NONRADIATIVE RATES OF SINGLE VIBRONIC LEVELS IN BENZENE SINGLET STATE

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(Received 3 October 1983)

ABSTRACT — A tunnel effect theory is applied to the calculation of the rate constants for internal conversion $S_1 \rightsquigarrow S_0$ and intersystem crossing $S_1 \rightsquigarrow T_1$ of single vibronic singlet levels of C_6H_6. Coupling between the optically excited modes and the accepting CH modes was considered in terms of relative CH bond displacements. Within this model good agreement with experimental data was found. The dependence of the calculated internal conversion rates and the fluorescence lifetimes on the excess vibrational energy of the excited state supports the view that $S_1 \rightsquigarrow S_0$ via direct population of CH modes or of CC modes is responsible for channel 3.

1 — INTRODUCTION

Extensive calculations of the nonradiative rates of single vibronic levels (s. v. l.) of benzene S_1 state have been presented in the literature [1-4], owing to their relevance to the theories of radiationless transitions in large molecules. Freed and coworkers [1, 2] have employed a molecular compound state formalism and have essentially calculated the relative nonradiative rates as a function of vibrational energy. The rate of nonradiative transition between two single vibronic levels, s and l, for a state s in a vibrational level $\{ n_a \}$, is given by

$$k_{sl}(m_a) = (2\pi/\hbar)\,|C^k_{sl}|^2 \sum_{\{n_a\}} \prod_{a \neq k} |<m_a|n_a>|^2 \, I[\Delta E_{sl}(\{m_a\})]$$

where $\{ m_a \}$ are the possible sets of final levels, $I(\Delta E)$ is a density of states weighted Franck-Condon factor and C^k_{sl} is the matrix element for the promoting mode k . Since only relative rates for the $S_1 \rightsquigarrow T_1$ transition were calculated the matrix element C^k_{sl} was not determined [1]. However the experimental results show that intersystem crossing (i.s.c.) is not the only important channel of decay in the isolated molecules, but that there is also an internal conversion (i.c.) to the ground state, $S_1 \rightsquigarrow S_0$, even from the lowest excited vibronic levels [5]. Estimations of the matrix elements for the $S_1 \rightsquigarrow T_1$ and $S_1 \rightsquigarrow S_0$ transitions by Freed et al. [2] gave absolute rates two orders of magnitude smaller for i.s.c. and ten orders of magnitude smaller for the i.c. process. Therefore, although the theory has been able to estimate relative rates in good agreement with experiment, it has not been able to reproduce absolute rates and treat properly i.c. and i.s.c. in benzene S_1 state.

We have employed a tunnelling formalism [3, 4] for such calculations. However only the effect of excess vibrational energy was considered and there was no attempt to treat the nonradiative rates of selected s.v.l.. Here we intend to extend such studies to calculate nonradiative rates of i.c. and i.s.c. in selected s.v.l. in C_6H_6, by employing a tunnel effect theory. Recently Jortner and Ulstrup [6] have shown that for nonradiative transitions of a large electronic energy-gap the molecular compound state theories can be reduced to the tunnel effect formalism for the Franck-Condon factors and the preexponential factor is given by $2 \, | C^k_{sl} |^2 \hbar^{-1} \nu$, where ν is the frequency of an effective vibrational mode. Nevertheless since the multiphonon nonadiabatic transition theories of Jortner and Freed provide underestimates of absolute rates in spite of extensive and difficult calculations of the matrix elements, we will employ the tunnel effect theory in its complete formalism.

2 — TUNNEL EFFECT FORMALISM

The tunnel effect theory for radiationless transitions has been extensively described [3, 7]. Consequently here we will only present the formalism employed in the present calculations. In spite of the fact that benzene S_1 state, at low pressures (~ 0.1 Torr), is in a pseudostatistical situation with respect to i.s.c. [5, 8], theory shows that in a large isolated molecule the average singlet decay is exponential and pressure independent [9]. Therefore the nonradiative rates can be estimated as it were for a statistical case in i.s.c. and i.c..

Of all the vibrational modes of an aromatic molecule the CH modes are the ones of the smallest reduced mass and consequently are the ones that provide the highest tunnelling rates for weakly displaced oscillators. In a previous study we have considered that the excess of vibrational energy in benzene was redistributed statistically between all the vibrational modes. The effect of vibrational energies in the nonradiative rates was a consequence of the population of the CH modes in high vibrational levels. Such an approach is adequate when intramolecular vibrational relaxation is a process faster than the radiative and nonradiative transitions. However in an isolated molecule such as S_1 benzene such approach is no longer valid. Therefore, except where otherwise stated, we have considered the CH modes with zero point energy, since no direct excitation of the CH modes was experimentally achieved. The effect of the vibrational excitation of other vibrational modes on the CH modes was considered by studying the coupling of these modes with the CC modes. The displacement of the C atom during a CC stretching in the S_1 state leads to a change of equilibrium position of the CH bond in the excited state, with respect to the equilibrium position of the CC and the CH modes in the final state. Such a change of the relative equilibrium position can decrease the barrier width for tunnelling and consequently increase the rates of radiationless transitions. Thus the increase of vibrational energy in a CC mode is translated in a displacement of the potential energy curves of the CH modes.

In the present calculation all the vibrational modes were taken as anharmonic. The potential curves were considered as Morse curves

$$V(x) = D_e\,(1 - e^{-\beta x})^2 \tag{1}$$

where $V(x)$ is the potential energy for a bond extension or contraction, x. The effective potential energy curve for n identical oscillators [7] is considered for coordinates of a symmetric motion and therefore $\beta = n^{1/4}\ 1.2177 \times 10^7\ \omega\ \sqrt{\mu/D_e}$ where ω is the frequency of the oscillator, μ its reduced mass and D_e the dissociation energy. The relative displacement for the origin of the effective potential energy for n oscillators is given by [10]

$$R = [\sum_i (\Delta r_i)^2]^{1/2} \tag{2}$$

where Δr_i is the change in bond length between the initial and the final electronic states.

The nonradiative transitions are considered to occur via a quantum mechanical tunnelling of oscillators through an energy barrier of the effective potential energy curves in two electronic states. If reflections are ignored and within the WKB approximation, the rate of tunnelling of a particle through a potential energy barrier [3] is given by

$$k_{nr} = 4\, f\, \omega\, [\, (D - E_v)\, E_v \,/\, D^2 \,]^{1/2} \,. \tag{3}$$

$$\exp \left\{ - \frac{4\pi}{\hbar} \int_{x_1}^{x_2} 2\mu \, [\, D_e (1 - e^{-\beta (x-R)})^2 + \Delta E - D_e (1 - e^{-\beta x})^2 \,]^{1/2} \, dx \right\}$$

f is a forbidden factor which has an electronic (and vibronic) nature and is treated as an empirical parameter. The rates k_{nr} are estimated for the CH stretches which are the ones of highest frequencies and lowest reduced masses, and consequently are the modes which have the largest Franck-Condon factors. In eqn (3) D is the energy of the crossing point of the potential energy curves involved in the transition, E_v the vibrational energy and ΔE the difference in electronic energy between the two states; x_2 is the coordinate of the turning point in the final state, isoenergetic with the initial vibronic state and x_1 is equal to R plus the relative change of origin due the coupling of the CH and CC modes. Such a coupling depends on the nature of the CC modes of vibration. For the C stretch 1 mode the change in the CC bond length at the turning points of vibration is added completely to R (CH) since both stretches are colinear; for the 6 and 16 modes the change in length of the projection along the CH directions was considered.

The relevant parameter for the i.c. $S_1 \rightsquigarrow S_0$ and $S_1 \rightsquigarrow T_1$ transitions are $\Delta r_{CH} = 0.0014$ nm for $S_1 \rightsquigarrow S_0$ [11] and $\Delta r_{CH} = 0.0004$ nm for $S_1 \rightsquigarrow T_1$ [12] and according to eqn (2) for 6 oscillators

$$R_{S_1 \rightsquigarrow S_0} = 0.00343 \text{ nm} \,,\; R_{S_1 \rightsquigarrow T_1} = 0.00098 \text{ nm} \,.$$

The electronic energies are $E_{S_1} = 38200 \text{ cm}^{-1}$ and $E_{T_1} = 29000 \text{ cm}^{-1}$. The characteristics of the potential curves for i.c. and i.s.c. gave higher rates for the transitions on the repulsive part of the potential energy curves.

As we have previously stated the forbidden factors are treated as empirical parameters. They reflect the role of the promoting modes which are difficult to assess in a quantitative manner [1, 13]. Heller et al. [1] consider that the population of a promoting mode effectively reduces the true energy gap for the nonradiative transition increasing the nonradiative rate and tentatively they consider a reduction of $1500\,cm^{-1}$. However by the same reasoning the maximum Franck-Condon factor for the accepting modes would have been obtained with a large population of the promoting modes which reduces the effective energy gap to zero. However in their own way the promoting modes have Franck-Condon restrictions. Therefore we will not consider any reduction in the effective energy gap for the electronic transition between the different electronic states since the role of the promoting modes is treated empirically by a forbidden factor. For i.s.c. processes between π, π^* states in aromatic molecules the spin forbidden factor is typically of the order of 10^{-5} - 10^{-6}, as revealed by the phosphorescence and absorption spectra [14]. For i.c. process the forbidden factor can only arise by symmetry considerations and is generally very weak (ca. 10^{-1}). Nevertheless symmetry does not seem to play any significant role in nonradiative internal conversion processes [15]. The forbidden factors were estimated such that the i.s.c. and i.c. rates, together with the radiative rate constant $2.2 \times 10^6 s^{-1}$ [16], reproduce the triplet ($\phi_T = 0.70$) and i.c. ($\phi_{ic} = 0.08$) quantum yields, from the lowest vibrational level in S_1 [5] and its nonradiative rates [16]. The forbidden factors were for the zero level $f_{ic} = 0.57$, $f_{i.s.c} = 0.82 \times 10^{-5}$. A set of data was calculated for all the other s.v.l. with the same value of $f_{i.s.c}$ and for $f_{i.c} = 0.57$ and $f_{i.c} = 1.0$.

3 — RESULTS AND DISCUSSION

Table 1 presents the results of the calculations which reveal that a tunnel effect formalism is able to give a fair account (within ca 20 % error) of the absolute rates of the nonradiative transitions in C_6H_6 in terms of i.c. and i.s.c. . Depending on the nature of the populated modes the best agreement is obtained with $f_{ic} = 0.57$ (modes 6^m and $6^m\,1^n$) and with no forbidden factor for the 1^n and $1^n\,16^p$ modes. Comparison between this

TABLE 1 — Nonradiative Rates of Single Vibronic Levels in Benzene S_1 State.

Levels	Energy above origin (cm^{-1})	k_{ic} ($10^6\ s^{-1}$)		k_{isc} ($10^6\ s^{-1}$)	k_{nr} ($10^6\ s^{-1}$)		
		$f_{ic} = 0.57$	$f_{ic} = 1.0$		Calc.		Obs. [16]
					$f_{ic} = 0.57$	$f_{ic} = 1.0$	
0	0	0.8	—	7.0	7.8	—	7.8
6^1	521	1.6	2.8	7.7	9.3*	10.5	9.3
6^2	1042	3.2	5.6	8.4	11.6*	14.0	9.9
1^1	923	1.4	2.4	7.7	9.1	10.1*	9.5
1^2	1846	2.2	3.9	8.4	10.6	12.3*	13.5
1^3	2769	3.8	6.6	9.2	13.0	15.8*	18.9
$6^1 1^1$	1444	2.7	4.7	8.4	11.1*	13.1	11.1
$6^2 1^1$	1965	5.4	9.6	9.2	14.6*	18.8	12.8
$6^1 1^2$	2367	4.5	7.9	9.2	13.7*	17.1	15.2
$6^2 1^2$	2888	8.8	15.5	10.2	19.0*	25.7	20.8
$6^1 16^1$	764	1.7	3.1	7.7	9.4	10.7	9.6
$6^1 16^2$	1007	1.9	3.3	7.7	9.6	11.0	11.6
$6^1 1^1 16^1$	1687	2.8	5.0	8.4	11.2	13.4*	13.7
$6^1 1^1 16^2$	1930	3.1	5.5	8.5	11.5	14.0*	16.4
$6^1 1^2 16^1$	2610	4.8	8.5	9.2	14.0	17.7*	21.7
$6^1 1^3$	3290	16.6	29.0	11.0	27.6	40.0	—

* Values closer to experimental data.

calculation and previous approaches [1, 2] is not valid, because the other models were adjusted to reproduce relative rates in terms only of $S_1 \rightsquigarrow T_1$ i.s.c.. However we can compare our range of discrepancy with respect to the experimental data (1.23) to the ones of Heller et al. [1] (1.66); for the $6^m\ 1^n$ progression the highest discrepancy is 1.14 and 1.18 respectively.

The present calculations can be employed to discuss the controversial problem of the nature of channel 3 in C_6H_6 [2, 4, 15, 17-22]. Upon excitation at 240 nm the rates of nonraditive decay in benzene increase so much that fluorescence emission becomes very weak. Due to the very fast rates the initial lifetime data was obtained by measurement of linewidths [17]. Based on such data several explanations were proposed such as radiationless transitions to another state [4, 21] or simply an enhanced i.c. [18], although strong doubts were raised about the possibility of i.c. being able to interpret channel 3. However since factors other than population relaxation could contribute to line broadening such as internal vibrational randomization, the need for direct fluorescence measurements was necessary. Such experiments were carried out recently by employing very fast laser pulses [15, 20]. The lifetime measurements confirm the very fast rates of nonradiative decays in this region, but are not identical to the linewidth measurements of Callomon et al. [17].

Theories of radiationless transitions predict an exponential dependence of nonradiative rates with an increase on the vibrational energy, E_v, of the excited state [3, 6, 13] as Fig. 1 reveals. The

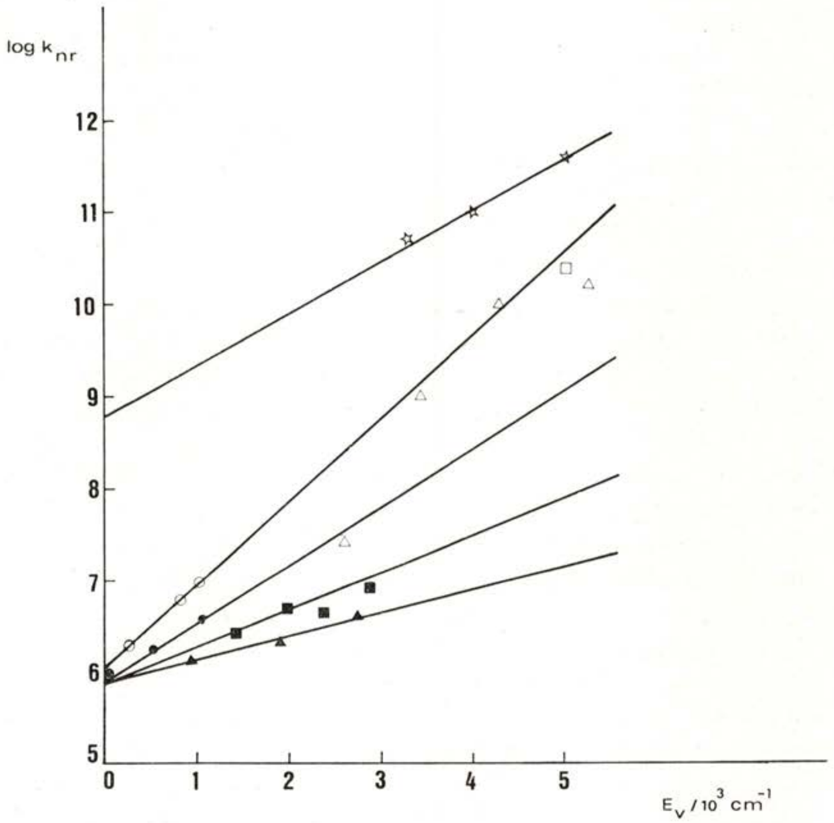

Fig. 1 — Vibrational energy dependence of the calculated i.c. rates ($f_{i.c.} = 0.57$) and channel 3 data: (●) 6^m, (■) $6^m\ 1^n$, (▲) 1^n, (○) $7^p\ 1^n$; Callomon's data [17] (☆), Takagi's [20] (□) and Wunsch's [15] (△).

interesting point is that although this behaviour was also present in Callomon's data, the rates extrapolate to rates ca. $6 \times 10^8\ s^{-1}$, at zero vibrational energy. Since much lower rates ($\sim 10^6\ s^{-1}$) were observed from this levels such a behaviour suggests the onset of another process at $3000\ cm^{-1}$ excess energy above S_1. However this is not the situation with the more recent data based on fluorescence lifetime studies. In particular the most accurate data which was based on one photon absorption and was pressure independent up to 20 torr (C_6H_6) allowed an estimation of a lifetime of 42 ps for the $7^1 1^2$ level. This level involves the direct population of a CH mode (7 mode). We have performed calculations for the i.c. rates with the population of a CH mode which has a faster E_v dependence than the 6^m or $6^m\ 1^n$ modes (Fig. 1). The data extrapolate well to the experimental value of Takagi et al. [20] at $E_v \simeq 4950\ cm^{-1}$. For other levels which do not involve the population of the CH modes, the data of Wunsch et al. [15] for the $14^q\ 1^n$ levels can also be interpreted reasonably well in terms of an i.c. process. At high excitation energies the data fits better the curve for the population of CH modes. However this data was not determined directly from lifetime measurements owing to the time resolution of the experimental system, but was estimated from the fluorescence intensities. The present results support the view that in C_6H_6 S_1 isolated state, in the current region of excitation ($E_v = 0$ to $5000\ cm^{-1}$), there are only two channels of nonradiative decay: the internal conversion $S_1 \rightsquigarrow S_0$ and the intersystem crossing $S_1 \rightsquigarrow T_1$. Channel 3 would be simply the result of a fast increase of internal conversion with the excess vibrational energy in S_1.

A final word should be said on the triplet yields in C_6H_6 as a function of vibrational energy. Since $S_1 \rightsquigarrow S_0$ increases faster than $S_1 \rightsquigarrow T_1$ the triplet yield decreases with an increase in excitation energy. Only recently the experimental techniques of supersonic free jets allowed some measurement of the triplet yields in isolated molecules as a function of vibrational energy. Otis et al. [22] have employed a supersonic molecular beam of C_6H_6 to ensure isolated molecule conditions. The singlet S_1 state is populated by a laser pulse and allowed to evolve in time. Following this, excited molecules are pumped by a second pulse which photoionizes the molecules in S_1 and T_1. The decays are analyzed in terms of a biexponential attributed to S_1, the fast component, and to T_1, the slow component. The ratio of the two components allows the estimation of the triplet yields. However such analysis is based on the statistical behaviour for the nonradiative transition in isolated excited C_6H_6. Fig. 2 reveals that benzene T_1 state is not on a statistical case. In fact the decay rates [22] of the vibrationally excited T_1 levels do not extrapolate to the T_1 decay rate in vapour phase at high pressures, $2 \times 10^3\ s^{-1}$ [23]; the extrapolated value is almost two orders of magnitude higher, $9 \times 10^4\ s^{-1}$, revealing that the hot triplet levels, T_1^v, have a different channel of decay than T_1^0. The decays are considered to

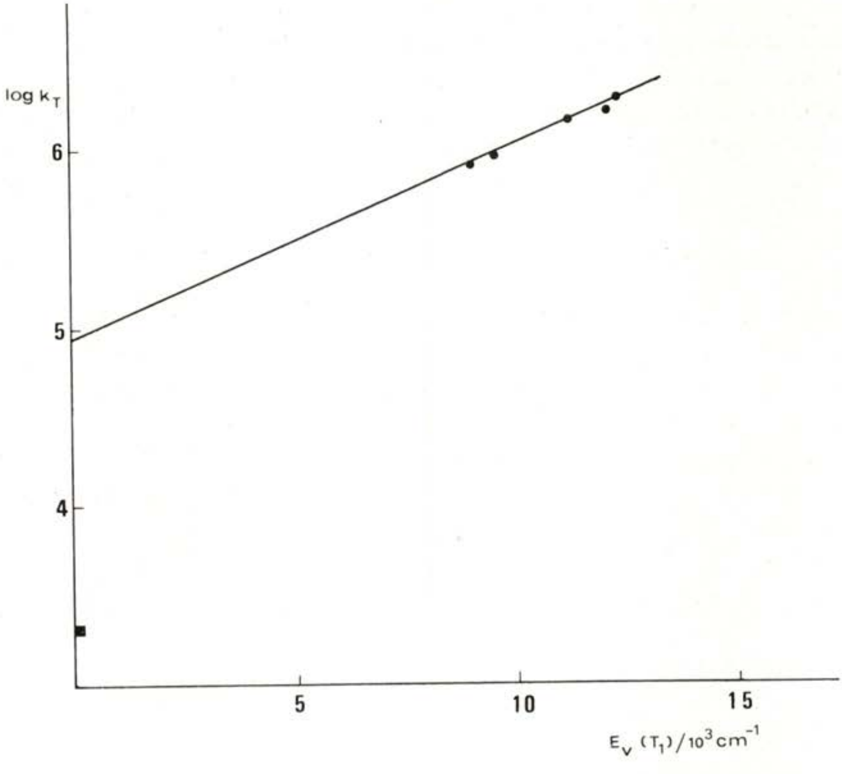

Fig. 2 — Logarithmic plot of the triplet decay rates k_T [22] as a function of triplet vibrational energy; triplet decay rate (■) from the thermally equilibrated T_1 state.

be $T_1^v \rightsquigarrow S_1\,(E_v(T_1) \geqslant E_{S_1} - E_{T_1})$ and $T_1^0 \rightsquigarrow S_0\,(E_v(T_1) < E_{S_1} - E_{T_1})$. Consequently the biexponential decay observed in the photoionization experiments may have some contribution of S_1 in the slow component and of T_1 in the fast component. Nevertheless in relative terms the analysis of Otis et al. [22] reveals a decrease in ϕ_T with an increase in E_v. Such a decrease is in reasonable agreement with the yields estimated from the calculated nonradiative transitions, as shown in Table 2. The best agreement is apparently with $f_{i.c} = 1.0$ but no conclusion can be made, because the absolute values of Otis et al. [22] may be subjected to some error owing to the assumption of a statistical behaviour.

TABLE 2 — Triplet Quantum Yields from Singlet Levels

Levels	E_v (cm^{-1})	Experimental Values		Calculated	
		a	*b*	$f_{ic} = 0.57$	$f_{ic} = 1.0$
6^0	0	0.62	0.70	—	—
6^1	521	0.58	0.65	0.67	0.61
$6^1 1^2$	2367	0.57	0.64	0.63	0.49
$6^1 1^3$	3290	0.29	0.33	0.40	0.28

a Values of ref [22].
b Values of ref [22] corrected for the yield 0.7 at zero level.

The yield for all the triplet vibronic levels from the zero singlet level calculated by Otis et al. [22] is smaller than the yield from the thermally equilibrated molecule (0.70). This difference cannot be due to the thermal population of higher singlet vibronic levels, because this would decrease ϕ_T even further. The discrepancy may be due to the assumption of the statistical behaviour for T_1. When the yields are corrected for $\phi_T = 0.70$ a better agreement is found with the calculated yields for $f_{i.c} = 0.57$ (Table 2).

We are grateful to INIC for financial support.

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