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Author
Dykstra, Clifford E.

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Clifford E. Dykstra, Robert R. Lucchese, and
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July 1977

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Electron Correlation Effects on the Excitation Energies

of the Lowest Triplet States of Glyoxal

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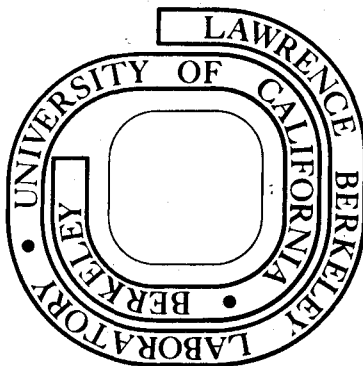
Department of Chemistry and the Materials and Molecular Research Division
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

Abstract

In an attempt to understand the ordering of excited states of glyoxal, the ^1A_g ground state and low-lying triplet states, ^3A_u, ^3B_u, and ^3B_g, have been studied with $\underline{ab}$ $\underline{initio}$ correlated wavefunctions. A double zeta basis set was used in the configuration interaction calculations, and $\sim 6,000$ Slater determinants were selected for each electronic state. The predicted CI adiabatic excitation energies T_e are 21,800 cm^{-1} (^3A_u), 25,100 cm^{-1} (^3B_u), and 29,300 cm^{-1} (^3B_g). The effects of d functions and higher (than double) excitations (unlinked clusters) have also been evaluated. For the ^3B_u state, both d functions and higher excitations raise the predicted T_e value, by perhaps as much as 5,000 cm^{-1}. For the ^3B_g state, d functions raise the predicted excitation energy but higher excitations have the opposite effect. It is concluded that the excitation energy of the ^3B_u state is dramatically increased by correlation effects, while T_e for the ^3A_u and ^3B_g states is markedly decreased by correlation.

Introduction

In a previous self-consistent field (SCF) study of glyoxal,[1] the ^3B_u state was predicted to lie 14,900 cm^{-1} above the ground state, but with a large uncertainty due to unknown basis set and correlation effects. The nature of the ^3B_u state made this result quite interesting since it was predicted to have a substantially contracted C-C bond length and an extended C=0 bond. Furthermore, it corresponds to a $\pi \rightarrow \pi^*$ excitation and is best described as a biradical. This is contrary to the notion of other theoretical[2-6] and experimental[7] work that the next lowest lying triplet after the observed $n \rightarrow \pi^*$ ^3A_u should be a ^3B_g state, also an $n \rightarrow \pi^*$ excitation.

The importance of further studies of glyoxal excited states is first of all theoretical since the excitation energy of the ^3A_u state was calculated[1] to be 26,850 cm^{-1} compared to a well determined experimental[8] value of 19,200 cm^{-1} and such a discrepancy should be understood. In addition, however, the theoretical prediction of excited state energies for unobserved states is important experimentally for confirming tentative identifications of states[7] and explaining energy transfer and relaxation processes.[9-10] Such importance is likely to carry over to larger molecules, such as methyl glyoxal[11-13] and biacetyl,[14-18] and some related molecules that may have qualitatively similar low-lying states. Indeed, SCF calculations on acrolein,[19] which is isoelectronic to glyoxal, showed a very similar prediction of a low-lying $\pi \rightarrow \pi^*$ state with major geometry differences, relative to the ground state. In this paper, we report the results of configuration interaction (CI) calculations

on the ^1A_g, ^3A_u, ^3B_u and ^3B_g states of trans-glyoxal. It is hoped that the dominant correlation effects on excitation energies are satisfactorily described by the methods adopted.

Theoretical Approach

As in previous studies of glyoxal,[1,20] a double-zeta basis of Dunning[21] contracted functions was used. SCF orbitals were used as the basis for the CI expansion and calculations were performed with the program BERKELEY.[22] Only triplet states were studied, largely because singlet state information can be inferred. The ^1B_g-^3B_g energy separation should correspond roughly to the experimentally known ^1A_u-^3A_u separation since all are $n \rightarrow \pi^*$ excitations. The ^1B_u state at the SCF level is predicted to be quite high in energy[1] and even with correlation effects is not likely to be low-lying. Only trans states were examined since the cis manifold of excited states will be similar, especially for the lowest states, with the ^3A_u corresponding to a $^3B_1$, ^3B_g to $^3A_2$, and ^3B_u to $^3B_2$.

Two series of theoretical calculations were performed, differing in the geometrical structures assumed for the excited states. In each case the ground state geometry was the equilibrium structure predicted earlier[1] from SCF theory. At this same geometry, CI <u>vertical</u> excitation energies were predicted for the three excited triplet states. In addition the SCF predicted excited state geometries were used to make CI calculations of the adiabatic excitation energies T_e. The ^3A_u and ^3B_u SCF equilibrium geometries are from reference 20 and the ^3B_g structure was determined in the present work. This structural information is summarized in Table I.

Two levels of CI are reported here. Both rely on the cumulative selection of configurations by perturbation theory, as developed by Shavitt and co-workers.[23,24] Given consideration were all Slater determinants differing by one or two spinorbitals from the appropriate Hartree-Fock configurations

$$^1A_g \ \ldots\ldots\ 5b_u^2\ 6a_g^2\ 1a_u^2\ 6b_u^2\ 1b_g^2\ 7a_g^2 \tag{1}$$

$$^3A_u \ \ldots\ldots\ 5b_u^2\ 6a_g^2\ 1a_u^2\ 6b_u^2\ 1b_g^2\ 7a_g\ 2a_u \tag{2}$$

$$^3B_u \ \ldots\ldots\ 5b_u^2\ 6a_g^2\ 1a_u^2\ 6b_u^2\ 7a_g^2\ 1b_g\ 2a_u \tag{3}$$

$$^3B_g \ \ldots\ldots\ 5b_u^2\ 6a_g^2\ 1a_u^2\ 1b_g^2\ 7a_g^2\ 6b_u\ 2a_u \tag{4}$$

In the first set of calculations, referred to as CI 1 hereafter, the six lowest occupied molecular orbitals were constrained to be doubly occupied. The summation threshold σ, the estimated effect of the deleted Slater determinants, was set at 0.02 hartrees. At their respective SCF equilibrium geometries, this means that 6773 (^1A_g), 6457 (^3A_u), 6132 (^3B_u), and 6186 (^3B_g) Slater determinants were included in the four CI treatments. In the second set of CI calculations, only four SCF molecular orbitals (the 1s-like orbitals on C and O) were constrained to be doubly occupied, but a higher σ value of 0.06 hartrees was imposed. This CI 2 treatment included 6513, 6245, 5701, and 5954 Slater determinants for the four electronic states of interest at their respective SCF equilibrium geometries. Although CI 1 and CI 2 involve rather different selection procedures, they should be of roughly comparable predictive reliability. The existence of two independent

sets of predictions also gives a zeroth order estimate of some of the errors to be expected.

All calculations were carried out on the Harris Corporation Slash Four minicomputer.[25] Typical computation times (for the ^3A_u state at its equilibrium geometry) were 1.8 hours for the SCF procedure including integrals, 0.9 hours for the four index transformation of integrals, and 1.7 hours for the remainder of the CI procedure. Since the cost of time on this small machine is only \$8/hour,[25] the cost of the present study was reasonably modest.

The validity of a double zeta basis set was also tested at the SCF level of theory. There a full set of six d-like functions (x^2, y^2, z^2, xy, xz, and yz multiplied times $e^{-\alpha r^2}$) was added to the carbon and oxygen atoms. Orbital exponents α were 0.75 for carbon and 0.80 for oxygen.

Results

The ^3A_u State

It seems sensible to discuss this $n \rightarrow \pi^*$ excited triplet state first, since the adiabatic excitation energy T_e is known to be 19,200 cm^{-1} from Ramsay's experiments[8]. Our results for this quantity are summarized in Table II and Figure 1. As mentioned in the introduction, the previous double zeta SCF study[20] predicted T_e = 26,900 cm^{-1}, corresponding to an error of 7,700 cm^{-1}. Both CI 1 and CI 2 improve considerably upon that result, with T_e predictions of 21,690 and 21,770 cm^{-1}. The remaining error of $\sim$ 2500 cm^{-1} ($\sim$ 0.3 eV) is probably about what should

be expected from this level of theory. At the SCF level, d functions are seen to raise the predicted T_e by 2200 cm^{-1}, but this effect will apparently be more than counterbalanced at the CI level. I.e., correlation effects involving d functions and/or higher excitations will be more important for the ^3A_u state than for the ground state.

The ^3B_u State

Table II and Figure 1 show that electron correlation has a truly dramatic effect on the position of this $\pi \rightarrow \pi^*$ triplet state. That is, the DZ CI excitation energy is $\sim$ 10,000 cm^{-1} higher than the previous[20] DZ SCF prediction. This means that electron correlation is much more important for the glyoxal ground state than for this ^3B_u excited state. Furthermore, at the SCF level d functions are seen to be 7,700 cm^{-1} more important for the ground state. Although this large correction is not likely to be directly additive with respect to the DZ CI T_e values, it does suggest that 24,000 cm^{-1} is a reasonable lower bound to the true adiabatic excitation energy of the ^3B_u state. It remains[20] true, of course, that this $\pi \rightarrow \pi^*$ triplet is a low-lying excited state of glyoxal and should be observable experimentally.

The ^3B_g State

Like the previously investigated[20] ^3B_u state (but to a significantly lesser degree), this $n \rightarrow \pi^*$ triplet has a geometry very different from that of the ^1A_g ground state. As with both the ^3A_u and ^3B_u states, at the SCF level the effect of d functions is to raise the predicted T_e value. CI however significantly lowers the adiabatic excitation energy, to $\sim$ 29,000 cm^{-1}. The latter prediction is in rough agreement with experimental estimates[7] for ΔE ($^1A_g - ^3B_g$). Since the plausible range

of excitation energies for the ^3B_u and ^3B_g states overlaps, it is not possible on theoretical grounds to say which lies lower. In any case, the present uncertainties are becoming sufficiently small and the two states now well enough characterized theoretically that a renewed experimental assault on glyoxal seems quite appropriate.

Vertical Excitation Energies

These results may be of considerable value in unraveling experimental glyoxal spectra, since both the ^3B_u and ^3B_g states have very different geometries from the gound state. Table III and Figure 2 summarizes the present predictions.

For the ^3A_u state, the vertical excitation energy of 23,100 cm^{-1} is only 1300 cm^{-1} above the adiabatic result. Of course, this difference would probably increase if a CI geometry optimization were carried out for the ^3A_u state. For the ^3B_g state, the vertical excitation energy is 7400 cm^{-1} higher than T_e. However, as predicted previously,[20] the difference between vertical and adiabatic separations is greatest, 16,200 cm^{-1} for the $\pi \rightarrow \pi^*$ ^3B_u state. We also see in Figure 2 that electron correlation actually reverses the SCF energy ordering of the ^3B_u and ^3B_g states at the vertical geometry.

Electronic Structure Considerations

Although the Hartree-Fock approximation is qualitatively correct for the ground states of most stable molecules, this is not intuitively obvious for many excited states. For this reason we give in Table IV the

weights of the most important configurations for each of the four electronic states studied. These results were obtained at the respective SCF equilibrium geometries of the four states.

Table IV shows that the electronic structure of all four electronic states is dominated by the Hartree-Fock configuration. Electron correlation is most important for the ^3B_g state, for which C_o = 0.925 implies that the SCF configuration amounts to 85.6% of the total wavefunction.

After the orbitals occupied in the Hartree-Fock description of the ground state, the $2a_u$ orbital is the most important. This is seen both in the excited state orbital occupancies and in the second, third, and fourth most important configurations in the CI description of the ground state. Similarly the $2b_g$ orbital follows the $2a_u$ in importance, being involved significantly in all four correlated wave functions.

Approximate Treatments of Higher Excitations

The fact that the coefficient of the SCF configuration spans a considerable range for the ^1A_g, ^3A_u, ^3B_u, and ^3B_g states suggests that higher excitations (e.g., triple and quadruple excitations) may affect some predicted correlation energies more than others. Although these so-called "unlinked clusters" are very difficult to treat variationally,[26] several approximate treatments are available. One of the most widely used in Davidson's formula[27] for the energy ΔE_Q due to quadruple excitations

$$\Delta E_Q = (1 - C_o^2)\Delta E_D \qquad (5)$$

where ΔE_D is the correlation energy due to double excitations. In the present work we have used (1) with ΔE_D replaced by ΔE_{SD} the correlation contribution from both single and double excitations.

A more recent approximate treatment of these effects has been formulated by Pople, Seeger, and Krishnan.[28] Their "size consistency" correction modifies a CI (including all single and double excitations) energy to yield the exact (given the basis set adopted) energy of an assembly of isolated identical two-electron systems. If $\cos\theta$ is set equal to C_0 and n is the number of valence electrons being correlated, the approximate total correlation energy ΔE is given by[28]

$$\Delta E = \frac{(n^2 + 2n\ \tan^2 2\theta)^{\frac{1}{2}} - n}{2(\sec 2\theta - 1)}\ \Delta E_{SD} \qquad (6)$$

Table V shows the results of applying both the Davidson and Pople formulas to the glyoxal excited states. For the ^3A_u state, the Pople correction yields a T_e value of 19,500 cm^{-1}, in remarkably close agreement with the experimental value,[8] 19,200 cm^{-1}. Unfortunately we must consider this result somewhat fortuitous, since corrections due to the neglect of polarization functions can be much greater than 300 cm^{-1}. For example, for formaldehyde a comparable theoretical calculation[29] on the lowest $n \rightarrow \pi^*$ triplet state yields an excitation energy $\sim$ 3000 cm^{-1} less than the experimental T_e. In this context, the Davidson prediction of T_e = 20,100 cm^{-1} is more representative of the reliability to be expected at this level of theory.

Although the Pople T_e value of 26,600 cm^{-1} for the ^3B_u state seems reasonable (except for the expected upward adjustment due to d functions), we are concerned about the ^3B_g value of 24,700 cm^{-1}. The Davidson value of 26,100 cm^{-1} (again, to be adjusted upward for the effects of d functions) seems more reasonable. We note that the Pople correction lowers the ^3B_g T_e prediction by 4,600 cm^{-1}, a very large energy change. Moreover, the ^3B_g-^1B_g separation should be[20] only about 3500 cm^{-1}, suggesting that if this ^3B_g value is correct the ^1B_g state may lie at T_e = 28,200 cm^{-1}. However, there appears to be no experimental evidence[30] for a singlet electronic state other than ^1A_u (the singlet counterpart of our ^3A_u state) below 30,000 cm^{-1}. In this sense the straight CI result of 29,300 for T_e (^3B_g) should be closer to the ultimate truth. The latter conclusion is also consistent with the fact that d functions raise the (^1A_g-^3B_g) separation by roughly the same amount that this separation is lowered by unlinked cluster effects, according to the Davidson approximation.

Concluding Remarks

The present research represents a very significant improvement over previous theoretical discussions of the electronic spectrum of glyoxal. It now seems clear that the ^3B_g, ^1B_g, and ^3B_u states of glyoxal are all low-lying, with T_e values certainly $\leq$ 35,000 cm^{-1}. Except for the observed ^1A_u and ^3A_u states, all other states of glyoxal should lie significantly higher. At this point, renewed investigations of the glyoxal spectrum in the 28,000-35,000 cm^{-1} range would be very welcome. Additional theoretical work is also called for, first to predict the

structures of the ^3A_u, ^1A_u, ^3B_g, ^1B_g, and ^3B_u states via methods including correlation. Secondly, very precise (say $\pm$ 1000 cm^{-1}) predictions of excitation energies will require the simultaneous inclusion of polarization functions and electron correlation.

Acknowledgments

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Table I. Equilibrium excited state bond lengths
and SCF energies.

	$R_{C-C}(\overset{\circ}{A})$	$R_{C=O}(\overset{\circ}{A})$	$E_{SCF}(a.u.)$
^1A_g [a]	1.508	1.215	-226.5182
^3A_u [b]	1.492	1.241	-226.3959
^3B_u [b]	1.353	1.356	-226.4504
^3B_g	1.372	1.292	-226.3525

[a] Ref. 20.

[b] Ref. 1. The ^3A_u C-C-O optimized angle of 121.0° was
assumed for equilibrium ^3A_u state calculations, but
is essentially the same as the ground state angle of
121.1° assumed for the structures of all other states.

Table II. Glyoxal adiabatic excitation energies, in hartrees and cm^{-1} relative to the ^1A_g ground state. Geometries used here were optimized separately for each electronic state at the double zeta (DZ) self-consistent-field (SCF) level of theory.

Level of Theory	DZ SCF	DZ + d SCF	CI 1	CI 2	Experiment
^1A_g	-226.5182	-226.6377	-226.8068	-226.8453	
^3A_u $(n \to \pi^*)$	-226.3959 26,800	-226.5054 29,000	-226.7080 21,700	-226.7461 21,800	19,200
^3B_u $(\pi \to \pi^*)$	-226.4504 14,900	-226.5346 22,600	-226.6964 24,200	-226.7308 25,100	
^3B_g $(n \to \pi^*)$	-226.3525 36,400	-226.4558 39,900	-226.6750 28,900	-226.7120 29,300	

Table III. Glyoxal vertical excitation energies. Energies are given both in hartrees and in cm^{-1} relative to the ^1A_g ground state.

Level of Theory	DZ SCF	DZ + d SCF	CI 2
^1A_g	−226.5182	−226.6377	−226.8453
^3A_u $(n \rightarrow \pi^*)$	−226.3940 27,300	−226.5079 28,500	−226.7403 23,100
^3B_u $(\pi \rightarrow \pi^*)$	−226.3680 33,000	−226.4730 36,200	−226.6576 41,200
^3B_g $(n \rightarrow \pi^*)$	−226.3231 42,800	−226.4377 43,900	−226.6770 36,900

Table IV. Electronic structure of four low-lying states of glyoxal. For each electronic state, we list all configurations having CI coefficient ≥ 0.05. Orbitals not occupied in the respective Hartree-Fock configurations are underlined.

$$^1A_g \text{ Ground State}$$

$$\ldots\ldots 1a_u^2\ 6b_u^2\ 1b_g^2\ 7a_g^2 \qquad\qquad 0.941$$

$$6b_u^2\ 7a_g^2\ 1a_u\ 1b_g\ \underline{2a_u\ 2b_g} \qquad -0.095$$

$$1a_u^2\ 6b_u^2\ 7a_g^2\ \underline{2a_u^2} \qquad\qquad -0.081$$

$$6b_u^2\ 1b_g^2\ 7a_g^2\ \underline{2a_u^2} \qquad\qquad 0.056$$

$$^3A_u \text{ State}$$

$$\ldots\ldots 1a_u^2\ 6b_u^2\ 1b_g^2\ 7a_g\ 2a_u \qquad 0.934$$

$$1a_u^2\ 1b_g^2\ \underline{7a_g^2}\ 6b_u\ \underline{2b_g} \qquad -0.104$$

$$1a_u^2\ \underline{7a_g^2\ 2a_u^2}\ 6b_u\ 1b_g \qquad -0.086$$

$$6b_u^2\ 1b_g^2\ \underline{2a_u^2}\ 1a_u\ 7a_g \qquad -0.055$$

$$6b_u^2\ 2a_u^2\ 1a_u\ 1b_g\ 7a_g\ 2b_g \qquad 0.050$$

Table IV continued

$$^3B_u \text{ State}$$

$$\cdots\cdots 6b_u^2 \ 1a_u^2 \ 7a_g^2 \ 1b_g \ 2a_u \qquad\qquad 0.942$$

$$6b_u^2 \ 7a_g^2 \ 2b_g^2 \ 1b_g \ 2a_u \qquad\qquad -0.077$$

$$6b_u^2 \ 7a_g^2 \ 1b_g^2 \ 1a_u \ 2b_g \qquad\qquad 0.075$$

$$6b_u^2 \ 7a_g^2 \ 2a_u^2 \ 1a_u \ 1b_g \qquad\qquad 0.066$$

$$6b_u^2 \ 7a_g^2 \ 1b_g \ 2a_u \ 2b_g \ 3b_g \qquad\qquad 0.050$$

$$^3B_g \text{ State}$$

$$\cdots\cdots 1a_u^2 \ 1b_g^2 \ 7a_g^2 \ 6b_u \ 2a_u \qquad\qquad 0.925$$

$$1a_u^2 \ 6b_u^2 \ 2a_u^2 \ 1b_g \ 7a_g \qquad\qquad -0.127$$

$$1a_u^2 \ 1b_g^2 \ 6b_u^2 \ 7a_g \ 2b_g \qquad\qquad -0.116$$

$$1b_g^2 \ 7a_g^2 \ 2a_u^2 \ 1a_u \ 6b_u \qquad\qquad -0.073$$

Table V. Approximate treatment of unlinked cluster contributions to the

correlation energies of four electronic states of glyoxal.

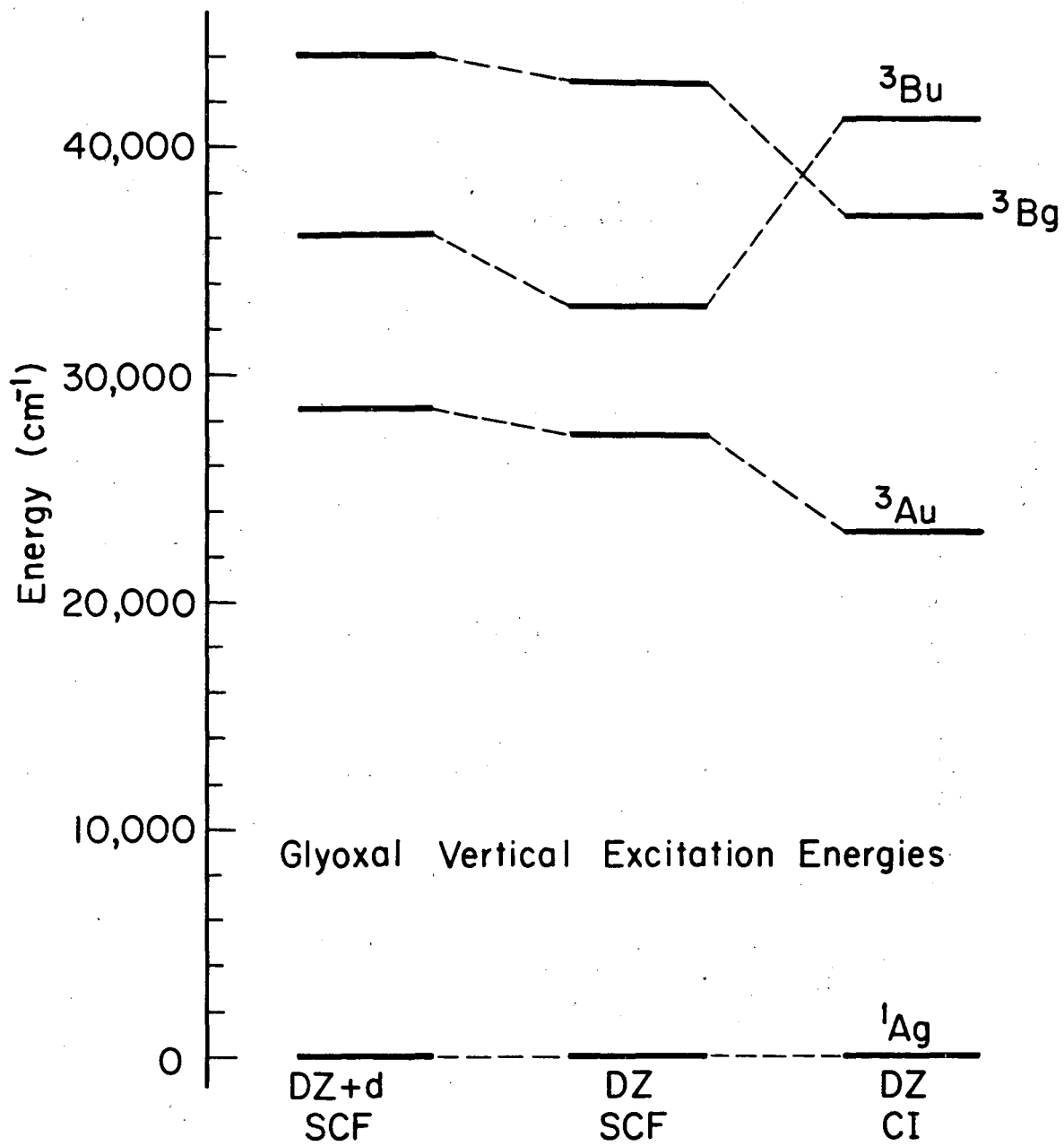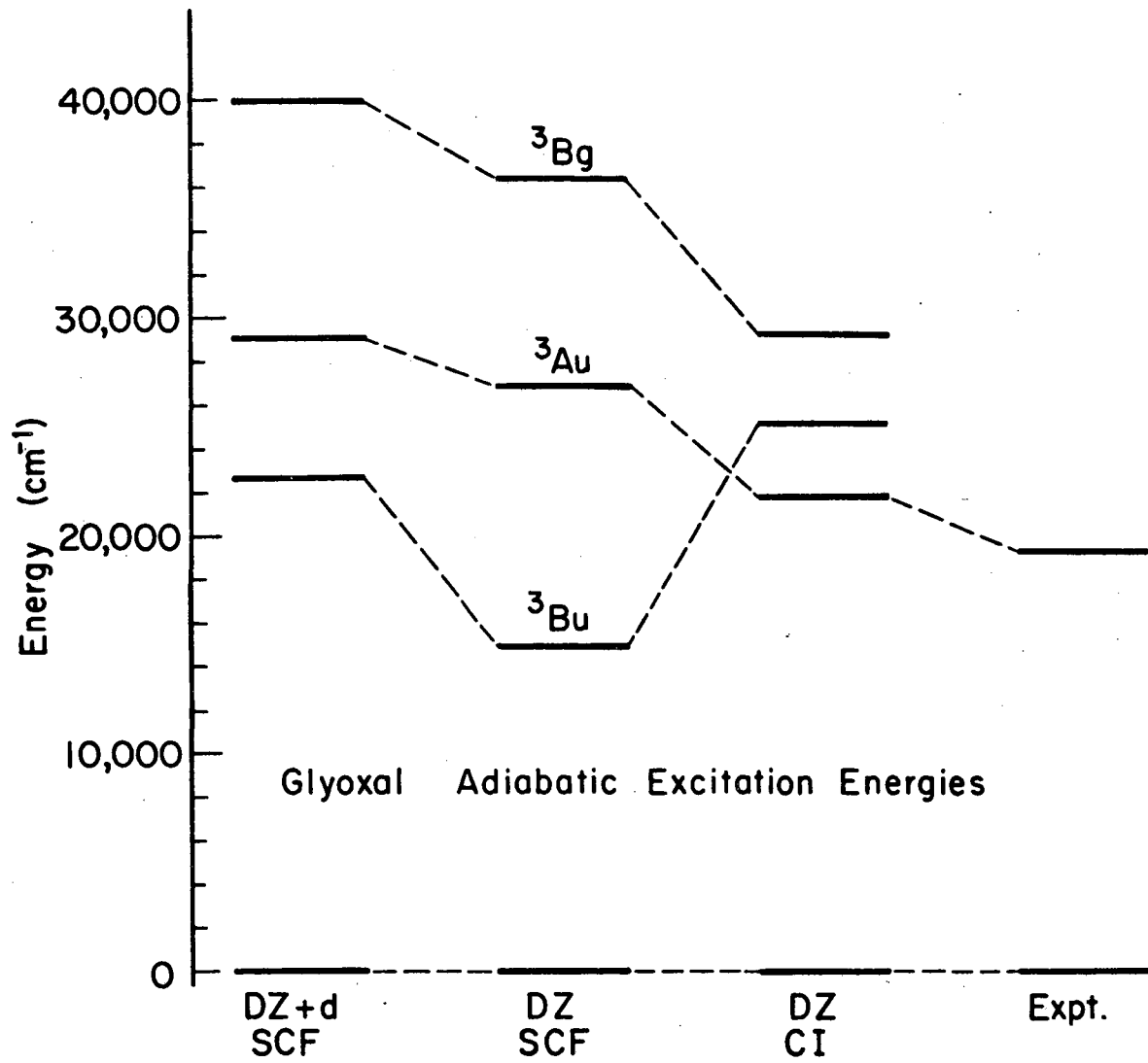|	CI 2 Excitation Energy (cm^{-1})	Davidson Approximation[a]		Pople Approximation[b]	
		Correction (hartrees)	Excitation Energy	Correction (hartrees)	Excitation Energy
^1A_g	---	0.0372	---	0.0426	---
^3A_u	21,800	0.0450	20,100	0.0532	19,500
^3B_u	25,100	0.0317	26,300	0.0363	26,600
^3B_g	29,300	0.0518	26,100	0.0636	24,700

[a]Reference 27.

[b]Reference 28.

Figure Captions

Figure 1. Adiabatic excitation energies T_e for the three lowest triplet

states of glyoxal. The three different levels of theory plotted

on the x axis are described in the text. DZ refers to a double

zeta basis set, SCF implies the use of self-consistent-field

theory, and CI is an abbreviation for the configuration interaction

method.

Figure 2. Vertical excitation energies for the three lowest triplet states

of glyoxal.

Glyoxal Vertical Excitation Energies

XBL775-3503

Glyoxal   Adiabatic Excitation Energies

XBL775-3502

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