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Vibronic Coupling in Carbonyl Compounds*

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The vibronic coupling integrals for a series of molecules containing carbonyl groups (formaldehyde, glyoxal, biacetyl) have been evaluated in the "floating orbital" scheme. The expression of the normal coordinates necessary for the evaluation of such integrals has been obtained through a MINDO/3 procedure, whereas the electronic wave functions were of CNDO/S type. The role of the main vibrations active in the coupling between the various states has been individuated and discussed with respect to spectroscopic properties, such as the induced intensities of forbidden bands, and to photophysical properties, such as the non-radiative deactivation of the lowest singlet state.

INTRODUCTION

Vibronic coupling, i. e. the interaction between the vibrational and electronic motions of a molecule, is one of the key properties to a full understanding of the photophysical and photochemical behavior of chemical compounds. Recent development of sophisticated experimental techniques, such as time-resolved single level vibronic absorption and fluorescence spectroscopy, Raman resonance and two-photon excitation spectroscopy has provided detailed information on the excited states of molecules and their coupling through vibrational modes. Two classes of organic molecules have been thoroughly examined: the alternant conjugated aromatics and the heteroaromatics. Both these classes of compounds have low-lying, weakly absorbing states because of symmetry reasons (the former) or because of orbital momentum (the heteroaromatics with the lowest singlet of $n\pi^*$ nature) and their transitions often appear dominated by vibronic borrowing from higher, strongly allowed $\pi\pi^*$ states. The main manifestations of vibronic coupling in radiative processes are the appearance of false origins of non-totally symmetric bands, of combination bands and change of frequency due to the distortion of the potential surfaces in the excited states. The influence of vibronic coupling in non-radiative processes is revealed by dependence of the lifetimes of the excited states on the pressure, solvent, temperature and the position of the substituents.

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Various theoretical frameworks have been developed in order to explain the physical effects of vibronic coupling. Among the most recent ones are the theory of Siebrand and coworkers[1], who stressed the importance of non--Condon effects in the treatment of such properties, and the theory of Lim and coworkers[2] who applied a quantum-statistical approach to the coupling of close excited states of $n\pi^*$ and $\pi\pi^*$ nature in the heteroaromatics (the so-called proximity effect). However, these schemes assumed the values of the vibronic integrals from experimental data or introduced them as variable parameters in the theoretical framework without direct numerical calculations.

In this paper we present a calculation of vibronic integrals of a series of well-individuated mono-carbonyl compounds (formaldehyde) and α-dicarbonyl compounds (glyoxal and biacetyl). The goal of this work is to provide a set of numerical estimates for the main vibronic terms and to investigate the role of the various vibrations in the processes of radiative and radiationless deactivation of the lowest excited states of carbonyl compounds.

PROCEDURE

The adiabatic and non-adiabatic vibronic coupling integrals can be expressed respectively by

$$V^{A}{}_{ab} = < \partial < \psi_a \,|\, H(Q) \,|\, \psi_b > \partial Q >_o \approx \; < \chi_a \,|\, < \varphi_a \,|\frac{\partial H}{\partial Q}|\, \varphi_b > Q \,|\, \chi_b > \tag{1}$$

$$V^{NA}{}_{ab} = \frac{< \psi_a \,|\, -\partial^2/\partial Q^2 \,|\, \psi_b >}{E_a - E_b} = V^{A}{}_{ab} \frac{\hbar\,\omega(Q)}{E_a - E_b} \tag{2}$$

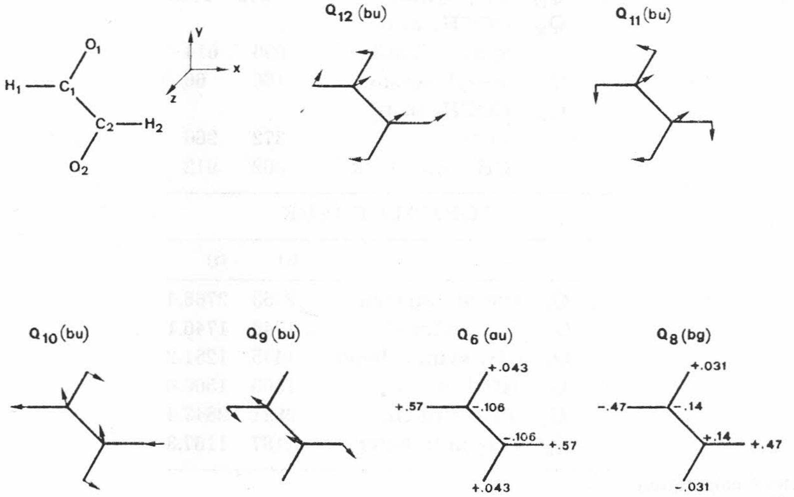
and their evaluation appears necessary for the induced transition moment

$$M^{i}(S_1, S_o) = \Sigma_i \, V^{A}{}_{1i} \, m_\alpha (S_i, S_o) \, \Delta E^{-1}{}_{1i} \tag{3}$$

where $m_\alpha (S_i, S_o)$ is the dipole moment along the α direction for the transition $S_o \longrightarrow S_i$, and ΔE_{1i} is the energy gap. On the other hand, the rate constant of internal conversion can be expressed through the Fermi's folden rule:

$$K^{ic} = \frac{2\pi}{\hbar} \,|\, V^{Na} \,|^2 \, \varrho \tag{4}$$

where ϱ is the density of states in the final manifold. A convenient method for evaluating the integrals in (1) and (2) has been recently proposed[3] and tested[4] for several organic molecules with satisfactory results. This method, based on the »floating orbital« scheme, takes particular advantage from the use of semi-empirical wave-functions based on the ZDO approximation. In the present calculation the wave-functions used were of CNDO/S type with a configuration interaction limited to 50 monoexcited configurations. Doubly excited configurations were not included in the calculations because we dealt with monoelectronic properties and also because the results of previous calculations on the same molecule did not appear modified by this inclusion, apart from the remotion of degeneracy between singlets and triplets on $n\pi^*$ nature[5]. Since the evaluation of integrals in (1) and (2) requires the knowledge of the Cartesian displacements along the various normal coordinates, a full vibrational calculation on the molecules under examination was performed, using a MINDO/3 program[7] implemented by the algorithm of McIver-Kormonicki for the optimization of the geometry.[6] Although some frequencies calculated by this method show the well-known deviations from the experimental ones,[7] the quality of the Cartesian displacements so obtained is to be considered consistent with the degree of approximation of the whole calculation. The calculated frequencies of the molecules examined are reported in Table I, whereas in Figure 1 the most relevant modes of glyoxal are shown.



Calculated Cartesian displacements for the relevant normal modes of glyoxal (C_{2h}).

TABLE I

Calculated Frequencies for the Most Relevant Modes of Glyoxal, Biacetyl, and Formaldehyde

GLYOXAL

			a)	b)
b_u	Q_9	CH stretch	3269	2835
	Q_{10}	C=O stretch	1981	1732
	Q_{11}	CH rock	1247	1312
	Q_{12}	CCO bend	355	338
b_g	Q_8	CH wag	969	1048
a_u	Q_6	CH wag	698	801.4
	Q_7	CC torsion	121	126.7

BIACETYL

			a)	c)
b_u	Q_{22}	CH anti stretch	3463	3012
	Q_{23}	CH symm. stretch.	3485	2925
	Q_{24}	C=O anti stretch.	1942	1706

	Q_{25}	CH_3 anti def.	1377	1418
	Q_{26}	CH_3 symm. def.	1278	1350
	Q_{27}	C—CH_3 anti stretch.	1179	1131
	Q_{28}	CH_3 anti rock	939	953
	Q_{29}	$COCH_3$ anti bend	495	544
	Q_{30}	$COCH_3$ anti rock	240	257
b_g	Q_{19}	CH_3 symm.	919	1288
	Q_{20}	$COCH_3$ anti symm. bend	606	614
a_u	Q_{16}	acetyl torsion	160	66
	Q_{14}	$COCH_3$ o. p. bend	372	960
	Q_{13}	CH_3 anti rock	862	912

FORMALDEHYDE

			a)	d)
a_1	Q_1	symm. stretch.	2753	2766.4
	Q_2	C=O stretch.	1746	1746.1
	Q_3	CH_2 symm. bend.	1445	1251.2
b_1	Q_4	HCH bend.	1500	1500.6
b_2	Q_5	anti stretch.	2831	2843.4
	Q_6	CH_2 anti bend	1167	1167.3

a) MINDO/3 calculation.
b) Ref. 9b.
c) Ref. 17.
d) Ref. 18.

RESULTS

Glyoxal

Being the simplest α-dicarbonyl compound, glyoxal has been the subject of numerous experimental[8,9] and theoretical studies.[5] In Table II the ordering and symmetry of the relevant molecular orbitals and singlet excited states are reported the (forbidden ^1A_g states have been omitted). As far as the vibronic coupling is concerned, the experimental data indicate that the active vibrational modes are (see Table I):

a) Q_8 (b_g)which is responsible for the induction of in-plane intensity in the transition $S_o \longrightarrow S_1$ (^1A_u).
b) b_u vibrations which couple S_1 to S_2 and S_3 with different energy gaps.
c) a_u symmetry vibrations which are responsible for the internal conversion $S_1 \dashrightarrow S_o$ process.

The calculated vibronic terms for the relevant vibrational modes are reported in Table III and the results can be summarized as follows:

a) Vibronic coupling in the radiative transition $S_o \longrightarrow S_1$ (^1A_u).

This is an allowed out-of-plane (z) transition, with a very small oscillator strength ($\sim 6.10^{-5}$). Also, it can borrow intensity from allowed in-plane transitions, namely from the $S_o \longrightarrow {}^1B_u$ and $S_1 \longrightarrow {}^1B_g$, through the only vibration of b_g symmetry, Q_8. This mode appears prominent in the absorption spectrum,

TABLE II

Calculated Orbital Energies and State Ordering for Glyoxal and Biacetyl

— GLYOXAL —

MO	Type	Sym.	E (a. u.)	State	Sym.	ΔE (eV)	f
13	π^*	b_g	1.42	S_{14}	$B_u\,(\pi\pi)$	12.9	0.29 (x, y)
12	π^*	a_u	— 1.14	S_7	$A_u\,(n\pi)$	9.56	0.015 (z)
11	n_+	a_g	—12.73	S_6	$B_u\,(n\sigma)$	9.55	0.091 (x, y)
10	n_-	b_u	—14.72	S_5	$B_u\,(\pi\pi)$	8.74	0.81 (x, y)
9	π	b_g	—15.65	S_4	$A_u\,(\sigma\pi)$	8.18	0.024 (z)
8	π	a_u	—17.96	S_3	$B_g\,(n\pi)$	7.93	0.0
				S_2	$B_g\,(n\pi)$	3.98	0.0
				S_1	$A_u\,(n\pi)$	2.93	0.0001 (z)

— BIACETYL —

19	π^*	b_g	.0802	S_{13}	$B_u\,(\pi\pi)$	11.57	0.075 (x, y)
18	π^*	a_u	—.0194	S_7	$B_u\,(\pi\pi)$	9.24	0.091 (x, y)
17	n_+	a_g	—.4317	S_6	$A_u\,(n\pi)$	9.11	.0022 (z)
16	n_-	b_u	—.5153	S_5	$B_u\,(\pi\pi)$	8.73	.8126
15	π	b_g	—.5400	S_4	$A_u\,(\sigma\pi)$	8.27	0.0004
14	π	a_u	—.5768	S_3	$B_g\,(n\pi)$	7.80	0.0
				S_2	$B_g\,(n\pi)$	4.12	0.0
				S_1	$A_u\,(n\pi)$	2.88	$< 10^{-5}$

where its intensity amounts to 86% of the O——O band.[8] The induced intensity, build over the 8_o^1 false origin has a dipole transition moment given by:

$$M_{xy} = \sum_{i \in B_g} \frac{V_{oi}}{E_i} < {}^1B_g(i) \,|\, r \,|\, S_1 > + \sum_{j \in B_u} \frac{V_{1j}}{E_j - E_i} < S_o \,|\, r \,|\, B_u(j) > \tag{5}$$

where

$$V_{oi} = < \chi^0{}_o \,|\, < S_o \,|\, \frac{\partial H}{\partial Q_8} \,|\, {}^1B_g(i) > Q_8 \,|\, \chi^1{}_1 >$$

$$V_{1j} = < \chi^0{}_o \,|\, < S_1 \,|\, \frac{\partial H}{\partial Q_8} \,|\, {}^1B_u(j) > Q_8 \,|\, \chi^1{}_1 >$$

In the present case the main contributions arise from the states $i = 2, 3$ and $j = 5, 6, 14$. From the values reported in Table III, one can observe that the borrowed intensity is not given predominantly by one or two states, but arises from many contributions with substantial cancellations. It is interesting to note that the intense $S_o \longrightarrow S_5$ $(\pi\pi^*)$ transition is not the most important one in the borrowing. In fact it turns out that $S_o \longrightarrow S_6$ $(n\sigma^*)$ is even more important in view of the large vibronic coupling (3810 cm^{-1}). Also very large are the contributions coming from the $S_1 \longrightarrow S_2$ and $S_1 \longrightarrow S_3$ transitions, which sometimes are neglected because of the supposed large energy gap $E_3 - E_o$ and $E_2 - E_o$. The total borrowed intensity corresponds to an oscillator

TABLE III

Vibronic Coupling Terms (cm^{-1}) and Transition Moments (eÅ) of Glyoxal and Biacetyl

GLYOXAL

b_g (Q_8)				
$V_{0,2}$	1462	$r_{1,2}$	—.157(x);	.452(y)
$V_{0,3}$	464	$r_{1,3}$	—.099(x);	—.765(y)
$V_{1,5}$	526	$r_{0,5}$	.359(x);	—.965(y)
$V_{1,6}$	3810	$r_{0,6}$	—.281(x);	—.175(y)
$V_{1,14}$	360	$r_{0,14}$	.416(x);	.287(y)

b_u	Q_9	Q_{10}	Q_4	Q_{12}
$V_{1,2}$	—173	—346	—260	— 108
$V_{1,3}$	191	1468	—486	—1364

a_u	Q_6
$V^{Na}{}_{0,1}$	119

BIACETYL

b_g (Q_{20})				
$V_{0,2}$	—1485	$r_{1,2}$	.158(x);	—.418(y)
$V_{0,3}$	— 203	$r_{1,3}$	.145(x);	.973(y)
$V_{1,5}$	878	$r_{0,5}$	.537(x);	—.879(y)
$V_{1,7}$	2109	$r_{0,7}$	.254(x);	.214(y)
$V_{1,13}$	— 987	$r_{0,13}$	.01265(x);	—.272(y)

b_u	Q_{24}	Q_{25}	Q_{26}	Q_{27}	Q_{28}	Q_{29}	Q_{30}
$V_{1,2}$	— 244	—162	—178	—87	298	93	214
$V_{1,3}$	—1661	26	693	1	—449	—829	143

a_u	Q_{14}	Q_{13}
$V^{NA}{}_{0,1}$	22	53

strength of 5.1×10^{-5} compared to the allowed one of 6.0×10^{-5}. The absolute values and especially the ratio between the values compare well with the experimental values of absorption intensity and radiative lifetime.[8]

b) Coupling of S_1 (^1A_u) with S_n (^1B_g) through b_u vibrations.

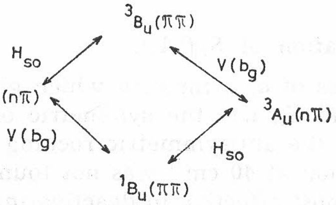
Strong coupling of S_1 with close lying excited states may have the effect of distorting potential energy curves thus enhancing the radiationless decay $S_1 \rightsquigarrow S_o$. This occurs when vibronic coupling is of similar size as $E_n - E_1$. In glyoxal the next two states, S_2, S_3, both of B_g symmetry, are by 1.04 and 5.0 eV higher than S_1, respectively. The results of the coupling brought about by the four b_u vibrations are also reported in Table III. We note that large vibronic coupling terms are found only for $V_{1,3}$ in correspondence with a larger energy gap (5 eV). The values for $V_{1,3}$ however, are much smaller as they are never larger than 5% of the energy gap $E_2 - E_1$. Thus, one can conclude that these couplings do not distort appreciably the potential energy curve of S_1.

c) Radiationless transition S_1 (^1A_u) $\rightsquigarrow S_o$ induced by a_u vibrations.

There are two vibrations of a_u symmetry: the CH wag (Q_6) and the torsion around the C—C bond (Q_7). The latter is unlikely to give rise to large vibronic coupling because of its low frequency. The mode Q_6 gives rise to $V_{0,1} = 3495$ cm^{-1} which corresponds to a non-adiabatic coupling

$$V^{NA}_{01} \equiv < \chi_o \,|< S_o \,| \frac{\partial}{\partial Q_6} \,| S_1 > \frac{\partial}{\partial Q} \,| \chi_1 > = V_{01} \frac{\hbar \omega}{E_1 - E_o} = 119 \text{ cm}^{-1}$$

This coupling, which is reasonably large, is responsible for the internal conversion to the ground state and can also affect the potential energy surface of S_1. However, time resolved single level fluorescence spectra[10] show that the frequency of Q_6 decreases in S_1 of 10% with respect to S_o, indicating that the vibronic coupling with upper states can be more important in distorting the surface of S_1 along this coordinate. Another channel of radiationless deactivation of S_1 is the intersystem crossing to the low-lying triplet states. According to the experimental results,[8] Q_8 appears to enhance the non-radiative decay of S_1. The channels for this decay should involve intermediate states of $\pi\pi^*$ nature (large spin-orbit coupling) and vibronic coupling both in the singlet or in the triplet manifold. Two possible schemes of the isc process induced by Q_8 (b_g) are:



Since the CNDO/S method is not able to distinguish between singlets and triplets of $n\pi^*$ nature it appears that a more refined treatment is necessary in order to evaluate the two different mechanisms. Moreover, other channels of deactivation of S_1 (^1A_u) are possible in molecules of C_{2h} symmetry through a_u vibrations as indicated by Drent and Kommandeur.[11] A more complete calculation including the H_{so} integrals for glyoxal and biacetyl is now in progress in this Institute.

Biacetyl

The calculated energies of singlet states, oscillator strengths and orbital ordering for biacetyl (C_{2h}) are reported in Table II, whereas in Table I the most relevant vibrations are shown. The PES data[11] show that the three highest bands appear at 9.55, 11.46, and 13.00 eV. This suggests the correlation $9.55 \longrightarrow n_+$; $11.46 \longrightarrow n_-, \pi_9$; $13.00 \longrightarrow \pi_8$. As for glyoxal, the most relevant vibrations for the vibronic coupling are of b_g, b_u and a_u symmetry.

a) Vibronic coupling in the radiative transition $S_o \longrightarrow S_1$ (^1A_u).

The absorption spectrum of this molecule in the visible region shows two main bands occurring at 437 and 490 nm, which have been attributed to the $S_o \longrightarrow S_1$ (^1A_u) and $S_o \longrightarrow T_1$ (^3A_u) transitions, whereas a band at 450 nm was preferably attributed to the transition $^1B_1 \longleftarrow {}^1A_1$ of the cis isomer.[12] Both the absorption bands of the trans biacetyl show false origin due to the vibronic borrowing of a b_g vibration at 530 cm^{-1} and to a lesser extent of

$Q\,(b_g)$ at 1315 cm^{-1}. The activity of the former mode is also present in the fluorescence spectrum (at 615 cm^{-1} in the ground state) and appears analogous to Q_8 of glyoxal. Indeed the calculated values of vibronic coupling for $Q_{20}\,(b_g)$ (Table III), parallel those found for glyoxal and the same conclusions can be drawn for this vibration. Moreover the activity of a mode at 517 cm^{-1} in the spin forbidden transition $S_o \longrightarrow {}^3A_u$ suggests that among the out-of-plane vibrations (b_g and a_u) Q_{20} is the most effective in the borrowing both in the spin allowed and spin vibronic processes.

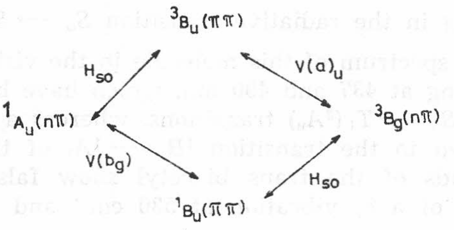
b) Coupling through b_u vibrations.

The coupling of S_1 with $S_2\,(b_g)$ and $S_3\,(b_g)$, lying at 1.24 and 4.92 eV higher than S_1 respectively, can occur through 9 b_u vibrations, as reported in Table I. As observed for glyoxal, the coupling $V_{1,3}$ is generally larger than $V_{1,2}$ and the vibrations most active are the skeletal modes Q_{24} (C=O stretching), Q_{29} (CCC bending) and the methyl deformation Q_{26}. Due to the large energy gap ΔE_{31}, the potential energy curve should not be affected by these couplings in the singlet manifold, whereas the coupling through b_u vibrations could result more effective in the triplet manifold where the presence of two close lying triplets of A_u and B_g symmetry ($\Delta E \simeq 2500$ cm^{-1}) has been inferred by several authors.[11,13]

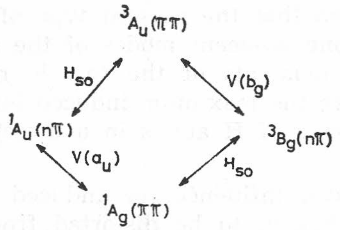
c) Radiationless deactivation of $S_1\,({}^1A_u)$.

There are two modes of a_u symmetry which give a sizeable non-adiabatic coupling between S_o and S_1, i. e. the symmetric out-of-plane bending of the $COCH_3$ groups (Q_{16}) and the antisymmetric rocking of the methyl groups (Q_{13}), (the other torsional motion at 40 cm^{-1} was not found effective in this process). The latter appears the most effective in deactivating S_1 *via* internal conversion and indicates that modes other than the skeleted ones (and especially the methyl group motions) can be active in the radiationless deactivation of S_1 in biacetyl.

The other important channel of deactivation of S_1, i. e. the intersystem crossing to a low-lying triplet of $\pi\pi^*$ nature, has been studied in detail by several authors,[11,13] who pointed out that more than one triplet seems involved in the process. In order to explain the small molecule behavior of biacetyl below excitation energies of 22500 cm^{-1}, a four-level scheme based on two singlets (${}^1A_u$ and ${}^1B_g$) and two triplets (${}^3A_u$ and ${}^3B_g$) has been proposed on the basis of the pressure dependence of the phosphorescence lifetime.[11b] The presence of a low-lying, strongly interacting triplet of B_g symmetry has been successively confirmed by Kaya et al.[13] by photoacoustic measurements. If this is the case two other mechanisms involving out of plane modes of b_g and a_u symmetry and the ${}^3B_g$ as final state could be competitive with mechanism (6), i. e.:



and



Formaldehyde

The ordering of singlet excited states of formaldehyde (C_{2v}) is reported in Table IV, whereas in Table V the calculated vibronic terms and induced intensities are shown. Among the three coordinates which can induce intensity to the transition $S_0\,(^1A_1) \longrightarrow S_1\,(^1A_2)$, $Q_4\,(b_1)$ out of plane bending which couples prevalently $^1A_2$ with $S_4\,(^1B_2)$ is the most relevant and brings about 70% of the total induced intensity along the y direction. The other two active vibrations are $Q_5\,(b_2)$, in plane antisymmetric stretching and $Q_6\,(b_2)$, antisymmetric bending, which induce intensity along the out of plane direction. These interactions are found to mix S_1 not only with the next S_2 state, but also with upper excited states: in fact the moment induced by Q_5 appears larger than that of Q_6, although $V_{1,2}\,(Q_6) > V_{1,2}\,(Q_5)$. The resulting induced moments are in satisfactory agreement both with the experiment[14] and more accurate cal-

TABLE IV

Calculated Singlet and Triplet Energies for Formaldehyde

FORMALDEHYDE

T_1	$A_2(n\pi)$	3.78	S_1	$A_2(n\pi)$	3.78	0.0
T_2	$B_2(\pi\pi)$	6.58	S_2	$B_1(n\pi)$	9.15	0.0103(z)
T_3	$B_2(\pi\pi)$	8.84	S_3	$B_2(\pi\pi)$	9.67	0.3344(x)
T_4	$B_1(n\pi)$	9.1	S_4	$B_2(\pi\pi)$	9.75	0.0731(y)
T_5	$B_2(\pi\pi)$	11.47	S_5	$B_1(\sigma\pi)$	12.19	0.0475(z)

TABLE V

Vibronic Coupling Terms for Formaldehyde (cm⁻¹) (The Last Three Lines Show the Induced Moments of Formaldehyde)

FORMALDEHYDE

$b_1\,(Q_4)$		$b_2\,(Q_5)$		$b_2\,(Q_6)$	
$V_{1,4}$	—455	$V_{1,2}$	48	$V_{1,2}$	—338
$V_{1,7}$	16	$V_{1,12}$	198	$V_{1,12}$	—294

M^{ind} %	a	b	c
$Q_4\,(b_1)$	72	66	66
$Q_5\,(b_2)$	27	26	21
$Q_6\,(b_1)$	<1	6	13

a) This calculation
b) Experimental, ref. 14.
c) *Ab initio* calculation, ref. 15.

culations[15] for Q_4 and Q_5, while the activity of Q_6 appears underestimated However, it is well known that the present type of calculation is subject to transfer of intensity among adjacent modes of the same symmetry.[16] Recent analysis of the induced moments of the two b_2 modes has shown that a description suitable to give the maximum induced intensity in the b_2 subspace would require displacements of H atoms in a direction perpendicular to the C=O group.[14]

Other factors wich can influence the induced moment distribution are the geometry, which is known to be distorted from planarity in the state $^1A_2$, and mixing of the coordinates in the excited state through the Duschinski effect.

CONCLUSION

In this paper we have presented a set of numerical results on the vibronic coupling integrals of three carbonylic compounds. The main vibrations responsible for induction of intensity in the absorption and emission spectrum were individuated and preliminary indications on the role of the modes in the radiationless transitions were drawn. While in formaldehyde the out-of-plane vibration was found dominating in the vibronic borrowing, in α-dicarbonyls the presence of in plane coupling between states of $n\pi^*$ nature can complicate the description of the channels of deactivation of S_1. Moreover, in biacetyl the methyl group appears to play a role in the photophysical processes, thus differentiating this molecule from the simplest term of the series, glyoxal. It turns out that the photophysical deactivation of S_1 in α-dicarbonyls is a multi-channel process and that a correct description of the phenomenon requires an accurate location of the levels and an appropriate evaluation of the spin-orbit and vibronic interactions. However, the method presented here, based on two relatively simple methods, such as MINDO/3 for the normal coordinates and CNDO/S for the vibronic integrals, appears to give a reasonable description of all the quantities under examination and allows the first interpretative steps of the photophysics of an important class of organic molecules such as the carbonyl compounds.

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SAŽETAK

Vibronsko sprezanje u karbonilnim spojevima

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Integrali vibronskog sprezanja za niz molekula koje sadrže karbonilne grupe (formaldehid, gliksal, biacetil) procijenjeni su prema obrascu »plutajućih orbitala«. Izraz za normalne koordinate, nužne za procjenu takovih integrala, dobiven je MINDO/3 postupkom, dok su elektronske valne funkcije bile CNDO/S tipa. Izdvojena je i razmatrana uloga glavnih vibracija aktivnih u sprezanju s obzirom na spektroskopska svojstva, kao što su inducirani intenziteti nedozvoljenih vrpci, i s obzirom na fotofizička svojstva, kao što je deaktivacija najnižeg singletnog stanja bez zračenja.