxide, and the C=S double-bond energy (128 kcal)¹⁶ is not comparably reduced relative to the standard C=O bond energy (179 kcal). Thus the energy of the third bond in C≡S is only about (170 - 128) = 42 kcal, making the formation of ethylenedione exothermic by roughly (146 - (2 x 42)) = 62 kcal. Again, one does not want to take such a crude estimate too seriously, but this simple bond-energy argument does encourage one to pursue quantitative theoretical studies.

The goals of the present theoretical study were then twofold: first, to examine the (CS)₂ system in the anticipation that it might have an enthalpic stability not present for the analogous CO dimer; and secondly to carry out a detailed theoretical study of the Σ _g³⁻ ground state of (CO)₂. The most reliable previous investigation of ethylenedione is that Haddon, Poppinger, and Radom,¹⁴ and these authors (HPR) concentrated on the lowest singlet electronic state of C O₂. Another unique aspect of the present research is the detailed prediction of vibrational frequencies, inasmuch as one of the most likely means of experimental detection of chemically bound C O₂ or C S₂ is matrix-isolation infrared spectroscopy.¹⁷

A. Theoretical Approach

Both C_2O_2 and C_2S_2 were examined by using standard double zeta plus polarization (DZ + P) basis sets of contracted Gaussian functions. For carbon and oxygen, the (9s 5p) sets of Huzinaga²⁰ were contracted to (4s 2p) following Dunning.³¹ For sulfur, Huzinaga's (11s 7p) primitive basis was contracted to (6s 4p) in the manner of Dunning and Hay.²² To each atom was appended a set of six d-like functions with orbital exponents $\alpha = 0.8$ (oxygen), 0.75 (carbon), and 0.6 (sulfur). Thus the complete DZ + P basis set has the designation C,O (9s5p1d/4s2p1d), and S(11s7p1d/6s4p1d).

With the DZ + P basis, the restricted Hartree-Fock method of Roothaan²³ was used to investigate C_2O_2 and C_2S_2 . Both equilibrium geometries and quadratic force constants²⁴ were determined by using analytic gradient techniques. The Cartesian force constants were subsequently subjected to a standard analysis²⁵ to yield harmonic vibrational frequencies.

The effects of electron correlation were investigated variationally by using the method of configuration interaction (CI).²⁶ The CI procedure included all (within certain classes) configurations differing by one or two electrons from the Hartree-Fock reference configuration, either 2 or 3. The core molecular orbitals $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, and $2\sigma_u$ (carbon and oxygen 1s-like orbitals) were held doubly

occupied in all configurations, and the corresponding (in a DZ-type basis set) four highest lying virtual orbitals were deleted from the CI procedure. Correspondingly, in the case of sulfur the 1s- and 2s-like orbitals are held doubly occupied and the two highest lying virtual orbitals were deleted from the CI. This yields the same configuration list as described below for $C O$. Furthermore, for the open-shell species, only the Hartree-Fock interacting space (those configurations having nonzero matrix elements with the SCF reference configuration) was included. Finally, the actual calculations were carried out not in $D_{\infty h}$ but its subgroup D_{2h} . With these specifications it may be stated that for $C O$ there are 17,415 configurations for the Σ state (3) 35,538 configurations for the Π dissociation limit, and 15,009 configurations for the closed-shell singlet state (2). Final estimates of energy differences were made by using Davidson's correction for higher excitations (unlinked clusters).

B. The Diatomics CO and CS

Since no experiments have been successfully carried out for the chemically bound $C O_{22}$ and $C S_{22}$, the component diatomics provide the only basis for comparison with experiment. For this reason, such information is included in Table I. In general, the agreement is reasonable and consistent with what one expects from SCF theory applied with good basis sets. For carbon monoxide, the ground and first excited state bond distances are shorter than experiment by 0.010 and 0.021 Å, respectively. For CS, the $X \Sigma_{1+}^3$ internuclear separation is 0.015 Å less than experiment, while the $a \Pi$ bond distance is spot-on.

The harmonic vibrational frequencies are too large by 9.3% for $X \Sigma_{1+}^3$ CO, 14.3% for $a \Pi$ CO, 8.6% for $X \Sigma_{1+}^3$ CS, and 6.1% for $a \Pi$ CS. Thus, on balance, it would appear that the DZ + P SCF level of theory does a bit better for CS than for CO. For the $X \Sigma_{1+}^3 - a \Pi$ separation, the Hartree-Fock approximation inherently predicts a separation less than experiment, since the triplet state is treated better by a single-configuration wave function than is the closed-shell singlet ground state. With DZ + P SCF, the CO separation is 124.7 kcal (experiment 139.2 kcal¹⁵) and the CS X-a energy difference is 63.4 kcal (experiment 79.1). In both cases the error in the SCF singlet-triplet separation with respect to experiment is ~ 15 kcal.

Since vibrational frequencies for $C O_{22}$ and $C S_{22}$ were

subsequently predicted only at the DZ + P SCF level of theory, the above results suggest that errors of the order of +10% should be expected there. However, the relative energies of $C O_{22}$ and $C S_{22}$ were also predicted by using correlated wave functions (see previous section for description), and accordingly smaller errors were anticipated. This notion is supported by the comparison of results obtained for the dissociation limits $X \Sigma_{1+} CO_{1+}$ + $X \Sigma_{1+} CO_{1+}$ and $X \Sigma_{1+} CO_{3+}$ + a ΠCO . As just noted, the DZ + P SCF value of this $X \Sigma_{1+}^3 - a \Pi$ separation is 124.7 kcal. However, the DZ + P CI and cluster-corrected 29 DZ + P CI methods predict 134.8 and 136.2 kcal, respectively, for the same energy difference. The latter result is only 2.9 kcal 15 less than the experimental value (139.2 kcal), and this error may be considered representative of the reliability expected for other energy differences predicted in the same way.

C. Geometrical Structures of Ethylenedione and Ethylenedithione

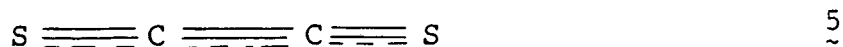
The predicted $D_{\infty h}$ stationary point geometries of the $3 - \Sigma_g$ electronic ground states of C_2O_2 and C_2S_2 are illustrated in Figure 1. For C_2O_2 , comparison with the earlier predictions of HPR¹⁴ show qualitative agreement. Their STO-3G (1.256 Å) and 4-31G (1.261 Å) values of the C-C bond distance are slightly less than the present DZ + P SCF value of 1.281 Å. All three levels of theory concur that the bond order of the C-C bond is about 2.5. Somewhat in contrast, the DZ + P SCF C-O bond distance is 1.168 Å, a bit shorter than HPR values 1.214 Å (STO-3G) and 1.186 Å (4-31G). The DZ + P SCF theoretical value of 1.168 Å places the C-O distance in C_2O_2 just about halfway between the formaldehyde $C=O$ double bond (1.203 Å)³⁰ and the carbon monoxide $C \equiv O$ triple bond (1.128 Å).¹⁵ On this basis one would conclude that the CO bond order is about 2.5 and sketch a valence structure of form:



This structure, among other problems, has a bond order of five about each carbon atom and should not be taken too seriously. Nevertheless, the short carbon-carbon distance is very different from that expected for a van der Waals molecule^{8,9} and obviously indicative of genuine chemical bonding.

For ethylenedithione, it is also apparent that the

mechanism of bonding is the same as for $\Sigma_g^{3-} \text{C}_2\text{O}$. At the DZ + P SCF level, the C-C distance r_e is only 0.005 Å shorter in C_2S than in C_2O and both bond distances imply a C-C bond order of about 2.5. In C_2S , the C-S distance of 1.563 Å is actually a bit closer to the triple bond of $\text{C}\equiv\text{S}$ (1.535 Å)¹⁵ than the $\text{C}=\text{S}$ double bond of thioformaldehyde (1.611 Å).³¹ Thus for ethylenedithione, one is again faced (strictly on the basis of geometrical data) with a bizarre valence structure:



incorporating three bonds of order 2.5.

In light of these remarkable geometries, it is important to point out that for unusual molecular species the correlation between bond distance and bond strength often breaks down. For example, the very weak (~ 3.3 kcal) bond in diatomic XeF_2 is only ~ 20% longer³² than that in XeF_4 , for which the first XeF bond has a dissociation energy of ~ 60 kcal.³³ A second example is the short but rather weak bond Cr_2 . Still other examples of short but weak aluminum-carbon bonds are given in the recent theoretical study of Fox and co-workers.³⁴ Therefore, one need not necessarily assume that these carbon-carbon bonds (in $\Sigma_g^{3-} \text{C}_2\text{O}_2$ and C_2S), which are sufficiently short to be classified of bond order 2.5, are necessarily very strong bonds in the conventional thermochemical sense.

D. Vibrational Frequencies

The DZ + P SCF harmonic vibrational analyses for linear ethylenedione and ethylenedithione are summarized in Table II. There, it is seen first of all that both linear structures are true minima on their respective potential energy hypersurfaces. This immediately rules out the possible cis and trans bent structures examined in some detail at lower levels of theory of HPR.¹⁴ However, the low-frequency bending modes of both molecules suggest that the energy surfaces are rather flat in the vicinity of these linear minima.

It is generally accepted that vibrational frequencies provide a fingerprint by which to identify functional groups.³⁵ Thus, for example, characteristic frequencies for carbon-carbon single, double, and triple bonds are respectively of the order of 1100, 1600, and 2100 cm⁻¹. However, before comparing the theoretical predictions with these "standard" frequencies, it is well to note that DZ + P SCF harmonic frequencies are typically of the order 12% greater than the observed stretching fundamentals. In an ordinary case, this 12% difference might be due to a combination of the effects of anharmonicity and neglect of electron correlation.³⁶ For this reason, we now reduce the ab initio C=C stretching frequencies of Table II to 2369 cm⁻¹ (C O) and 1879 cm⁻¹ (C S) prior to comparison with experiment.^{2 2} Even so, both frequencies clearly fall within the sphere of carbon-carbon multiple bonding. It would, however, be a

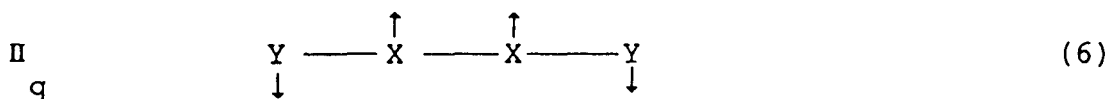
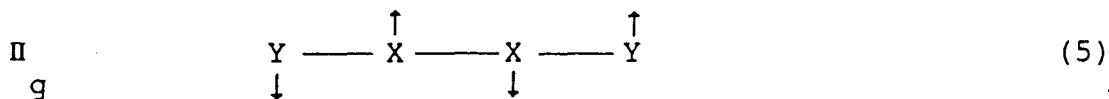
mistake to conclude that the high CC stretching frequency in C_2O_2 proves that a triple bond is present, since the proximity of the CC and CO stretching frequencies makes possible considerable mixing in the final vibrational analysis. In contrast, the lower frequency CS stretching (see Table I: $\omega_e = 2170 \text{ cm}^{-1}$ for diatomic CO vs. 1285 cm^{-1} for diatomic CS) does not mix as effectively with the CC stretching in C_2S_2 . One would conclude that the predicted CC stretching frequency of 1879 cm^{-1} for C_2S_2 is more nearly isolated, and hence subject to standard group-frequency analysis, ^{35,37} than the predicted frequency at 2369 cm^{-1} for C_2O_2 .

In like manner, the characteristic frequencies ³⁷ of C-O single, double, and triple (diatomic CO of course is the only known example) bonds are 1050 , 1700 , and 2143 cm^{-1} . However, such a direct comparison with the theoretical values is not appropriate, since it is well-known that the presence of multiple bonds in close proximity gives rise to asymmetric and symmetric stretching frequencies separated by a considerable difference. For example, the CO_2 molecule clearly has two C=O double bonds, but the observed stretching frequencies, ⁴⁰ at 2349 and 1388 cm^{-1} , are separated by 961 cm^{-1} . This is admittedly an extreme case, since the two C=O bonds are immediately adjacent, and, for the carbon suboxide molecule $O=C=C=C=O$, the observed C=O frequencies, ⁴¹ at 2258 cm^{-1} (Σ_g^+) and 2185 cm^{-1} (Σ_u^+) are separated by only 73 cm^{-1} . Clearly, the C_2O_2 molecule studied here, with predicted CO stretching frequencies of

1745 and 913 cm^{-1} , is closer to CO than to C O . Furthermore, comparison of the present C O frequencies (1745, 913 cm^{-1}) with those for CO (2349, 1388 cm^{-1}) suggests somewhat less than CO double bond character for the CO bonds in C O .

For carbon-sulfur bonds, a typical stretching frequency is 700 cm^{-1} , while in thioformaldehyde the $\text{C}=\text{S}$ mode lies at 1059 cm^{-1} and for diatomic $\text{C}\equiv\text{S}$, $\nu = 1273 \text{ cm}^{-1}$. Moreover, the adjacent $\text{C}=\text{S}$ frequencies in CS are 1533 and 658 cm^{-1} , while those separated by two bonds in C S (carbon subsulfide) are 1663 and 485 cm^{-1} . In this light the theoretical CS stretching frequencies at 1127 and 531 cm^{-1} would appear to be characteristic of the system with two interacting weak $\text{C}=\text{S}$ double bonds. In this sense the vibrational frequencies of the Σ_g^+ ground states of C O and C S are consistent in predicting CO and CS bond orders significantly less than the 2.5 suggested by the theoretical molecular structures.

An interesting prediction seen in Table II is that the Π_u bending frequency is the higher for C O , while the bending frequency of Π_g irreducible representation is significantly higher for C S . Note in this regard that these symmetry species correspond qualitatively to the following nuclear motions:



Displacement (5) is seen to lead to trans structures, while normal coordinate (6) moves the molecule into cis geometries. Thus it is seen that $C O_{2 2}$ is more favorable energetically toward cis bent structures, while $C S_{2 2}$ prefers trans distortions from equilibrium by a significant amount.

The known molecule most like $C O_{2 2}$ might appear to be cyanogen, $C N_{4 1 2 2}$, the vibrational frequencies of which are known. However, the CC single-bond stretching frequency of $C N_{-1}$ is only 851 cm^{-1} , much less than the 2369 cm^{-1} predicted here for $C O_{2 2}$. Note that this result is consistent with the former's longer C-C bond distance (1.397 \AA) compared with the 1.281 \AA C-C distance predicted here for $C O_{2 2}$. Furthermore, the CN stretching frequencies ($2330, 2148 \text{ cm}^{-1}$) appear to interact rather weakly compared to the separation of 832 cm^{-1} found for $C O_{2 2}$. Thus we conclude that the two CN fragments in $C N_{2 2}$ are much more weakly bound in this well-characterized molecule than for the experimentally unknown $C O_{2 2}^3 - \Sigma_g^-$ electronic ground state.

E. Relative Energies

The laboratory preparation of ethylenedione or ethylenedithione requires a measure of thermochemical stability. Should either C_2O_2 or C_2S_2 lie energetically below the respective ground-state dissociation limits $CO + CO$ or $CS + CS$ by more than a van der Waals dissociation energy, then a new absolute minimum for the energy hypersurface could be claimed. However, since the dimer electronic ground states are of Σ_g^- symmetry, all that is required for thermochemical stability is a significant potential well relative to the separated diatomic dissociation limit $X \Sigma^+ + a \Pi$. In this light, a summary of the theoretical relative energies are presented in Table III and Table IV.

As noted earlier by HPR,¹⁴ ethylenedione is not the absolute minimum on the C_2O_2 potential surface. However, every level of theory reported in Table III yields a Σ_g^- ground state strongly bound relative to the lowest triplet $CO + CO$ dissociation limit. Not anticipated from previous studies^{13,14} of C_2O_2 is the fact that polarization basis functions (d functions on each atom) decrease the predicted dissociation energy from 93.1 kcal (4-31G basis) to 65.4 kcal (DZ + P basis). This is of course contrary to what is typically found²² and is due to the fact that d functions are especially important in describing the triple bonds of the separated CO molecules. Electron correlation has a relatively small effect on the predicted value of D_e (OC-

CO), which is increased by 8.3 kcal to 73.7 kcal (DZ + P CI). Finally, the Davidson correction for unlinked clusters²⁹ increases the predicted dissociation energy by 0.5 kcal to 74.2 kcal.

In contrast, Σ^g_{3-} ethylenedithione is the absolute minimum on the C_2S_2 energy hypersurface. This result is predicted at each of the three levels of theory considered here. Relative to the lowest CS + CS triplet dissociation limit, the DZ + P SCF value of D_e (SC-CS) is 117.1 kcal, but the dissociation energy relative to two ground-state CS molecules is only 38.0 kcal (DZ + P). These DZ + P SCF dissociation energies are, however, somewhat increased when the effects of electron correlation are variationally considered.

F. Concluding Remarks

A very simple and crude bond-energy argument presented in the introduction suggests that $S=C=C=S$ might have a thermochemical stability (relative to the dissociation limit $CS + CS$) much greater than the analogous oxygen compound $O=C=C=O$, which lies energetically above two ground-state CO molecules. This seemingly naive suggestion has been confirmed in the present theoretical study, in the sense that the Σ^g_{3-} ground state of ethylenedithione is predicted to be the absolute minimum on the C_2S_2 potential energy hypersurface, lying 39 kcal below $X^1\Sigma^+ CS + X^1\Sigma^+ CS$. Therefore, we are convinced that C_2S_2 is a "makable" molecule and look forward to experimental efforts to this end. Since the monomer CS itself is not a very stable species, we appreciate that the production of gram quantities of C_2S_2 is unlikely. However, matrix-isolation infrared spectroscopy,¹⁷ electron spin resonance techniques,³⁸ or molecular beam studies³⁹ would all appear to be viable approaches to the experimental identification of ethylenedithione. Although the Σ^g_{3-} state of C_2O_2 lies ~ 65 kcal above $X^1\Sigma^+ CO + X^1\Sigma^+ CO$, this metastable species nevertheless lies 74 kcal below its lowest spin-allowed dissociation limit and should also be detectable in a carefully designed experiment.

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Table I. Comparison between theory and experiment for the diatomic molecules CO and CS. Experimental bond distances and vibrational frequencies are from Huber and Herzberg, reference 15.

CO		Total Energy (hartrees)	Bond Distance (Å)	Harmonic Vibrational Frequency
1 + Σ	SCF	-112.75878	1.118	2372
Experiment		--	1.128	2170
3 Π	SCF	-112.56011	1.185	1992
Experiment		--	1.206	1743
CS				
1 + Σ	SCF	-435.30706	1.520	1396
Experiment		--	1.535	1285
3 Π	SCF	-435.20609	1.569	1204
Experiment		--	1.569	1135

Table II. Predicted harmonic vibrational frequencies for the linear Σ_g^- ground states of OCCO and SCCS. All entries are in cm^{-1} and determined at the DZ+P SCF level of theory. The equilibrium geometries about which the vibrational analyses were performed are seen in Figure 1. The frequencies in parentheses have been empirically reduced by 12% from the ab initio values.

Normal Mode Symmetry	C O 2 2	C S 2 2	Description
Σ_g^+	2653 (2369)	2104 (1879)	C-C stretch
Σ_u^+	1954 (1745)	1262 (1127)	Asym. C-X stretch
Σ_g^+	1023 (913)	595 (531)	Sym. C-X stretch
Π_u	345 (308)	199 (178)	Cis bend
Π_g	277 (247)	485 (434)	Trans bend

Table III. Relative energies of the $3 - \Sigma_g^-$ ground electronic state of C_2O relative to the symmetry allowed $X^1\Sigma^+ + a^3\Pi_{22}$ dissociation limit and relative to the lowest $X^1\Sigma^+ + X^1\Sigma^+$ dissociation limit. The experimental $X^1\Sigma^+ - a^3\Pi$ separation used here is 139.2 kcal.¹⁵

O=C=C=O Method	$3 - \Sigma_g^-$ Absolute Energy (kcal)	Relative to $X^1\Sigma^+ + X^3\Pi$ CO (kcal)	Relative to $X^1\Sigma^+ + X^1\Sigma^+$ CO (kcal)
STO-3G UHF ^a	-222.37464	-91.8	47.9
4-31G UHF ^a	-225.03124	-93.1	46.1
DZ+P RHF	-225.39997	-65.4	73.8
DZ+P CI	-225.90646	-73.7	65.5
Davidson Corrected ^b	(-225.97106)	-74.2	65.0

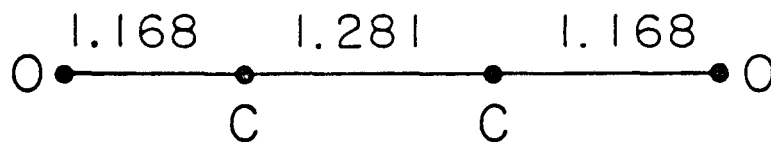
^a Haddon, Poppinger, and Radom, reference 14.

^b Not a variational result.

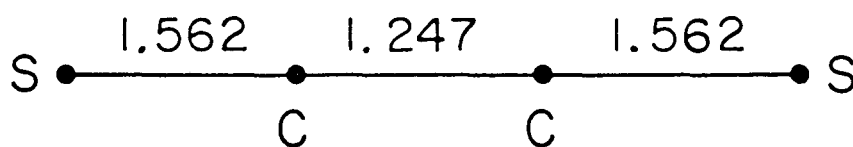
Table IV. Relative energies of the Σ ground electronic state of C_2S relative to the dissociation limits. The experimental $X \Sigma - a \Pi$ separation used here is 79.1 kcal.

S=C=C=S Method	$3 -$ Absolute Σ Energy g (hartrees)	Relative to $1^+ \Sigma CO + 1^+ \Sigma CO$ (kcal)	Relative to $1^+ \Sigma CO + 3 \Pi CO$ (kcal)
DZ+P SCF	-870.67470	-117.1	-38.0
DZ+P CI	-871.11686	-120.8	-41.7
Davidson Corrected (-871.18209) ^a		-118.5	-39.4

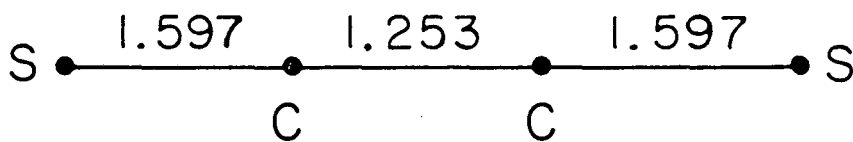
^a Not a variational result.



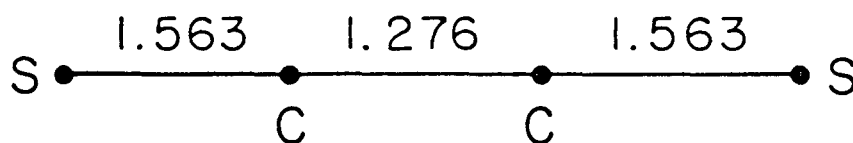
DZ + P



STO-3G



4-31G



DZ + P

IV. RELATIVISTIC CONTRIBUTIONS IN METHYLENE

In recent years there has been much interest in the singlet-triplet energy separation in methylene. Until recently there has been a "large" (~ 10 kcal) discrepancy between the theoretical prediction¹⁻¹² for the separation and the experimental determination¹³⁻¹⁹ of this quantity. It has been suggested by several authors that the origin of the remaining discrepancy (~ 1 kcal) may lie in the neglect of relativistic effects in the theoretical calculations. The older experimental values have taken the range from 6 to 19.5 kcal/mole. The largest of these values is that obtained by Zittel *et al.*¹⁸ and although it is a precise assignment (± 0.7 kcal/mole) questions have been raised about the interpretation of the data. Reevaluation of the quantity⁸ would lower the value to about 9 kcal/mole. A recent investigation by Hayden *et al.*¹⁹ using a molecular beam of CH_2CO ² places the separation energy at 8.7 ± 0.5 kcal/mole. Several theoretical studies¹⁻¹² have been completed and all lead to values around 11 kcal/mole and the most complete of these, a large CI with a large basis set yields 10.5 ± 1.5 kcal/mole.¹² Allowing for the uncertainties in both the theoretical and experimental values, there is still a discrepancy to be resolved.

It has been suggested by several authors²⁰⁻²³ that the origin of this problem may lie in the neglect of relativistic effects in the theoretical calculations. The carbon

atom would be the main contribution in these effects and Feller and Davidson²⁰ used Desclaux's²⁴ average configurational Dirac-Hartree-Fock atomic calculations to propose a relativistic correction to the singlet-triplet separation.

Assuming the electron configuration of the carbon atom to be $2s^2 2p^1$ and $2s^2 2p^1$ for the A and B states respectively, their relativistic differential was 1.5 kcal/mole (525 cm^{-1}).

This estimate was questioned by Wood and Pyper²¹ who noted that the atomic calculations were in error due to an incorrect comparison of relativistic and non-relativistic calculations. They subsequently carried out relativistic and non-relativistic atomic calculations and deduced a smaller correction of 120 cm^{-1} . A more recent study by Davidson et al.²³ provided actual calculations on methylene by treating the important terms of the Breit-Pauli Hamiltonian within a first order perturbation scheme. This yields a relativistic correction for the singlet-triplet separation of 0.07 millihartrees or ($\sim 15 \text{ cm}^{-1}$). They showed some of this discrepancy was due to the incorrect assumption of $2s^2 2p^1$ and $2s^2 2p^1$ hybridization in the two states of CH_2 .

In the Davidson study and the research to be presented here, the non-relativistic Hamiltonian is modified to include relativistic terms formulated in the Breit-Pauli Hamiltonian. These terms are expanded to first order in α^2 where α is the fine structure constant, so typically these terms are used in first order perturbation calculations. But as noted by Cowan and Griffin²⁵, including these terms

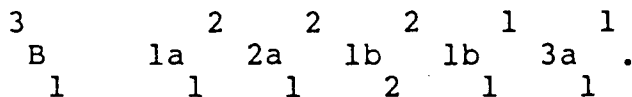
as part of a total Hamiltonian does give results that agree well with the full Dirac-Fock calculations. This is dependent on restricting behavior near the nucleus appropriately, which will be described later in more detail. In this research the relativistic problem has been treated in both manners, as a first order perturbation and in addition as a part of the total Hamiltonian for an SCF and CI calculation.

A. Theoretical Approach - Electronic Structure

A large basis set of essentially TZ (triple zeta) type quality was used for the SCF and CI calculations. This basis set is that recommended by van Duijneveldt²⁶ and is described by the nomenclature (11s 7p 3d) contracted to (8s 5p 3d) on carbon and (6s 1p) contracted to (4s 1p) on the hydrogens. The exponents on the d polarization functions are 0.25, 0.75, and 2.25. The p polarization function on the hydrogen has an exponent of 1.0. This basis set should be sufficiently flexible to correctly describe the methylene system for both the ¹A and ³B states.

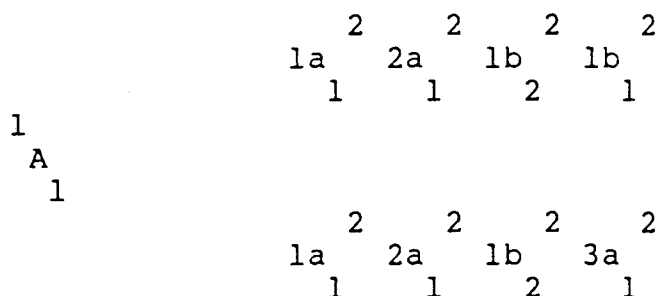
Rather than carry out an theoretical study to determine the equilibrium structure, the experimentally determined geometries were used throughout these calculations. Since the aim of this study is to help resolve the discrepancy between theory and experiment these may be taken as a better starting point for the calculation. For the ³B state this structure was determined to be C-H: 1.075 Å, and the H-C-H angle: 133.9°. The ¹A structure was determined to be C-H: 1.11Å, and the H-C-H angle: 104°.

The ³B state arises from the electronic configuration:



Within the SCF approximation this state can be treated as a

single Slater determinant so a single Hartree-Fock reference configuration is used in the SCF and later for the CI calculation. The CI calculation was limited to a single and double excitation configuration list which resulted in 4474 configuration for the B^3 state. The A^1 state, the first excited state, is for linear geometries, a doubly degenerate state arising from the electronic configurations:



When this is the case an adequate SCF description requires the use of both of these configurations and is termed a two configuration SCF or TCSCF. The TCSCF is a special limited case of the multi-configuration SCF or MCSCF which has been described in detail by several authors.²⁹ Both of these states are used as references in the CI calculation which in this case involves 6195 configurations for the singles and doubles configuration list. Both of these configuration sets are generated requiring the $1a_1$ orbital to remain doubly occupied, and keeping the 28th or highest unoccupied orbital unoccupied, not participating in the CI.

B. Theoretical Approach - Relativistic Problem

In the treatment of relativistic effects, the approximate Breit - Pauli relativistic Hamiltonian^{30,32} was used as a starting point, given in its general form in the absence of external magnetic fields by:

$$\begin{aligned}
 H = & \sum_j \frac{1}{2} \vec{p}_j^2 - \sum_j \frac{\alpha^2}{8} \vec{p}_j^4 + \sum_j \alpha^2 \pi_{ex}(\vec{r}_j) \\
 & + \sum_j \frac{\alpha^2}{2} \vec{s}_j \cdot (\vec{E}_{ex}(\vec{r}_j) \times \vec{p}_j) + \sum_{j < k} \frac{1}{r_{jk}} \\
 & - \sum_{j < k} \frac{\alpha^2}{2} \vec{p}_j \cdot (\frac{RR}{R^3} + \frac{1}{R}) \cdot \vec{p}_k \\
 & + \sum_{j=k} \frac{\alpha^2}{1/R} \vec{s}_j \cdot (\vec{R} \times \vec{p}_k) \\
 & - \sum_{j, j=k} \frac{\alpha^2}{2} \frac{1}{R^3} \vec{s}_j \cdot (\vec{R} \times \vec{p}_j) \\
 & - \sum_{j < k} \frac{\alpha^2}{2} \vec{s}_j \cdot (\frac{3RR}{R^5} - \frac{1}{R}) \cdot \vec{s}_k \\
 & - \sum_{j < k} \frac{8\pi \alpha^2}{3} (\vec{R})_{jk} \cdot \vec{s}_j \cdot \vec{s}_k - \sum_{j < k} \alpha^2 \pi(\vec{R})_{jk}
 \end{aligned}$$

Where $\vec{R} = \vec{r}_j - \vec{r}_k$, $\vec{E}_{ex}(\vec{r}) = -\nabla V_{ex}(\vec{r})$, and $\pi_{ex}(\vec{r}) = Z\delta(\vec{r})$ for a point nucleus.

In order to simplify the calculation terms were

selected from the Hamiltonian to include the major relativistic effects while dropping those negligible for light atoms.²³ These terms are described below as H_{251} , H_2 , H_3 , and H_4 and as demonstrated by Cowan and Griffin²⁵¹ these terms pick up the major corrections. Pyykko³² that the relativistic corrections are dominated by the mass velocity, Darwin and spin orbit terms for heavier many electron systems. In the case of light atoms, omission of the spin orbit term does not seriously affect the results. This stems from the fact that the majority of the relativistic contribution comes from the s electrons and of course the spin orbit coupling is zero.

Using atomic units the terms used are given by:

$$H_1 = -\frac{\alpha^2}{8} \sum_i p_i^4$$

$$H_2 = \frac{\alpha^2}{2\pi} \sum_A \sum_i Z_A \delta(\vec{r}_{iA})$$

$$H_3 = -\frac{\alpha^2}{\pi} \sum_{i<j} \delta(\vec{r}_{ij})$$

$$H_4 = -8\pi \frac{\alpha^2}{3} \sum_{i<j} \vec{s}_i \cdot \vec{s}_j \delta(\vec{r}_{ij})$$

The only terms included were those expected to contribute for a molecule with atoms of low atomic number.³⁰ The first term is the mass velocity contribution which takes into

account the change in the rest mass of the electron with velocity. As the velocity of the electron approaches the speed of light the mass increases. Looking at a hydrogen-type atom one can see the effect this has on the electron orbit. The Bohr radius for the hydrogen atom is given by the formula:

$$a_0 = \frac{\hbar^2}{m_e} .$$

Thus as the mass increases a relativistic contraction occurs. Along with this contraction a corresponding relativistic SCF expansion will occur in the outer d and f shells. Term two is the Darwin interaction term which has two parts, the one electron and the two electron part. The probability for an electron being at the nucleus is represented by the $1/r$ operator and the instantaneous interaction of two electrons is represented by the $1/r_{ij}$ term. This one-electron Darwin term results from the reduction of a four-component Dirac spinor to a two component form. In this case the electron is no longer a point charge but is a diffuse charge distribution. The effect of this is to reduce both the nuclear-electron attraction and electron-electron repulsion. Interaction between the spin magnetic dipole moments of two electrons is included in the fourth term. In practice for an antisymmetric wavefunction, term four is equal to minus twice the third term, so it need not be calculated.

Two sets of calculations have been carried out. In the

first treatment the terms H_1 , H_2 , H_3 have been calculated via perturbation theory. These results are summarized in Table II. In this approach the matrix elements are calculated over primitive basis functions (i.e., uncontracted Gaussian functions) then multiplied by appropriate contraction coefficients and density matrix elements and summed together. The results are in very good agreement with previous calculations of this type by Davidson and co-workers.²³ The small discrepancies in the actual values for each of these terms may be attributed to differences in basis set, geometry, and SCF vector convergence.

The contribution of this research is the extension beyond the simple perturbation type calculation. Within the normal non-relativistic Hartree-Fock formalism the relativistic Hamiltonian elements are added in, the integrals treated in the same manner as the normal non-relativistic one and two electron integrals. The Hartree-Fock equations are then iterated on to self consistency. By including these integrals in with the normal integrals and using this "relativistic" wavefunction for the reference SCF wavefunction a CI calculation may be carried out that can be labeled a relativistic CI. This provides the framework for the calculations summarized in Table I.

Calculation of the integrals necessary for these terms in the Breit-Pauli Hamiltonian requires relatively simple modifications of the existing program for the calculation of multi-center integrals. The first two

terms, the mass velocity and one-electron Darwin term involve integrals of only one electron, where the mass velocity term may be evaluated using conventional gaussian quadrature techniques. Evaluation of the Darwin term involves integration over a Dirac delta function and the term requires no actual integration calculation. The two electron Darwin term also reduces to a simpler problem via integration over a Dirac delta function. Here the remaining integral looks like a "super overlap" integral and requires integration over only one variable which again may be computed using gaussian quadrature techniques. The integral list and driver program are the same as the program used for the SCF integral calculation and relativistic calculation can easily be incorporated into the existing scheme. A very simple modification (changing the integral read) allows the relativistic CI to follow, and convergence is again rapid.

Within an SCF scheme, however, there is an important complication with the behavior of the mass velocity term. As noted by several authors,^{25,31} in the Breit-Pauli Hamiltonian the mass velocity term diverges in the region close to the atomic origin. This is a consequence of the power series expansion in α^2 of the relativistic kinetic energy operator. For Gaussian basis sets, the total Breit-Pauli relativistic kinetic energy contribution for s functions with exponents of the order $1/\alpha^2$ or larger becomes negative, yielding unrealistic wavefunctions and energies if corrections above first order in α^2 are included. The relati-

vistic kinetic energy correction can be limited to first order in the region of the nucleus if the basis set contraction is chosen carefully. Using the non-relativistic SCF contraction coefficients, high exponent s functions are heavily contracted with much smaller exponent functions, effectively avoiding the problem of this divergence.

C. Results

Table I contains the relativistic and non-relativistic results of the SCF and CI calculations for both the singlet and triplet states of methylene. A glance across the table shows that the results are reasonable, the relativistic SCF calculation lowers the energy by slightly more than the first order perturbation calculation. This is expected given the added flexibility inherent in the SCF calculation. Comparing the totally non-relativistic SCF-CI calculation and the totally "relativistic" SCF-CI calculation it is seen that the addition of relativistic effects has little effect on the CI contribution to the energy. In both calculations the CI lowers the energy by approximately the same amount. This is an indication that most of the relativistic effect has already been incorporated at the SCF level of theory. As for the intermediate calculation, the NR SCF-RCI, indicates, the relativistic effects may almost entirely incorporated in again by addition of the relativistic integrals into the CI.

Both the A_1 state and the B_1 state results follow these trends, but of particular interest here is the energy difference between these two states for each set of calculations. Table II summarizes these results and the first order perturbation results for comparison.

It can be seen that all the calculations predict a small relativistic correction to the singlet-triplet split-

ting in methylene. The correction for this separation obtained from first order perturbation theory is 19 cm^{-1} and the addition of the full relativistic CI calculation only changes the separation energy to 20 cm^{-1} . For comparison, relativistic SCF calculations have been carried out on the 3^3 P and 3^5 S states of the carbon atom with the same basis set and Hamiltonian as described for methylene. The relativistic contribution to the 3^3 P- 3^5 S separation is 97 cm^{-1} , which compares fairly well with prediction of 120 cm^{-1} by Wood and Pyper²¹ using a Dirac-Fock type calculation. Since the relativistic effect is due mainly to s core electrons, a Mullikan population analysis was carried out. The population on the carbon atom in the 3^3 B state of methylene was found to be $s^{1.5} p^{2.6}$ and for the 3^1 A state, $s^{1.3} p^{2.9}$, where the precise change in s population is .256. This indicates,²³ as was previously noted by Davidson, Feller, and Phillips, that the assumption made in earlier papers that the carbon atom is $s^2 p^2$ and sp^3 in the singlet and triplet states of methylene, is incorrect. Assuming that the s change is the major contribution to the relativistic correction, a simple correction factor may be applied to Wood and Pyper's results for methylene. This multiplication factor changes their correction to 30 cm^{-1} which is in close agreement with the calculations given here.

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Table I. Relativistic and Non-relativistic SCF and CI Energies in Atomic Units using the Breit-Pauli Hamiltonian

State	(a) E	(b) E	(c) E	(d) E	(e) E
3 B	-38.9336	-38.9476	-39.0646	-39.0780	-39.0784
1 A	-38.9169	-38.9308	-39.0480	-39.0615	-39.0619

(a) Non-relativistic self-consistent field.

(b) Relativistic self-consistent field.

(c) Non-relativistic configuration interaction with non-relativistic self-consistent field.

(d) Relativistic configuration interaction with non-relativistic self-consistent field.

(e) Relativistic configuration interaction with relativistic self-consistent field.

Table II. Relativistic Corrections to the $A^1 - B^3$ Separation of Methylene using the Breit-Pauli Hamiltonian

Method	Relativistic Contribution		
	in milliHartree	in kcal/mole	in cm^{-1}
First Order Perturbation	0.087	0.055	19
Relativistic Self-Consistent Field	0.090	0.056	20
Relativistic Configuration interaction with non-relativistic self-consistent field	0.090	0.056	20
Relativistic Configuration interaction with relativistic self-consistent field	0.091	0.057	20

V. CONCLUDING REMARKS

The research presented here represents what is hopefully only a small portion of the cooperative science between theoreticians and experimentalists. Theoretical chemistry has developed into a discipline that is capable of quantitative predictions of chemical properties. Although precise agreement for many predictions is not yet possible, the errors in prediction are understood to a high degree and limits of disagreement can be established.

In particular, the research on the molecular ion HO^+_{2} shows the cooperative effort. This ion was tagged as one of interest to Professor Saykally, a molecular spectroscopist at U. C. Berkeley. Identification and characterization of ions that can be made in only small quantities is a difficult task and guidelines for a wavelength search are very helpful. Although this particular ion has not yet been observed experimentally, the theoretical predictions of its spectra have already been of use. The O-H stretching fundamental, the only frequency that lies within the experimental range of the Saykally apparatus, lies at ~ 3200 cm^{-1} . Thus the HO^+_{2} ion was eliminated as a possible source of the ~ 3500 cm^{-1} spectral line that has since been identified as H_2O^+ . In fact, this final identification was aided by calculations done by Colvin and coworkers.

The techniques for calculating anharmonic corrections could in principle be applied to larger systems but at

present the application is limited by available computer power. With the addition of only one atom, a four atom system, the problem becomes quite large, where the major difficulty lies in the description of the potential energy surface.

The relativistic techniques and programs described here may be of use for other small systems. In particular, the first row transition metals could be studied and the relativistic effects explored. By the time atoms as large as second row transition metals are considered, this level of treatment is no longer adequate. For these atoms the spin-orbit coupling term becomes as important as electron-electron repulsion and interatomic interactions, and more terms need to be included in the Hamiltonian.

As computing power increases the number of problems that may be addressed successfully, using the methods outlined here, becomes larger and larger. This industrial innovation coupled with continued development of derivative techniques, more elegant configuration interaction approaches, and yet unknown techniques will move ab initio molecular orbital theory further into the realm of the every day experimental world.

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