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Author

Dykstra, Clifford E.

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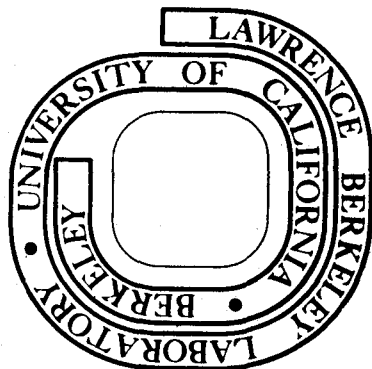
Clifford E. Dykstra and Henry F. Schaefer III

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ELECTRONIC STRUCTURE OF DICARBONYLS: GLYOXAL EXCITED STATES*

Clifford E. Dykstra**

and

Henry F. Schaefer III

Department of Chemistry

and

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

* Work performed under the auspices of the U.S. Energy Research
and Development Administration.

** Du Pont Graduate Fellow

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ABSTRACT

Excited electronic states of glyoxal, $(\text{CHO})_2$, have been studied by ab initio self-consistent field (SCF) methods using a double-zeta basis set of contracted gaussian functions. The vertical excitation energies from the optimum ground state geometry were determined for 20 trans and 20 cis excited states. These included all singlet and triplet $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations and the lowest $n \rightarrow \sigma^*$ excitations. Geometry optimization was performed for the three lowest cis and trans states. Two very low-lying unobserved triplet states, trans 3B_u and cis 3B_2 , are predicted by these calculations to be within about $15,000 \text{ cm}^{-1}$ of the corresponding ground states, making them the lowest excited states of glyoxal. The next lowest lying states were the observed trans 3A_u , 1A_u and cis 1B_1 , for which the geometry optimization provides a basis for comparison with experiment. The experimentally observed states arise from an $n \rightarrow \pi^*$ excitation, but surprisingly the lowest triplets arise from $\pi \rightarrow \pi^*$ excitations. The geometry of these $\pi \rightarrow \pi^*$ triplets is strikingly different from that of the ground state and is in closer correspondence with a biradical structure.

INTRODUCTION

While many excited states of carbon monoxide, formaldehyde and other carbonyl molecules have been identified,¹ fewer states of the simplest dicarbonyl, glyoxal, have been observed. Brand identified the first excited states of trans-glyoxal as 1A_u and 3A_u from his vibrational analysis of the 4550 Å absorption band.² Following the description of McMurry,³ these states were associated with an $n(a_g) \rightarrow \pi^*(a_u)$ excitation. Extensive high resolution spectroscopic studies have been made by Ramsay and coworkers.⁴⁻⁶ In addition, they made the first observation of the cis form of glyoxal and identified the 1B_1 excited state in rotational analysis of a band at 4875 Å.⁷⁻⁹ This state is associated with an $n(a_1) \rightarrow \pi^*(b_1)$ excitation and a 3B_1 state is presumed to occur in the same region. There has been no direct observation of other glyoxal excited states, though a simple molecular orbital picture suggests a total of 32 $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states.

In addition to their spectroscopic interest, the excited states of glyoxal are important photochemically. Glyoxal has been found to photodissociate into hydrogen, carbon monoxide, formaldehyde and CHO radicals.¹⁰⁻¹⁴ And the dissociation product

yields have been related to individual electronic states.¹⁴⁻¹⁶

The reactive chemistry of carbonyl molecules also depends on the nature of the excited states. For instance, Yardley has proposed the existence of either a biradical intermediate or a charge-transfer complex between 3A_u trans-glyoxal and olefins.¹⁷

Finding additional excited states by direct absorption spectroscopy appears limited because transitions from the ground state to some of the possible low-lying states are dipole forbidden. Specifically, these are the A_g and B_g states of trans-glyoxal and the A_2 states of cis-glyoxal. Also, higher energy states may be more difficult to identify because of the observed increasing diffuseness in the spectrum at shorter wavelengths.¹ Recently, a 1B_g state of glyoxal has been tentatively identified at about $30,000 \text{ cm}^{-1}$ above the ground state, with the forbidden transition presumably induced by interaction with the solvent in a matrix.¹⁸ In biacetyl, $\text{CH}_3\text{COCOCH}_3$, the observed change from small molecule to statistical or large molecule behavior in radiationless relaxation has been attributed to a 3B_g state occurring energetically near the 3A_u state.¹⁹ This may support the possibility of a low-lying singlet-triplet pair of B_g states in glyoxal.

With only three excited states of glyoxal clearly identified and potential difficulties in extending experimental excited state information, theoretical considerations are appropriate. Theoretical methods may be useful in predicting the ordering of excited states and in providing some basis to support indirect experimental state identifications. And, in fact, several semi-empirical studies have considered glyoxal and dicarbonyl excited states.²⁰⁻²⁴ Both Hug and coworkers²⁰ and McGlynn and coworkers²¹, using CNDO calculations, indicate that of the $n \rightarrow \pi^*$ excitations, the lowest two should be $a_g \rightarrow a_u$ for trans and $a_1 \rightarrow b_2$ for cis followed by $a_g \rightarrow b_g$ and $a_1 \rightarrow a_2$. For both cis and trans, the separations between the two excitations were found to be about 1 ev in both calculations. In the more conventional notation used here, b_2 and b_1 representations are necessarily interchanged compared with the usage of Hug and McGlynn. This gives a B_1 state for their $a_1 \rightarrow b_2$ (now $a_1 \rightarrow b_1$) excitation, as observed.

Unfortunately, only Kato and coworkers considered $\pi \rightarrow \pi^*$ states in addition to $n \rightarrow \pi^*$ states.²⁴ Their results are in agreement with the ordering of $n \rightarrow \pi^*$ excitations, but in addition, they show a $\pi \rightarrow \pi^*$ 3B_u state occurring between 3A_u and 3B_g $n \rightarrow \pi^*$ states. Furthermore, the ordering of ground state n and π

orbitals is somewhat unexpectedly close. Ab initio calculations on the ground state ²⁵⁻²⁷ have been in reasonable agreement with this ordering of the valence molecular orbitals (MO's). And as already pointed out, ²⁷ this suggests $\pi \rightarrow \pi^*$ excitations could be among low-lying states. As yet, no ab initio calculations of glyoxal excited states have been reported.

THEORETICAL APPROACH

Used in the calculations was a double-zeta basis set of Dunning-contracted gaussian functions,²⁸ C(9s 5p/4s 2p), O(9s 5p/4s 2p), and H(4s/2s). In calculations on the ground state of glyoxal,²⁷ this basis set has compared favorably with those used in other ab initio calculations.^{25, 26, 29, 30} A detailed review of basis sets has been presented elsewhere.³¹

In the previous calculation on the ground state,²⁷ the closed shell occupancies were confirmed to be

$$\dots 5b_u^2 6a_g^2 1a_u^2 6b_u^2 1b_g^2 7a_g^2$$

for the trans form (C_{2h} symmetry) and

$$\dots 6a_1^2 5b_2^2 1b_1^2 6b_2^2 1a_2^2 7a_1^2$$

for the cis form (C_{2v} symmetry). The π out-of-plane orbitals transform as a_u and b_g for trans and a₂ and b₁ for cis. The n or oxygen non-bonding orbitals are the highest filled a_g, b_u, a₁ and b₂ MO's. A pictorial representation of the π and π^* MO's is given in Figure 1. The orbitals are ordered by increasing number of nodes. While the representation may suggest a possible ordering of excited states, calculations were performed for all possible n \rightarrow π^* and $\pi \rightarrow \pi^*$ excitations because of the close spacing of n and π ground state MO's.

Excited state occupancies were made by promoting one electron from each n and π orbital to an unfilled orbital. As shown in Tables I and II, for both cis and trans forms, there are ten such occupancies arising from all $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ and two $n \rightarrow \sigma^*$ excitations. Each occupancy, of course, can produce a singlet and triplet state for a total of 40 states. Single configuration self-consistent-field (SCF) calculations were performed for these 40 states. Arbitrary numerical prefixes have been assigned to distinguish states of the same symmetry. Of course, only for the lowest state of each symmetry are the present calculations truly variational. The vertical excitation energy was calculated for all states. This is the energy of a given state at the geometry which is optimum for the cis or trans ground state.²⁷ Excited state calculations were performed only for the planar forms of the molecule. For gauche forms, the symmetry is reduced to C_2 , for which only A and B states are defined, and there is no longer a unique correspondence between orbital occupancies and electronic states. Hence, the simplest reasonable ab initio description of many of the analogous gauche electronic states of glyoxal would require configuration interaction.

With the interest of comparing SCF results with experiment, a partial geometry optimization was performed for the observed states. Comparison of these optimized results with experiment may enable one to precisely predict the energies of unobserved states. From ground state results, it was expected that carbon-hydrogen bond length and CCH angle optimization would not improve the energy as much as optimizing the carbon-carbon and carbon-oxygen bond lengths and perhaps the CCO angle. For 3A_u , 1A_u , 3B_1 and 1B_1 , these last three structural parameters were quite nearly optimized by a simple parabolic fit of energy to parameter value, fitting one parameter at a time. The changes in energy for the CCO angle were small and so, only the C-C and C-O bond lengths were optimized in the two lowest unobserved states, 3B_u and 3B_2 .

RESULTS AND DISCUSSION

The calculated energies of the forty excited states at geometries corresponding to the cis or trans ground state optimum structures are given in Tables I and II, and represented in Figure 2. The lowest vertical excited states are the observed $1-A_u$ ($n \rightarrow \pi^*$) and $1-B_1$ ($n \rightarrow \pi^*$) states, though their energies relative to the ground state are higher than experimentally determined. Next are the trans $1-^3B_u$ and cis $1-^3B_2$ states, both $\pi \rightarrow \pi^*$ excitations, and then another set of $n \rightarrow \pi^*$ states, $1-B_g$ and $1-A_2$. Transitions to the $1-B_g$ state from the trans ground state and to the $1-A_2$ state from the cis ground state are dipole forbidden. The positions of states lying above around $60,000 \text{ cm}^{-1}$ should be treated skeptically since Rydberg states (not treated here) become important in that region. The $n \rightarrow \sigma^*$ states were quite high in energy and need not be considered in discussions of the low-lying electronic states of glyoxal.

For all occupancies, the triplet state is lower in energy than the singlet and for most, the singlet and triplet are fairly close. The exceptions are the two B_u ($\pi \rightarrow \pi^*$) trans excitations and the two B_2 ($\pi \rightarrow \pi^*$) cis excitations. For these, the singlets were as much as $40,000 \text{ cm}^{-1}$ higher than the corresponding triplets. These large singlet-triplet separations may be in part an artifact of the chosen basis set, which did not include diffuse or Rydberg-type functions. For an increasing number of $\pi \rightarrow \pi^*$ singlet states, it is now becoming clear that a purely

valence-like description of the electronic structure is inadequate.³²⁻³⁴ However, several test calculations using diffuse $p\pi$ functions lowered the total energies of these $\pi \rightarrow \pi^*$ singlet states by less than 0.01 hartree.

The geometry optimization gave rather minor changes for the $n \rightarrow \pi^*$ states, but substantially lowered the 3B_u and 3B_2 states. The results are shown in Table III. The promotion of an electron to the lowest π^* MO, with a node between carbon and oxygen, produced a lengthening in the C-O separation for 3A_u , 1A_u , 3B_1 and 1B_1 . Also, the carbon-carbon distances were slightly shortened for these states. The CCO bond angle changed little for the trans singlet and triplet but did increase in the cis states. For 3B_u and 3B_2 , an electron is excited from a π MO with no nodes to the lowest π^* MO. In the ground state, the filled π MO is energetically just above the second highest occupied orbital (see ref. 27). At vertical excitation, the 3B_u and 3B_2 , as expected, lie above the 3A_u and 3B_1 , respectively. But at the equilibrium geometry for the 3B_u and 3B_2 states, the carbon-carbon bond length is contracted by about 0.15 Å and the carbon-oxygen bond length is about 0.15 Å longer than in the ground state. Their energies now become lower than any other excited state.

The calculated dipole moments of the cis states are given in Table IV. The dipole moment of the lowest $n \rightarrow \pi^*$ B_1 singlet and triplet is about the same as the ground state. For most excitations, the singlet and triplet have very nearly equal dipoles. The exceptions are the 1- B_2 ($\pi \rightarrow \pi^*$) and 3- B_2 ($\pi \rightarrow \pi^*$). Not surprisingly, these are the same excitations which gave the large singlet-triplet separations.

Prediction of States

Several factors must be considered when predicting the physical observability of states on the basis of SCF calculations. Aside from the quality of the chosen basis set, one must estimate effects of geometry optimization, correlation energy, and differences in vibrational zero-point energies between states. The partial geometry optimization of the 3A_u , 1A_u and 1B_1 states and the complete optimization of the cis and trans ground states,²⁷ can be used to estimate some of the unknown effects. The partially optimized singlet states are about 9000 cm^{-1} above experimental 0-0 excitation energies. The 3A_u state is also about 30% higher in energy than experimentally found. A more complete geometry optimization and possible differences in zero-point energies could probably account for no more than 1000 cm^{-1} of the discrepancy.

The remaining errors are due either to incompleteness of the basis set or correlation effects. In light of this, it is interesting to note a recent Hartree-Fock (i.e., large basis set) study of the $n \rightarrow \pi^*$ singlet and triplet states of formaldehyde.³⁵ There Garrison et al. found the SCF excitation energies to lie $\sim 8000\text{ cm}^{-1}$ below experimental values. This would at first suggest that the glyoxal excitation energies are too high because of the basis set. To test this, vertical excitation energies were calculated for formaldehyde using the same basis set as with glyoxal. The geometry used was the experimentally determined ground state structure.¹

The results of these calculations, shown in Table V, agree with the larger basis set study³⁵ in finding the $n \rightarrow \pi^*$ energies too low. This suggests that the excitation energy errors introduced by our double zeta basis may be quite small for glyoxal. However, this in turn implies that the true Hartree-Fock excitation energies in glyoxal are too high, whereas in formaldehyde the opposite is the case. This result cautions us against models in which glyoxal is thought of as a superposition of two formaldehyde molecules. Interestingly, an analogous model has been successfully used by Dunning, Hosteny and Shavitt³³ to discuss the electronic states of butadiene in terms of those of two ethylene units.

Our conclusion at the present time concerning correlation effects in glyoxal is that they are somewhat unpredictable and can result in errors as large as $9,000 \text{ cm}^{-1}$ in Hartree-Fock excitation energies. Should more experimental information become available, it would be possible to calibrate SCF results for related systems, e.g., acrolein, and thus make rather accurate semi-empirical predictions.

We can now attempt to estimate the positions of the next set of $n \rightarrow \pi^*$ states. The four $1-B_g$ and $1-A_2$ states were calculated to have vertical excitation energies greater than $40,000 \text{ cm}^{-1}$. The π^* MO for these and the lower pairs of states is the same. Since the n orbitals are largely non-interacting, we expect the same geometry changes, correlation effects, and SCF error as with excitation from the other n orbital. Therefore, we estimate that the $1-^3B_g$ state occurs about $29,000 \text{ cm}^{-1}$ to $35,000 \text{ cm}^{-1}$ above the ground state, with the $1-^3A_2$ perhaps slightly lower. In correcting the singlet state energies, it is possible that the singlet-triplet separation should be larger than calculated. However, cis excitations which gave particularly large singlet-triplet separations had substantially different dipoles. We consider the reasons for this later, but at this point, we note the agreement in dipole moments of the $1-^3A_2$ and $1-^1A_2$ states. Then, the similarity of these states and the analogous trans states with the lower observed $n \rightarrow \pi^*$ states, places the singlets above the triplets at an energy which can be taken as the experimental $^1A_u - ^3A_u$ difference, roughly 3000 cm^{-1} . This could support the recent experimental identification¹⁸ of a 1B_g state.

Perhaps the most critical estimate is required for the two low-lying $\pi \rightarrow \pi^*$ triplets. Once again, we expect that further geometry optimization would not significantly change the energies of the $1-^3B_u$ and $1-^3B_2$ states. Lacking a configuration interaction

calculation, correlation effects are difficult to estimate reliably as discussed earlier. But the surprisingly low energies of these $\pi \rightarrow \pi^*$ states suggests that their correlation energies may be less than that of the glyoxal ground state. Thus, the 3B_u may occur between $12,000 \text{ cm}^{-1}$ and $22,000 \text{ cm}^{-1}$ of the ground state, after estimating the theoretical uncertainty. Similarly, the 3B_2 state might be found between $11,000 \text{ cm}^{-1}$ and $21,000 \text{ cm}^{-1}$ above the cis ground state. While $21,000 \text{ cm}^{-1}$ and $22,000 \text{ cm}^{-1}$ represent upper limits to the calculation uncertainty, spectroscopic studies⁴⁻⁹ at energies as low as about $18,000 \text{ cm}^{-1}$ do not indicate the presence of these states. Thus, it seems likely that these will be the lowest excited states of glyoxal.

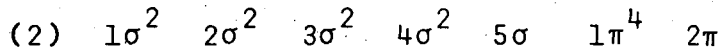
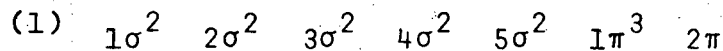
In the vertical excitation energies, a very substantial break is found between the states so far considered and the higher states. Since even a sizeable downward correction would not place these among the low-lying states, no attempt has been made to predict the true energies of the higher states.

The 1A_u and 1B_1 states demonstrate an internal consistency of the calculations. Spectroscopic results have placed the 1B_1 about 335 cm^{-1} below the 1A_u state^{4,8} using the determined value⁸ for the ground state cis-trans separation of 1125 cm^{-1} . If instead, the calculated separation²⁷ of about 2070 cm^{-1} is used, the 1B_1 state will be 600 cm^{-1} above the 1A_u . And this compares well with a difference of 715 cm^{-1} in the partially optimized, calculated 1B_1 and 1A_u state energies.

Electronic Structure

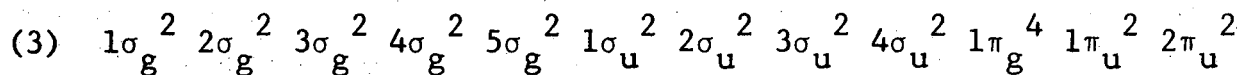
The underlying interest in ab initio calculations on dicarbonyls is to attempt to relate the electronic structure and hopefully, chemical properties of the whole system to the simpler electronic structure of a carbonyl group. And this should be useful in understanding the chemistry of large carbonyl systems. In ground state calculations,²⁷ a comparison between carbon monoxide, $(CO)_2$ and glyoxal made possible a better interpretation of the ordering of n and π valence MO's. The excited states show an even more significant relationship.

Many excited states of carbon monoxide have been observed and studied experimentally.^{1,36} In an ab initio configuration interaction study of carbon monoxide, O'Neil and Schaefer found a dominant configuration for eleven bound states including the observed states.³⁷ Two occupancies were found to yield the eight experimentally observed states:



The states arising from occupancy 1 have a fairly small singlet-triplet separation.³⁶ But the $\tilde{a} \ ^3\Pi$ state and $A \ ^1\Pi$ state, which arise from occupancy 2, differ in energy by about 2 ev. This is suggestive of the $1-B_u$, $3-B_u$, $1-B_2$ and $3-B_2$ excitations in glyoxal.

The probable existence of a carbon monoxide dimer has been shown in theoretical calculations.³⁸⁻⁴⁰ Potential curves have been obtained showing three bound states of $(CO)_2$ in a constrained linear ($D_{\infty h}$) arrangement, with the lowest state, $^3\Sigma_g^-$, being bound with respect to the lowest available dissociation limit. The occupancy which gives rise to these states is,



This occupancy, however, does not correlate (for collinear geometries) with the ground state occupancies of two CO molecules. In fact, the interaction between ground state CO molecules is repulsive (except for the long range attraction), both in a linear arrangement³⁸ and non-linear approaches.²⁷ However, by going to pathways of sufficiently low symmetry, it appears⁴⁰ that the $^1\Delta_g$ state of $(CO)_2$ can dissociate readily to two ground state CO molecules. The lowest dissociation limit accessible to the $^3\Sigma_g^-$ state of $(CO)_2$ is $\tilde{X}^1\Sigma^+$ plus $\tilde{a}^3\Pi$. Finally, occupancy 3 of the dimer correlates, though not uniquely, with the $1-B_u$ and $1-B_2$ electron occupancies of glyoxal.

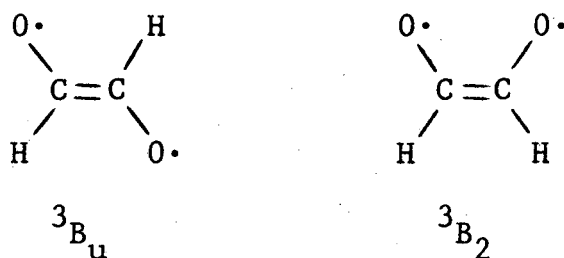
This three-way correlation of excited states and occupancies is also indicated by the structures of the CO, (CO)₂ and glyoxal states. Experimentally, the carbon monoxide bond length is about 0.1 Å longer in the $\tilde{a}^3\Pi$ state than in the ground state. Similarly, the C-O bond length is about 0.14 Å longer in the 3B_u and 3B_2 states of glyoxal than in the ground state. The minimum in the C-C distance potential for CO-dimer was found to be 1.335 Å.³⁸ For the analogous glyoxal states, we find the C-C distance to be 1.353 in the trans form and 1.350 Å in the cis form.

Correlation of additional states is much more difficult, since occupancy 1 of carbon monoxide has two open-shell π MO's. Such a correlation will not be unambiguous and can give doubly excited glyoxal states. The most important result of the discussion of CO, CO-dimer and glyoxal states is the rationalization of the low-lying 3B_u and 3B_2 states. Specifically, an electronically excited CO monomer is required to form the ground state of (CO)₂ and in glyoxal, this state becomes a very low-lying $\pi \rightarrow \pi^*$ state.

Explanation of the anomalous singlet-triplet separation and dipole differences of the 1-B_u, 3-B_u, 1-B₂ and 3-B₂ excitation requires examination of the wavefunctions. Considering as an example

the $1-B_2$ states, we note that only a few orbitals provide different singlet-triplet contributions to the total dipole moment. Among these are the filled $1b_1$ and open shell $2b_1$ MO's. Their net contribution is greater for the singlet than the triplet, but in addition, the relative magnitudes of their contributions is reversed between the singlet and triplet. In addition, atomic Mulliken populations and the orbitals themselves show remarkable differences between the singlet and triplet. Basically, the $1b_1$ and $2b_1$ MO's tend to be more delocalized in the triplet than singlet. In the singlet, the filled $1b_1$ MO is localized on the oxygens, whereas in the triplet it is the half-filled $2b_1$ MO which is localized on the oxygens. Immediately, this accounts for the larger dipole moment of the singlet. The half-filled $1a_2$ orbital is similar in both singlet and triplet. Standard quantum mechanical arguments would say that the unpaired singlet electrons, with opposite spin, can occur at the same spatial positions where highly repulsive, but in the triplet can not. For the $2b_1$ orbital, this produces greater singlet state localization. With the two $1b_1$ electrons now forced to localize on the oxygens, the singlet-triplet energy separation is increased. The plausibility of this interpretation may be enhanced when CI wavefunctions for these states are available. For the other $\pi \rightarrow \pi^*$ excitations, the arguments are analogous.

Of perhaps primary importance in this work, is the nature of the predicted low-lying 3B_u and 3B_2 states. We first point out that the localization of the b_1 MO's causes the states to be biradicals. This is consistent with the CO-dimer state, ${}^3\Sigma^-$, which has been described as a biradical³⁸ and which correlates with the glyoxal $\pi \rightarrow \pi^*$ triplets. It is worthwhile to note that the singlet states which arise from the same excitation are not biradicals because of the singlet-triplet $1b_1-2b_1$ MO reversal in localization. The carbon-carbon bond of the 3B_u and 3B_2 states is essentially a double bond, consistent with the bond length shortening, and thus the structures can be represented as



As with ${}^3\Sigma^-$ CO-dimer, the high reactivity of a biradical could make the observation of these states difficult.

As mentioned earlier, another model in terms of which to discuss the electronic spectrum of glyoxal involves the superposition of two H_2CO molecules. This sort of "molecules in molecules" model has been successfully used to describe several excited electronic states of butadiene recently.³³ In the same spirit we present in Figure 3 a correlation of

the lowest triplet states of glyoxal with the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states of formaldehyde. Note of course that this model applies only to geometries of glyoxal rather comparable to those of formaldehyde. And we see that at the ground state equilibrium geometry, the $n \rightarrow \pi^*$ state of glyoxal is indeed the lowest excited state, as is the case for formaldehyde. However, changes upon excited state geometry optimization are so severe as to bring into question the validity of this simple model. In addition, Figure 3 shows that at the vertical geometry the lowest $\pi \rightarrow \pi^*$ state falls below the second $n \rightarrow \pi^*$ state. Thus one can reasonably conclude that the "coupling" of the two fragments is rather strong in glyoxal.

The final consideration of this work is the correlation of cis and trans excited states. The complicated pattern of vertical excitations in Figure 2 has several interesting features. After placing the $1-^3B_u$ and $1-^3B_2$ states below the $1-A_u$ and $1-B_1$ states, respectively, it can be seen that the A_u trans states correlate with higher energy A_2 cis states. Similarly B_1 states correlate with higher B_g states. This would indicate that population of the unobserved A_2 and B_2 states could probably be followed by isomerization. If there is little or no barrier to the isomerization, then the existence of these states might explain short wavelength diffuseness in the glyoxal spectrum. At still higher energies, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ states are considerably mixed. There will be several

avoided crossings and some $n \rightarrow \pi^*$ states of one isomer will be found to correlate with $\pi \rightarrow \pi^*$ states of the other isomer.

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Table I. Trans-Glyoxal Excited States.^a

<u>Excitation</u>	<u>Open Shell MO's</u>	<u>State Symmetry</u>	<u>Triplet Energy</u>	<u>Singlet Energy</u>
Ground State	-	1 A _g	-	-226.5182
n→π*	7a _g 2a _u	1 A _u	-226.3940	-226.3741
π→π*	1b _g 2a _u	1 B _u	-226.3680	-226.1762
n→π*	6b _u 2a _u	1 B _g	-226.3231	-226.3074
π→π*	1a _u 2a _u	1 A _g	-226.2480	-226.2450
n→π*	7a _g 2b _g	2 B _g	-226.2224	-226.2114
π→π*	1b _g 2b _g	2 A _g	-226.1511	-226.1474
n→π*	6b _u 2b _g	2 A _u	-226.1495	-226.1385
n→σ*	7a _g 7b _u	2 B _u	-226.1082	-226.0904
π→π*	1a _u 2b _g	3 B _u	-226.0814	-225.9734
n→σ*	7a _g 8a _g	3 A _g	-226.0188	-226.0072

^a Each excited occupancy produces a singlet and triplet state of the given symmetry type. Arbitrary numerical prefixes distinguish states of the same symmetry. Energies correspond to vertical excitation and are in atomic units.

Table II. Cis-Glyoxal Excited States.^a

<u>Excitation</u>	<u>Open Shell MO's</u>	<u>State Symmetry</u>	<u>Triplet Energy</u>	<u>Singlet Energy</u>
Ground State	-	$1 A_1$	-	-226.5088
$n \rightarrow \pi^*$	$7a_1$ $2b_1$	$1 B_1$	-226.3899	-226.3705
$\pi \rightarrow \pi^*$	$1a_2$ $2b_1$	$1 B_2$	-226.3628	-226.1856
$n \rightarrow \pi^*$	$7a_1$ $2a_2$	$1 A_2$	-226.3314	-226.3164
$\pi \rightarrow \pi^*$	$1b_1$ $2b_1$	$1 A_1$	-226.2468	-226.2430
$n \rightarrow \pi^*$	$6b_2$ $2b_1$	$2 A_2$	-226.2086	-226.1971
$n \rightarrow \pi^*$	$6b_2$ $2a_2$	$2 B_1$	-226.1474	-226.1365
$\pi \rightarrow \pi^*$	$1a_2$ $2a_2$	$2 A_1$	-226.1420	-226.1382
$n \rightarrow \sigma^*$	$7a_1$ $7b_2$	$2 B_2$	-226.0888	-226.0669
$n \rightarrow \sigma^*$	$7a_1$ $8a_1$	$3 A_1$	-226.0812	-226.0699
$\pi \rightarrow \pi^*$	$1b_1$ $2a_2$	$3 B_2$	-226.0705	-225.9613

^a Vertical excitation energies are in atomic units.

Table III. Optimized excited states. The carbon-carbon bond length, carbon-oxygen bond length and carbon-carbon-oxygen angle were optimized for the lowest excited states. Bond lengths are in Å and angles are in degrees.

	State	R_{CC}	R_{CO}	\angle_{CCO}	Energy (a. u.)	Energy Relative to g.s. (cm^{-1})
<u>Trans</u>	$1A_g$ g.s.	1.508	1.215	121.1	-226.5182	0.0
	1^3A_u	1.492	1.241	121.0	-226.3959	26,850
	1^1A_u	1.494	1.244	121.7	-226.3766	31,090
	1^3B_u	1.353	1.356	121.1 ^a	-226.4504	14,890
<u>Cis</u>	$1A_1$ g.s.	1.516	1.213	123.2	-226.5088	0.0
	1^3B_1	1.492	1.236	124.7	-226.3921	25,620
	1^1B_1	1.494	1.241	125.1	-226.3733	29,740
	1^3B_2	1.350	1.356	123.2 ^a	-226.4480	13,340

^a Not optimized; ground state value assumed.

Table IV. Excited state dipole moments. By symmetry, all trans-glyoxal states have a zero dipole moment. Cis excited state dipole moments were calculated from the SCF wavefunctions corresponding to vertical excitation. Values are in Debyes.

	$1A_1$ (g.s.)	4.79		
1	3B_1	4.76	1	1B_1 4.80
1	3B_2	3.04	1	1B_2 5.13
1	3A_2	4.12	1	1A_2 4.32
1	3A_1	4.52	1	1A_1 4.53
2	3A_2	4.29	2	1A_2 4.28
2	3B_1	3.64	2	1B_1 3.67
2	3A_1	2.92	2	1A_1 2.91
2	3B_2	1.07	2	1B_2 0.73
3	3A_1	3.08	3	1A_1 2.86
3	3B_2	3.78	3	1B_2 4.75

Table V. Formaldehyde Electronic States.^{a,b}

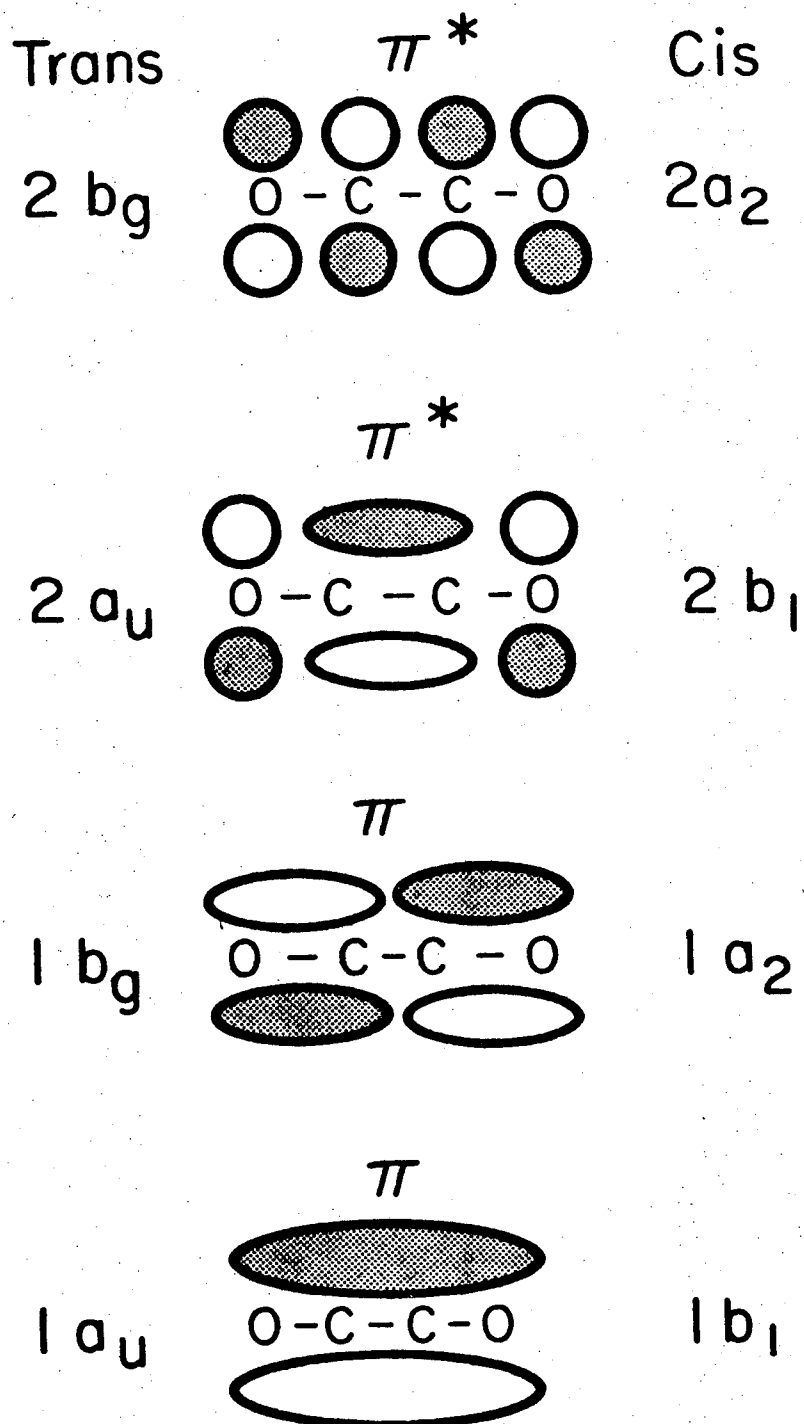
<u>Excitation</u>	<u>State</u>	<u>Energy (a.u.)</u>	<u>Excitation Energy (cm⁻¹)</u>
Ground State	¹ A ₁	-113.8295	0.0
n → π [*]	³ A ₂	-113.7426	19,100
	¹ A ₂	-113.7286	22,100
π → π [*]	³ A ₁	-113.6738	34,200
	¹ A ₁	-113.6674	35,600
σ → π [*]	³ B ₁	-113.5737	56,200
	¹ B ₁	-113.5401	63,500
n → σ [*]	³ B ₂	-113.4909	74,300
	¹ B ₂	-113.4732	78,200

^a Calculations were done with the same basis set as that used for glyoxal. Energies correspond to vertical excitation at the experimentally determined geometry¹ of the ground state.

^b Note that the π → π^{*} ¹A₁ state calculated does not correspond to physical reality, as it has a large Hamiltonian matrix element with the ¹A₁ ground state of formaldehyde. CI calculations place this state much higher. See, e.g., S. D. Peyerimhoff and R. G. Buenker, in Chemical Spectroscopy and Photochemistry in the Vacuum-Ultraviolet (Reidel, Dordrecht-Holland, 1975).

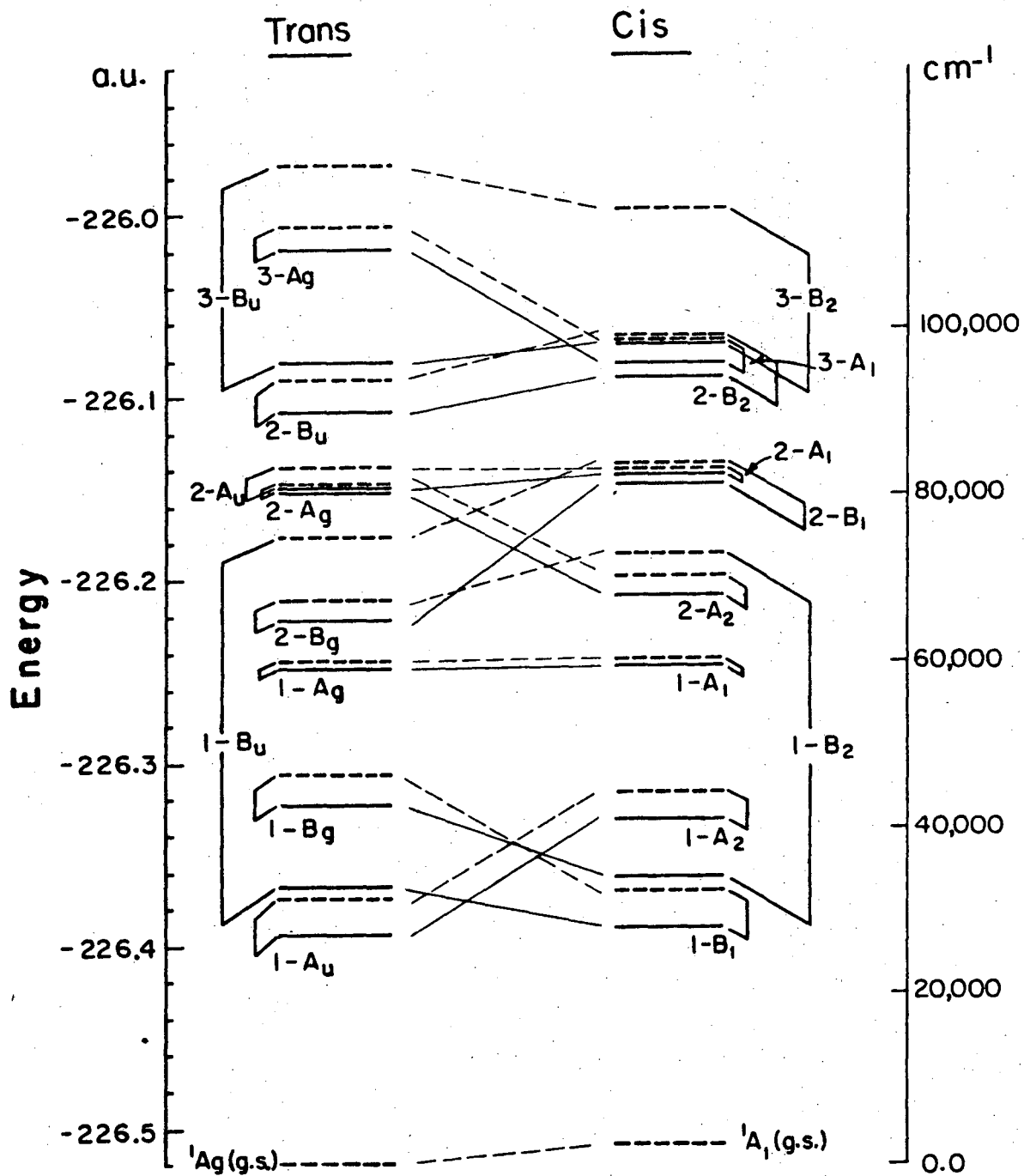
FIGURE CAPTIONS

- Figure 1. Qualitative representation of glyoxal π and π^* molecular orbitals. Shading represents the phase difference between lobes.
- Figure 2. The excited states of glyoxal. Energies correspond to vertical excitation from the cis or trans ground state. Triplet states are shown with solid lines and singlet states with broken lines. Symmetry state designations are given for each singlet-triplet pair of states and correspond to excitations given in Tables I and II. Correlation lines between cis and trans states connect states which must correlate on the basis of symmetry, but do not represent any internal rotation potentials.
- Figure 3. Correlation of the lowest triplet states of glyoxal with those of two formaldehyde molecules.



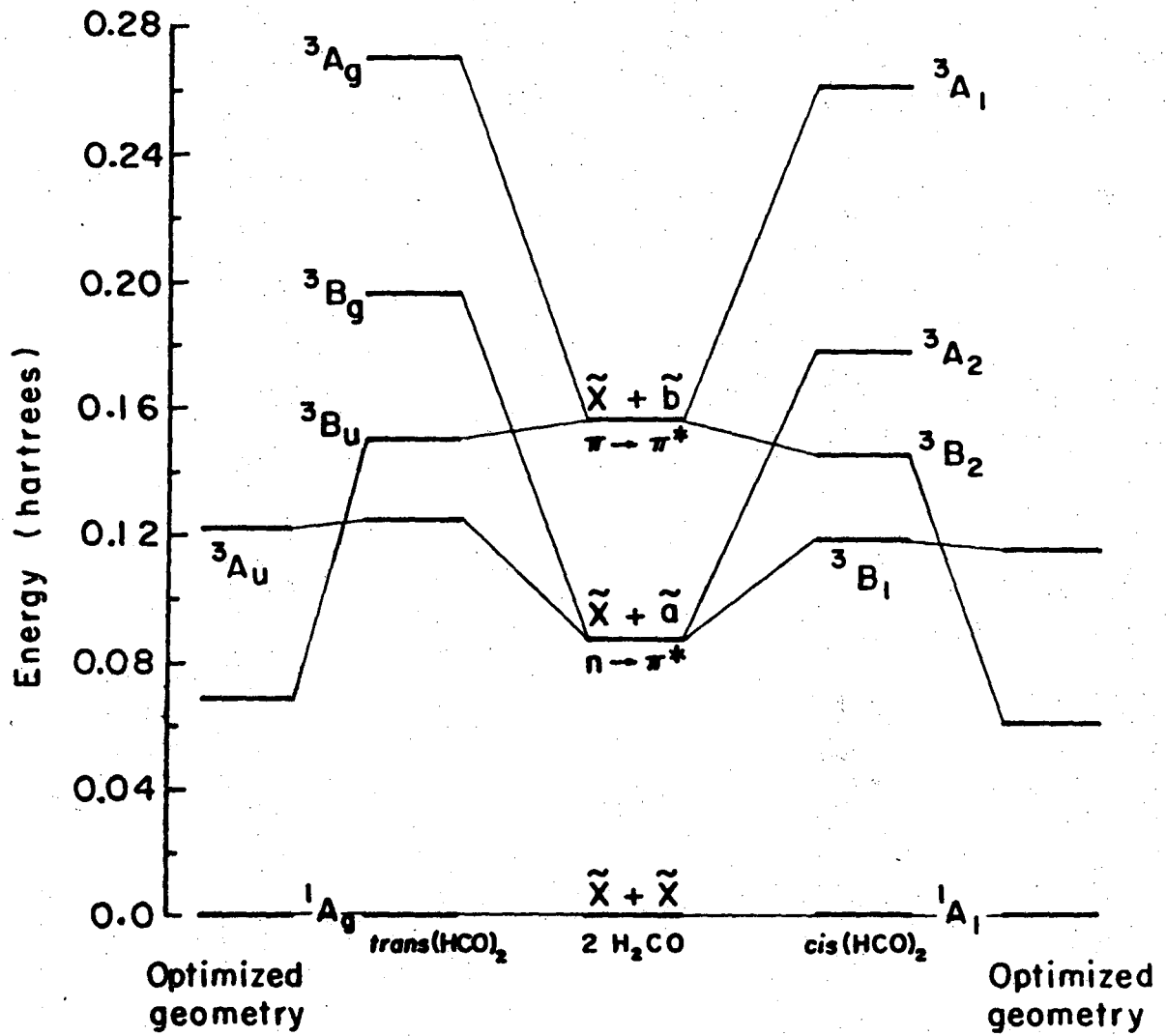
XBL753-2581

Fig. 1



XBL753-2580

Fig. 2



XBL754-2756

Fig. 3

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720