effects which may modify the $S_1 - T$ electronic matrix elements. A good correlation between the cross sections and intermolecular potential well depths has been found [5].

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### K7
### The Photodissociation, with Pulsed Synchrotron Radiation, of $H_2$ and $D_2$ near 750 Å

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Emission of the Balmer $\alpha$, $\beta$ and $\gamma$ lines of atomic H and D were observed when $H_2$ and $D_2$ were irradiated below 750 Å with synchroton radiation from the ACO storage ring at Orsay. The excitation spectra were recorded together with that from the Lyman $\alpha$ emission below 850 Å and the lifetime of the $\beta$ emission was measured by single photon counting.

The excitation spectra were structured and some of the peaks could be correlated with the absorption spectrum in this region. The spectra indicate that the atoms are formed principally by predissociation from the initially excited Rydberg states in the region just above each energy threshold.

### L7
### Photochemistry of Ru(II) Complexes in Non-Aqueous Solvents

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Tris(bipyridyl)ruthenium(II) is now frequently used as a sensitizer for transition metal complexes, both for luminescence and for photochemistry. However, in solvents less polar than water, it does undergo a photochemical reaction itself. Although this reaction has only a small quantum yield $(10^{-3})$, it must still be taken into account in sensitization studies because the ruthenium complex has a very high extinction coefficient in the visible region and it is therefore used in quite low concentrations.

The reaction of the $NCS^-$ salt in DMF leads to two products, one of which is the $cis(Ru(bipy)_2(NCS)_2)$, and the other is the $cis(Ru(bipy)_2(NCS)(DMF))^+$. The former is formed from an ion paired excited state with a quantum yield:

$$\Phi = \Phi_{ip}\frac{K_{ip}(NCS^-)}{1 + K_{ip}(NCS)^-}$$

with $\Phi_{ip} = 1.4 \times 10^{-3}$ and $K_{ip} = 55 \pm 10$.

The second species is formed with a quantum yield of ca. $3.2 \times 10^{-4}$, independent of $(NCS^-)$. The photochemical reaction is quenched by $O_2$ to the same extent as is phosphorescence, thus the phosphorescing triplet state is also directly involved in the photoreactions.

### O2
### Intramolecular Excimers

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Formation of intramolecular excimers with molecules A-$(CH_2)_n$-A has in general been observed only for $n = 3$, e.g. for 1,3-diphenylpropane but not for 1,4-diphenylbutane (Hirayama [1]). The only

exception to this Hirayama rule ($n$ = 3)
published to date is the 1,4-di-(1-naphthyl)
butane, where a weak emission ascribed to
an intramolecular excimer was observed,
but only at low temperatures (Chandross
and Dempster [2]). Studies of dinaphthyl-
propane [2] and of bicarbazolylpropane
[3 - 5] essentially confirmed the gener-
ality of the $n$ = 3 rule.

In order to clarify the factors gover-
ning the generality of the Hirayama rule,
the fluorescence of a series of $\alpha$, $\omega$-di-(3-
pyrenyl)-alkanes, $Py(CH_2)_n Py$, with $n$ =
2,...,16 and 22 was studied. It was felt
that the steric and statistical reasons which
have been invoked to explain the Hiraya-
ma rule could be less important than the
magnitude of the stabilization energy of
the intramolecular excimer. Pyrene was
chosen because of its large excimer stabil-
ization energy. For $Py-(CH_2)_n-Py$, in
methylcyclohexane(MCH) solution (1.0 ×
$10^{-5}M$) at room temperature, intramole-
cular excimer emission was observed for
all dipyrenylalkanes investigated, except
for $n$ = 7. Thus in contrast to the systems
previously investigated, excimer fluores-
cence is clearly not restricted to the case
where $n$ = 3.

The intensity of excimer emission
shows a minimum for $n$ = 7, 8, in a pat-
tern reminiscent of *i.a.* the cyclization
yield of $\omega$-oxy acids as a function of chain
length, as reported by Stoll and Rouvé in
1935, see [6].

In the series of $\alpha,\omega$-di-(3-pyrenyl)al-
kanes a variation of the energy of the ex-
cimer emission maximum with the length
of the $CH_2$-chain is observed.

An investigation of the time depen-
dence of the monomer and excimer fluor-
escence after pulse excitation ($N_2$-laser),
reveals *i.a.* a non-exponential decay when
the monomer fluorescence of *e.g.* Py-
$(CH_2)_4Py$ and $Py(CH_2)_9Py$ is studied at the
zero-zero transition at room temperature.
This behaviour can be explained by assum-
ing that the repopulation of the monomer
from the initially formed excimer is an
important process for $Py(4)Py$ and $Py(9)$
Py at room temperature. For 1,3-di-(9-
phenanthryl)propane, $Phen(CH_2)_3Phen$,
an emission from an intramolecular ex-
cimer could not be observed over a large
temperature range, in contrast to Phen–
$(C=O)$–$(CH_2)_2$–Phen where a new emis-

sion at longer wavelength could in fact be
measured.

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## O3
## Photophysics of diphenylpolyenes
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Observations have been made of the
fluorescence lifetime ($\tau$) and quantum
yield ($\phi_F$) of the first four all-*trans* di-
phenylpolyenes (*trans*-stilbene, diphenyl-
butadiene, diphenylhexatriene and di-
phenyloctatetraene) in seven solvents
from −50 to 50 °C.

The radiative lifetime $\tau_F$ (= $\tau/\phi_F$) ex-
hibits several anomalies.

1. $\tau_F$ exceeds the theoretical radiative
lifetime $\tau_A$ calculated from the integrated
absorption spectrum.

2. $\tau_F/\tau_A$ increases with the polyene
chain length.

3. $\tau_F/\tau_A$ increases with the degree of
departure from mirror symmetry between
the fluorescence and absorption spectra.

4. $\tau_F/\tau_A$ increases with the Stokes shift
between the absorption and fluorescence
maxima.

5. $\tau_F$ depends markedly on the solvent.

6. $\tau_F$ increases with increase in temper-
ature.
Similar anomalies occur in the retinol po-
lyenes.

The following model is proposed to
account for the behaviour. A polyene has
a $^1A_g$ ground state and $^1B_u$ and $^1A_g(^1A_g*)$
excited states which are adjacent. After
Franck–Condon excitation of the all-*trans*
configuration ($\theta$ = 0° ) by the allowed $^1B_u$
← $^1A_g$ absorption transition, molecular
relaxation occurs. The phenyl groups rot-
ate through a relative angle $\theta$ about the