

# COMPREHENSIVE CHEMICAL KINETICS

EDITED BY

C.H. BAMFORD MA, ScD, FRS, and C.F.H. TIPPER Ph.D, DSc

VOLUME 24

## MODERN METHODS IN KINETICS

ELSEVIER

# COMPREHENSIVE CHEMICAL KINETICS

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# CHEMICAL KINETICS

EDITED BY

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## Preface

This volume covers roughly the same area of kinetics as was reviewed in Section 1 (Volumes 1–3), that is the practice and theory of the subject, concentrating mainly on advances which have been made since the early volumes were published about thirteen years ago. Chapter 1 reviews some modern photochemical techniques, detailing the development of lasers and the enormous increase in speed and complexity of electronic devices used for signal detection and processing with reference to the study of fluorescence decay. The kinetic aspects of mass spectrometry are covered in Chapter 2, a full discussion being given of unimolecular ionic reactions, including kinetic isotope effects and energy release during decomposition of ions, together with field ionization kinetics and photoion–photoelectron coincidence. On the more theoretical side of kinetics, the use of computers in the analysis of complex reactions and simulation of the mechanism through modelling, with the mathematical techniques involved, is considered in Chapter 3 (particularly with respect to the pyrolysis of hydrocarbons and thus oil feedstocks) and in Chapter 4 the basic RRKM theory of unimolecular reactions is developed from elementary principles, since the theory is widely used to interpret the behaviour of thermal and photochemical reactions (see, for example, Chapters 2 and 5). Finally, the distribution of energy in the products of simple gas-phase reactions between neutral species is reviewed, including the main experimental methods of investigation, particularly crossed-molecular beams, and the nature of the reaction potential energy surfaces involved.

*Liverpool*  
*May 1982*

C.H. Bamford  
C.F.H. Tipper

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# Modern Photochemical Techniques: the Study of Fluorescence Decay

I. STUART McDERMID

## 1. Introduction

It is now some twelve years since the first volumes of this series were published. Perhaps the most significant advances during that time, particularly for the photochemist, have been the further development of lasers and the tremendous increase in speed and complexity of electronic devices used for signal detection and processing. These have spawned a number of new techniques for the study of kinetics and drastically modified some of the traditional methods. The aim of this chapter is to show how and where some of these techniques can be applied.

An area which has expanded greatly as a result of these new developments is the study of the dynamics of excited states. This chapter reviews the advances in this field. Attempts have been made to show where specific techniques are best applied and where problems may arise. For example, ways in which kinetics theory can be used to extract collision-free information when the laboratory experiments can only be carried out at relatively high pressures ( $\gtrsim 0.1$  Torr) are discussed. Different modern techniques for recording fluorescence decay curves are explained with indications of their individual advantages and disadvantages. The measurement of very long lifetimes,  $\gtrsim 100 \mu\text{s}$ , poses special problems, especially at low pressure, due to geometrical considerations and the fact that the molecule can travel a large distance within its radiative lifetime. Methods of estimating potential errors in these experiments are presented. Finally, the use of optical multichannel analysers for the study of time-resolved fluorescence emission spectra is discussed.

## 2. General characteristics of a laser source

Laser devices have become of great importance in chemical studies and applications and, before discussing some of the applications of lasers in kinetic measurements, it is worth reviewing the fundamental characteristics of a laser. Many different substances have been found to exhibit laser action when suitably pumped and lasers are now available at thousands of wavelengths from the vacuum ultraviolet to the submillimeter wave region. Figure 1 shows some of the lasers which can be used in

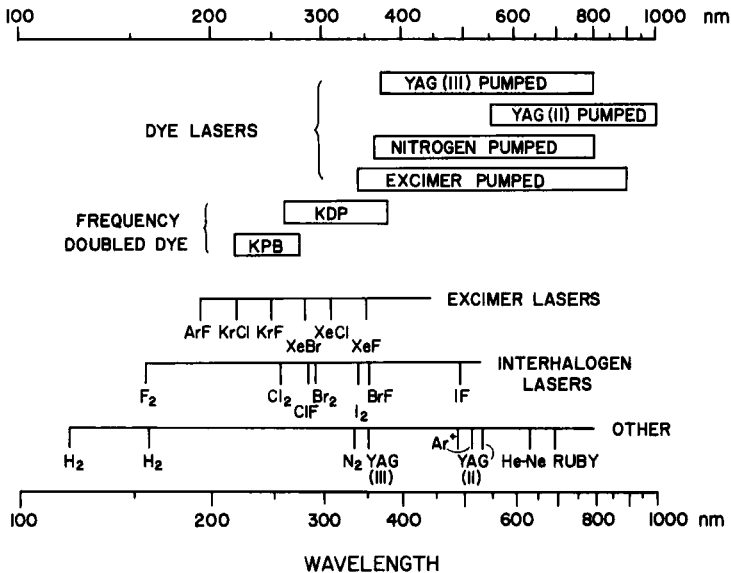


Fig. 1. Some useful laser sources in the visible and ultraviolet spectrum. For infrared lasers and also a more complete listing of laser lines see, for example, ref. 1. YAG (II) and YAG (III) signify the second and third harmonics, respectively, of the neodymium:YAG laser. KDP, potassium dihydrogen phosphate, and KPB, potassium pentaborate, are frequency doubling crystals.

the wavelength range from 100 to 1000 nm. The characteristics and properties of individual lasers are beyond the scope of this chapter. There is a number of reviews and books concerning lasers and laser technology [1, 2] to which the reader can refer for specific details.

## 2.1 POWER AND COHERENCE

Lasers are not very efficient devices at present and the average power emitted is usually less than that of a conventional light source. However, when it is considered that the energy of the laser is emitted in a narrow beam, the energy density per unit solid angle is very much greater than other light sources. Also, even a small amount of energy when compacted into a short pulse of a few picoseconds can have very high power. A terawatt ( $10^{12}$  W) can easily be produced in a laser of modest size.

Because of the good spatial coherence, the beam can be focused to a small spot, the size of which is given by  $f\delta\theta$  where  $f$  is the focal length and  $\delta\theta$  is the beam divergence of the laser. For a laser beam in which the divergence is close to diffraction limited, it is possible to focus it down to a size of a few times the wavelength. This produces an optical field with extremely high power per unit area. The high powers available allow the investigation of non-linear phenomena. Within the limits of this review, the main application for the high power densities available is for the

photodissociation or photoionization of molecules to produce species whose kinetics can then be studied.

## 2.2 TUNABILITY

The ability to tune the frequency of a laser whilst maintaining a narrow output bandwidth is particularly useful to the chemist and spectroscopist. The frequency of each laser can be tuned within the (generally) narrow fluorescence linewidth around the proper frequency by adjusting the resonant frequency of the optical cavity. In the case of a laser operating on a single atomic or vibronic transition, this range is very small,  $\lesssim 0.01 \text{ \AA}$ . For a molecular system, such as the excimer lasers, the range may cover one or more vibrational bands giving a tuning range of  $\lesssim 10 \text{ \AA}$ . In many instances, the tuning range can be increased by using an appropriate method to shift the frequency of the laser transition, e.g. by Raman shifting in a suitable medium [3–5].

An alternative to shifting the resonant frequency is to utilize a laser medium with a wider bandwidth or to increase the bandwidth with some external influence. An example of the latter method is the high pressure molecular gas laser. This utilizes pressure broadening of the line profile to increase the range of continuous tunability. In some cases, if the pressure can be raised high enough, the vibrational–rotational lines overlap and the laser can be continuously tuned over a wide range. For example, in the  $\text{CO}_2$  laser, overlap of lines occurs at 10–15 atm, providing continuous tuning in the 9–11  $\mu\text{m}$  region [6, 7].

### 2.2.1 The dye laser

The best example of a laser with a wide fluorescence bandwidth over which it is continuously tunable is the dye laser. A number of high efficiency dyes are available which, when suitably pumped, cover the spectral region from about 300 nm to 1  $\mu\text{m}$ . The fluorescence bandwidth of the individual dyes varies, but is typically 25–50 nm. By using the non-linear optical response of certain crystals for second harmonic generation (SHG), the wavelength range of the dye laser can be extended down to 217 nm in the ultraviolet. Because it covers such a wide range in an important part of the electromagnetic spectrum and because it can be easily and continuously tuned through this region, the dye laser has found many applications in kinetics and spectroscopy.

A later section of this review is concerned with experimental techniques for the measurement of relaxation processes. There are many studies of these processes in the literature and, in the larger proportion of the recent studies, pulses from tunable dye lasers have been used for the initial excitation. Therefore, a brief description of some pulsed dye lasers is given below.

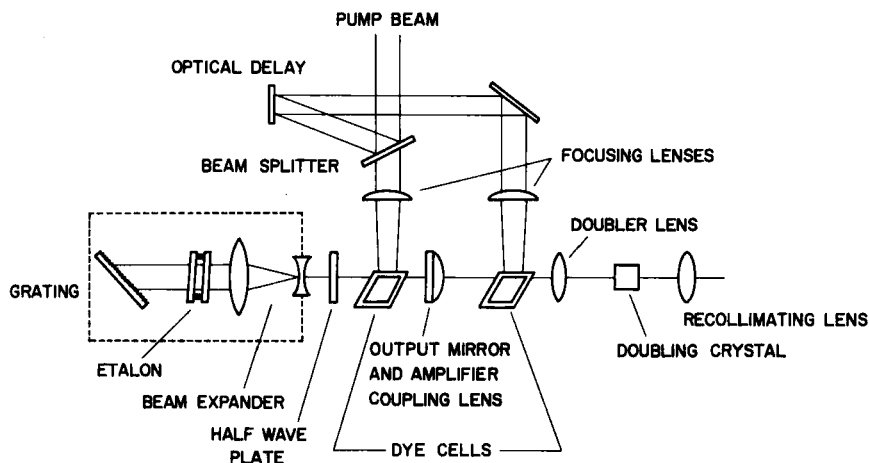


Fig. 2. A typical pulsed, tunable dye laser, of the Hansch design, in an oscillator—amplifier configuration. Suitable pump lasers are  $N_2$ , excimer and Nd:YAG-harmonics. The broken line represents a pressure chamber which is required to scan the wavelength if an air spaced Fabry—Perot etalon is used. With solid etalons, tuning is achieved by tilting the etalon and the pressure chamber is not required.

### 2.2.2 The pulsed dye laser

A typical dye laser cavity of the Hansch design [8, 9] is shown in Fig. 2. Such systems are typically pumped by pulsed lasers with a pulse length of 2–50 ns. Some suitable pump lasers are nitrogen (331.7 nm), second and third harmonics of neodymium YAG (532 nm, 355 nm) and excimer lasers (e.g. XeCl, 308 nm; XeF, 351 nm, etc.). In this example, coarse wavelength tuning is accomplished by the use of a grating at one end of the optical cavity. Combining this with a beam expander so that more lines of the grating are illuminated typically produces an output laser bandwidth (FWHM) of the order of  $0.5 \text{ cm}^{-1}$ . This output bandwidth can be further reduced to  $\sim 0.001 \text{ nm}$  by installing an etalon (Fabry—Perot) into the cavity. The tunability is maintained even with the etalon installed since the transmission wavelength of the etalon can be tuned by tilting the etalon or, in the case of an air-spaced etalon, by changing the pressure or refractive index of the gas between the Fabry—Perot plates.

This type of laser produces output pulses which are typically between 1 and 10 ns duration and are well suited to provide initial excitation in the study of the decay of excited states and other transient effects in small molecules. Many fundamental processes, however, occur on a time scale much shorter than the 1–10 ns resolution available with dye lasers of the type discussed above. These processes, such as the relaxation of large biological molecules and dyes in solution, exciton decay and migration in solids, charge-transfer and other non-radiative transfer processes between molecules, and many more, take place on a picosecond time scale.

Therefore very narrow excitation pulse widths are necessary, for example, to measure sub-nanosecond relaxation times. A number of methods for generating picosecond laser pulses have been devised and several reviews of these techniques are available [10, 11].

### 2.2.3 Synchronously pumped picosecond dye lasers

Picosecond pulses can be produced in a number of different types of laser systems. As an example, a brief description is first given of a synchronously pumped c.w. dye laser such as can be readily assembled from commercially available units. Generation of repetitive subnanosecond pulses in a c.w. laser by mode-locked synchronous pumping was first described by Harris et al. [12]. The essential features of such a system are shown in Fig. 3. In this system, an acousto-optically mode-locked ion laser is used to pump the dye laser. In order to achieve synchronous pumping, the length of the dye cavity must be adjusted so that the dye laser intermode spacing is an integral multiple of the pump mode-locker frequency.

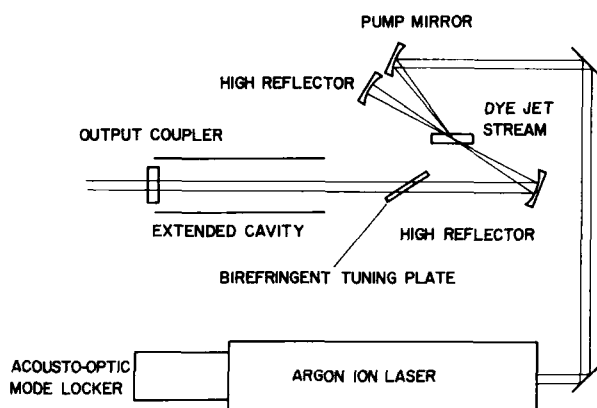


Fig. 3. Diagram of a synchronously pumped picosecond-pulse dye laser.

The output is thus a continuous train of pulses separated by the dye cavity round-trip time. Even though the pump laser pulses may be of the order of 200 ps long, dye laser pulses of less than 10 ps can be achieved by synchronous pumping. This is because the dye molecules have extremely large stimulated emission cross-sections and the dye laser pulse passing through the dye stream immediately de-excites the dye molecule, in a few picoseconds, by stimulated emission [13].

Longer pulse-to-pulse separations and more energy per pulse can be obtained by cavity dumping (Fig. 4). To achieve this, the partially transmissive output coupler on the dye laser is replaced by a cavity dumping system comprising an acousto-optic deflector at the focus of a highly reflective folded cavity. Each time the cavity dumper is activated, the energy circulating within the laser cavity is deflected out of it. In the

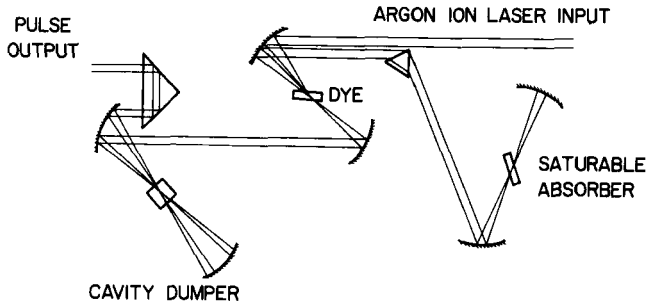


Fig. 4. Diagram of a cavity dumped, passively mode-locked dye laser. In this version, the saturable absorber is in a free flowing dye stream. In more recent experiments, the saturable absorber flows in contact with a 100% reflectivity resonator mirror (see text).

normal synchronously pumped system, the energy coupled out of the laser is only a small fraction of the total energy in the cavity. By cavity dumping, this power is accessed directly, producing higher energy pulses with peak powers in the kilowatt range. When used in the cavity dumped mode, the laser can operate single-shot or at MHz repetition rates and with pulse lengths of less than 20 ps.

#### 2.2.4 Passive mode-locking of dye lasers

An alternative to the synchronous pumping method for generating picosecond pulses in a dye laser is passive mode-locking using a saturable absorber inside the laser resonator. A saturable absorber is a material whose absorption decreases as light intensity increases and thus a short high peak power pulse suffers less loss in the absorber than a longer, less intense pulse of the same energy. Passive mode-locking of a dye laser was first observed by Schmidt and Schafer [14] who successfully modulated the output of a flashlamp pumped Rhodamine 6G laser with the saturable absorber DODCI (3,3'-diethyloxadicarbocyanine iodide).

In early experimental systems, tunable picosecond pulses were obtained from both Rhodamine 6G and Rhodamine B dye lasers by employing a diffraction grating as one laser-resonator reflector and by immersing the output mirror in the DODCI solution [15]. In a typical arrangement now used, the saturable absorber solution is contained in a cell and is in optical contact with a 100% reflectivity resonator mirror [16, 17]. The laser bandwidth and frequency are controlled with an intracavity Fabry-Perot etalon. Because of variations in the gain of the laser dye and in the absorption of the mode-locking dye as the wavelength is changed, it is necessary to vary the concentration of the absorber so that, for each wavelength, the laser operates just above threshold. The wavelength range covered by flashlamp pumped mode-locked dye lasers now extends from 465 to 805 nm using a range of different dyes and saturable absorbers [11].

The c.w. dye laser can also be passively mode-locked and two different arrangements have been used. The first employed two free flowing dye streams, one for the laser dye and the other for the absorber (see Fig. 4) [18, 19]. In the alternative arrangement, the saturable absorber dye flows in a narrow channel of variable thickness (0.2–0.5 mm) and in contact with a 100% broadband reflectivity mirror. With an absorber thickness of 0.5 mm, output pulses of  $\sim 1$  ps duration have been obtained [20]. Pulses as short as  $\sim 0.3$  ps were produced when the DODCI cell length was shortened to 0.2 mm. The subpicosecond pulses produced in this arrangement were transform-limited in bandwidth.

In summary, the laser provides the photochemist with a light source which is powerful, directional, monochromatic, and possibly tunable. The beam can be on continuously, or pulsed with pulse widths as short as a few picoseconds.

### 3. Fluorescence decay

#### 3.1 INTRODUCTION

The applications of lasers in kinetic studies are essentially twofold. Firstly, they can be used to produce a particular species. This might be a vibration–rotationally defined quantum state of a molecule [21], or it could be an ion [22–24] or fragment [25–28] produced by photoionization or photodissociation [29, 30] of some parent. The combination of specific frequency, short pulse duration and high powers makes selective control of chemical reactions possible. Secondly, they can be used as detectors of specific species and quantum states [31, 32]. There are a number of different methods of using lasers to detect small concentrations of a species in a chemical reaction. Lin and McDonald [33] have broadly reviewed the generation and detection of reactive species in static systems with particular emphasis on the use of lasers for this purpose.

Here, the techniques concerned with the measurement of the kinetics and dynamics of excited states produced by laser excitation will be discussed in detail. The narrow-band tunable dye laser is very useful in these studies since the frequency of the laser can be tuned into coincidence with a particular transition in a molecule, producing a well-defined excited state. The examples which follow are principally concerned with electronic excitation to a particular vibrational–rotational level. Similar techniques can be applied to the study of vibrational distributions [34] and relaxation in a particular electronic state, the difference being that the excitation and emission wavelengths are much longer (infrared) and different lasers and detectors must be used for this spectral region.

Some impression of the specificity of narrow-band laser excitation can be gained from Fig. 5. This figure shows a section of the high resolution



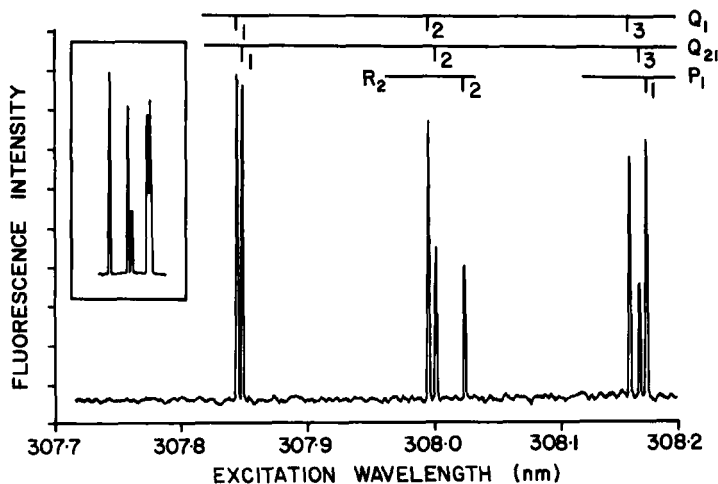


Fig. 5. High resolution laser excitation spectrum of the 0-0 band in the  $A^2\Sigma-X^2\Pi$  system of the OH radical. The widths of the peaks in the spectrum reflect the Doppler width of OH at room temperature,  $\Delta\nu_D^{298} = 0.009 \text{ \AA}$ . (After ref. 35.)

excitation spectrum of the 0-0 band of OH  $A^2\Sigma-X^2\Pi$  measured by McDermid and Laudenslager [35]. A nitrogen laser pumped dye laser operating in an oscillator-amplifier configuration and with an air spaced etalon was frequency doubled in KDP to provide excitation wavelengths near 308 nm with a bandwidth of  $< 0.001 \text{ nm}$ . The wavelength of the laser was scanned while monitoring the total undispersed fluorescence perpendicular to the beam with a photomultiplier. The width of the peaks in this spectrum is the Doppler width and hence, in this case, the resolution is limited by the temperature rather than the bandwidth of the excitation laser. Note how even the satellite lines in the spectrum are clearly resolved and separated from the main branches. By tuning the laser to one of the spectral features, OH could be produced in a specific electronic, vibrational, rotational level. Even a specific  $\Lambda$  doublet in the excited state could be produced and measurements of the kinetics and dynamics of this well-defined state could be made by some of the techniques discussed below.

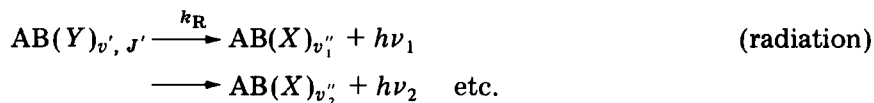
### 3.2 THEORY

The measurement of fluorescence decay times can provide information on a number of fundamental processes. Consider the following kinetic scheme. The molecule AB in its electronic ground state ( $X$ ) is irradiated by a short, narrow bandwidth pulse of light at a wavelength which corresponds to the transition to the vibronic level ( $Y$ ) $_{v', j'}$ , viz.



Following this initiation step, there are a number of both radiative and

non-radiative pathways for the decay of this excited state. At low pressures, where the gas kinetic collision rate is low enough for the majority of the excited molecules to undergo radiative decay before suffering a collision, the fluorescence will be the pure spontaneous emission spectrum from the initially excited state,



This is illustrated in Fig. 6.

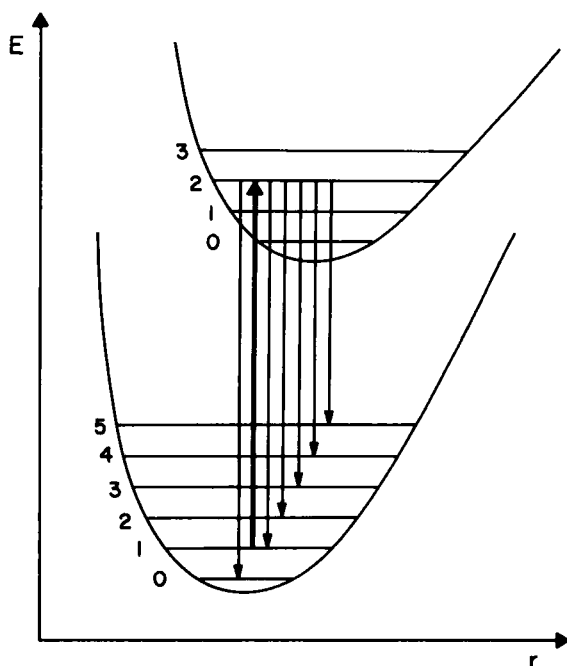


Fig. 6. Schematic diagram showing the possible vibrational transitions seen in emission from an unrelaxed excited state following laser excitation in the 2—1 band.

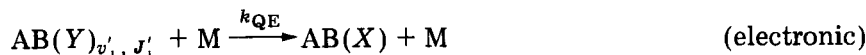
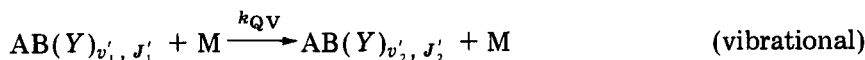
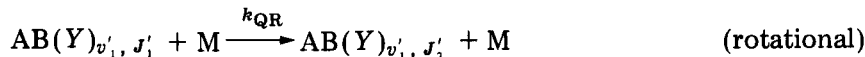
The wavelength of the fluorescence will show a progression into the red of the transitions to the different vibrational levels of the ground state. the intensities of these vibrational transitions will be governed by the Franck—Condon factors and transition probabilities. The number of rotational lines associated with each vibrational transition depends on the nature of the two electronic states concerned. If a ground state vibrational level above  $v'' = 0$  was excited initially, then there will also be fluorescence at shorter wavelengths to the exciting line.

In the absence of collisions, the only processes which can compete with radiation are spontaneous processes such as predissociation and intersystem

crossing, e.g.



At higher pressures, where the number of collisions within the radiative lifetime increases, relaxation processes are important.



The first two of these processes, rotational and vibrational relaxation, do not usually cause a loss of fluorescence. The molecule is still in an electronically excited state and can radiate but at different wavelengths from the initial state. It is therefore possible to observe these relaxation processes by using some method to disperse or select the wavelength of the fluorescence.

Thus if  $[\text{AB}^*]_0$  is the initial concentration of excited AB molecules following the laser pulse, the decay of  $\text{AB}^*$  is given by

$$[\text{AB}^*] = [\text{AB}^*]_0 \exp \{-(k_{\text{R}} + k_{\text{NR}} + k_{\text{Q}} [\text{M}])\} \quad (1)$$

If wavelength selective detection of the fluorescence is used such that only fluorescence from the initially excited state is observed, then

$$k_{\text{Q}} = k_{\text{QR}} + k_{\text{QV}} + k_{\text{QE}}$$

However, when the total undispersed fluorescence is measured, then  $k_{\text{QR}}$  and  $k_{\text{QV}}$  have no observable effect (but see later) and  $k_{\text{Q}} = k_{\text{QE}}$ . The decay constant is thus  $k_{\text{R}} + k_{\text{NR}} + k_{\text{Q}} [\text{M}]$  and the observed fluorescence lifetime ( $1/e$  time) is

$$\tau_{\text{OBS}} = \frac{1}{k_{\text{R}} + k_{\text{NR}} + k_{\text{Q}} [\text{M}]} \quad (2)$$

It is clear that, by changing the experimental conditions and/or detection wavelength, limiting values can be found for all of the quantities mentioned above from measurements of the fluorescence decay time. The effects of collisional and spontaneous processes can be separated by conventional Stern—Volmer analysis [36]. The concentration,  $[\text{M}]$ , of quenching molecules is varied and the reciprocal of the observed lifetime is plotted against the concentration of M. The quenching rate coefficient is thus obtained from the slope and the intercept gives the rate coefficient for the spontaneous relaxation processes, which is usually the natural lifetime of the excited state. In cases where the experiment cannot be carried out under collision-free conditions, this is the only way to measure the natural lifetime from observation of the fluorescence decay.

### 3.3 COLLISIONS AND ENERGY TRANSFER

In an actual experiment, it is frequently not possible to work under conditions where there are no relaxation effects. The usual reason for this is that the intensity of the fluorescence becomes too weak to observe as the concentration of excited molecules is reduced. The lowest pressures which can be used are defined by a number of parameters; the strength of the transition, the power of the laser and the detection efficiency of the system are among the most important. It therefore follows that, in interpreting the results of lifetime measurements, one must consider carefully the possible effects of rotational and vibrational redistribution in the excited state. In a regular unperturbed state where there is little or no change in radiative lifetime with changes in rotational and vibrational level, the effects of relaxation are not observable so long as the fluorescence is still detected with the same efficiency. However, if the excited state is perturbed, for example by predissociation, then the effects of redistribution must be carefully studied.

Some interesting examples of the effects of rotational and vibrational relaxation on the fluorescence decay profile of levels near and above a predissociation are provided by the studies by Clyne and McDermid [37–40], and Clyne and Heaven [41, 42] on the  $B-X$  systems of the hetero- and homo-nuclear diatomic interhalogens.

To take one example, let us consider the effects of rotational relaxation in BrF. The excited  $B^3\Pi(O^+)$  state in BrF is crossed by another  $O^+$  state which leads to predissociation of the  $B$  state in vibrational levels 7 and 6. The initial study of the dynamics of the  $B$  state was carried out in a discharge flow system where the minimum operating pressure was  $\sim 50$  mTorr. The gas-kinetic collision rate coefficient at 298 K for He + BrF( $B$ ) collisions is  $\sim 4.4 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Thus, at the minimum pressure of 50 mTorr, the average time between collisions of excited BrF molecules and helium buffer gas is  $\sim 1.5$   $\mu$ s. This time is short compared with the radiative lifetime of BrF (42–56  $\mu$ s [43]) and therefore significant redistribution in the excited state can occur before it radiates.

The experimental results for  $v' = 7$  [37] showed that the lowest ( $\sim 15$ ) rotational levels exhibited single exponential decay with a decay constant that was essentially independent of  $J'$ . These levels were then assumed to be stable and unaffected by the predissociation. For much higher initial rotational states,  $J' \geq 28$ , the observed lifetime was dramatically shortened. A very rapid initial decay was observed followed after a few microseconds by a slower decay. On increasing the pressure, the initial fast decay was hardly affected but the intensity of the longer-lived decay component increased as more molecules were transferred by rotational relaxation out of the initially formed predissociated state into lower-lying stable states.