

reaction. Conversely, the addition of molecular oxygen increases the ethylene quantum yield from 0.14 to 0.38 at a total pressure of 1 Torr.

From these results it is not obvious what mechanism is responsible for such an effect. However, the involvement of excited *triplet* intermediates may be assumed:



Direct absorption of a photon leads to the formation of a *singlet* excited molecule. This excited molecule decomposes into two *triplet* excited molecules etc. Triplet–triplet annihilation processes are well known in the liquid phase but are not often included in gaseous chemical systems.

Collision-induced radiationless transitions in CS₂

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We measured the quenching rate constants of CS₂ vapour (¹A₂ and ³A₂ states) by laser-induced fluorescence with the gases CS₂, CO₂, O₂, NO, C₂H₅OH, CH₃OH, C₂H₅NO₂, CCl₄ and CH₃CN. The emission was measured in regions centred at 4480 and 5860 Å. The quenching cross sections were obtained for both electronic states. Stern–Volmer plots at 4480 Å for the ³A₂ state show saturation effects for CH₃CN, C₂H₅NO₂ and O₂, whereas only O₂ produces such effects at 5860 Å. The quenching cross sections correlate with the molecular parameters defined in the Thayer–Yardley model for collision-induced radiationless transitions. The decay of CS₂ obeys this model for the two states involved.

Energy selection experiments in glassy matrixes: the fluorescence spectrum of isobacteriochlorin

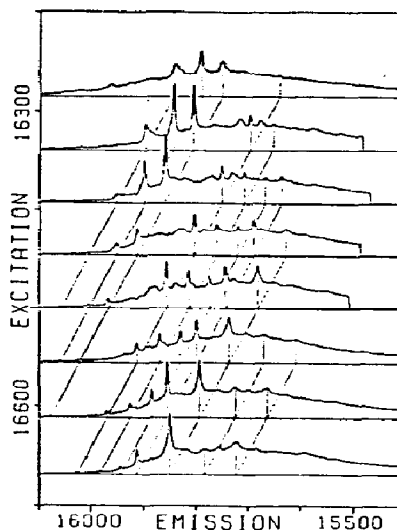
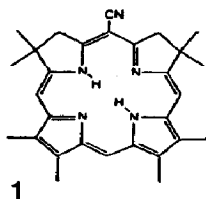
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The fluorescence spectrum of a synthetic isobacteriochlorin 1 was studied in a glassy matrix at low temperature. It consists of a single strong 0–0 band and very little vibronic structure. Excitation into a region 400 - 900 cm⁻¹ above the

$S_1 \leftarrow S_0$ energy with a narrow-band laser, however, results in well-structured and excitation-wavelength-dependent emission spectra. It is shown that a site selection effect is responsible for this behaviour.

A set of fluorescence spectra of isobacteriochlorin in 3-methylpentane at 4.2 K excited at eight different frequencies is shown. We note that the line pattern varies enormously from one spectrum to another. A comparison of two spectra taken at random would hardly indicate that they result from the same compound.



Photochemical and photobiological properties of haematoporphyrin derivatives

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Derivatives of haematoporphyrin (HpD) have been introduced in the diagnosis and therapy of cancer because of their selective retention in tumours, their characteristic fluorescence and their efficiency as photosensitizers. We analysed HpD with respect to (a) chemical composition, (b) cellular uptake of the components, (c) relative efficiency of the components in sensitizing photo-inactivation of cancer cells, (d) fluorescence spectra and fluorescence quantum yields and (e) quantum yields of singlet oxygen production. The major components of HpD, as analysed by high pressure liquid chromatography, are (listed in order of decreasing water solubility) (1) two stereoisomers of haematoporphyrin, (2) two stereoisomers of each of two positional isomers of *o*-acetyl