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DIATOMIC SULFUR: LOW LYING BOUND MOLECULAR ELECTRONIC STATES OF S_2

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Abstract

We present here the results of self-consistent field (SCF) and configuration interaction (CI) type calculations on thirteen low-lying electronic states of diatomic sulfur. The basis set was one of double zeta quality augmented with polarization functions. The CI space for each electronic state consisted of all configurations constructed from single and double excitations of electrons from the valence orbitals of the Hartree-Fock configuration.

There are several significant findings of this study. First, we report the discovery of a previously unobserved and bound $^1\Pi_u$ state which lies approximately 37,000 cm^{-1} above the ground state. This state dissociates to two ground state sulfur atoms. Second, we provide new predictions of excitation energies and properties for the three states $e^1\Pi_g$, $c^1\Sigma_u^-$ and $B''^3\Pi_u$. These states were suspected or known to be bound, but experimentally determined properties were uncertain. Finally, we find that systematic application of a formula of Davidson, which estimates the contribution of unlinked energy terms in a singles and doubles CI calculation, leads to improved predictions of excitation energies.

I. Introduction

There are many good reasons for experimental as well as theoretical interest in diatomic sulfur. Lasing has been observed in two different systems of the S_2 electronic spectrum, and in one of these a wide range of tunability is probable.[1,2] Also, it is interesting to compare S_2 with O_2, since the two molecules have an identical electronic valence structure. Finally, S_2 is a molecule about which much is yet to be learned experimentally, and for which ab initio calculations have not been performed. Indeed, very few quality ab initio calculations have been done on second row diatomic molecules.

The oxygen molecule is very well-characterized experimentally. However, although a great deal is known about the electronic structure of S_2[3], there are several ambiguities remaining. Table I summarizes the experimentally determined excitation energies of these two molecules. For only four of the thirteen low-lying electronic states studied here is information known with certainty. The ground $X^3\Sigma_g^-$ and $B^3\Sigma_u^-$ states are well-known from numerous studies[3] of $B \rightarrow X$ transitions, the same transitions which give rise to the lasing mentioned above. A second set of well-studied features are those of the $B'^3\Pi_g \rightarrow A^3\Sigma_u^+$ and $B'^3\Pi_g \rightarrow A'^3\Delta_u$ transitions. Studies of these transitions[4] establish quite accurate information on the A and A' states involved and their relative energies. The energies of the B', A, and A' states relative to the ground state are known only indirectly by comparing the dissociation energies of the A and A' states with that of the X state. The B' state itself is so predissociated that transitions from the v = 1 state are unobserved. Although, in principle, transitions from the lowest vibrational state are enough to determine most properties of interest, comparison

of several vibronic bands is usually needed to establish properties with certainty.

Another question of experimental interest concerns whether the $^1\Pi_u$ state exists as a bound species. This state arises from the configuration

$$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4\ 3\sigma_u^2\ 4\sigma_g^2\ 4\sigma_u^2\ 5\sigma_g^2\ 2\pi_u^4\ 2\pi_g\ 5\sigma_u \quad ,$$

which also gives rise to a $^3\Pi_u$ state. The $^3\Pi_u$ state is believed to exist as a bound state whereas no evidence exists for the presence of a bound $^1\Pi_u$ state.

Experiments on S_2 in 1962 by Meakin and Barrow[5] resulted in the observations of bands at 13,985.5 and 13,451.9 cm^{-1} which were then assigned to transitions $e^1\Pi_g \rightarrow c^1\Sigma_u^-$. However, in the later work on the $B' \rightarrow A,A'$ transitions referenced above the band at 13,451.9 cm^{-1} was assigned to the $B' \rightarrow A$ system. Thus, the proposed value of T_0 = 23,500 cm^{-1} for $c^1\Sigma_u^-$ of Barrow and du Parcq[3] is questionable since it was based on the assignment made earlier by Meakin and Barrow. (Also questionable are the properties they predicted for the $e^1\Pi_g$ state which were based on these two assignments.) Another reason for suspecting the earlier assignment is that it results in an ordering of the three closely spaced states c, A', A which is different than the ordering observed in O_2. Barrow and du Parcq's[3] assignments for the c state combined with those of Narasimham, et al.,[4] for the A and A' states give an ordering $A'^3\Delta_u$ (T_0 = 20974), $A^3\Sigma_u^+$ (21971), $c^1\Sigma_u^-$ (23550), whereas in O_2 the analogous states are ordered $c^1\Sigma_u^-$ (32660), $C^3\Delta_u$ (34320), $A^3\Sigma_u^+$ (35010).[6] Since all three states in both molecules

arise from the same valence electronic configuration of ... $\pi_u^3 \pi_g^3$, it would be surprising if the orderings were different in O_2 and S_2. Indeed, work by Scott, Raftery and Richards on modified Hund-type rules for linear molecules[7] gives a theoretical basis for the ordering to be as in O_2. However, a reliable value of T_o for the c state of S_2 has yet to be obtained.

One of us has performed matrix isolation experiments observing chemiluminescence upon diffusion of sulfur atoms in an argon matrix.[8] Two previously unobserved progressions have been assigned to the $c^1\Sigma_u^- \rightarrow a^1\Delta_g$ and $A'^3\Delta_u \rightarrow X^3\Sigma_g^-$ systems. Good calculations on the a, b and c states, whose excitation energies are uncertain, will help confirm the assignments. In addition, it would be useful to verify the T_o of the c state (20250 ± 250 cm^{-1}) derived from experiment as smallest among the c, A, and A' states.

A final point in question concerns the location and properties of the $B''^3\Pi_u$ state. The B → X transition of S_2 has been studied by fluorescence from cryogenic matrix samples by Brewer and Brabson[9] and by thermoluminescence by several groups (reference 10 and references therein). Recently, Long[11] suggested that the B'' → X transition plays a role in this S_2 matrix emission. Although the B'' state has never been observed previously, there is evidence for a $^3\Pi_u$ state a few hundred wave numbers below the B state. The evidence exists in the form of perturbations on the B state vibrational energy levels as suggested by Barrow and du Parcq[3] and Ricks and Barrow.[12] More information is needed about the B'' state to answer this important question. (It is interesting to note here that the B'' state of O_2 perturbs the B state. It is not, however, a bound state.[13])

In view of the present state of research on diatomic sulfur, it seemed appropriate to perform quality ab initio calculations on this molecule. It was hoped that such calculations could help answer some of the questions posed on the electronic states mentioned above. Furthermore, calculations on other low-lying states of S_2 could be valuable to future workers by providing reasonable estimates of bond lengths, excitation energies and vibrational frequencies. Certainly such calculations are unnecessary for the well-characterized states of S_2, such as the $X^3\Sigma_g^-$, $B^3\Sigma_u^-$, $A^3\Sigma_u^+$ and $A'^3\Sigma_u$ states, since the accuracy of the experimental information on these states is well-established. However, by performing calculations on these states as well as the lesser known ones, we may hope to obtain an estimation of the error our predictions may have for those lesser known states.

II. The Calculations

There were thirteen electronic states studied in this work. These were all possible states arising from four different electronic configurations:

$$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4\ 3\sigma_u^2\ 4\sigma_g^2\ 4\sigma_u^2\ 5\sigma_g^2\ 2\pi_u^4\ 2\pi_g^2 \qquad (1)$$

$$\ldots\ 5\sigma_g^2\ 2\pi_u^3\ 2\pi_g^3 \qquad (2)$$

$$\ldots\ 5\sigma_g^1\ 2\pi_u^4\ 2\pi_g^3 \qquad (3)$$

$$\ldots\ 5\sigma_g^2\ 2\pi_u^4\ 2\pi_g^1\ 5\sigma_u^1 \qquad (4)$$

The first electronic configuration gives rise to three states ($X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$), the second to six ($c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$, $B^3\Sigma_u^-$, $f^1\Delta_u$, $^1\Sigma_u^+$), the third to two ($B'^3\Pi_g$, $e^1\Pi_g$), and the fourth to two ($B''^3\Pi_u$, $^1\Pi_u$).

The calculations on these states were of ab initio quality and involved self-consistent field calculations (SCF) followed by configuration interaction calculations (CI). Each of these aspects of the calculation will be discussed separately.

The basis set was one contracted from a (11s7p) set of gaussian primitives generated by Huzinaga to a [6s4p] double zeta set by Dunning,[14] then augmented with a set of d functions (zeta = 0.6) for polarization. Various basis sets were tried before this one was decided upon. The criterion for a good basis set was that reasonable properties can be predicted for the ground state of S_2. This criterion was based on the hope that a basis set which was good for the ground state would be about

as good for all the excited states studied here. This seems reasonable in view of the fact that all states arise from electronic configurations (1)-(4) which are low level excitations from the ground state configuration into other valence orbitals. This was equivalent to assuming that the molecular orbitals of the excited states were quite similar to those of the ground state, and that all excited states studied were valence-like rather than Rydberg-like. This assumption was reasonable in all but one or two cases, which will be discussed later in Section III.

As can be seen from Table II, the polarization functions are necessary to give any binding of ground state S_2 at the experimental geometry of 1.889 Å. To see if diffuse functions needed to be added to the (6s4p1d) basis, an extra set of s (zeta = 0.05813) and p (zeta = 0.04347) functions were added. These orbital exponents were selected by the Raffenetti-Ruedenberg even-tempered criterion.[15] As can be seen from Table II, these diffuse functions result in a significant lowering of energies for both the atom and the molecule. However, the potential curves of the [6s4p1d] basis, with and without the diffuse functions are essentially parallel, so it was thought that the diffuse functions were unnecessary. The presence of diffuse functions did improve the ^3P-^1D energy separation, but not enough toward the experimental value of 26.4 kcal to warrant the extra computational effort involved with leaving them on.

Basis sets optimized for SCF calculations may or may not be adequate for configuration interaction (CI) calculations. Furthermore, CI calculations of different qualities may have different basis set requirements. The CI calculations performed here involved all single and double excitations of the twelve valence electrons of the electronic state under consideration.

In other words, for each calculation, electrons in core orbitals $1\sigma_g^2$ ... $3\sigma_u^2$ were held frozen. This resulted, of course, in different numbers of configurations for each electronic state, but roughly equivalent treatments for each state as far as the size of the interaction space was concerned. The average size of the interaction space was about 3000 configuration.

In Table III a comparison is presented of results of both different basis sets and different sizes of interaction spaces. The shorthand notation "u3s3p" is used to denote that all single and double excitations from molecular orbitals constructed primarily from the 3s and 3p (valence) orbitals of sulfur were used. This is the interaction space described above and used in the remainder of the study. Similarly, "u3p" is the above space made smaller by the freezing of the $4\sigma_g$ and $4\sigma_u$ electrons.

It can be seen at a glance that combination A is unsatisfactory at the CI level as it was at the SCF level. This result clearly indicates a shortcoming of the basis set. It is clear from the table that the [6s4pld] basis set is adequate. As for the interaction space size, clearly the larger one can afford to use, the better. We chose combination C over B, even though the two are nearly equivalent for the ground state of S_2, because correlation in the $4\sigma_g$ and $4\sigma_u$ orbitals may be important for excited states of S_2, particularly the $^1\Pi_g$, $^3\Pi_g$ states formed from the ... $5\sigma_g\ 2\pi_u^4\ 2\pi_g^3$ occupancy.

It may be disturbing to note that even the best calculations here do not give a very good value for the dissociation energy of the ground state of S_2. This is a rather well-known limitation of a single and double excitation CI caused by size inconsistency.[16] Basically, it means that although a singles and doubles calculation may be adequate at close-to-equilibrium geometries, it may become less so at larger atomic separations. Indeed,

this is not difficult to understand if one recognizes that to get an energy for S_2 with the sulfur nuclei infinitely separated that is comparable to twice the singles and doubles CI energy of a single sulfur atom, one would have to include at least quadruple excitations in the CI calculation on S_2. Naturally, therefore, the size inconsistent dissociation energies of Table III are much too small, since a singles and doubles calculation does much better for the atom than the molecule. This problem would not occur, of course, if one were to perform a full CI, i.e., one which included not only single and double excitations but also triple, quadruple, etc., excitations.

Nor can an estimate of the dissociation energy be obtained from a singles and doubles calculation on S_2 at large internuclear separation. This is true because it would take six configurations made from S_2 molecular orbitals to describe two ground state sulfur atoms, one of which is a quadruple with respect to the reference configuration of S_2 near equilibrium.[17] Since this configuration is absent in a singles and doubles CI, such a wave function becomes a less and less accurate representation as the nuclei separate and the energy does not converge to that of two sulfur atoms.[18]

The issue is illustrated schematically in Figure 1. Hopefully, at geometries near equilibrium, the singles and doubles energy curve will be nearly parallel to the actual curve, and, hence, accurate vibrational properties may be calculated. A rule of thumb is that vibrational frequencies (ω_e) will be slightly too large and vibrational asymmetry parameters ($\omega_e x_e$) will be unreliable as obtained from the singles and doubles calculations here.

Just as it was hoped that the basis set chosen would be about equally good for all the electronic states studied, it was hoped that the configuration

space chosen (all single and double excitations from one reference configuration) would treat each state equivalently. This is assumed to be true when the reference configuration describes the electronic state quite well and constitutes at least 90% of the CI wave function. This will not be the case at large internuclear separations or where there is considerable interaction with energetically neighboring states of the same symmetry. This latter situation will arise particulary for the higher excited states near the Rydberg "continuum" where the problem is known as Rydberg poisoning. For Rydberg-like states, our calculations are inadequate not only at the CI level, but also at the SCF level due to the absence of diffuse functions in the basis set. Experimentally, it is believed that the Rydberg-like states of S_2 have energies starting at about 55,000 cm^{-1} above the energy of the ground state.[3] Therefore, one must be suspicious of calculated properties of states lying 50,000 cm^{-1} or greater above the ground state. (Unfortunately two of the states studied here may fall into this category: $f\,^1\Delta_u$ and $^1\Sigma_u^+$.)

To facilitate the calculations, real orbitals (e.g., π_x, π_y) were used instead of complex ones (e.g., π_+, π_-). In developing an SCF energy expression for a wave function which is an eigenstate of orbital angular momentum (Λ) as well as spin (S,m_S), one soon encounters integrals which are neither of Coulomb nor exchange type. The presence of these integrals prevented correct SCF calculations from being done on many states (e.g., all those arising from a $\pi_u^3\,\pi_g^3$ configuration) until 1971 when J. B. Rose and V. McKoy[19] demonstrated that those troublesome integrals could be expressed as linear combinations of Coulomb and exchange integrals. In the SCF calculations of this work, SCF energy expressions developed by Rose

and McKoy are used. This results in energies reflecting those of eigenfunctions of orbital angular momentum, even though real orbitals are used throughout.

The CI calculations were performed using the newly developed BERKELEY system of programs.[20] The calculations were done utilizing only the D_{2h} subgroup of the full ($D_{\infty h}$) symmetry of the molecule. Some states which belong to different irreducible representations in $D_{\infty h}$ belong to the same one in D_{2h}. (For example, both the $B\,^3\Sigma_u^-$ state and the $A'\,^3\Delta_u$ state belong to the ^3A_u representation in the D_{2h} group.) When this happens one must obtain not one but the two lowest eigenvectors of the CI Hamiltonian matrix. Unfortunately, this results in solving a larger problem than would be necessary if the calculation were done in full symmetry.[21] This does not affect the accuracy of the results, however, and higher eigenvalues of the CI Hamiltonian matrix are variational.

Spectroscopic constants were determined for each state by fitting the energies at five internuclear distances near equilibrium to a fourth degree polynomial then using the fitting parameters to analytically determine such values as r_e, B_e, ω_e, and α_e.[22]

The calculation of properties for a large number of electronic states, especially those well characterized experimentally, allows us to test an empirical correction, which has become known as the Davidson correction,[23] as to its effectiveness in improving predictions of properties by configuration interaction calculations of the type employed here. The correction formula estimates the effect of unlinked cluster energy terms which are included in a singles and doubles level CI calculation and which contribute to the size inconsistency. In principle, application of the formula to a

singles and doubles CI energy should give an energy which reflects the effects of higher excitations (triples and quadruples) were they to be included. The formula is $\Delta E_Q = (1-C_o^2)\Delta E_{SD}$ where ΔE_Q is the predicted energy lowering of the higher excitations, C_o is the coefficient of the reference (Hartree-Fock) configuration in the normalized CI wavefunction, and ΔE_{SD} is the energy lowering of the singles and doubles CI calculation relative to the SCF energy.

III. Results

The results are presented in Table IV along with what we feel are the best experimental results for comparison. For most states total energies were computed for seven to ten different internuclear distances near equilibrium. In some cases this was not enough points to adequately determine all the spectroscopic constants. In particular the rotational asymmetry parameter, α_e, was very sensitive to the fit. For several cases we do not feel we have calculated enough points to adequately define the potential curve for the determination of α_e, and so no values are predicted. For the calculation of vibrational frequencies, the average percent difference with experiment is about 24% at the SCF level and 10% at the CI level. Much better agreement is obtained for the calculation of bond lengths, where the percent difference with experiment is 3% at the SCF level and 1% at the CI level. Of course, the calculation of these average percent differences includes our predictions for the $f\,^1\Delta_u$ and $^1\Sigma_u^+$ states, for which these calculations should be worst since they are near the Rydberg continuum. The percent differences are considerably smaller for the lower states.

The Davidson correction was applied <u>once</u> to each electronic state at the potential minima predicted by the singles and doubles CI calculations. This gives the rows of Table IV labeled CI+. It is certainly possible to apply the Davidson correction to each point (i.e., other than the minimum) of the singles and doubles CI energy curve, but it is not clear that this will necessarily yield better results. The formula seems to be most valid when a singles and doubles CI wavefunction is itself already a good approximation to the true wavefunction. This is the case when the molecule

is near equilibrium. However, if there is very strong configuration interaction as at distorted geometries or highly excited electronic states, it may not be clear which configuration qualifies as "the reference configuration" whose coefficient is to be used as c_o in Davidson's formula. In particular, when the formula was applied to the entire singles and doubles CI curve for the $c^1\Sigma_u^-$ and $f^1\Delta_u$ states (both highly correlated), unsatisfactory values for the spectroscopic constants were determined.[26] Since the Davidson correction seems to diverge for certain states we felt that applying it once for each state at the minimum predicted by the singles and doubles CI would be better than applying it to the entire singles and doubles curve. This is especially so since our prime concern was the prediction of excitation energies, for which an equal treatment of each state is essential.

As can be seen from Table IV and Figure II, in all cases where experimental excitation energies are known with some degree of certainty, application of the Davidson correction to the singles and doubles CI results decreases the discrepancy between theory and experiment. The average percent difference between experiment and theory at the singles and doubles CI level for the several states that are well-known experimentally is 16%. After application of Davidson's correction formula, this is reduced to about 7%. Agreement is much better still if one leaves out of consideration the $f^1\Delta_u$ and $^1\Sigma_u^+$ states. With these states left out, the average singles and doubles CI error of 13% drops to 5% upon application of Davidson's correction. Of course, not much importance should be attached to these percentages; we quote them only to emphasize the goodness of the correction formula.

It was remarked in the previous section that dissociation energies could not be accurately calculated for two related reasons: lack of size consistency and the absence of enough configurations for proper dissociations to sulfur atoms. Since the Davidson correction estimates the energy of size inconsistency of a singles and doubles CI, there is some justification for applying it to the ground state calculation of S_2 at the minimum predicted by the singles and doubles CI and not to the atomic sulfur singles and doubles CI, and then taking differences for an estimate of the dissociation energy. Davidson's correction lowers the minimum of the ground state energy curve by 15.8 kcal. When this is added to the dissociation energy of 66.5 kcal predicted by $E(2S)-E(S_2)$ in Table III for the basis set used, the result of 82.3 kcal is much closer to the experimental value of 101 kcal. We emphasize that this is certainly neither a consistent nor rigorous way to treat the size consistency problem, but only note that the magnitude and trends are consistent with reality.

It is distressing to note that the singles and doubles CI does a particularly poor job predicting the excitation energy of the $B\ ^3\Sigma_u^-$ state. The energy of this state is extremely well-known experimentally. We attribute the shortcoming of our singles and doubles CI to the fact that this state, which arises from the $\ldots 5\sigma_g^2\ 2\pi_u^3\ 2\pi_g^3$ occupancy, interacts quite strongly with another $^3\Sigma_u^-$ state from the $\ldots 5\sigma_g\ 2\pi_u^4\ 2\pi_g^2\ 5\sigma_u$ occupation. (The situation is just as in O_2.[13]) A proper treatment of the B state should include single or single and double excitations from this second configuration as well. However, since our goal was to predict excitation energies, we were required to treat all states equally, and this called for CI calculations for each state that included single and

double excitations from one configuration only. It is interesting to note that for this state the Davidson correction results in the largest percent change in predicted excitation energy.

IV. Concluding Remarks

In this work we have predicted the presence of a bound $^1\Pi_u$ electronic state of S_2 with spectroscopic constants as listed in Table IV. This state has not been identified experimentally and it is not bound in the O_2 molecule. Judging from the accuracy of our calculation of the energy of the $B''\ ^3\Pi_u$ state which arises from the same orbital occupation as the $^1\Pi_u$ state, we predict the $^1\Pi_u$ state to be at about 37000 cm^{-1} above the ground state.

We have also provided new estimates for properties and excitation energies (again, see Table IV) of the $e^1\Pi_g$, $c^1\Sigma_u^-$, and $B''^3\Pi_u$ states. Our predictions for the e and c states differ significantly from earlier work.[3,5] The ordering given by this study for the three closely spaced states c, A', A now agrees with that predicted by modified Hund-type rules for linear molecules[7] and with matrix isolation work by Lee and Pimentel.[8] As for the e state, judging from the accuracy of our calculations of the energy of the $B'^3\Pi_g$ state, which arises from the same orbital occupation as the e state, we predict the e state to be near to and below about 43000 cm^{-1} above the ground state.

The B'' state, whose presence as a bound state had been postulated to exist[3,12], we predict to lie about 400 cm^{-1} below the B state. This state could certainly account for the perturbation of the B state observed in the B → X system mentioned earlier. A more thorough investigation (see, e.g., reference 13) is needed to determine the detailed mechanism of the B-B'' interaction in S_2.

We hope this work will be of value to future workers by providing

them with estimates of spectroscopic properties for these thirteen electronic states of S_2.

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21. The re-use of the formula tape (see reference 20 for details of the workings of the CI program) for states of the same representation in D_{2h} compensated for effort lost by solving the larger problem.

22. Formulas used are from Herzberg's Spectra of Diatomic Molecules, page 108 (Van Nostrand Reinhold Company, New York, 1950). It is our feeling that not enough data was calculated to obtain $\omega_e x_e$, the vibrational asymmetry parameter. Please note, however, that the formula for $\omega_e x_e$ (III, 79) on page 93 is incorrect and should have "+j" instead of "-j".

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26. In other words, our use of Davidson's correction is quite different from that of Rosenberg, Ermler, and Shavitt, J. Chem. Phys. 65, 4072 (1976), where it was applied to each point of a ground state H_2O potential surface with excellent results.

Table I. Comparison of experimentally determined excitation energies (in cm^{-1}) of O_2 and S_2 for the electronic states studied in this work.

O_2 [a]		S_2 [b]	
$^1\Sigma_u^+$	(c)	$^1\Sigma_u^+$	$\sim$ 45100
$^1\Delta_u$	88278	$f\,^1\Delta_u$	$\sim$ 41600
$^1\Pi_g$	unbound	$e\,^1\Pi_g$	$\sim$ 37000 [e]
$^3\Pi_g$	unbound	$B'\,^3\Pi_g$	14326+A' ($\sim$ 35300) [d]
$^1\Pi_u$	unbound	$^1\Pi_u$	
$^3\Pi_u$	unbound	$B''\,^3\Pi_u$	$\leq$ 31700
$B^3\Sigma_u^-$	49358	$B^3\Sigma_u^-$	31689
$A^3\Sigma_u^+$	35007	$A^3\Sigma_u^+$	21971 [d]
$C^3\Delta_u$	34319	$A'^3\Delta_u$	20974 [d]
$c^1\Sigma_u^-$	32664	$c^1\Sigma_u^-$	$\sim$ 20000 [e]
$b^1\Sigma_g^+$	13121	$b^1\Sigma_g^+$	$\sim$ 8500
$a^1\Delta_g$	7882	$a^1\Delta_g$	$\sim$ 4700
$X^3\Sigma_g^-$	0	$X^3\Sigma_g^-$	0

(a) From Reference 6.

(b) From Reference 24, unless noted.

(c) Calculations (see reference 17) predict this state to be bound, although it is yet to be observed experimentally.

(d) From reference 4.

(e) See Text.

Table II. Comparison of different basis sets at the SCF level.

Basis Set	$E(^3P)$	$E(^1D)$	ΔE, kcal	$S_2 X^3\Sigma_g^-$ (1.889 Å)	$E(2S) - E(S_2)$, kca
A. [6s4p]	-397.46774	-397.41462	33.2	-794.92152	-8.8
B. [6s4p1d]	.46774	.41462	33.2	-795.00038	40.7
C. [7s5p1d]	.46942	.41712	32.8	-795.00369	40.7

Table III. Comparison of different basis sets at the CI level[†,‡]

Basis Set/CI Space	$E(^3P)$	$S_2 X^3\Sigma_g^-$ (1.889 Å)	$E(2S)-E(S_2)$, kcal
A. [6s4p] u3s3p	-397.49598	-794.98855	- 2.1
B. [6s4p1d] u3p	.51379	-795.14768	75.4
C. [6s4p1d] u3s3p	.57155	.24914	66.5
D. [7s5p1d] u3p	.51605	.15155	75.0
E. [7s5p1d] u3s3p	.57445	.25409	66.0

[†]At these levels of CI, the energy of S_2 in the limit of infinite internuclear separation is different than twice the energy of a sulfur atom. See the discussion in the text.

[‡]The experimental dissociation of $X^3\Sigma_g^-$ S_2 is 101 kcal/mole.[24]

Table IV

Comparison of Theoretical and Experimental Results for Thirteen Electronic States of S_2

State	D_{2h} Size of CI Space	Method[a]	T_o, cm^{-1}	T_o, cm^{-1}	r_e, Å	ω_e, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}
$1\Sigma_u^+$		SCF	72500	b+65800	2.026	650	0.2566	0.0011
	5529	CI	59700	b+49900	2.128	500	0.2326	
		CI+	53800	b+44800				
		Expt.[b]	45100	b+36624.7	--	428.5	--	--
$f^1\Delta_u$		SCF	61400	a+54600	2.030	660	0.2556	0.0011
	5529	CI	49700	a+44300	2.138	500	0.2305	0.0010
		CI+	44100	a+39300				
		Expt.	~ 41600	a+36875.45	2.1555	438.32	0.22704	0.00178
$e^1\Pi_g$		SCF	37000	c+24400	2.160	280	0.2257	
	2915	CI	43000	c+25700	2.143	430	0.2293	
		CI+	43300	c+25400				
		Expt.[c]	(~37000)	(c+13451.8)	(~2.08)	(533.7)	(~0.25)	--
$1\Pi_u$		SCF	49300	49300	2.154	500	0.2270	0.0009
	3051	CI	41600	41600	2.243	400	0.2094	0.0012
		CI+	37600	37600				
		Expt.						
$B'^3\Pi_g$		SCF	33900	A'+20600	2.120	460	0.2345	
	2939	CI	35400	A'+17100	2.106	450	0.2375	0.0023
		CI+	35300	A'+16200				
		Expt.[d]	35300	A'+14326	2.08	~ 500	0.244	--

$B^3\Sigma_u^-$		SCF	50100	50100	2.033	650	0.2549	0.0011
	5827	CI	38300	38300	2.142	490	0.2296	0.0017
		CI+	32500	32500				
		Expt.	31689	31689	2.168	434	0.2244	0.0018
$B''^3\Pi_u$		SCF	41400	41400	2.135	510	0.2310	0.0009
	3078	CI	35200	35200	2.219	430	0.2139	
		CI+	32100	32100				
		Expt.	$\leq$ 31700	$\leq$ 31700	< 2.28	--	> 0.2029	--
$A^3\Sigma_u^+$		SCF	14000	A'+710	2.156	510	0.2267	0.0014
	5747	CI	18900	A'+640	2.176	580	0.2224	0.0016
		CI+	19700	A'+620				
		Expt.[d]	21971	A'+997	2.15	482.15	0.2248	0.0014
$A'^3\Delta_u$		SCF	13300	13300	2.148	520	0.2284	0.0014
	5827	CI	18300	18300	2.168	480	0.2242	0.0016
		CI+	19100	19100				
		Expt.[d]	20974	20974	2.146	488.2	0.2285	0.0015
$c^1\Sigma_u^-$		SCF	12600	12600	2.140	527	0.2301	0.0014
	5653	CI	17300	17300	2.160	489	0.2257	0.0017
		CI+	17900	17900				
		Expt.[e]	$\sim$ 20000	$\sim$ 20000	--	--	--	--
$b^1\Sigma_g^+$		SCF	6730	6730	1.877	813	0.2989	0.0012
	4562	CI	9790	9790	1.914	732	0.2874	0.0015
		CI+	8960	8960				
		Expt.	$\sim$ 8500	$\sim$ 8500	--	700.82	--	--

$a^1\Delta_g$		SCF	6730	6730	1.877	813	0.2989	0.0012
	4562	CI	5440	5440	1.907	746	0.2897	0.0014
		CI+	4820	4820				
		Expt.	$\sim$ 4700	$\sim$ 4700	1.8987	702.35	0.29262	0.00173
$X^3\Sigma_g^-$		SCF	0	0	1.876	819	0.2994	0.0012
	2948	CI	0	0	1.900	760	0.2920	0.0015
		CI+	0	0				
		Expt.	0	0	1.889	725.668	0.29541	0.00158

(a) Unless otherwise stated the experimental data is from reference 24.

(b) This data is from reference 25. Note that this state is different from any of the $^1\Sigma_u^+$ states listed in reference 24.

(c) The experimental data for the $e^1\Pi_g$ state was based on an assignment later shown to be incorrect. See text.

(d) This data is from reference 4.

(e) This data is from reference 8. Also see text.

Figure Captions

Figure 1. Schematic representation of the size consistency problem. Curve A: SCF level calculation; Curve B: Singles and doubles level CI calculation; Curve C: Exact, or size consistent calculation, using the same basis set; Point D: Twice the energy of an atom as calculated by a singles and doubles level CI.

Figure 2. Relative energies (T_o) of the thirteen states of S_2 studied in this work. The third column is the result of systematically applying the Davidson correction to the singles and doubles CI calculation. Dashed lines in the experimental column signify uncertain information.

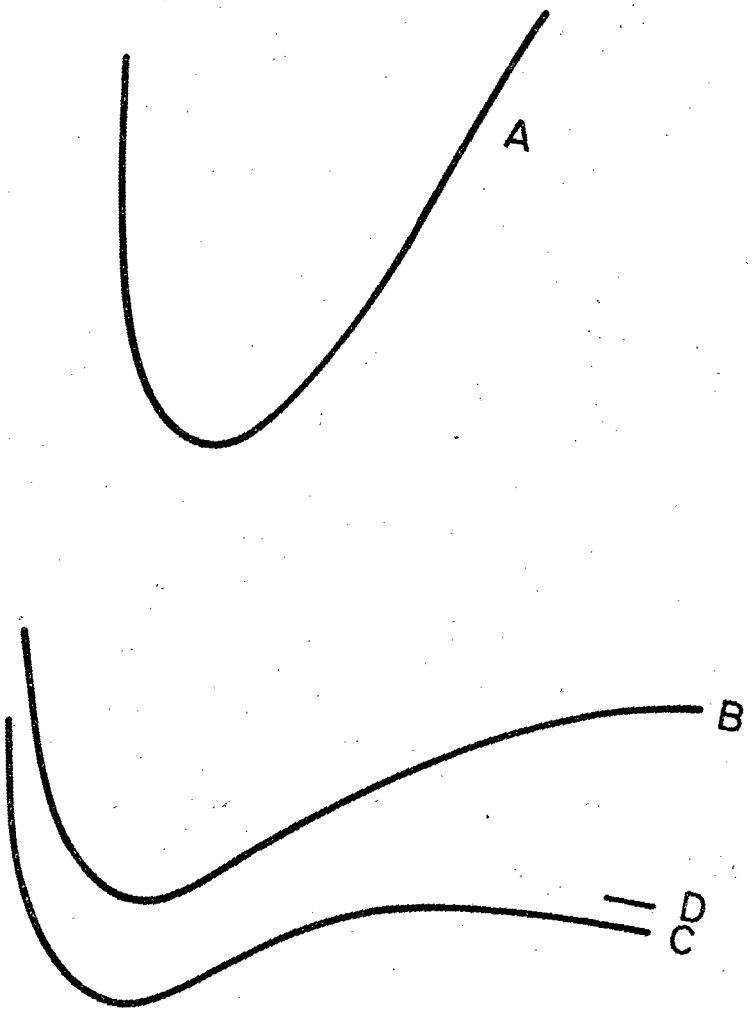

Figure I

XBL 787-9839

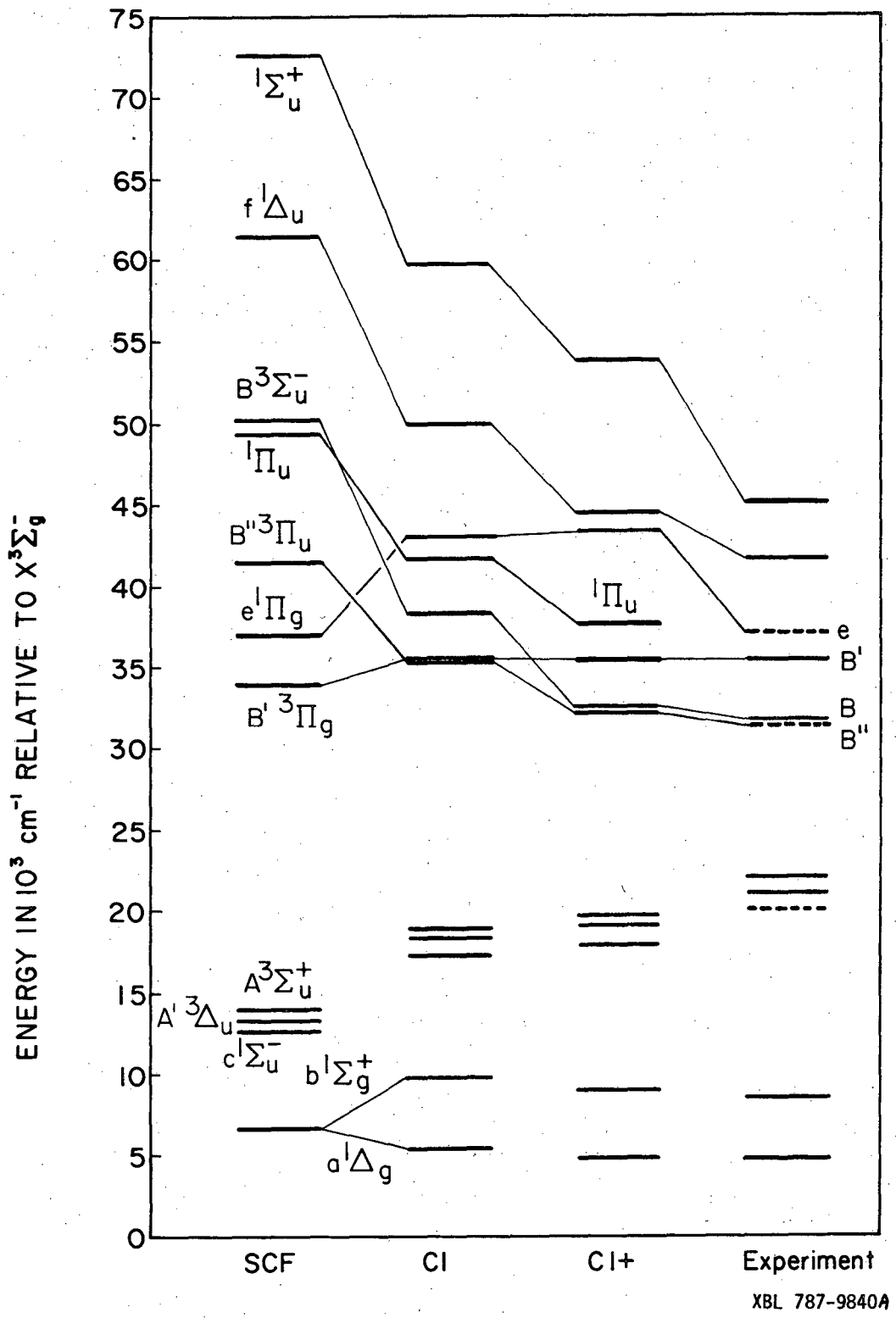
ENERGY IN 10^3 cm^{-1} RELATIVE TO $X^3\Sigma_g^-$
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
$^1\Sigma_u^+$
f $^1\Delta_u$
$B^3\Sigma_u^-$
$^1\Pi_u$
$B''^3\Pi_u$
e $^1\Pi_g$
$B'^3\Pi_g$
$^1\Pi_u$
e
B'
B
B''
$A'^3\Delta_u$
$A^3\Sigma_u^+$
$c^1\Sigma_u^-$
$b^1\Sigma_g^+$
$a^1\Delta_g$
SCF
CI
CI+
Experiment
XBL 787-9840A

Figure 2

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