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PURCHASE OF AN ARRAY PROCESSOR TO ENHANCE QUANTUM
CHEMISTRY CALCULATIONS(U) NORTH DAKOTA STATE UNIV FARGO
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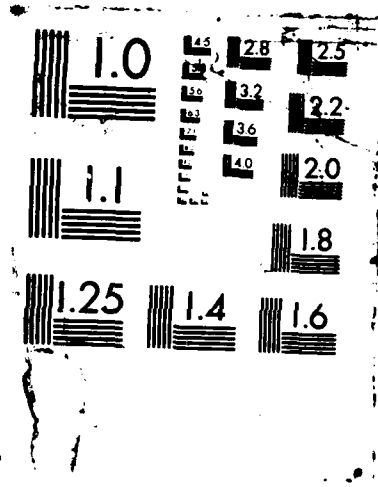
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Hewlett-Packard six pen color plotter and a Tektronix 4307 color graphics terminal. In addition to the matching dollars provided by the University, North Dakota State University also provided a much improved air conditioning system for the computer room and has very recently provided the hardware necessary to interface the VAX with the NSFNET supercomputers. The reliability of the VAX has been outstanding, and several research projects have already been initiated using the system.

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**PURCHASE OF AN ARRAY PROCESSOR TO ENHANCE QUANTUM
CHEMISTRY CALCULATIONS**

FINAL REPORT

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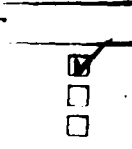
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[The original proposal was to add an array processor to the VAX 11/750, previously purchased with a DoD grant, in order to increase the throughput by a factor of five. However, after extensive comparative studies of array processors and stand-alone computers, it was concluded that none of the available array processors in the accessible price range were sufficiently reliable and that the desired factor of five increase in speed might not be achieved. Therefore, the alternative of trading in the VAX 11/750 on a new stand-alone computer was considered as an alternative. Benchmark tests were developed using the program GAMESS, and these benchmarks combined with known reliability led us to purchase a VAX 8530, manufactured by Digital Equipment Corporation. This computer, configured with 16 megabytes of real memory, 1.35 gigabytes of disk space, a tape drive, a printer, and a console, provides us with approximately six times the throughput of the 8530, thereby exceeding our expectations. Interfaced with the computer and purchased as part of the grant, are a Hewlett-Packard six pen color plotter and a Tektronix 4307 color graphics terminal. In addition to the matching dollars provided by the University, North Dakota State University also provided a much improved air conditioning system for the computer room and has very recently provided the hardware necessary to interface the VAX with the NSFNET supercomputers.

The reliability of the VAX has been outstanding, and several research projects have already been initiated using the system.] These are summarized below.

A. Gas Phase Acidities, M.S. Gordon, A. Koster, and D.R. Gano, research in progress.

An important question related to stabilities of pentacoordinated silicon anions is the effect of substituents on XH_n gas phase acidities. Preliminary calculations have been carried out at the minimal basis set level for the compounds $XH_{n-1}Y$, where $X=C, N, O, Si, P, S$, and $Y=CH_3, NH_2, OH, F, SiH_3, PH_2, SH$, and Cl . This is now being followed up with much higher level calculations. 3/or



Codes

A-1

B. Theoretical Studies of the Reactions of Si_n^+ with Methylsilane, L.P. Davis, L.W. Burggraf, K. Nguyen, M.S. Gordon, and K. Raghavachari, research in progress.

In a recent experimental paper, Bondybey and co-workers reported a FT-MS study of the reactions of cationic silicon clusters with methylsilane. The experiments were only able to determine the molecular formulas of the products. Since there are a very large number of possible products, even for $n=1$, and since there are many isomeric forms for most of the products, we have embarked on a combined ab initio/MNDO study of the possible reactions, with particular interest in determining the relative thermodynamics and barrier heights for the competing reactions. Several possible products of the reaction $\text{Si}^+ + \text{CH}_3\text{SiH}_3$ are predicted to be formed with release of energy at the MP2/6-31G(d) level of theory. These include (exothermicities in parentheses) $\text{H}_2\text{CHSiH}_2^+ + \text{H}$ (5.9 kcal/mol, $\text{SiCH}_3^+ + \text{SiH}_3$ (4.7), $\text{SiH}_2\text{CH}_2\text{Si}^+ + \text{H}_2$ (20.7), $\text{H}_3\text{SiCHSi} + \text{H}_2$ (5.0), $\text{H}_3\text{SiSiCH}_3^+$ (45.2), $\text{SiHSiH}_2\text{CH}_3^+$ (38.3), $\text{SiH}_3\text{CH}_2\text{SiH}^+$ (46.0), $\text{SiH}_2\text{SiHCH}_3^+$ (53.5), $\text{SiH}_2\text{SiH}_2\text{CH}_2^+$ (47.0). The remaining products are predicted to be uphill in energy. The next step in the process is to investigate the barrier heights for the exothermic reactions in order to develop an understanding of the mechanism of the overall process.

C. Theoretical Study of the, Lowest Triplet Potential Energy Surface of Si_2H_2 , S. Koseki and M.S. Gordon, J. Phys. Chem., in press.

As part of a comprehensive investigation of reactions which may be important in chemical vapor deposition (CVD), we have embarked on a study of the singlet and triplet potential energy surfaces of disilyne.

Binkley had determined that there are two minima corresponding to a bent $^3\text{A}''$ silasilene structure (with the planar triplet apparently the transition state for the inversion motion) and a twisted ^3B disilyne. However, the addition of zero point vibrational energies to his results reverses the energy order of the bent and planar silasilene structures. Our more extensive calculations verify

this result, and we predict the minimum to be planar, rather than bent. This C_{2v} structure is predicted to be the global minimum on the triplet potential energy surface. The second Binkley minimum, obtained with unrestricted Hartree-Fock (UHF) wave functions, is also questionable, since this state is UHF unstable. Also, at the MP4/6-31++G(d,p)//UHF/6-31G(d,p) level both planar cis and trans disilyne are found to be more stable than the twisted form found by Binkley. Unfortunately, the UHF wave functions for the two planar structures are also unstable. This suggests that a multiconfigurational approach is needed. At the FV MCSCF/6-31G(d,p)//MCSCF(4,4)/6-31G(d,p) level of computation, trans planar disilyne is indeed found to be lower in energy than the nonplanar structure. The potential energy surface for the rotation about the Si-Si bond has also been investigated using MCSCF wave functions, revealing the existence of three local minima: the cis-bent (C_s), twisted (C_2), and trans-bent (C_{2h}) structures. The rotation barrier from trans-bent to cis-bent is about 11 kcal/mol, while there is only a small barrier between the cis-bent and twisted structures. The latter might disappear at higher computational levels, because it is caused by a strong avoided crossing with a higher electronic state, and external correlation may be important.

D. Theoretical Study of the Singlet Potential Energy Surface of Si_2H_2 , S. Koseki and M.S. Gordon, in progress.

The pertinent reactions on the singlet surface include the isomerization of disilyne to silasilene and the dissociation of both isomers to $Si_2 + H_2$. At the RHF/6-31G(d,p) level, the transition state for the isomerization from planar singlet silasilene to the global Si_2H_2 minimum bridged disilyne is planar with one partially formed Si-H-Si bridge bond formed by the attack of one of the two Si-H bonds on the empty 3p orbital of the terminal silicon of silasilene. The MP4(SDQ)/6-31G(d,p) barrier for the reaction is only 4.1 kcal/mol. An MCSCF/6-31G(d,p) calculation with 7 active orbitals and 6 active electrons yields a similar value of 5.3 kcal/mol. The reverse barrier is found to be 14.7 and 7.1

kcal/mol, respectively, by the two methods. Since there is relatively little configurational mixing on this part of the surface, it is expected that the MP4 results are more accurate.

Extensive calculations at the full valence (FV) MCSCF/6-31G(d,p) level apparently detect a transition state leading from bridged disilyne to $\text{Si}_2 + \text{H}_2$, with a barrier of 43.8 kcal/mol. A long range minimum is also detected on this surface, at a 2.42 Å separation of the two fragments. The barrier for the dissociation is only 1.9 kcal/mol higher than this long range minimum, so the latter may disappear at higher computational levels. The vibrational frequencies along this path have also been studied, and this will lead to an analysis of the free energy path. This is particularly exciting, because it will allow an investigation of temperature effects on the reaction energetics.

The C_{2v} (least motion) path leading from planar silasilene to $\text{Si}_2 + \text{H}_2$ is symmetry forbidden. Because large configurational mixing is expected along this reaction path, the C_s transition state has been determined at the (7 orbital, 6 electron) MCSCF level; however, because the calculation is complicated by a bifurcation that occurs along this path, so that an intrinsic reaction coordinate (IRC) calculation cannot in itself identify the reactants and products connected by this transition state. More extensive calculations on this surface are under way.

The alternative dissociation of silasilene to $\text{SiH}_2 + \text{Si}$ has also been investigated using an MCSCF(6,6)/6-31G(d,p) wave function. It is found that the barrier for this reaction is much larger than that for the isomerization to bridged disilyne, so the latter is probably the preferred path.

E. Vibrational Dependence of the Lowest Electronic Transition in Disilene, S. Koseki and M.S. Gordon, research in progress.

This is a study of the dependence of the energy difference and the transition dipole moment between the ground state and the singlet ($\pi \rightarrow \pi^*$)

state on motions along some of the normal modes (Q_i) in Si_2H_4 , in an attempt to understand the vibrational structure of the UV spectrum of this molecule. Since the lowest ($\pi \rightarrow \pi^*$) and ($\sigma \rightarrow \sigma^*$) states are very close to each other in energy and belong to the same irreducible representation, the approach we are taking is to use MCSCF + CI wave functions to determine the Q -dependence of the vertical excitation energy and transition moment. The particular vibrational motions of interest are rotation about the Si-Si bond and flapping of the SiH_2 groups.

As expected, it is generally found that Si_2H_4 is a much "floppier" molecule than ethylene. Rotation about the central X-X bond is much easier for $\text{X}=\text{Si}$ than for $\text{X}=\text{C}$. The same is true for the flapping of the XH_2 groups. Because internal rotation partially breaks the π bond and therefore destabilizes the ground state, both motions decrease the excitation energy to the first excited state. What is not so obvious is that the oscillator strengths for both molecules and for both types of distortion have their maxima at the planar structure.

F. The Reaction of SiH_2 With O_2 , S. Koseki and M.S. Gordon, research in progress.

The first step in this study has been to determine the minima on the singlet and triplet potential energy surface of O_2SiH_2 . At the RHF/3-21G* level of theory, seven such singlet minima with positive definite force fields have been found, the lowest energy isomer being dihydroxysilylene, $\text{Si}(\text{OH})_2$. The lowest of the six triplet UHF/3-21G* minima has the same structure and is predicted to be 50 kcal/mol higher in energy than the lowest singlet. The large singlet-triplet splitting for $\text{Si}(\text{OH})_2$ is consistent with previous calculations on SiF_2 . The next steps in this problem are to re-examine the minima with MCSCF wave functions and then to study the potential energy surfaces for the dissociation and isomerization reactions.

G. Algorithms and Accuracy Requirements for Computing Reaction Paths, K.K. Baldrige, M.W. Schmidt, D. Bartol, B.C. Garrett, M.J. Redmon, R. Steckler, D.G. Truhlar, and M.S. Gordon, J. Phys. Chem., in press.

Recent advances in electronic structure theory allow the direct computation of gradients, and sometimes higher derivatives, of potential energy surfaces with only a small increase in computational effort over the calculation of the energy itself. This development has led to increased interest in minimum energy paths (MEP's, sometimes referred to as intrinsic reaction coordinates or IRC's) computed by the method of steepest descents and in using these paths as a first step in the prediction of reaction dynamics. This work was initiated to address the question of the accuracy with which the reaction path must be calculated, for a given level of electronic structure theory, in order to converge the calculation of the IRC and of thermal rate constants based on reaction paths and reaction path potentials. To this end, both ab initio and empirical potential energy surfaces have been used. The ab initio surfaces are those for the reactions $\text{HCN} \rightarrow \text{HNC}$ and $\text{H}_2 + \text{CH}_3 \rightarrow \text{H} + \text{CH}_4$, both computed with HF/STO-3G wave functions. The empirical surfaces are for the latter reaction and for $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$.

Several algorithms have been used to compute the reaction paths. The simplest approach is the simple gradient-following method. Here, an initial step off the saddle point is taken in the direction of the normal mode corresponding to the imaginary frequency. Subsequently, small steps are taken in the direction of the negative of the gradient (either toward reactants or toward products) in mass-weighted or mass-scaled cartesian coordinates. More sophisticated algorithms which take advantage of the knowledge of previous energies and gradients can also be devised. Those tested in the current work are the nth order Adams-Moulton method with either fixed (FAM) or variable (VAM) step sizes and the fixed-step-size Adams predictor method (FAP). The FAP method of order zero (FAPO) is identical to the simple gradient-following method

described above, and FAP1 is equivalent to a quadratic fit of the surface using two previous gradients and a previous geometry. Finally, a stabilization method (ES), originally proposed by Ishida, Morokuma, and Komornicki (J. Chem. Phys., 66, 2153 (1977)) and refined by Schmidt, Gordon, and Dupuis (J. Am. Chem. Soc., 107, 2585 (1985)) is used as well. It is found that to converge the FAPO method in general requires very small step sizes (on the order of $0.001 \text{ (amu)}^{1/2}\text{-bohr}$, and that higher order methods do not result in much improvement. The ES method does converge the reaction path much more rapidly than the other methods, but this approach is more time-consuming since it requires the calculation of additional gradients. Nonetheless, the ES approach allows a much larger step size, so it may well be the method of choice.

H. Development of the GAMESS Computer Code, M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S. Koseki, M.S. Gordon, S.T. Elbert, and B.T. Lam, QCPE, 7, 115 (1987).

The General Atomic and Molecular Electronic Structure System (GAMESS) has become one of the most sought after quantum chemistry programs. Originally written by Dupuis, Spangler and Wendoloski (NRCC Software Catalog Program QG01, 1980), the code was taken over by the NDSU Quantum Chemistry Group (with continuing support from AFOSR), in collaboration with S.T. Elbert at Iowa State and B. Lam at Ottawa. Now available at most of the National Science Foundation Supercomputer Centers and in IBM, CRAY, SCS, VAX, CDC, and UNIX versions, GAMESS is an electronic structure program which is capable of predicting:

1. the molecular and electronic structure of molecules;
2. transition states and barrier heights for chemical reactions;
3. minimum energy paths (IRC's) for chemical reactions;
4. vibrational frequencies and normal modes;
5. Franck-Condon factors and oscillator strengths;
6. various molecular properties, including

- a. dipole, quadrupole, and octopole moments,
 - b. electrostatic potentials,
 - c. electric field and electric field gradients,
 - d. virial theorem,
 - e. electron density and spin density,
 - f. Mulliken and Lowdin populations,
7. localized molecular orbitals by the Boys method.

The development and implementation of several other features are currently in progress. These include the computation of vibronic and spin-orbit coupling matrix elements, the calculation of analytical second derivatives of the energy, and interfacing with the dynamics program POLYRATE for the prediction of reaction rates.

The computations are made using ab initio quantum mechanical methods, using gaussian orbital basis sets of sizes varying from minimal to near Hartree-Fock. Wave functions may be of the RHF, UHF, ROHF, GVB, MCSCF, or CI type, with analytical energy gradients available for all but the latter.

I. Modifications of GAUSSIAN82, K.K. Baldrige and M.S. Gordon.

As noted above, GAUSSIAN82 has been modified to facilitate its interface with POLYRATE. The most important modification is the addition of the IRC codes, so that the minimum energy path for a chemical reaction can be generated with wavefunctions correlated using perturbation theory. Related to this is the automation of the scaling all correlation (SAC) method. This is a procedure developed in this laboratory for scaling the correlation energy obtained with perturbation theory. These modifications will shortly be incorporated into GAUSSIAN86

J. Aromatic Metals, K.K. Baldrige and M.S. Gordon, J. Am. Chem. Soc., submitted.

The concept of "aromaticity" (perhaps more properly referred to as ring delocalization stabilization) is a somewhat arbitrary one, but a quantitative

measure of the stabilization of a cyclic compound due to delocalization of the pi electron density may be obtained using "isodesmic" reactions. These are reactions in which each formal bond type is conserved, the advantage being that computational errors at the Hartree-Fock level are minimized. Two particular types of isodesmic reaction, bond separation reactions and superhomodesmotic reactions, are particularly useful for the present purposes. In a bond separation reaction the aromatic ring (e.g., benzene) is broken into its smallest component parts (e.g., three ethanes and three ethylenes) in a properly balanced reaction. The reaction enthalpy then measures the stabilization relative to these components. The disadvantage to this approach is that the resultant stabilization arises not only from the ring structure, but also from the ordinary conjugation of alternating single and double bonds. Superhomodesmotic reactions overcome this difficulty (at the expense of much greater amounts of computer time) by relating the parent ring compound to a conjugated molecule of the same size (e.g., 1,3,5-hexatriene).

In this study both types of reaction are being used at the RHF/3-21G* level to probe the "aromaticity" of C, Si, Ge, Sn, N, P, As, and Sb in six-membered rings and of N, P, As, Sb, O, S, Se, and Te in five-membered rings. As expected, the energy differences are much smaller for the superhomodesmotic than the bond separation reactions, since there is a much smaller change on going from reactants to products in the former. So far, however, the trends observed for the two types of reactions are essentially the same. For example, silabenzene is found to be about 70% as aromatic as benzene, while the corresponding value is roughly 88% for phosphorus vs. nitrogen. Replacing Si with Ge or P with As in the six-membered rings has very little effect on the stabilization, according to the bond separation reactions, with the corresponding ratios being 98% and 94%, respectively. Continuing this trend, Sb is almost as effective as As in stabilizing the metallobenzene, whereas

stannobenzene is only two thirds as aromatic as germabenzene. The corresponding superhomodesmic reactions are currently under investigation for the fourth and fifth period atoms. In the five-membered rings a dramatic drop in stabilization is observed on going from N to P. Indeed, the supehomodesmic reaction predicts the phosphorus compound to be less stable than its acyclic analog. On the other hand, the order of stabilization for the group VI elements is $S > Se > O, Te$. This is related to the strain in the oxygen ring relative to the other group VI five-membered rings and is in good agreement with available experimental rate data.

K. Silabicyclobutanes and Silacyclobutenes, J.A. Boatz and M.S. Gordon, J. Phys. Chem., in press.

The structures, vibrational frequencies, and bent bond lengths are predicted for the bicyclobutanes $C_nSi_{4-n}H_6$ ($n=0-4$), and for their cyclobutene analogs. The strain energies are predicted using the appropriate homodesmic reactions. The same reactions can be used to predict heats of formation when those of the reference compounds are known. It is found that the bonds in these compounds can be very bent, the most dramatic example being the isomer of $Si_2C_2H_6$ in which the two silicons are in the bridge positions. In this compound the internuclear distance is a very unusual 2.15 Å, whereas the bent bond length is a more "normal" single bond length of 2.3 Å. Some of the compounds, particularly the bicyclobutanes with bridging Si-Si bonds, actually have two minima, one with a normal bridehead bond length and one with a rather stretched bridgehead bond. Because the latter is so long, preliminary calculations suggest that there is considerable diradical character. Therefore, it is not entirely clear which of the two isomers is more stable. Additional calculations are proceeding in this laboratory to determine the relative energies.

L. Three-Membered Rings, J.A. Boatz and M.S. Gordon, J. Am. Chem. Soc., submitted.

The molecular structures and vibrational frequencies for the three-membered rings C_2H_4X and Si_2H_4X have been calculated at the RHF/6-31G(d) level of theory, for $X=CH_2$, NH, O, SiH_2 , PH, S. Ring strain energies and heats of formation have been predicted at the MP2/6-31G(d)//HF/6-31G(d) level, using the appropriate homodesmic reactions. The thermodynamics of the insertion of X into the $CH_2=CH_2$ and the $SiH_2=SiH_2$ double bonds to form the corresponding ring compounds have been calculated at the same level of theory. The strain energies and heats of formation are both within 2 kcal/mol of the experimental values where the latter are known. The insertion exothermicities are not quite as accurate, because the reactions are not homodesmic.

Because of the extreme sensitivity of the electron density to basis set in many of these three-membered rings, we have found that the bent bond analysis must be carried out with a basis set which contains at least two sets of d orbitals on the ring atoms. Otherwise, spurious maxima and minima appear along a bond. The bent bond analysis is very revealing. The internuclear base bond internuclear distances are found to decrease considerably as the electronegativity of the apex group is increased. This is accompanied a planarization of the base C_2H_4 or Si_2H_4 moiety. This has led some authors to suggest that the structure of these three-membered rings is becoming more and more like a pi complex between the apex group and the X_2H_4 moiety. However, the bent bond analysis clearly shows that the actual (bent) bond lengths are the same as those expected for normal single bonds, and no double bond character is apparent. This is verified by Mulliken population analyses which show little pi overlap for either the C-C or Si-Si bonds.

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