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A TUNNEL EFFECT MODEL FOR RADIATIONLESS TRANSITIONS IN AROMATIC MOLECULES

A process of a tunelling effect in the potential surfaces of the C-H stretching vibrational modes is proposed in order to interpret the radiationless transitions in aromatic molecules. The agreement with the experimental data is found to be good both qualitatively and quantitatively.

The radiationless transitions in large molecules, and particularly in the aromatic hydrocarbons have been a very active field of study, not only experimentally, but also from a theoretical point of view (1, 2). Apart from some early work of Franck and Sponer (3) and Ross and co-workers (4, 5), the problem of the radiationless transitions in big molecules was dominated by two papers of Robinson and Frosch (6, 7) where the importance of Franck-Condon factors and density of states was emphasized. Although not easily amenable to an absolute calculation, the model has been very useful qualitatively and was well explored in a semi-empirical way by Siebrand (8, 9). More recently, the approach of Robinson and Frosch was considered formally wrong (2) and more sophisticated theories were developed by Rice, Jortner, Freed and co-workers (2) and Fischer and others (10). These later approaches lack the qualitative simplicity of the model of Robinson and Frosch and only recently have some calculations been done with them (11, 12), mainly in relation to the ratio of rates because the absolute values are some orders of magnitude lower than the experimental rates. The Franck-Condon factors do not seem as important as has been claimed, and in fact in 1968 Ting (13) clearly stated that the calculated Franck-Condon integrals were 10^{-10} - 10^{-7} times smaller than it was required to calculate radiationless rates of the right order of magnitude.

Since the aromatic hydrocarbons are relatively rigid molecules, no crossing between the potential surfaces of their vibrational modes is expected. Although having spacial points in common, as figure 1 shows, no isoenergetic transitions between different electronic states can occur via those points, because the Franck-Condon factors are too small. Therefore, only a tunneling process from the turning points of the vibrations of one electronic state to the other can give a possible mechanism for a radiationless conversion, as Ross and co-workers expressed in their early approaches (4, 5).

The tunnel crossing between two electronic states, say between C and B (fig. 1), requires not only the tunnelling of an electron, but also the simultaneous tunnelling of the oscillator, since for an isoenergetic transition the molecule finds itself in a different geometrical configuration, after the transition. Within the W.K.B. approximation (5a) it can be shown that the rate of conversion is given by

$$k = \nu \exp\left(\frac{-2\pi}{h}\sqrt{2m\,(I_e - E_e)}\,.\,\Delta x\right)\cdot$$
$$.\exp\left(\frac{-2\pi}{h}\sqrt{2\mu\,(D - E_v)}\,.\,\Delta x\right) \tag{1}$$

ν is the frequency of the vibrational mode, i. e., the number of times that the oscillator can try the transition in a unit of time. The two exponential functions express the probability of tunnelling of the electron and of the oscillator as independent events, i.e., within the Born-Oppenheimer approximation. Each exponential represents the probability of a particle to tunnel a barrier of width Δx, i.e., the horizontal distance between the potential surfaces at the energy of the transition. Therefore, I_e is the ionization of one electron in the molecule, E_e the electronic energy of the initial electronic state, m the mass of the electron, μ the reduced mass of the oscillator, E_v the vibrational energy and D the energy barrier for a free change of geometry of the oscillator. D is the dissociation energy of the vibration (D_e) when the radiationless transition occurs on the expansion of the vibration.

If the crossing occurs on the compression of the oscillator, D is the energy at the crossing point of the two potential surfaces. It can be high if the electronic states are close together and, consequently, the radiationless transition can only occur from the attractive side of the potential energy curve, i.e., when the oscillator is in distension. However, if the electronic energy gap is high ($\sim 40.000\ cm^{-1}$) the energy of the crossing point of the repulsive curves, relative to the initial state, is of the same order of magnitude as D_e. For two harmonic oscillators with the same vertical axis of symmetry the frequency factor should be 2ν, but in fact such situation is not common and is only presented as such in figure 1 with an illustrative purpose.

There are several modes of vibration in an aromatic molecule, but the one of highest frequency and lowest reduced mass is the C-H stretching mode. The other modes being of lower frequency and (or) higher reduced mass have a very much smaller tunnelling rate. Therefore, the radiationless conversions should be dominated by the C-H stretching modes of vibration, a well known fact for a long time (8, 9). The transitions from the potencial curves of these modes should be mainly to the potential energy surfaces of the same vibrational modes, because the curves of the other modes are much wider and Δx should be, consequently, higher.

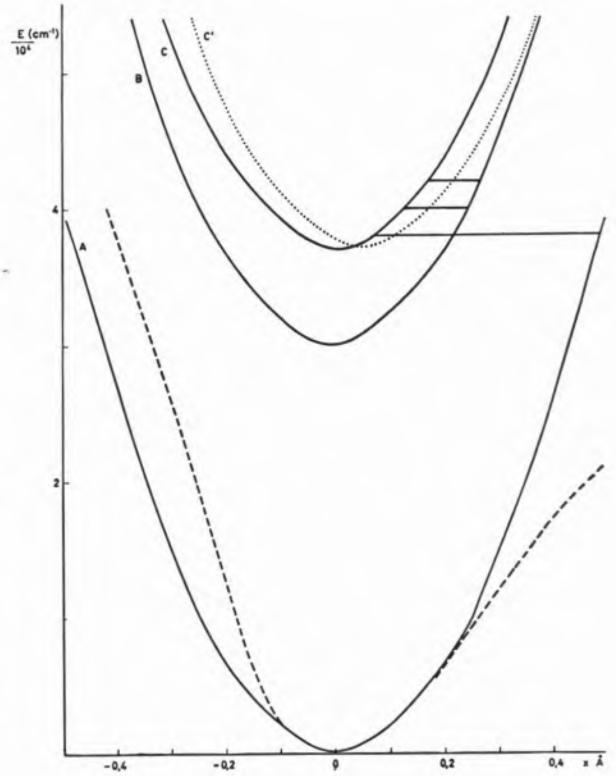

Fig. 1

Potential energy curves of the C-H vibrational stretching mode in several electronic states. (— harmonic oscillators; ...displaced harmonic oscillator; --- anharmonic oscillator).

Let us now test the model with a few examples of the radiationless conversions in the aromatic molecules, considering in equation (1) only the parameters for the C-H stretching mode. For an internal conversion $S_2 \rightarrow S_1$ (say between C′ and B (fig. 1)) differing by $7000\ cm^{-1}$, with an $I_e = 9$ eV, $E_{S_2} = 35\,000\ cm^{-1}$, and $D_e = 100$ Kcal/mol, a rate $k_{S_2 \rightarrow S_1} = 9 \times 10^{11}\ s^{-1}$ is found with $\Delta x = 0.1$ Å. Such value is in perfect agreement with the experimental data, which varies typically between $1.6 - 0.3 \times 10^{12}\, s^{-1}$ (14). In benzene the value is only $4 \times 10^{10}\, s^{-1}$ and in azulene $k_{S_2 \rightarrow S_1} \simeq 2.0 \times 10^9\, s^{-1}$, which causes the molecule to fluoresce from S_2 with a high quantum yield, even in solution. This has been always a puzzling question for the current theories of radiationless transitions, but it can be well explained within the present model. In fact if there was a small or virtually no displacement between S_2 and S_1, Δx would be ca. $0.2 - 0.3$ Å and k would vary between $5 \times 10^9\, s^{-1}$ and $10^8\, s^{-1}$. Even a higher Δx could be possible, particularly with anharmonic functions, and the internal conversion rates could be even much smaller.

Now let us look at the rate $S_1 \rightarrow S_0$ from the lowest vibrational level. With the Δx and E- taken from figure 1 for the electronic states B and A (anharmonic function) $k_{S_1 \rightarrow S_0} \simeq 10^6$ as expected since internal conversion is not normally an important process at the low vibrational levels in S_1. However, if the rate is calculated for an excess of 8,000 cm^{-1} in the vibrational energy, then $k_{S_1 \rightarrow S_0} \simeq 3 \times 10^8\, s^{-1}$. This rate is probably too high because the dissociation energy of the C-H bond was used as a value for D, and since the crossing is on the repulsive side of the potential energy curves, a higher value of D should have been used. Neverthless, this explains well the increase in the rate from a given electronic state with an increase of vibrational energy, a qualitative effect that was predicted when looking at the decrease of Δx from C to B with the increase in the vibronic energy (fig. 1).

Experimentally such effect has been observed in naphthalene (15, 16) and has been invoked in the interpretation of the pressure effect on the fluorescence and triplet yields in benzene (17). The actual values found by FORMOSINHO and PORTER (15) vary from $k \gtrsim 10^6\, s^{-1}$, at the lowest vibrational levels, to $k = 2.3 \times 10^7\, s^{-1}$ at an 8000 cm^{-1} of excess vibrational energy in S_1. Furthermore, equation (1) predicts that such increase should be an exponential function of the vibrational energy, an effect found in the steady state fluorescence studies of naphthalene (15) and in the fluorescence decays when the correct quantum yields are used (16, 18). The variation of the rates with the vibrational energy content of the electronic states should be smaller for radiationless transitions between states of a smaller electronic energy gap because the rates are already closer to the frequency factor. In fact, in naphthalene, for the experimental conditions mentioned above, only an increase of 4 times was observed for the conversion $S_1 \rightarrow T_2$ (or T_3) (15). A calculation for the rate between the states C′ and B gave the same value for an increase of 8,000 cm^{-1} in C′, although, of course, the absolute agreement must be regarded to a small extent as fortuitous. From these considerations it is clear that studies in solution at different temperatures will reveal apparent activation energies, due to the thermal population of high vibronic levels. Such effect has been observed in benzene (19).

Internal conversion between triplet states seems to be very small ($\sim 10^6\, s^{-1}$) in the vapour phase at low pressures (15) and ca. $10^{10}\, s^{-1}$ in solution (15,20). This should be due to small relative displacements between the triplet potential energy functions. The effect of collisional perturbations will change the shapes of the potential surfaces (21) and the displacements, and this may cause a great increase in the nonradiative rates (15,17). It is not clear why apparently the displacements in the singlets are larger than in the triplets, but a possible reason could be the different Fermi correlation effects in these two kinds of electronic states.

The intersystem crossing rates involve a spin forbidden factor in the frequency ν' (ν' is a more general frequency term that may include the spin forbidden factor). The magnitude of such factor depends on the mechanism of the spin coupling between the singlet and triplet states and decreases with the increase of the electronic energy gap ΔE ($\nu' \propto \Delta E^{-2}$). As far as S_1 is concerned it should be coupled more strongly to the triplet levels nearer to such singlet state. This seems to agree with several experimental data on the photophysical processes of the aromatic compounds (15, 17, 22, 23). Direct coupling with T_1 should be normally very small. Since internal conversion between triplet states can be very small (ca. $10^6\, s^{-1}$) at low pressures, the smallness of the coupling $S_1 \rightarrow T_1$ eliminates some of the arguments against the reversibility of the intersystem crossing process from S_1, proposed by ASHPOLE, FORMOSINHO and PORTER (23) in order to explain the pressure dependence of triplet formation of some aromatic vapours.

Apparent activation energies are also expected for the intersystem conversion from S_1, although smaller than for the process $S_1 \rightarrow S_0$. Such effect will be observed not only if the coupled state is higher in energy than S_1, but also when it is lower.

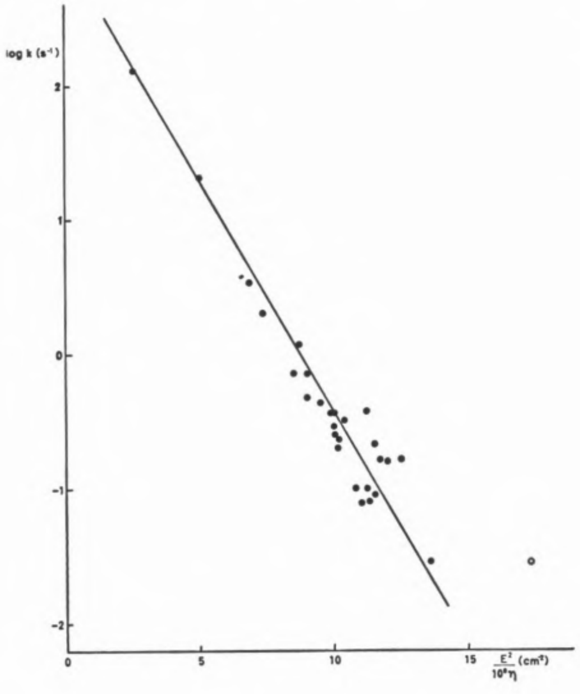

Fig. 2

Logarithmic plot of the non-radiative triplet decay rate constant k versus $\frac{E^2}{\eta}$ *(E energy of the triplet state; η relative number of H atoms in the molecule; o benzene).*

Therefore, some care should be exercised in the interpretation of the temperature effects on the fluorescence quantum yield studies in solution, although the present model does not exclude the possibility of a double intersystem crossing process from S_1.

As fig. 1 illustrates for an electronic transition from the same state (say C) to several others, Δx increases when the electronic energy difference increases and, consequently, as equation (1) shows, k decreases. This is the well known energy-gap law of the triplet lifetimes studied by SIEBRAND (23). Owing to the order of magnitude of the energy gaps involved (ca. 25,000 cm^{-1}) the transition $T_1 \rightarrow S_0$ occurs on the attractive side of the potential surfaces of the C-H stretching mode. Therefore the non-radiative triplet decay rate, k, should be plotted against some exponential function of the triplet energy E. A careful analysis of the potential energy curves near the dissociation limit shows that $\Delta x \propto E^2$ for the energy region where triplet states are located. Assuming no displacement between the potential surfaces of S_0 and T_1, log k should be studied directly as a function of E^2. Figure 2 shows such plot for $\frac{E^2}{\eta}$ where η is the relative number of hydrogen atoms in the molecule $\left(\eta = \frac{\eta_H}{\eta_H + \eta_C}\right)$.

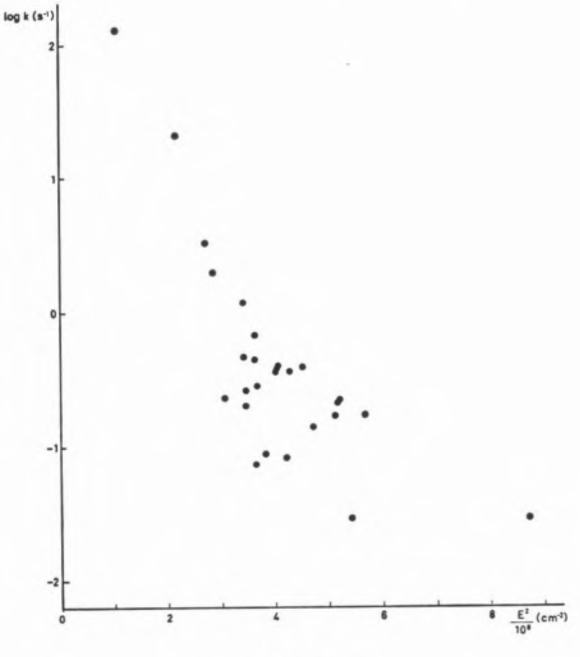

Fig. 3

Similar plot as in fig. 2 but against E^2.

The parameter η was also used before by SIEBRAND in his studies (23). Figure 3 shows the plot of log k versus E^2. As the figures clearly show the correlation is much better with $\frac{E^2}{\eta}$ and this reveals the need to take the relative number of active modes for the radiationless conversions into account. In view of this experimental correlation, equation 1 should probably be refined as follows

$$k = \nu' \exp\left(-\frac{2\pi}{h} \sqrt{2m\,(I_e - E_e)} \,.\, \Delta x \right) .$$
$$.\, \exp\left(-\frac{2\pi}{h} \sqrt{2\mu\,(D - E_v)} \,.\, \frac{\Delta x}{\eta} \right)$$

As expected no correlation was found between log k and $\frac{E^{1/2}}{\eta}$ or $E^{1/2}$ as is required for an harmonic oscillator.

The correlation also shows that the factor

$$\nu' \exp\left(-\frac{2\pi}{h} \sqrt{2m(I_e - E_e)}\ \Delta x \right)$$

is more or less constant for all the hydrocarbons. Although the coupling between T_1 and S_0 should increase when E_T decreases, E_e decreases and the exponential term increases. So, it seems that both factors compensate somehow. The lack of ionization data for all the hydrocarbons plotted in the figures does not allow a more quantitative test.

Benzene (0 in fig. 2) does not seem to fit the correlation curve, but this could be due to some difference in the electronic frequency factor or (and) to any displacement of its triplet function.

Although I believe the presented explanation is the correct one, I should say that SIEBRAND's empirical correlation (23) of log k with $\frac{E - 4000}{\eta}$ (cm^{-1}) for the protonated compounds, and with $\frac{E - 5{,}500}{\eta}$ (cm^{-1}) for the deuterated derivatives, is not «a priori» incompatible with this model. It would require a displacement of the triplet curves by ca. 0.2 Å in order to explain the energy subtracting factor of 4000 cm^{-1}. This does not agree very well with the absence of strong displacements in the triplet states. Furthermore, Δx should be proportional to E^n with $n > 2$ because T_1 will be closer to the dissociation limit of the C-H potencial curve in S_0. For the deuterated compounds the displacement would be greater (ca. 0.3 Å) in order to account for the higher subtracting energy factor contrary to what would be expected.

A factor of $k = 10^3$ is found by extrapolating the data of fig. 2 to zero energy. With the electronic data available for naphthalene (14) a value of $3\text{-}5 \times 10^4\ s^{-1}$ is found for ν'. Such a value should be the maximum rate observed in an intersystem crossing process from T_1, and this is in agreement with the triplet lifetimes studies in the vapour phase (25) that show a maximum rate of ca. $10^4\ s^{-1}$. Since through this model the rates of radiationless transitions are very sensitive to displacements and shapes of the potential curves, some effect should be expected at least for the lower rates of crossing. Such theoretical prediction agrees well with the smaller apparent activation energy found for $k_{T_1 \rightarrow S_0}$ in solid matrices (26) than in the liquid (27) and the vapour phase (25).

The decrease of the nonradiative rates on deuteration is very easily accounted for by expression (1), since there is a decrease in the frequency and an increase in the reduced mass of the oscillator. The average experimental decrease is ca. 10^{-1} (14). The calculated decrease for $E \simeq 25\,000\ cm^{-1}$ is about 10^{-2}. However for any small displacement, in contraction, of the C-D stretching, the crossing of the repulsive parts of T_1 and S_0 can occur for a smaller energy in the deuterated compounds. With this decrease in D, transitions from the repulsive side of the potential curve would also occur in the deuterated hydrocarbons and this, obviously, will make the calculated factor in better agreement with the experimental data. For transitions between electronic states very close in energy ($\sim 1000\ cm^{-1}$) the displacement of the C-D potential curves will correspond to a decrease in Δx compared to the same electronic states of the protonated compounds, and an inverse deuterium effect can be observed.

In this discussion we have considered only direct rates, i. e., non-equilibrium situations. When, for example, a $S_1 \rightarrow S_0$ transition occurs, the oscillator, due to the Franck-Condon principle, will keep its velocity factor and Δx will increase progressively after the transition. The coupling with many other vibrational modes redistributes the vibrational energy, avoiding the break of the C-H bond, and makes the recurrence time of the reverse transition $S_0 \rightarrow S_1$ very long, in fact, for this case, much longer than the intermolecular collision that will cause vibrational relaxation.

Consequently, the internal conversion $S_1 \rightarrow S_0$ is irreversible. Only when the rates are similar and fast as it is the case of $S_1 \rightarrow T_J$ and $T_J \rightarrow S_1$ could such equilibrium be attained at low pressures, as the experimental observations confirm (21, 28).

The effect of collisions on the photophysical process of the S_1 states needs also a short discussion. The $S_1 \rightarrow S_0$ transitions occur as it was shown, on the repulsive side of oscillator potential curves, and therefore are probably not very sensitive to collisions. But the $S_1 \rightarrow T_J$ transitions occur on the attractive side of the potential curves, the side of the energy surfaces more sensitive in shape and probably in displacements to collisional perturbations. Consequently, in some conditions, an isolated aromatic molecule will have only an internal conversion from S_1 and its fluorescence decay will be exponential. At low pressures, when the molecule suffers ca. one average collision in the lifetime, the collisional perturbation on the attractive part of the potential surfaces of S_1 and T_J can cause or enhance an intersystem crossing process, which is reversible, and the fluorescence decays become non-exponential. That was the explanation proposed by FORMOSINHO and PORTER (15) to conciliate the reversibility of intersystem crossing in aromatic molecules, apparently the only kinetic explanation of the pressure effects on the fluorescence and triplet yields of those compounds, with the exponential fluorescence decays observed with some molecules under isolated conditions (16, 18, 29). Here only a stronger theoretical support is given within the present model.

Although this paper is mainly concerned with aromatic molecules, some generalizations can be made. For example, for small molecules such as NO_2 and SO_2, particularly interesting for their long fluorescence lifetimes, if there are no great changes of geometry in some of the electronic excited states, no crossing of the potential surfaces will occur. Consequently a tunnelling mechanism could be applied to the radiationless transitions in these molecules. However, since now there is not a dominating mode for the tunnelling effect, each space of the normal coordinates should be analyzed. The long fluorescence lifetimes of those molecules could be due to an equilibrium situation caused by a reversible crossing between S_1 and another state with a higher density of vibronic levels. Another possible explanation is given by a tunnelling radiationless transition from S_1 to a different electronic state and to a different vibrational mode of higher reduced mass or (and) lower frequency. From such a state the radiationless transition to S_1 becomes more difficult and the energy is trapped for a longer time.

In conclusion, in spite of its simplicity, the presented model seems to agree quantitatively well with the published data on radiationless transitions and can be easily handled quantitatively and qualitatively enabling an evaluation of the displacement and the shape of the potential surfaces of the C-H stretching vibrational modes in different electronic states. Furthermore it seems to show whether a radiationless conversion occurs on the repulsive or on the attractive part of the potential surfaces which might be of photochemical interest.

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REFERENCES

1. Henry, B. R. and Kasha, M., *Ann. Rev. Phys. Chem.*, **19**, *161 (1968)*.
2. Jortner, J., Rice, S. A. and Hochstrasser, R. M., *Adv. Photochem.*, **7**, *149 (1969)*.
3. Franck, J. and Sponer, H., *J. Chem. Phys.*, **25**, *172 (1956)*.
4. Hunt, G. R., McCoy, E. F. and Ross, I. G., *Austral. J. Chem.*, **15**, *591 (1962)*.

5. McCoy, E. F. and Ross, I. G., *Austral. J. Chem.*, **15**, *573 (1962)*.

5.a Messiah, A., «Mécanique Quantique», Dunod, Paris, 1959, p. 199.

6. Robinson, G. W. and Frosch, R. P., *J. Chem. Phys.*, **37**, *1962 (1962)*.

7. Robinson, G. W. and Frosch, R. P., *J. Chem. Phys.*, **38**, *1187 (1963)*.

8. Siebrand, W., *J. Chem. Phys.*, **44**, *4055 (1966)*.

9. Siebrand, W., *J. Chem. Phys.*, **46**, *440 (1967)*.

10. Schlag, E. W., Schneider, S. and Fischer, S. F., *Ann. Rev. Phys. Chem.*, **22**, *465 (1971)*.

11. Fischer, S., Schlag, E. W. and Schneider, S., *Chem. Phys. Letters*, **11**, *583 (1971)*.

12. Heller, D. F., Freed, K. F. and Gelbart, W. M., *J. Chem. Phys.*, **56**, *2309 (1972)*.

13. Ting, C. H., *Photochem. Photobiol.*, **9**, *17 (1969)*.

14. Birks, J. B., «Photophysics of Aromatic Molecules», Interscience Publishers, London, 1970.

15. Formosinho, S. J. and Porter, G., Work in course of publication.

16. Beddard, G. S. and Porter, G., Work in course of publication.

17. Formosinho, S. J., and Silva,, A. M., to be published.

18. Laor, U. and Ludwig, P. K., *J. Chem. Phys.*, **54**, *1054 (1971)*.

19. Greenleaf, J. R. and King, T. A., Proc. Intern. Conf. Luminescence, Akademiai Kiadó, Budapest, 1968, p. 212.

20. Liu, R. S. H. and Edman, J. R., *J. Am. Chem. Soc.*, **91**, *1492 (1969)*.

21. Kroto, H. W. and Dias, J. J. C. T., *Mol. Phys.*, **18**, **773** *(1970)*.

22. Ashpole, C. W., Formosinho, S. J. and Porter, G., *Proc. Roy. Soc. (London) Ser. A*, **323**, *11 (1971)*.

23. Keavell, A. and Wilkinson, F., *J. Chim. Phys.*, xx, *125 (1970)*.

24. Siebrand, W., «The Triplet State», Ed. by Zahlan et al., Cambridge University Press, 1967, p. 31.

25. Ashpole, C. W., Formosinho, S. J., Porter, G. and West, M. A., *J. C. S. Faraday Transactions I*, In publication.

26. Jones, P. F. and Siegel, S., *J. Chem. Phys.*, **50**, *1134 (1950)*.

27. Langelaar, J., Rettscknick, R. P. H. and Hoytink, G. J,, *J. Chem. Phys,*, **54**, *1 (1971)*.

28. Formosinho, S. J., Porter, G. and West, M. A., *Chem. Phys. Letters*, **6**, *7 (1970)*.

29. Abramson, A. S., Spears, K. G. and Rice, S. A., *J. Chem. Phys.*, **56**, *2291 (1972)*.

RESUMO

Apresenta-se uma nova teoria para as transições não-radiativas em moléculas aromáticas, baseada na possibilidade de tais processos ocorrerem por um efeito túnel dos modos de vibração C-H. O modelo apresentado está em bom acordo com vários dados experimentais.