

Chapter 11

Computational Model for the Electronic Excitation and Deactivation of Glyoxal

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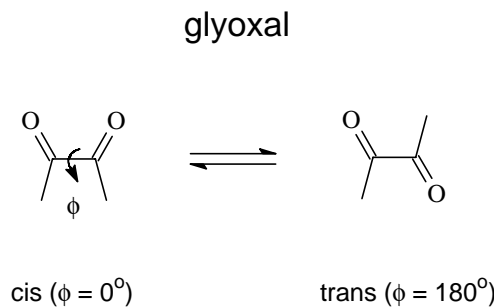
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11.1 Introduction

Glyoxal is an attractive and very intriguing molecule. A relevant structural feature is the internal rotation to give two isomers:



and this point gives a particular complexity and even ambiguity to the study of the ground and excited state behaviour and reactions.

Among the many facts because glyoxal is important, like being an intermediate in the mechanism of hydrocarbon oxidation in the atmosphere^{1,2}, we selected it for assaying the capability of contemporary computational procedures to explain the behaviour of polyatomic systems in front of light, and even the understanding of one of the most interesting reactions in chemistry: the “triple whammy” or internal decomposition after light excitation of this very simple system of 6 nuclei to three molecules (two CO and a H₂) upon internal rotation of the C – C bond.

The most important features of the spectroscopy and excited states have been described long time ago³. A review of further references on spectroscopy, coupling between lowest singlet and triplet states, energy transfer, van der Waals complexes and stimulated emission pumping is included in a recently appeared paper⁴ and some of the most relevant theoretical approaches^{5,6,7,8,9,10,11,12,13,14,15,16,17} were also produced recently.

In fact, several kinds of photochemical reactions are reported. The primary dissociation channel at room temperature appears to be^{18,19,20,21}:



The second is the above mentioned triple decomposition and could be described as the unimolecular reaction giving CO and H₂^{4,22,23}, and showing an important yield under low energy (440 nm) photon irradiation. This is a very significant case when a molecule undergoes decomposition into three other molecules in a single step. It is known as the “Triple Whammy Channel” (TWC):



Evidences are reported about other possible channels as the one occurring after irradiation above the first absorption band (193, 248, 308 and 351 nm), giving a typical Norrish I carbonyl decomposition reaction²⁴:



and the production of a rare formaldehyde isomer^{22,15}:



We will focus our attention in this paper to channel (2). It has been experimentally studied recently in the above cited paper. Process (3) have received little attention until now, from the very theoretical point of view, maybe due to the common nature of it in carbonyl compounds.

Pioneering works were published decades ago^{7,8} on channel (2) when an exercise of intelligent use of symmetry with limited (from nowadays point of view) computational resources permitted a description of the “triple whammy channel” (TWC). An important refinement

about the theoretical behaviour of glyoxal excited states has been further published in 1989 by Profs. Scuseria and Schaefer. However, very recent papers^{15,16,17} began to find new pathways from the theoretical point of view, and gave the very last word on this intriguing and very paradigmatic reaction where theory has supported experimental gas phase photochemistry to interpret and even suggest results.

In the case of TWC, our present calculations confirm that the reaction is possible after the population of a high vibrational level of the *cis* isomer ground state. It must drive the reaction *via* a *swinging* (non planar *cisoid*) transition state (TS_{TWC}) to CO and H₂ as reported by other authors^{15,17}. Such TS_{TWC} is experimentally represented by an activation barrier between 38.4 and 55.1 kcal mol⁻¹. Then, a fact to be described is that 440 nm photons (64.9 kcal mol⁻¹) must act in one of the following ways:

- a) direct population of the excited electronic state S1 of the *cis* isomer followed by radiationless deactivation to the TS_{TWC};
- b) direct population of TS_{TWC} of the *cis* isomer ground state by light absorption;
- c) population of a vibronic level of the *trans* isomer leading to isomerization to the *cis* isomer by an internal rotation and then accessing to the TS_{TWC}.

Options a) and b) seem not very much visited because the proportion of existing *cis* molecules at room temperature is non significant to absorb light and populate any of the excited states of it. However, option c) would mean to overcome an internal *torsional* barrier previous to TWC. A mechanism must be proposed for a *trans* glyoxal molecule to isomerize and then decay to TS_{TWC}. We searched several pathways to explain this process from the theoretical point of view and propose some hypothesis based in a high level computational model, including a detailed intrinsic reaction path after very accurate correlated *ab initio* calculations.

11.2 Procedures

Quantum mechanical approaches have been used for building the theoretical model. *Ab initio* SCF procedures included in Gaussian 94 package of programs²⁵ were mainly followed. 6-31G(d,p) and 6-311G(d,p)[#] basis sets²⁶ were selected to reach a good level in theoretical consistency at the Hartree - Fock level. Given the necessity of optimising ground state geometries by considering electron correlation and the very expensive nature of these calculations when they must be performed in several points of a hypersurface, the perturbative Møller - Plesset with double excitations (MP2) procedure has been used. This is a very consistent method to take into account correlation energy, although it is known that we are including the large majority, but all, of this very sensitive energy correction. The results show that we improved, in general, previous calculations at the CCSD/DZ+P level.

Singly excited states have been calculated either with fixed molecular geometries and also optimising the excited states by the CIS (configuration interaction of single excitations) procedure included in the Gaussian program. It is known that SCF MO procedure optimises those electronic states where electronic densities have non zero values. Therefore, virtual molecular orbitals are non-optimised at all during a normal SCF energy minimization and the purpose of

[#] This notation has been simplified to 6-31G** and 6-311G**, respectively, across this paper.

CIS is to improve the representation, only from this point of view, by providing a new and degenerate molecular wave function (i.e., with the same total energy) with a better overall orbital distribution. This is the reason because calculated electron excitations and geometry optimisations of excited states take sense after CIS.

Our calculations of the non planar transition state of glyoxal and the reaction path were performed at a very high level of Hartree Fock theory with correlation consistent, valence split triple zeta, polarization and diffuse basis functions in each shell (Dunning's AUG-cc-pVTZ) including MP2 correlation energy corrections, with full optimisations and without symmetry restrictions. It would be interesting to notice that a single scratch read-write file amounted 14 GB in hard drives, during each calculation.

Sometimes in this work calculations at both restricted and unrestricted Hartree - Fock (RHF and UHF) levels have been performed to test their abilities in the field of excited state modelling. The non-usual use of UHF in a closed shell system, like this one, was attempted because it could enhance the quality of the basis in excited state optimised geometries where bonding is critical, like certain transient species. As expected, no spin contamination was detected at all.

Single electron excitations of molecular valence orbitals with the appropriate configuration interaction were also calculated by the NDOL method²⁷ and using the program written by one of the authors²⁸ (LM). This is essentially an improvement of the traditional methods based in fully orthogonal and not explicit basis sets (NDO), that considers always experimentally originated and different parameters for atomic *s* and *p* orbitals, contrary to the fully empirical choice of *sp* orbitals in Pople's methods. Semiempirical MNDO-PM3 method²⁹ was also used for scanning the ground state hypersurface, by means of the MOPAC6 program version for PC's³⁰.

11.3 Results and Discussion

In the following discussion we represent electronic states as S_n and T_n for singlets and triplets, respectively, where $n=0$ is for the ground, and $n=1,2$ for the excited states. The molecular geometry corresponding to a certain state is represented between brackets and the symbols remain as STATE_ENERGY[STATE_GEOMETRY].

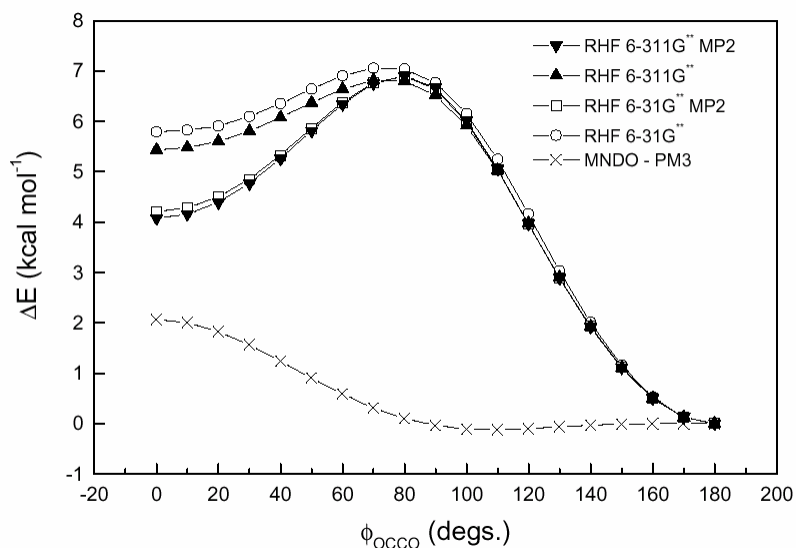


Figure 1. Energy surface corresponding to possible values of O-C-C-O torsion angle in S0[S0] state at different levels of theory.

A. Molecular properties. Since the main intramolecular reaction is the *trans* - *cis* isomerization by internal rotation around the C - C bond, scanning of this torsion angle in the ground state (S0), and leaving to relax all other coordinates, has been used to test the abilities of different methods and basis sets to reproduce the expected isomeric structures. Fig. 1 shows the most relevant results. It can be realized that semiempirical MNDO-PM3 method is unable to predict the right stable species, giving a minimum at a torsion angle of about 110° following a near to flat path until the *trans* conformer. On the other hand, a double zeta basis set in valence atomic orbitals (6-31G**) is giving quite the same results as the corresponding triple zeta (6-311G**). However, scanning with the inclusion of electron correlation at the MP2 level introduces a significant change. It invariably stabilizes the *cis* isomer with respect to non electron correlated calculations. The barrier is only slightly dropped, as it can be seen in Table 1, contrary to the statements in a previous work where they considered glyoxal as a “surprising example of a situation in which electron correlation has a major effect on a barrier to internal rotation” in the S0 state. Our most accurate calculation (MP2/6-311G**) gives a barrier height for a transition state up to 6.74 kcal mol⁻¹, with respect to the lowest energy *trans* isomer. The scanned reaction coordinate is mostly composed in this case by the torsion angle, showing a value of 79.4° in such transition state, i.e. displaced to the *cis* side as expected according the Hammond postulate. Experimental value for $\Delta H_{\text{cis-trans}} = 4.45 \pm 0.14$ kcal mol⁻¹³¹ is in good agreement with the calculated $\Delta E_{\text{cis-trans}} = 4.09$ kcal mol⁻¹. Other experimental^{32,33} values also approach it very well (see notes in Table 1). An important consequence of this calculation is that glyoxal occurs with an abundance of 99.9 % of the *trans* isomer at room temperature.

Table 1. Internal rotation in the ground state

	$\Delta E_{cis-trans}$ ($kcal\ mol^{-1}$)	E^* ($kcal\ mol^{-1}$)	ϕ^* (degs.)
6-31G**	5.64	7.15	75.0
6-311G**	5.43	6.84	74.8
MP2/6-31G**	4.21	6.91	78.8
MP2/6-311g**	4.09	6.74	79.4
CCSD/DZ+P ^a	4.59	6.09	76.5
Exp. ^b	4.45	-	-

a.- ref. 9

b.- ref. 31. Other experimental values are $3.30\ kcal\ mol^{-1}$ [ref. 32] and $3.85\ kcal\ mol^{-1}$ [ref. 33]

Ground state molecular geometry is not a particular interest of this paper because all relevant information were already obtained in the previous works. However, our results are comparable to them and in good agreement with experimental data (see Table 2).

Table 2. Significant data on molecular geometry

	r_{CC} (Å)		r_{CO} (Å)	
	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
neutral molecules				
6-31G**	1.517	1.528	1.185	1.181
6-311G**	1.517	1.528	1.185	1.181
MP2/6-31G**	1.514	1.526	1.224	1.221
MP2/6-311G**	1.523	1.537	1.213	1.210
CCSD/DZ-P ^a	1.527	1.541	1.220	1.216
exp.	1.525 ^b	1.505 ^b 1.514 ^b		
radical cation				
MP2/6-311G**	1.874	1.931	1.152	1.148
S1[S1]				
6-311G**	1.505	1.508	1.196	1.193
T1[T1]				
6-311G**	1.499	1.500	1.198	1.195

a.- ref. 9

b.- cited in ref. 9

Dipole moment of the *cis* isomer is also reported to be close to 3.40 D. The corresponding calculated value with our best basis set (MP2/6-311G**) in S0[S0] is 4.21D, not too far from the experimental result.

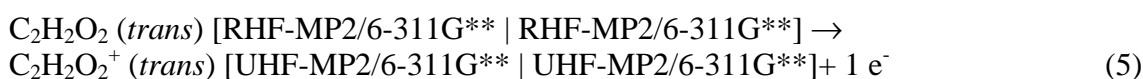
Table 3. HOMO eigenvalues

	- ϵ_{HOMO} (ev)			IP (ev) observed ^a
	<i>Trans</i>	<i>cis</i>	<i>TS</i>	
<i>6-31G** / 6-31G**</i>	11.68	11.57	11.37	9.48
<i>NDOL / 6-31G**</i>	8.49	8.56		
<i>6-311G** / 6-311G**</i>	11.69	11.56	11.38	
<i>NDOL / 6-311G**</i>	8.44	8.51		
<i>6-31G** / MP2/6-31G**</i>	11.99	11.87	11.65	
<i>NDOL / MP2/6-31G**</i>	8.79	8.82		
<i>6-311G** / MP2/6-311G**^b</i>	11.95	11.82	11.62	
<i>NDOL / MP2/6-311G**</i>	8.70	8.76		

a.- ref. 4.

b.- The calculated ΔE corresponding to the ionization reaction of the *trans* isomer at this level of theory gave an adiabatic IP of 9.54 ev, in excellent agreement with such experimental value. This theoretical value for *cis* isomer is 9.44 ev. See text.

Ionization potential is an accurate quantity of a property related directly with electronic states and serves for probing the quality of energetic values given by the selected theoretical methods. We compared the experimental value reported in the Herzberg's book corresponding to the appearance potential in mass spectrometry (presumably after an electron impact excitation) of 9.48 ev with the absolute value of our HOMO eigenvalues, according the Koopman's theorem (see Table 3). This is a surprising result, given the fact that our highest level calculations surpasses by about 2.5 ev the experimental value (expectedly corresponding to the *trans* form). An important point is that such MP2/6-311G** optimized geometry of the *trans* isomer brings a plausible value of 8.70 ev when the orbital calculation is performed with the *a priori* approximated NDOL method. An accurate calculation of the reaction:



gives an energy difference of 9.54 ev, in excellent coincidence with the reported value. The corresponding theoretical result for the *cis* isomer is 9.44 ev. A plausible explanation for the large difference is that Koopman's values are vertical IP's, while those calculated according reaction (5) are adiabatic, and the geometry changes between ionic and neutral species are important (see table 2), in coincidence with our theoretical results.

Table 4. Electron excitations to S1^a

	Vertical		Adiabatic		Observed	
	<i>trans</i> ¹ A _u	<i>cis</i> ¹ B ₁	<i>trans</i> ¹ A _u	<i>cis</i> ¹ B ₁	<i>trans</i> ^b ¹ A _u	<i>cis</i> ^c ¹ B ₁
<i>CIS/6-311G** / 6-311G**</i>	29710	28580	29280	27910	22206.7	20510
<i>NDOL / 6-311G**</i>	22020	23500				
<i>CIS/6-311G** / MP2/6-311G**</i>	28621	27552				
<i>NDOL / MP2/6-311G**</i>	21710	22150				

a.- cm⁻¹. This values for planar forms are the same if calculations are performed at the RHF or UHF level.

b.- Ref. 32. Ref. 3, p. 635, reported 21973.4 cm⁻¹ for adiabatic ¹A_u ← ¹A_g.

c.- ref. 6 and references therein.

Comparisons of calculated electron excitations with experimental values give similar conclusions, as it is shown in Table 4. The reported^{3,34} adiabatic absorption maximum corresponding to the *trans* isomer (¹A_u ← ¹A_g) is only comparable with vertical NDOL values obtained with the *ab initio* optimised geometries. The *ab initio* adiabatic numerical result with the best basis functions (*CIS/RHF 6-311G**/RHF 6-311G***) is 6414 cm⁻¹ above the experiment. The (*NDOL | MP2/6-311G***) vertical transition is much nearer to the experimental value. It must be pointed out that geometry differences are not large among S₀, S₁ and T₁ states of planar stable forms of glyoxal^{35,36} (see table 2), and consequently, adiabatic and vertical values must be similar. NDOL reverses the tendency giving the lower value to the *trans* isomer. In this particular respect, CIS calculations are plausible, as well as in differences between *cis* and *trans* transitions (theory: 1370 cm⁻¹ vs. experiment: 1697 cm⁻¹). A remarkable success of CIS results is the ability to calculate values for adiabatic absorption transitions (between pure electronic states), given the electron excitation corresponding to the molecular geometry of the first excited singlet (S₁) and the ground state (S₀) geometry and relative energy.

Excited triplet state results are shown in Table 5. They are better described by CIS calculations, contrary to previous results. NDOL results are not shown because this theoretical method is not including exchange terms in constructing the CI matrix, due to the strict orthogonality imposed to basis functions. Therefore, there are no difference between singlet and triplet values when transitions are forbidden by symmetry, as all nπ* states are. Values of CIS options (*CIS-RHF 6-311G**/RHF 6-311G***), as shown in Table 5, are closer to the experimental value of 19197 cm⁻¹, or “only” 3575 cm⁻¹ above.

Table 5. Electron excitations to T1^a

	Vertical		Adiabatic		Observed
	<i>trans</i> ³ A _u	<i>cis</i> ³ B ₁	<i>trans</i> ³ A _u	<i>cis</i> ³ B ₁	
<i>CIS/6-311G** / 6-311G**</i>	23187	22131	22772	21386	19197
<i>CIS/6-311G** / MP2/6-111G**</i>	22120	21076			

a.- cm⁻¹

b.- ref. 3, p. 635, for adiabatic ³A_u ← ¹A_g. A value of 19205 cm⁻¹ has been reported more recently (ref. 33)

It is remarkable that differences in energies between *trans* and *cis* isomers are very reduced from the 4.09 kcal mol⁻¹ of the S₀[S₀] state (*MP2/6-311G***, table 1) or 5.43 kcal mol⁻¹ (6-

311G**, table 1), to $1.53 \text{ kcal mol}^{-1}$ (6-311G**, table 6) in the $S_1[S_1]$ state and $1.48 \text{ kcal mol}^{-1}$ (6-311G**, table 6) in the $T_1[T_1]$ state. This fact leaves only activation energies and lifetimes as the main factors determining the population of different isomers in the excited states. It also points to favour isomerisations within the potential surfaces of the excited states.

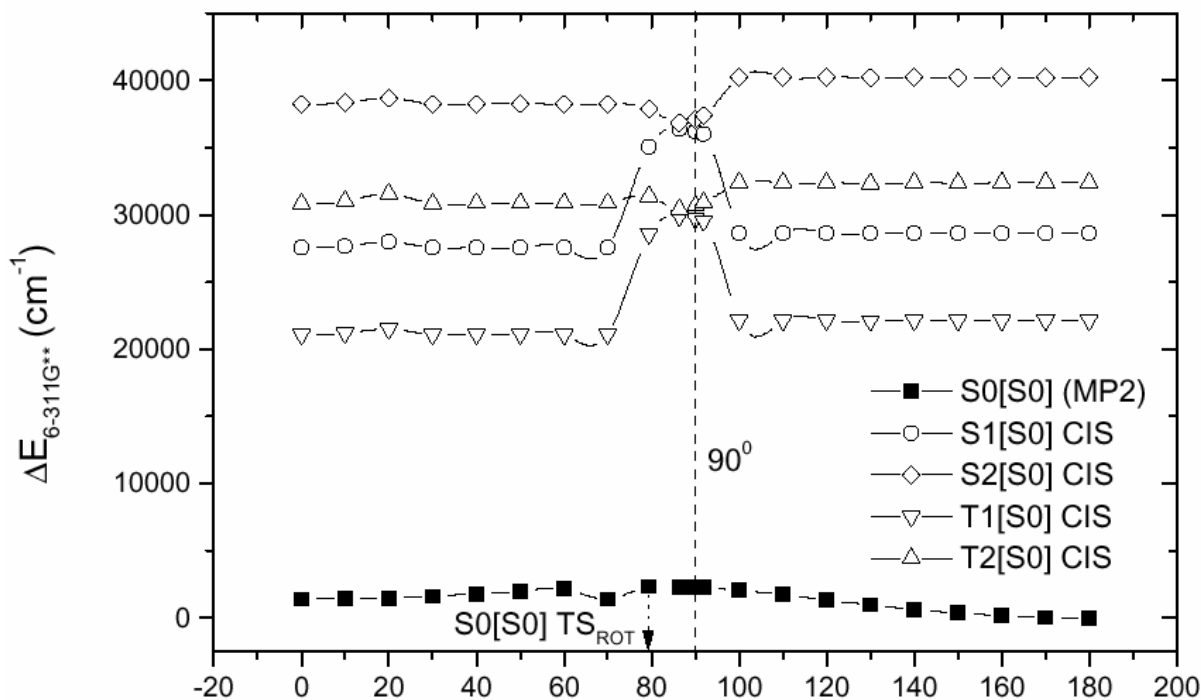


Figure 2. Scanning of ground state $S_0[S_0]$ and $n\pi^*$ excitations to $S_1[S_0]$, $S_2[S_0]$, $T_1[S_0]$, and $T_2[S_0]$ at the CIS/6-311G** | MP2/6-311G** level with respect to possible values of O-C-C-O torsion angle.

Fig. 2 shows a scanning of the main torsion angle ϕ_{OCCO} vs. relative S_0 ground state and corresponding vertical energies of S_1 , S_2 , T_1 and T_2 , at the S_0 geometry. The scanning was performed by relaxing to optimise all geometrical coordinates but the torsion angle at the RHF-MP2/6-311G** level, in steps of 10° each. An orbital analysis of calculated transitions shows that lower lying excited states are of $n\pi^*$ origin. Therefore, fig. 2 is a very descriptive graphics and show us the behaviour of all those excitations converging to degenerate, in their respective singlet and triplet manifolds at the point where CHO planes are perpendicular together, i.e. $\phi = 90^\circ$. Crossings in the region of $70 - 100^\circ$ indicate that in this very distorted geometries both near to degenerate triplets are lower than singlet states. It also would mean a very easy intersystem crossing upon internal rotation in excited species.

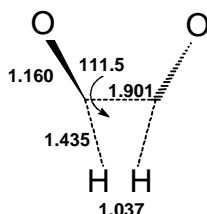
B. Transition state of the “triple whammy channel” (TS_{TWC}). The corresponding transition state (TS_{TWC}) was evaluated by shock wave experiments. The activation barrier in the low-pressure limit was $E_{a0} = 38.4 \text{ kcal mol}^{-1}$. The reported experimental activation energy, corresponding to the high-pressure limit, was $E_{a\infty} = 55.1 \text{ kcal mol}^{-1}$. The best photochemical yield was obtained after irradiation to the second harmonic of the torsional mode in the first

excited singlet state (7_0^2 of S1) and it is about 29 % higher than the one obtained upon excitation in the 0_0^0 of S1. It means a precise energy of $64.8 \text{ kcal mol}^{-1}$ after the very accurate experimental value of S1 that has been recently reported.

A very recent paper reports a non-planar TS_{TWC} , in the ground state, by Hartree-Fock and hybrid density functional methods with split valence and polarized basis sets [HF/3-21G, BH&HLYP/6-311G(d,p) and B3LYP/6-311G(d,p)] with a torsion angle between $90\text{-}110^\circ$ and an activation energy $\Delta E^\ddagger \approx 59.0 \text{ kcal mol}^{-1}$. This non-planar TS was also a logical conclusion of another very recent paper that finds a very abnormal behaviour if the reaction comes from the *cis* isomer population.

We carried out an independent calculation where such a non-*cisoid*, but *swinging*, TS_{TWC} was found and the internal reaction coordinate was followed in 41 steps. At this level of theory the reaction coordinate for the simple isomerisation shows a value of 78.1° (101.9° from the *trans* isomer) for the torsion angle in the corresponding transition state (TS_T), i.e. displaced to the *cis* (0°) side, as expected according to the Hammond postulate. The energy barrier height for interconversion is $6.20 \text{ kcal mol}^{-1}$ and the *trans* (180°) conformer is favored by $4.57 \text{ kcal mol}^{-1}$, in excellent agreement with the reported value of $4.45 \pm 0.14 \text{ kcal mol}^{-1}$ ¹³¹. According to a simple Boltzmann distribution, it means that the *trans* glyoxal isomer state is populated to 99.9 % at room temperature and, consequently, the *cis* isomer is quite absent and unable to be significantly excited by light. Therefore, any photochemical behaviour after a *cisoid* TS_{TWC} is very non-probable.

This *swinging* TS_{TWC} in S0 shows the following structure at our level of calculation:



where interatomic distances are in Ångstrom's and the torsion angle is 111.5° (68.5° from the *trans* isomer).

The reaction coordinate for the TWC is, mainly, the H-H distance. Our extensive calculation of such internal reaction coordinate pathway, with this basis set, took 55 days, 13 hours, 7 minutes and 19.5 seconds of a 350 MHz CPU time in an IBM-RS6000 workstation, without interruption. If we follow it from the very beginnings, fig. 3 depicts the process. Each point in both curves represents a calculated step in the reaction path. At 180° (i.e. the *trans* isomer), when the torsion starts, both hydrogen nuclei are separated by 3.161 \AA and the C-C bond length is 1.515 \AA . The true reaction path simulation begins at 114.1° (65.9° from the *trans* isomer). Hydrogen's are separated by 2.768 \AA at this point, although the C-C bond is only slightly stretched to 1.523 \AA . Then, the process goes steadily up to the swinging TS_{TWC} , with the above-mentioned geometry, and at $\Delta E^\ddagger = 64.2 \text{ kcal mol}^{-1}$ with respect to the *trans* isomer. This value is also in excellent agreement with the experimental finding of $64.8 \text{ kcal mol}^{-1}$ for the best photochemical yield, as mentioned above. It must be noticed that this barrier energy in the electronic ground state can be attained after light excitation to S1, because it corre-

sponds to $\approx 22500 \text{ cm}^{-1}$, that is above both experimental and theoretical vertical transitions of the $n\pi^*$ absorption. It means any kind of *in situ* $S0 \leftarrow S1$ internal conversion before for beginning the “triple whammy” reaction.

The reaction goes then forward by the H-H distance coordinate to converge in the H_2 molecule at 0.74 \AA , when the two carbon monoxide molecules are separated by the C---C distance of 2.409 \AA .

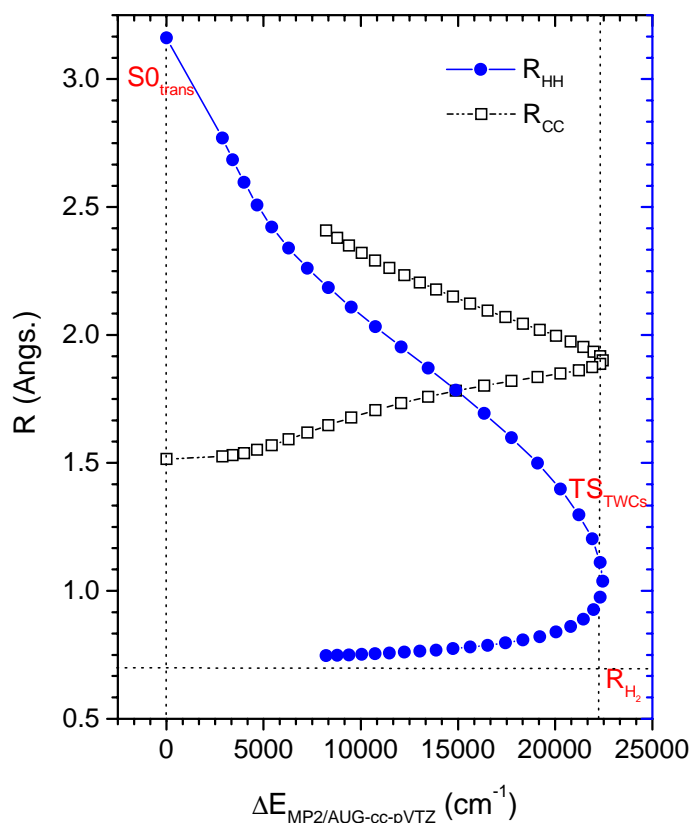


Figure 3. Internal reaction coordinate pathway as represented by the H-H distance. The graphic also shows the C-C distance as a measure of the molecule fragmentation.

11.4 Conclusions

Simple Hartree Fock calculations, even at the valence shell triple zeta with polarization 6-311G**, is not sufficient to reproduce the appropriate equilibrium energies in gas phase of this α di carbonyl compound. At least an MP2 correlation energy correction must be included to account all effects, over all in the *cis* isomer.

Ionization potentials, as obtained for vertical IP's from the Koopman's theorem, are not correctly predicted with high level calculations, although in this case the approximate HF NDOL theory predict them correctly. However, when adiabatic IP's are deduced from the dif-

ference of energies between the neutral form and the radical cation, the coincidence of theory and experiment is quite perfect.

The coincidence between absolute values for excitation energies as calculated by HF CIS procedures and experimental data is very poor. Normally, singlet transitions are overestimated for more than 6000 and triplets more than 3000 cm^{-1} . However, relative values are reliable. On the other hand, using accurately calculated geometries to obtain the HF NDOL vertical transitions approached much better the experimental absolute values.

As differences in energies between *trans* and *cis* forms in excited states are significantly lower than the ones in ground state, it remains only the activation energies and the lifetimes as the main factors determining the population of different isomers in the excited states. It also points to favour isomerisations within the potential surfaces of the excited states. However, the existence of a *swinging* transition state in the ground state has been modelled by theoretical means, in contraposition to the former theoretical model of a *cisoid* TS. The energy value of TS $\Delta E^\ddagger = 64.2 \text{ kcal mol}^{-1}$ is in excellent agreement with the experimental finding of 64.8 kcal mol^{-1} for the best photochemical yield. It must be noticed that this barrier energy in the electronic ground state can be attained after light excitation to S1, because it corresponds to $\approx 22500 \text{ cm}^{-1}$, that is above both experimental and theoretical vertical transitions of the $n\pi^*$ absorption. It means any kind of *in situ* $S_0 \leftarrow S_1$ internal conversion before for beginning the “triple whammy” reaction.

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