

## A QUANTUM MECHANICAL ANALOGUE OF THE STERN-VOLMER EQUATION

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We discuss the role of interference effects in intramolecular electronic energy quenching of an excited electronic state of a large molecule. For a small electronic energy gap the Stern-Volmer relation is obtained in the limit of strong coupling, while in intermediate cases the (pressure dependent) quantum yield may exhibit a minimum. This prediction was experimentally verified for the radiative decay of the singlet excited state of biacetyl.

## 1. INTRODUCTION

The classical Stern-Volmer (SV) equation which is widely utilized to account for electronic energy quenching,

$$Y = \left(1 + \frac{k_q}{k_f}[Q]\right)^{-1} \quad (1)$$

relates the emission quantum yield  $Y$ , the quenching rate constant  $k_q$ , the quencher concentration  $[Q]$  and the "pure" radiative lifetime  $(k_f)^{-1}$ . In this note, we present a quantum mechanical electronic energy quenching scheme, which yields the SV relation as a limiting case, and discuss the role of interference effects which will yield interesting deviations from the classical behaviour.

## THE TWO-LEVELS SYSTEM

We consider strong interstate coupling within a small polyatomic molecule, or between two excited electronic states of a large molecule which are separated by a small energy gap. It is well known [1] that no electronic relaxation will be induced by strong coupling between a small number of vibronic levels within an "isolated" (collision free) molecule in the low gas phase. The lower electronic manifold  $\{|l_j\rangle\}^*$  cannot act as a dissipative quasicontinuum. When this molecule

is externally perturbed by an inert gas, the electronic (non-radiative) relaxation characteristics of any  $|si\rangle$  level in the higher excited electronic state will be determined by a consecutive decay mechanism [2] through the  $|lj\rangle$  states. Collisions which occur during the lifetime of the excited state provide a vibrational relaxation broadening mechanism for the  $|lj\rangle$  states, whereupon at finite  $[Q]$  the fluorescence quantum yield will be reduced relative to unity and the experimental fluorescence decay pattern will be modified. These features pertain to the occurrence of electronic relaxation in the externally perturbed "small" molecule.

As the density of strongly coupled states in the  $|l\rangle$  manifold which are approximately degenerate with a given  $|si\rangle$  level is low for a "small" molecule\*\*, we can reasonably consider a simplified model which consists of two strongly coupled vibronic-levels system (fig. 1). A single vibronic level,  $\phi_s$ , of the higher electronic state

\*  $l$  and  $s$  will denote the lower and the higher electronic levels, while  $j$  and  $i$  refer to the vibronic components of these levels, respectively.

\*\* In what follows we assert that the small molecule case is exhibited also by an excited state of a large molecule characterized by a small effective energy gap. In this case, we have to allow for strong coupling of  $\phi_s$  with a small number of  $\phi_l$  states (or a single  $\phi_l$ ) and weak coupling with a large number of  $\phi_l$  states (or a single  $\phi_l$ ) and weak coupling with a large number of  $\phi_l$  states.

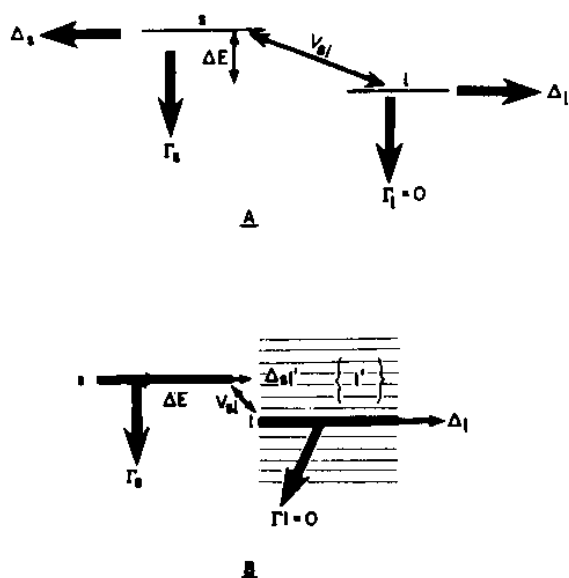


Fig. 1. A schematic representation of the two relevant vibronic levels and their decay widths. A. The two level model system. B. Interstate coupling in an excited state of a large molecule characterized by a small energy gap.  $|s\rangle$  is strongly coupled with  $|l\rangle$  and weakly coupled with the manifold  $\{|l'\rangle\}$ . The latter coupling may provide a width  $\Delta_{sl}$  to the nonradiative decay of  $|s\rangle$ .

$|s\rangle$  is active both in absorption and in emission from the ground state by a total radiative width  $\Gamma_s$  [the "pure" radiative lifetime obtained from the integrated oscillator strength being  $(\Gamma_s)^{-1}$ ]. The other zero order level,  $\phi_l$ , of the lower electronic state  $|l\rangle$  is optically inactive, i.e.  $\Gamma_l = 0$ . This situation is well documented in real life provided that the  $|s\rangle$  and  $|l\rangle$  states of the "small" molecule correspond to a singlet and to a triplet state respectively\*. The time evolution of the compound state of the system  $\Psi(t) = C_s(t)\phi_s + C_l(t)\phi_l + \dots$  can be represented within the framework of the Wigner-Weisskopf approximation by the decay matrix [2, 3]

$$\begin{pmatrix} E_s - \frac{1}{2}i\gamma_s & v_{sl} \\ v_{ls} & E_l - \frac{1}{2}i\gamma_l \end{pmatrix}, \quad (2)$$

with the initial condition  $C_s(0) = 1$ . Here  $E_s$  and  $E_l$  correspond to the energies, while  $\gamma_s = \Gamma_s + \Delta_s$  and  $\gamma_l = \Delta_l$  represent the widths of the zero order states  $\phi_s$  and  $\phi_l$ , respectively.  $\Delta_s$  is the nonradiative width of the  $\phi_s$  state, which can arise from electronic relaxation to the ground

\* The extension of the argument with the initial condition  $C_s(0) = 1$  for finite  $\Gamma_l$  is straightforward [2] and is of interest when the  $|l\rangle$  state corresponds to a singlet state which decays radiatively to the higher vibronic components of the ground electronic state.

state, to a weakly coupled dense manifold  $\{\phi_{l'}\}$  corresponding to the excited state (but not to the strongly coupled level  $\phi_l$ ) and from vibrational relaxation (if  $\phi_s$  is not the vibrationless level).  $\Delta_l$  represents the nonradiative width of the  $\phi_l$  zero order state which again can arise from the contribution of vibrational relaxation within the  $|l\rangle$  manifold and from electronic relaxation to the ground state.  $v_{sl}$  represents the nonadiabatic coupling matrix element between the states  $\phi_s$  and  $\phi_l$ .

### 3. CHARACTERISTICS OF THE RADIATIVE DECAY

The differential photon counting rate  $\dot{P}(t)$  integrated over the whole energy region is [2]

$$\dot{P}(t) = \Gamma_s |C_s(t)|^2 \quad (3)$$

while the quantum yield,  $Y$ , for emission is given by

$$Y = \int_0^\infty dt \dot{P}(t) = \Gamma_s \int_0^\infty |C_s(t)|^2 dt. \quad (4)$$

An explicit solution of these equations can be recast in the form [2]

$$\begin{aligned} \dot{P}(t) &= \Gamma_s |C_s(t)|^2 \\ &= \Gamma_s \{ (a^2 + b^2) \exp[-\gamma_1 t] + (c^2 + d^2) \exp[-\gamma_2 t] \\ &\quad - 2 \operatorname{Re}(a + ib)(c - id) \exp[-\frac{1}{2}(\gamma_1 + \gamma_2)t] \\ &\quad \times \exp[-i(\beta_1 - \beta_2)t] \} \\ &\quad \times \{ (\beta_1 - \beta_2)^2 + [\frac{1}{2}(\gamma_1 - \gamma_2)]^2 \}^{-1/2}, \end{aligned} \quad (5)$$

where  $\Delta E = E_s - E_l$ .  $\beta_1, \beta_2$  correspond to the energies while  $\gamma_1$  and  $\gamma_2$  represent the widths (reciprocal decay times) of the states which diagonalize the decay matrix and are given by

$$\beta_{1,2} = \operatorname{Re} \lambda_{1,2}; \quad \gamma_{1,2} = -2 \operatorname{Im} \lambda_{1,2}, \quad (6)$$

where

$$\begin{aligned} \lambda_{1,2} &= -\frac{1}{2} \{ \Delta E + \frac{1}{2}i(\gamma_s + \gamma_l) \\ &\quad \mp [(\Delta E + \frac{1}{2}i(\gamma_s - \gamma_l))^2 + 4|v_{sl}|^2]^{1/2} \} \end{aligned} \quad (7)$$

and the auxiliary terms in (5) are

$$\begin{aligned} a &= \beta_1 - \Delta E, & b &= \frac{1}{2}(\gamma_1 - \gamma_l), \\ c &= -\beta_2 - \Delta E, & d &= \frac{1}{2}(\gamma_2 - \gamma_l). \end{aligned} \quad (8)$$

The general expression [eq. (4)] for the quantum yield takes the form

$$Y = \left\{ \frac{a^2 + b^2}{\gamma_1} + \frac{c^2 + d^2}{\gamma_2} - 2\operatorname{Re} \frac{(a+ib)(c-id)}{\frac{1}{2}(\gamma_1 + \gamma_2) + i(\beta_1 - \beta_2)} \right\} \times \{(\beta_1 - \beta_2)^2 + [\frac{1}{2}(\gamma_1 - \gamma_2)]^2\}^{-1}. \quad (9)$$

Eqs. (8) and (9) display the features of the decay characteristic of the initially excited  $\phi_S$  state via direct radiative and electronic relaxation channels, and via coupling to an intermediate level which in turn decays nonradiatively by vibrational relaxation. These results lead to the following conclusions.

(a) The time resolved decay pattern will exhibit radiative interference effects provided that the spacing of the states which diagonalize the decay matrix is comparable to their mean width, i.e.

$$|\beta_1 - \beta_2| \approx \frac{1}{2}(\gamma_1 + \gamma_2). \quad (10)$$

Eqs. (6) and (7) then lead to the condition

$$\operatorname{Re}\{(\Delta E + \frac{1}{2}i(\gamma_S - \gamma_I))^2 + 4|v_{SI}|^2\}^{1/2} \approx \frac{1}{2}(\gamma_S + \gamma_I). \quad (10a)$$

Several physical situations can be visualized which satisfy the requirement for the observation of quantum beats

$$\Delta E \ll |v_{SI}| \approx \frac{1}{2}(\gamma_S + \gamma_I) \quad (11)$$

or alternatively

$$|v_{SI}| \ll \Delta E \approx \frac{1}{2}(\gamma_S + \gamma_I) \quad (12)$$

and finally

$$\Delta E \approx |v_{SI}| \approx \frac{1}{2}(\gamma_S + \gamma_I). \quad (13)$$

Relation (11) corresponds to the strong coupling situation (i.e.  $|v_{SI}| \gg |\Delta E + \frac{1}{2}i(\gamma_S - \gamma_I)|$ ) while relation (12) corresponds to the weak coupling limit (i.e.  $|v_{SI}| \ll |\Delta E + \frac{1}{2}i(\gamma_S - \gamma_I)|$ ). On the other hand, eq. (13) describes an intermediate coupling situation.

(b) No observable interference effects in the radiative decay will be encountered when the mean width of the independently decaying states considerably exceeds their spacing, i.e.

$$\gamma_S + \gamma_I \gg \Delta E, v_{SI}. \quad (14)$$

In this case, the decay will be fast on the time scale for the onset of the oscillation.

(c) Quantum beats will not be amenable to experimental observation when the level spacing considerably exceeds their mean width, i.e.

$$\gamma_S + \gamma_I \ll \Delta E, v_{SI}. \quad (15)$$

Under these circumstances, the fast oscillation will be averaged out by the measuring apparatus. (d) The quantum yield [eq. (9)] is not necessarily a monotonously decreasing function of the width  $\gamma_I$ . This conclusion is apparent from numerical calculations which demonstrate that for intermediate cases i.e.  $\Delta E \approx v_{SI} \approx \gamma_S \approx \gamma_I$ ,  $Y$  can exhibit a minimum. In this case the time resolved decay will exhibit interference effects in the vicinity of the minimum.

(e) The quantum yield is expected to exhibit the Stern-Volmer quenching equation in the strong coupling limit. When  $|v_{SI}| \gg |\Delta E + \frac{1}{2}i(\gamma_S - \gamma_I)|$  we have for eq. (8)  $a = -c = -v_{SI}$  and  $b = d = \frac{1}{2}(\gamma_S - \gamma_I)$  whereupon eq. (9) leads to

$$Y = \frac{\Gamma_S}{\gamma_S + \gamma_I}. \quad (16)$$

It is interesting to note that this relation exhibits a simple branching ratio. We shall now invoke the following assumptions: (1) the vibrational relaxation width  $\gamma_I$  is proportional to the concentration  $[Q]$  of the perturbing gas (which is valid for relatively low pressure gas phase quenching), i.e.  $\gamma_I = \Delta_I^0[Q]$ ; (2) the external perturber does not affect  $\gamma_S$ , i.e. vibrational relaxation of the  $\phi_S$  state is negligible\*. (This assumption is strictly valid for the vibrationless level of the  $|s\rangle$  state.) Eq. (16) can now be recast in the form

$$Y = \left[ \frac{\gamma_S}{\Gamma_S} + \frac{\Delta_I^0}{\Gamma_S}[Q] \right]^{-1}, \quad (16a)$$

which represents a somewhat more general Stern-Volmer relation allowing for additional nonradiative decay channels of  $\phi_S$ . Obviously, when  $\Delta_S = 0$ , i.e.  $\gamma_S = \Gamma_S$ , we retain eq. (1) in the strong coupling limit.

(f) It is interesting to note that the Stern-Volmer quenching relation which is exhibited in the strong coupling limit does not, in principle, exclude the occurrence of quantum beats in  $\dot{P}(t)$ .

Such a situation will be realized when

$$|\gamma_S - \gamma_I|, \Delta E \ll |v_{SI}| \approx \gamma_S + \gamma_I. \quad (17)$$

This condition can be satisfied only provided that  $\Delta E \ll \gamma_S \approx \gamma_I \approx |v_{SI}|$  and will be encountered only for a system which simultaneously satisfies the following severe restrictions: (1) near degeneracy of the zero order levels; (2) small nonadiabatic coupling (i.e.  $|v_{SI}| \approx \Gamma_S$ ); (3) a narrow range of  $\gamma_I$  values (i.e. over a small concentra-

\* Introduction of vibrational relaxation in the  $|s\rangle$  manifold will lead to considerable complications as it will connect states which can still decay radiatively and thus contribute to  $Y$ .

tion region of the perturber). It is highly improbable that these conditions will be realized in real life. We may thus conclude that in practice a two-levels system where the fluorescence quantum yield obeys the Stern-Volmer relation will not exhibit quantum radiative interference effects.

The simple model discussed herein is expected to be useful for the understanding of the radiative decay of collisionally perturbed small molecules and the lowest excited singlet state of a large molecule which is separated by a small energy gap from the lower lying triplet. Many heterocyclic molecules and carbonyl compounds correspond to the second case.

#### 4. MODEL CALCULATIONS

We have performed numerical calculations\* of the dependence of the fluorescence quantum yield [eq. (9)] on the width  $\gamma_l$  for the intermediate case ( $\Delta E \approx \nu_{sl} \approx \gamma_s$ ) and for the strong coupling situation. From the results displayed in fig. 2 we conclude that in the strong coupling [curve (1)] the SV relation is, of course, obeyed. On the other hand, in the intermediate case [curve (2)] the quantum yield exhibits an extremely interesting behaviour first decreasing at relatively low

\* We have chosen  $\gamma_s = \Gamma_s \approx 10^{-6} \text{ cm}^{-1}$  which corresponds to the radiative decay time of a spin allowed symmetry forbidden  $n-\pi$  transition.

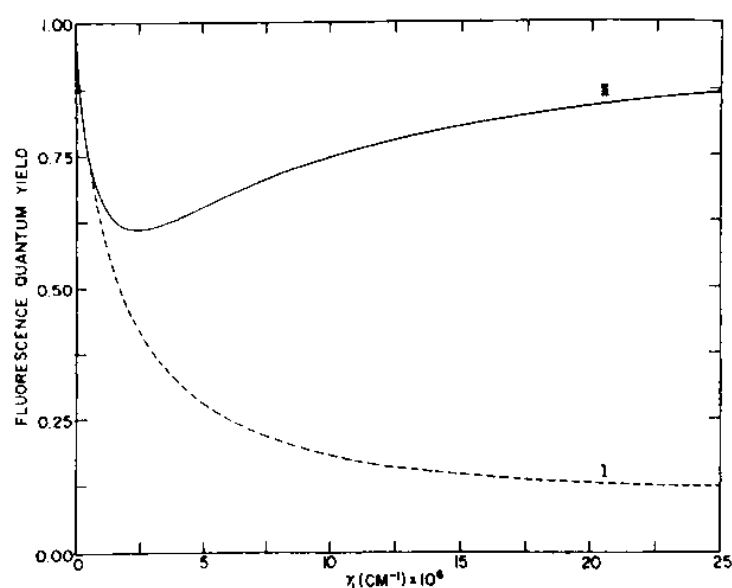


Fig. 2. Fluorescence quantum yield versus relaxation width of the  $l$ -level. I.  $\Delta E = \nu_{sl} = 1 \times 10^{-4} \text{ cm}^{-1}$ ;  $\gamma_s = 1 \times 10^{-6} \text{ cm}^{-1}$ . II.  $\Delta E = \nu_{sl} = 1 \times 10^{-6} \text{ cm}^{-1}$ ;  $\gamma_s = 1 \times 10^{-6} \text{ cm}^{-1}$ .

$\gamma_l$  values and subsequently increasing. The appearance of a minimum in the quantum yield curve in the intermediate case occurs when the energy parameters are so chosen that  $\gamma_1 + \gamma_2 \approx |\beta_1 - \beta_2|$  or  $\gamma_s + \gamma_l \approx \Delta E$  (fig. 2) which corresponds to the maximum overlap of the two levels\*\*. We may conclude that the increase of the quantum yield for larger  $\gamma_l$  in the region  $\gamma_s + \gamma_l > \Delta E$  is a pure quantum mechanical effect which could not have been explained classically. To demonstrate the role of radiative interference effects we present in fig. 3 the (normalized)  $\hat{P}(t)$  values [eq. (5)] calculated for the same energy parameters  $\Delta E$ ,  $\nu_{sl}$  and  $\gamma_s$  as used for curve (2) of fig. 2 and for selected values of  $\gamma_l$ . Curves (1) and (2) of fig. 3 satisfy eq. (13) and thus reveal quantum beats. Curve (3) satisfies relation (14) and does not reveal radiative interference effects, while the nonexponential decay curve (4) corresponds to the minimum of the quantum yield. We may thus conclude that in the intermediate case which exhibits a minimum in the  $Y - \gamma_l$  (or the  $Y - [Q]$  curve), quantum beats will be experimentally observed in the pressure region where the quantum yield decreases before reaching its minimum.

\*\* Comparing the condition  $\gamma_1 + \gamma_2 \approx |\beta_1 - \beta_2|$  with eq. (13) indicates that the minimum of  $Y$  corresponds to the onset of the erosion of observable quantum beats in the time resolved decay.

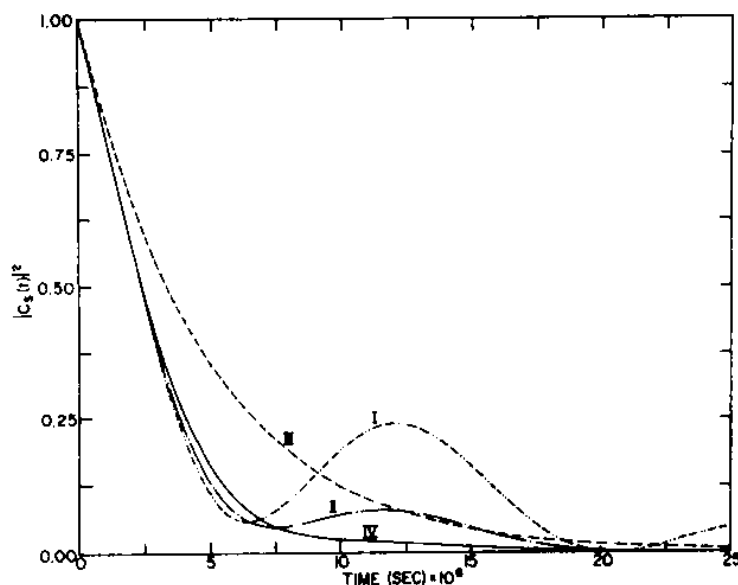


Fig. 3. Population in the  $s$  level,  $|C_s(t)|^2$ , versus time. I.  $\gamma_l = 1 \times 10^{-8} \text{ cm}^{-1}$ . II.  $\gamma_l = 1 \times 10^{-6} \text{ cm}^{-1}$ . III.  $\gamma_l = 1 \times 10^{-4} \text{ cm}^{-1}$ . IV.  $\gamma_l = 2.5 \times 10^{-6} \text{ cm}^{-1}$ .  $\gamma_s = 1 \times 10^{-6} \text{ cm}^{-1}$  in all cases.

## 5. EXPERIMENTAL VERIFICATION OF THE MINIMUM IN THE QUANTUM YIELD

A minimum in the fluorescence quantum yield was experimentally observed in the decay of the excited singlet state of biacetyl perturbed by He gas. The experimental procedure was similar to that previously employed for monitoring IR emission resulting from intersystem crossing in molecules [4]. The experimental setup consisted of a brightly polished aluminium sphere in which low pressure (0.05 torr) biacetyl, perturbed by He gas (0-6 torr), can be excited through a small aperture and the resulting fluorescence emission can be detected through another aperture. The low quantum yield ( $\approx 3 \times 10^{-3}$ ) of the biacetyl fluorescence requires a sensitive detection system described elsewhere [4]. Fig. 4a reveals the relative quantum yield of biacetyl fluorescence for excitation by the 4358 Å Hg line. No minimum is observed and a (low pressure) SV plot will result in a straight line. Fig. 4b exhibits the results of a similar experiment for excitation by the 4047 Å Hg line. A profound minimum in the fluorescence yield is observed. Excitation at 3650 Å results in a monotonously decreasing quantum yield with increasing He pressure which obeys the SV relation.

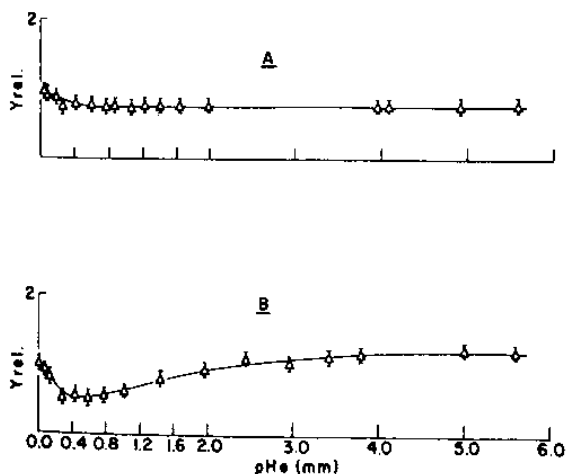


Fig. 4. Experimental relative fluorescence versus He pressure. A. for 4358 Å excitation. B. for 4047 Å excitation. The initial pressure of biacetyl is 0.05 mm in both cases.

## 6. CONCLUDING REMARKS

Approximate estimates of the total density of states,  $\rho$ , in the triplet manifold of biacetyl which are quasidegenerate with the lowest excited state indicate that for 4358 Å excitation  $\rho \approx 100/\text{cm}^{-1}$  [5] while for 4047 Å excitation  $\rho \approx 10^4/\text{cm}^{-1}$  [6]. One particular  $|si\rangle$  singlet

state will not couple to all these triplet states with the same efficiency, as the majority of states in the triplet manifold will be characterized by wrong symmetry and/or small Franck-Condon factors. The weakly coupled states  $|lj\rangle$  may provide a dissipative statistical decay channel characterized by the width  $\Delta_{sl} = 2\pi |v_{sl}| \rho_l$ . As is evident from eq. (9) this width will lead to the reduction of the overall quantum yield. Furthermore, within the excitation bandwidth not all  $|si\rangle$  will couple with the same efficiency. Those which dissipate effectively into the quasi continuum will give rise to a further reduction of the overall quantum yield. From the low pressure fluorescence spectra, evidence for the latter effect is obtained [6].

A small number of  $|lj\rangle$  levels will be strongly coupled to  $|si\rangle$  and may lead to interference effects. By performing a quantum yield experiment as a function of wavelength one will hopefully find some excitation energy for which the requirement  $\Delta E \approx \gamma_s \approx \gamma_l \approx |v_{sl}|$  is fulfilled for some (strongly coupled)  $|si\rangle$  and  $|lj\rangle$  pairs, and where a minimum in the pressure dependent quantum yield will be observed. The actual situation for biacetyl has been given in fig. 1b. The width  $\Delta_{sl}$  results from interaction between  $|si\rangle$  and the  $|lj\rangle$  manifold and is pressure independent. At low vibrational excitation in the singlet manifold we can neglect (pressure induced) vibrational relaxation between these states at the low pressures region employed herein (up to 5 mm He). The vibrational relaxation width  $\Delta_{ll'}$  originates from the relaxation between  $|lj\rangle$  and  $\{|lj'\rangle\}$  and since the vibrational excitation in the triplet is much higher than in the singlet manifold, the density of states is high there and the relaxation is pressure dependent.

An attempt was made to fit the experimental curve to the theoretical one. Good results are obtained with  $\Delta E = 3 \times 10^{-4} \text{ cm}^{-1}$ ,  $v_{sl} = 1.7 \times 10^{-4} \text{ cm}^{-1}$ ,  $\gamma_s = 10^{-4} \text{ cm}^{-1}$  ( $\Gamma_s = 10^{-6} \text{ cm}^{-1}$ ) and  $\gamma_l = 1.9 \times 10^{-3} \times (\text{pressure/torr}) \text{ cm}^{-1}$ . The quantity  $\gamma_s$  provides a good order of magnitude for the quantum yield ( $\approx 3 \times 10^{-3}$ ). The value of  $\gamma_l$  (which was chosen to fit the value of  $Y$  at the minimum) is somewhat larger than the value which corresponds to the simple gas kinetic collision frequency. The probability of meeting the condition  $\Delta E \approx v_{sl}$  depends on the density of states in the triplet manifold. At 4358 Å excitation the density of triplet states is too low and no interference effects are expected. On the other hand, for 4047 Å excitation the density of triplet states is  $\approx 10^4 \text{ cm}^{-1}$  and a single (or few) strongly coupled state(s) can presumably be lo-

cated sufficiently close to the  $|si\rangle$  level and a minimum will be exhibited in the quantum yield. Finally, at higher (3650 Å) excitation energy the density of states is high,  $\Delta E$  (average) is too low compared to  $\gamma_s$  and  $\nu_{sl}$  and the excited state will exhibit a normal SV quenching pattern [see eq. (16)].

We conclude that under appropriate conditions the minimum in the quantum yield, which is due to an entirely quantum mechanical effect, is amenable to experimental detection.

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