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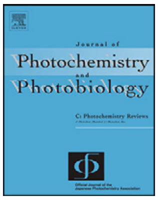

Review

New concepts in photochemistry and photophysics: Photochromic and other type molecules

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ABSTRACT

It is now clear for the first time that photochemistry can compete with vibrational relaxation within a singlet state. This possibility has not been generally considered, or believed possible, prior to the considerations given herein. It is also evident that both the nature of the vibrational/vibronic mode and the vibrational level excited within a given mode can markedly affect the experimentally determined quantum yields of photochemistry $\Phi_{PC}(n)$ and fluorescence $\Phi_F(n)$ in multi-atom systems, where n is the nth level. There is not just one quantum yield of fluorescence (F) or photochemistry (PC), but there are many that can exist. Since the yields of PC depend on the vibrational/vibronic level excited, the new concepts of Φ_V and Φ_{PC} inevitably arise $\Phi_V = k_V/(k_V + k_{PC})$ and $\Phi_{PC} = k_{PC}/(k_{PC} + k_V)$. Φ_{PC} measures the efficiency of photochemistry from a given level within a given mode in competition with vibrational relaxation between the given level and a lower one. Φ_V measures the efficiency of vibrational relaxation between a given level and a lower one. The magnitude of the photochemical yield is largely dictated by the nature of the mode excited within a given electronic state as well as the level that is excited. Φ_V and Φ_{PC} have no parallel in previously existing experimental or theoretical photophysics/photochemistry. In general, relaxation from the 0 level of an upper state S_x ($x = 2, 3, \ldots$) does not occur via vibrational levels of any lower energy states.

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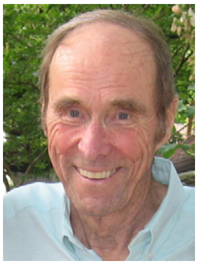


Ralph attained his PhD from Florida State University in 1955. He has published 200 papers mostly involving talented colleagues worldwide. They have been broad ranging and multi-faceted mostly involving: photophysics, photochemistry, topics such as photochromism, molecular spectroscopy, electron attachment and model visual pigments.Prof. Becker was the first to publish on and patent many of the photochromic compounds of the pyran-chromene types now used in many optical arrangements.He wrote the first definitive text on "Theory and Interpretation of Fluorescence and Phosphorescence" published in 1969, translated in 1970 into several languages as well as a general chemistry text with a co-author in 1980: translated into Japanese, German and Spanish.He has been a visiting professor or lecturer at universities in the U S A, Canada, Central and South America, Western and Eastern Europe and Asia, including India, Japan and South Korea.

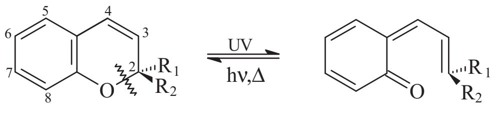
Gianna Favaro graduated in Chemistry from the University of Padua (Italy); she has been lecturer in Physical Chemistry and related subjects at the Universities of Padua, Bologna, and Perugia. Free docent of Physical Chemistry since 1971, she has been associate professor (1982-1986) and then full professor of Physical Chemistry at the University of Perugia. She has been a member of the Standing Committee of the European Photochemistry Association (EPA), president of the Italian Group of Photochemistry (GIF) and coordinator of the Interdivisional Group of Photochemistry of the Italian Chemical Society (GIDF). Retired since 2008, she is still involved in several scientific engagements.Scientific co-ordinator of several national research projects on the spectroscopic and kinetic study of photochromism and art materials, she has authored over 140 articles concerning electronic spectroscopy, photoinduced energy transfer, photosensitization, photokinetic studies on photochromic compounds and on materials of interest for cultural heritage.

1. Introduction

This review will describe new and unique concepts, models, mechanisms and appropriate equations not previously considered in the fields of photochemistry (PC) and photophysics (PP). New considerations are necessary with the simultaneous presence of photochemistry and/or photophysics and competing vibrational relaxation process(es). The foregoing should open up new opportunities for fundamental research in photochemistry and photophysics as well as opportunities for research in applied photochemistry and photophysics. A shorter report on this subject has been published elsewhere [1].

2. First observation of absorption spectrum versus fluorescence excitation spectrum

The first hint of a potentially unique find came in 1966 when we noticed that the fluorescence (F) excitation spectrum of a photoactive 2,2-diethylchromene (see Scheme 1) was significantly different from the absorption spectrum [2]. In this work, we showed that photochromic behavior was present with substitution at any position, or with benzo-condensation, as long as the chromene (or pyran) unit was present, see Scheme 1. Some qualitative ideas for the behavior were given. Proof of the nature of the product was also determined [3]. A patent on a large number of substituted chromenes and benzo condensed chromenes was issued in 1971 [4].



Scheme 1. Photochromic reaction of 2,2-diethylchromene.

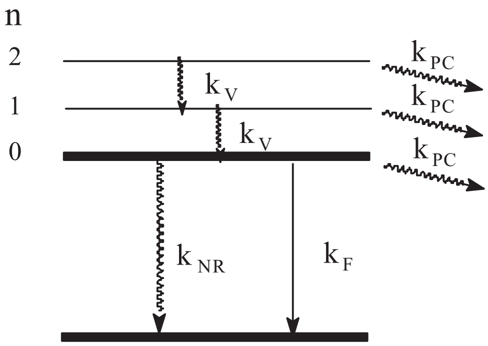


Fig. 1. Model for the fate of quanta absorbed into any vibrational level of any mode of any excited electronic state S_x ($x = 1$ in figure) excluding intersystem crossing (even if triplet formation occurred from $n = 0$, k_T is included in k_{NR}).

3. Quantum yields of fluorescence as a function of vibrational mode and level excited

In 1969 [5] a much expanded and quantitative explanation was made of the phenomenon seen earlier. Here, the relative quantum yields of F, Φ_F^{rel}, were determined for all the vibrational/vibronic levels in each of the excited states for 2,2-diethylchromene and 5,6-benzochromene. It was found that Φ_F^{rel} markedly varied, up to 10-fold, as a function of (a) the electronic state, (b) the vibrational mode and (c) the vibrational level that were excited. Comparison was made to a molecule of similar structure to 2,2-diethylchromene except the O atom was replaced by $-CH_2$ (1,2-dihydronaphthalene). In this case, excitation over fifteen wavelengths between 296 nm and 250 nm (first entire transition) did not result in any deviation (±5%) of the Φ_F^{rel} and no photochemistry was observed over irradiation times comparable to that used for the chromene and the benzochromene.

4. Development of a mechanism and equations for the dependence Φ_F on vibrational mode and level

A mechanism and associated equations were developed to understand the strong dependence of Φ_F on the particular vibrational/vibronic mode and level excited for molecules that underwent PC. Also, we determined that no phosphorescence was present and in later works [6,7], no triplet transient was found for chromenes and benzochromenes except for a small amount of triplet ($\Phi_T \sim 0.1$) for molecules having a 7,8-benzochromene core. Therefore, it was considered that photochemistry was in competition with vibrational relaxation at every vibrational/vibronic level within a given mode. With this premise, the fraction of molecules that relax from an upper (n) vibrational/vibronic level to a lower ($n-1$) vibrational level within a given mode is:

$$\frac{k_V}{k_V + k_{PC}} \tag{1}$$

where k_V is the vibrational relaxation constant (called k_{IC} in Ref. [5]) and k_{PC} is the photochemical rate constant as shown in Fig. 1.

For an nth level:

$$\Phi_F^{rel}(n) = \left[\frac{k_V}{k_V + k_{PC}}\right]^n \tag{2}$$

A plot of log $\Phi_F^{rel}(n)$ versus n should give a straight line with a slope equal to log $[k_V/(k_V + k_{PC})]$ and from this the ratio of k_V/k_{PC} could be obtained. There was a wide variation in the ratio as a function of the state and mode that was excited (~4-fold) for the chromene and benzochromene.

We also were able to show the foregoing phenomenon occurred in other types of photoactive/photochromic compounds such as