PHOTOCHEMISTRY
OF
CHLOROPENTAFLUOROACETONE

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by

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SCOPE AND CONTENTS:

When chloropentafluoroacetone in the gas phase at room temperature is electronically excited in the ultraviolet region, emission is observed. This emission is assigned to a transition from the $^1(n,\pi^*)$ state. Deactivation of the vibrationally excited singlet state can occur when the ketone is excited at short wavelengths. The internal heavy atom effect on both radiative and radiationless transitions from the excited singlet state is relatively small. The quenching of the chloroketone molecules in the zeroth vibrational level of the excited singlet state has been studied and the probable quenching mechanisms proposed. Intersystem crossing from the excited singlet state to the triplet state is an important process in the gas phase at room temperature. However, phosphorescence is observed only in matrices at low temperatures, e.g. 77°K. The internal heavy atom effect on radiative and radiationless transitions from the triplet state in the matrix at low temperature is small.

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CHAPTER 1

INTRODUCTION

HISTORICAL

Light must have intrigued man from the very beginning. Poets, philosophers and scientists alike have wondered at the burning sun, the twinkling stars and the soothing moon in this limitless universe of ours! Curiosity of man to understand the effect of light on different substances eventually led to the development of a new field of research known as "Photochemistry". This field has now become a powerful tool in the study of reaction mechanisms and also has practical applications.

Among the applications of photochemistry, one of the first, successfully explored by Alexander the Great, was the design of a time piece for his soldiers consisting of a chemically treated cloth which changed color under the action of sunlight(1). However, the early discoveries and studies of photochemical reactions were mostly accidental rather than systematic. Before the development of quantum mechanical theories the effect of light was not properly understood. As a result, between 1850 and 1920 a number of photochemical reactions were discovered but their usefulness was limited. Ciamician reviewed(2) the general state of photochemistry, before the advent of quantum theory and he urged scientists to make use of the vast amount of solar energy. Ciamician and Silber(3) and Paterno(4), are among the pioneers greatly responsible for the development of photochemistry.

In the 1950's important theories concerning the electrically excited states were developed and new spectroscopic and analytical techniques became available. These developments reduced the difficulty in characterizing the complex products and gave promise of control of photochemical reactions. One of the main advantages of a photochemical reaction is its selectivity. Photochemistry has made phenomenal progress in the last 15-20 years both in basic theoretical aspects as well as in its applications. A historical review will not be attempted since a number of books(5,6) and reviews(7-10) have recently considered the general area of photochemistry.

GENERAL

In a photochemical reaction activation to initiate a process is provided by absorption of a photon of light by the system. The interaction of photons with molecules and the physical and chemical processes which follow absorption of light are of importance to a photochemist in elucidating the mechanism of a particular reaction system. The sequence of events in a photochemical reaction includes the primary photochemical processes which involve the electronically excited states.

The primary photochemical process is best defined by Noyes et al.$^{(11)}$ as "The primary photochemical process comprises the series of events beginning with the absorption of a photon by a molecule and ending either with the disappearance of that molecule or with its conversion to a state such that its reactivity is statistically no greater than that of similar molecules in thermal equilibrium with their surroundings."

Photochemical laws:

Over the years important and basic laws of photochemistry have been recognized.

The first law according to Grotthus (1817) and Draper (1843) states, "Only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule."

The second law put forward by Stark and Bodenstein (1908-13) and Einstein (1912-13) may be stated as, "The absorption of light by a molecule is a one-quantum process, so that the sum of the primary process-quantum yields must be unity."

The quantum yield may be defined for a given system as follows:

$$\text{Quantum yield, } \phi = \frac{\text{Number of molecules undergoing a particular process}}{\text{Number of quanta of light absorbed by the system}}$$

In applying the second law the primary quantum yield should not be confused with the over-all yield which may be greater than unity since the secondary thermal chain reactions may follow the primary processes. The applicability of the law depends on the relatively short lifetime of the excited molecule and modest level of light intensity. In laser beams or flash photolysis where the intensity is very high some excited species may absorb a second quantum of light.

The third important law in photochemical studies is the combined Beer-Lambert law which describes the absorption of a monochromatic beam of light by a homogeneous absorbing system. This law may be expressed as

$$\log \frac{I_o}{I} = \varepsilon c \ell \qquad (1\text{-}1)$$

where I_o represents the intensity of monochromatic light incident at the front of a column of a single absorbing species of concentration, c (mole/liter); I is the intensity of the light beam transmitted through the column of material, ℓ cm in length; and ε (litres/mole-cm), the molar extinction coefficient, is a constant for a given pure absorbing species at a given wave length and temperature. The law strictly applies to cases where molecular associations are absent (which is usually the case in gaseous state).

Energy level diagram:

The absorption of light excites a molecule from its stable ground state to a higher energy level. A number of such levels are available to a molecule. Figure (1.1) shows an energy diagram which illustrates the important processes involving electronically excited states. For simplicity only three states, the ground state (S_0), the first excited singlet state (S_1) and the first triplet state (T_1) are shown. In the singlet state the spins of electron are paired whereas in the triplet state the spins are unpaired.

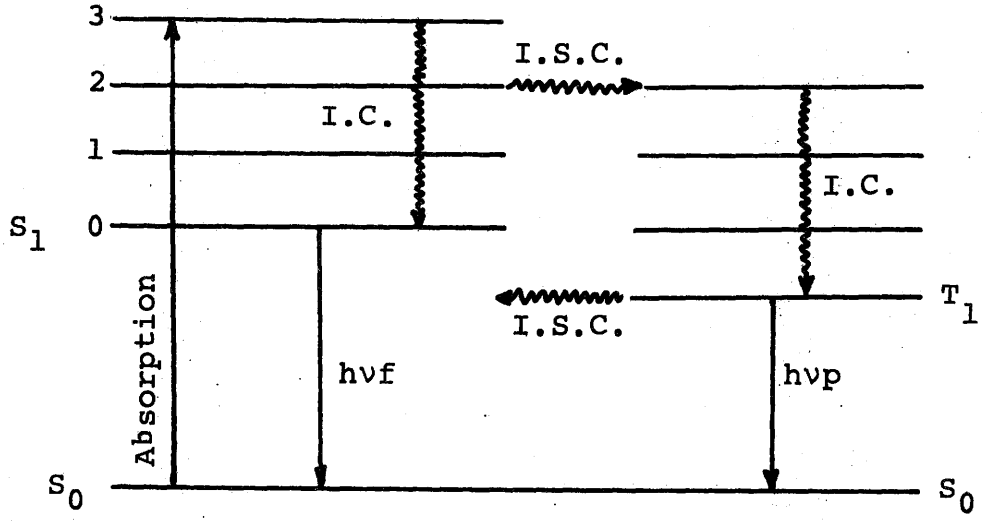


Figure 1.1

Jablonski diagram showing the different modes of dissipating excitation energy

The numbers 1, 2 and 3 represent the vibrational levels which are shown only for excited states. The wavy arrows indicate the radiationless processes which are either intersystem crossing (i.s.c.) or internal conversion (i.c.). $h\nu_f$ and $h\nu_p$ are fluorescence and phosphorescence respectively. The processes leading to chemical changes, e.g. dissociation, are not shown in the figure.

The excited states reached by the absorption of light possess excess energy, as a result these states may be occupied only for short times and could be more reactive than normal molecules. The various modes of deactivation of this excess energy can be grouped into the following classes:

Radiative process

These processes comprise fluorescence and phosphorescence. Chemists class fluorescence as the phenomenon of emission resulting from the transition between states of same multiplicity ($S_1 \rightarrow S_0 + h\nu_f$) whereas the emission termed phosphorescence involves the transition between states of different multiplicity ($T_1 \rightarrow S_0 + h\nu_p$). Physicists, on the other hand, use the criterion of lifetime for distinguishing between fluorescence and phosphorescence. The mean lifetime of fluorescence normally varies between 10^{-6} and 10^{-9} sec. The phosphorescence life time of most molecules varies from 10^{-3} to 10 sec. The transitions between states are governed by selection rules. For example, transitions between states of different multiplicity are "forbidden" and those between states of same multiplicity are "allowed". As a result, fluorescence is short-lived and phosphorescence is long-lived. Because of the "forbidden" nature of the triplet→singlet transition the triplet state is a metastable state.

Radiationless processes:

A radiationless process converts one electronic state to another without involving the absorption or emission of radiation. Excess vibrational energy which results from a radiationless transition is carried away rapidly as heat by collisions with surrounding molecules. Two extremely important types of radiationless processes are:

(1) Internal conversion between different electronic states of like multiplicity, i.e. $S_1 \rightsquigarrow S_0$ or $T_2 \rightsquigarrow T_1$, and

(2) Intersystem crossing between states of different multiplicity, e.g. $S_1 \rightsquigarrow T_1$ or $T_1 \rightsquigarrow S_0$).

These processes have been treated by several authors (12-17). Robinson and Frosch (14,15) consider that the transition rate is governed by intramolecular interactions and base their calculations on the vibrational overlap or Franck-Condon factors. This theory has been applied to the radiationless transitions in aromatic hydrocarbons.

All radiationless processes are iso-energetic and involve some type of energy transfer, i.e., transfer of energy from excited molecule to its environment. This energy transfer may be large (electronic energy transfer) or relatively small (vibrational, rotational or translational energy transfer). As mentioned earlier singlet→triplet or triplet→singlet transitions are "forbidden". However, this is an approximation based on the assumption that the orbital and spin angular momenta of various electrons in atoms or molecules do not couple, i.e. when Russell-Saunders coupling is valid. Russell-Saunders coupling is valid only for light atoms and breaks down for heavy atoms. This interaction between spin and orbital angular momenta is probably the most important single factor allowing intersystem crossing(18). Thus, the heavier the atoms in a molecule, the more important is spin-orbit coupling. The same effect of heavy atoms can be observed even when the heavy atom is not in the molecule but only in its proximity, since Kasha (19) has shown that singlet→triplet absorption is enhanced by solvents containing heavy atoms, e.g. iodine. Also, the presence of heavy atoms either in the molecule or in its vicinity greatly enhances intersystem crossing from the excited singlet state to the lowest triplet state in aromatic molecules and hence increases the phosphorescence yield at the same time decreasing fluorescence yield(20).

The nature of the orbitals involved in electronic transitions plays a very significant role in the amount of spin-orbital coupling in a molecule which does not possess heavy atoms(21). For example, most carbonyl compounds undergo intercombinational transitions at rates 10 to 10^4 faster than analogous unsaturated hydrocarbons and $S_1 \rightsquigarrow T_1$ process dominates the fluorescence from carbonyl compounds.

In addition to the processes shown in figure 1.1 and described above, there are a number of primary photochemical processes such as (i) intramolecular decomposition, (ii) dissociation into radicals, (iii) photoisomerization, (iv) photosensitized reactions, (v) photoaddition, (vi) hydrogen atom abstraction, (vii) intramolecular rearrangement, (viii) photoionization and (ix) electron transfer. Two important aspects of the unimolecular primary processes are predissociation and photodecomposition.

(1) Predissociation:

Excitation from the ground state S_0 yields a molecule in an excited state S_1 which would be stable in the absence of another repulsive excited state S_2. If the excitation gives a molecule in a vibrational level of S_1 above its intersection with S_2, the molecule will, during its vibrational motion, pass through a point at which the potential as well as the kinetic energies in the two states are equal. In the neighbourhood of this point the molecule may cross over to the repulsive state S_2 and dissociate. The S_2 state need not necessarily be repulsive for dissociation to occur. Dissociation from the S_2 state will occur provided the vibrational level to which the molecule is excited lies above the dissociation of S_2.

In polyatomic molecules with a large number of vibrational degrees of freedom states such as S_2 are very common and potential energy surfaces often cross. If the excited state corresponds to an energy greater than the bond-dissociation energy of some bond in the molecule, then the molecule excited to S_1 may cross over to S_2 and dissociate.

(2) Photodecomposition:

Photodecomposition is often one of the routes of dissipation of excitation energy. This occurs when the vibrational level of S_1 reached by excitation is one of the continuous set lying above the dissociation energy of the state S_1 and is characterized by the fact that the absorption in this region is continuous.

After this discussion of some aspects of general photochemistry, the following sections briefly survey the photochemistry of carbonyl compounds. In the past few years excellent reviews(11,23,24) have appeared on the photochemistry of carbonyl compounds. Here only the salient features of the photochemistry of compounds directly related to present research will be described. Emphasis will be laid on the emission studies of ketones.

Configuration of Carbonyl Compounds:

Before dealing with the configuration of the carbonyl group it may be useful to describe very briefly the common molecular orbitals. They are: (1) sigma-bonding (σ), sigma antibonding (σ^*), pi-bonding (π), pi-antibonding (π^*) and nonbonding (n) orbitals.

σ-orbitals form the basis for single bonds between two atoms. The electrons located in such orbitals are strongly bonding and localized. π-orbitals are associated with the multiple bonds and the electrons in these orbitals are delocalized over two or more nuclei. σ and π orbitals have σ* and π* antibonding counterparts respectively. Certain heteroatoms, such as oxygen, containing "lone pair" electrons introduce an n orbital. These orbitals are localized on one particular atom and have no anti-bonding counterpart.

If one ignores the σ and the lower energy orbitals which are not expected to take part in electronic transitions in the ultraviolet region the ground state configuration (S_0) of the carbonyl group may be written as

$$S_0 = (\pi_{CO})^2(n_O)^2(\pi^*_{CO})^0(\sigma^*_{CO})^0$$

where molecular orbitals increase in energy. The excitation at highest wavelength corresponds to promotion of an electron from the highest occupied orbital to the lowest unoccupied orbital. The common transitions, resulting from absorption of the ultraviolet radiation, between different molecular orbitals for the carbonyl group are given in table 1.1 below.

Table 1.1

Excited state configuration of carbonyl group

Designation Transition	Resulting state	Configuration
n→π*	n,π*	$(\pi_{CO})^2(n_O)^1(\pi^*_{CO})^1(\sigma^*_{CO})^0$
π→π*	π,π*	$(\pi_{CO})^1(n_O)^2(\pi^*_{CO})^1(\sigma^*_{CO})^0$
n→σ*	n,σ*	$(\pi_{CO})^2(n_O)^1(\pi^*_{CO})^0(\sigma^*_{CO})^1$
π→σ*	π,σ*	$(\pi_{CO})^1(n_O)^2(\pi^*_{CO})^0(\sigma^*_{CO})^1$

Each of the states shown in table 1.1 above may be a singlet or a triplet. However, only singlet and triplet, n,π^* and π, π^* states are formed by absorption in the ultraviolet region. Most studies of carbonyl compounds have investigated the n,π^* (singlet and triplet) states, as the $n \to \pi^*$ transitions require the least energy and absorb radiation ($f \simeq 10^{-2}$ to 10^{-4}) in a convenient ultraviolet region.

The $n \to \pi^*$ transition is electronically "forbidden". However, the transition can occur due to certain perturbations. For example, the $n \to \pi^*$ transition can occur from the planar ground state to an excited state in which the nuclei are bent out of the plane. In case of formaldehyde the ground state is planar whereas the upper states, both singlet and triplet, are non-planar(25,26). In the excited singlet and triplet states the plane of CH_2-group is inclined to C=O axis by 20° and 38° respectively. The $\pi \to \pi^*$ transition is electronically "allowed" and lies higher in energy than the $n \to \pi^*$ transition. The $\pi \to \pi^*$ transition in the carbonyl compounds usually takes place below 200 nm and results in an intense absorption. However, very little work has been done in this region.

Simple ketones which contain only one carbonyl group absorb between 350 and 220 nm with maximum occurring around

300 nm. This is a relatively weak absorption band. Another rather strong absorption region is between 200 and 150 nm. The former is due to an $n \rightarrow \pi^*$ transition and the latter corresponds to a $\pi \rightarrow \pi^*$ transition.

For diketones, particularly when the two carbonyl groups are adjacent to each other, the absorption is shifted toward longer wavelength. For example, the gas phase absorption spectrum of 2,3-butanedione (biacetyl) extends from 200 to 467 nm with the maximum around 400 nm(27,28). The carbonyl compounds absorb in the convenient region, are relatively simple to handle and exhibit all the important aspects of photochemical behaviour. These features are probably responsible for the exhaustive photochemical study of carbonyl compounds.

Primary photochemical processes in carbonyl compounds:

In this section the primary processes in the photochemistry of carbonyl compounds are described in detail. These processes are contained in the following mechanism which is similar to that suggested by Noyes et al.(11).

$$A + h\nu \rightarrow {}^1A^n \qquad (1.2)$$

$$ {}^1A^n \rightarrow \text{Dissociation} \qquad (1.3)$$

$$ {}^1A^n + M \rightarrow {}^1A^o + M \qquad (1.4)$$

$$ {}^1A^o \rightarrow A + h\nu_f \qquad (1.5)$$

$$ {}^1A^o \rightarrow A^n \qquad (1.6)$$

$$A^n + M \rightarrow A + M \qquad (1.7)$$

$$^{1}A^{o} \rightarrow {}^{3}A^{n} \tag{1.8}$$

$$^{3}A^{n} \rightarrow \text{Dissociation} \tag{1.9}$$

$$^{3}A^{n}+M \rightarrow {}^{3}A^{o} + M \tag{1.10}$$

$$^{3}A^{o} \rightarrow A + h\nu_{p} \tag{1.11}$$

$$^{3}A^{o} \rightarrow A^{m} \tag{1.12}$$

$$A^{m}+M \rightarrow A + M \tag{1.13}$$

$$A^{n} \rightarrow \text{Dissociation} \tag{1.14}$$

A is a ketone molecule in its ground state and M represents an inert gas. Superscripts 1 and 3 indicate the excited singlet and triplet states respectively and n and m represent the upper vibrational levels. Reaction (1.2) is the photo-excitation of the compound being studied. Reactions (1.3) and (1.9) represent the dissociation from the excited states whereas reaction (1.14) represents the dissociation from the vibrationally excited ground state. The products formed from different electronic states may not be the same.

The vibrational deactivation represented by reactions (1.4), (1.7), (.10) and (1.13) is shown as a strong collisional process, i.e., the excess vibrational energy is removed in one collision. In certain cases, to be discussed later, there is evidence that the excess vibrational energy is removed by a cascade through vibrational levels, a weak collisional process. Reactions (1.5) and (1.11) are fluorescence and phosphorescence respectively. The emission from the simple ketones in the gaseous phase often consists of both fluorescence and phosphorescence. The relative importance of fluorescence and phosphorescence depends on the individual compound under investigation and on the experimental conditions. The change in fluorescence and phosphorescence as a function of some experimental parameter may be useful in interpreting the mechanism of the system.

Reaction (1.6) indicates the internal conversion from the excited singlet state to the ground state whereas reactions (1.8) and (1.12) are the examples of the inter-system crossing. The triplet state with high vibrational energy, formed by crossover from the excited singlet state may dissociate or be deactivated by collisions to lower vibrational levels. The triplet state in the lower vibrational levels may intersystem cross to the ground state of phosphorescence.

It should be emphasized that the mechanism given above is only a general one. Certain reactions may be absent in some cases and the relative importance of each reaction will depend on the individual system. In the following sections the photochemistry of (1) monoketones, (2) diketones, and (3) halogenated ketones is discussed briefly.

Acetone:

The ultraviolet absorption spectrum of acetone extends from 220 to 350 nm(11, 29). The emission spectrum starts from 380 nm. Thus there is no overlap between the absorption and the emission spectra of acetone. However, the 0-0 band for singlet state has been suggested to lie around 360 ± 20 nm(11) and this is equivalent to about 79 Kcal per mole. The photochemical studies place the triplet state of acetone at about 77 K cal per mole above the ground state(11). The gap between the long wave limit of the absorption spectrum and the short wave limit of the emission spectrum suggests that the geometries of the lower and upper electronic states differ significantly. The maximum absorption is around 272-282 nm and there is evidence of structure from 295 nm to longer wave lengths(30-32). This indicates that the upper state has some stability, although photochemical dissociation occurs throughout the absorption region.

Spectroscopic investigations have provided information about the excited states of acetone undergoing dissociation and emission. The luminescence from acetone excited by 313 nm at room temperature extends from 470 to 380 nm with a maxima around 450 nm(23). The emission consists of both fluorescence and phosphorescence. The fluorescence lifetime of acetone in n-hexane is 2.5×10^{-9} sec at room temperature(33). The phosphorescence lifetime of the acetone vapor (pressure > 100 torr) at 25°C is 2×10^{-4} sec (34). The total emission yield is about 2×10^{-2} (35,36) and phosphorescence accounts for about 90% of the emission yield.

Quenching of phosphorescence by oxygen ($k_q = 8.2 \times 10^7$ M^{-1} sec^{-1}) follows a Stern-Volmer mechanism(37). In a reinterpretation of the emission data of acetone, O'Neal(38) suggests that the fluorescence is independent of acetone pressure and the phosphorescence-quenching by acetone does not obey a Stern-Volmer mechanism. This is a consequence of two decomposition processes, one from the upper vibrational levels of the triplet state and another from the triplet state in thermal equilibrium, i.e. the ground vibrational level. The acetone-phosphorescence in gas phase is quenched by biacetyl(39,40) aliphatic aldehydes(41) and unsaturated hydrocarbons(42) by energy transfer mechanism.

$$^3A^0 + Q \rightarrow A + {}^3Q \, . \qquad (1.15)$$

The quenching of the phosphorescence of acetone by olefins was explained by Lee et al.(43). They consider that the quenching ability is a function of overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor. The larger the overlap the higher is the quenching efficiency.

The triplet state of acetone is shown to be extensively populated, the yield approaching unity at room temperature(44). The low phosphorescence efficiency was ascribed to a relatively efficient radiationless decay process involving intersystem crossing to the ground state ($T_1 \rightsquigarrow S_0$, $k = 1.25\times10^5 \text{ sec}^{-1}$)

Abrahamson(45) studied the triplet energy transfer. in the solutions of carbonyl compounds and olefins and suggested that the transfer occurs via a chemical intermediate, triplet state oxetane. Recently Turro and Wriede(46) have reported the photocycloaddition of acetone to 1-methoxyl-1-butene to form oxetanes. Their data indicate that both the excited singlet and triplet states of acetone are involved in the oxetane formation and the rate constants for attack of acetone singlets or triplets on a given butene are almost equal. The mechanism is supposed to involve singlet or triplet biradicals. Photocycloaddition of acetone to 1,2-dicyanoethylene has also been reported(47) and is supposed to involve attack of the excited singlet state acetone on the olefin to form oxetanes.

Biacetyl:

The long wave limit of the ultraviolet absorption spectrum of biacetyl is 467 nm(27,28) and the short wave limit of fluorescence is between 440 and 450 nm(11). The 0-0 band for singlet states is suggested to lie around 450 nm, i.e.

the energy separation between the ground and the first excited singlet states is 64 K cal/mole. Sidman and McClure(48) put the short wave limit of fluorescence at 437 nm (65.4 K cal/mole). The energy of the triplet state is placed at 55 K cal/mole above the ground state. Conjugation of the adjacent carbonyl groups has, thus, lowered the energy of the excited singlet and triplet states.

The emission consists of both fluorescence and phosphorescence with respective lifetimes of about 11 × 10^{-9} sec (ketone = 25 torr)(49) and 1.8 × 10^{-3} sec (ketone > 1 torr)(50) at 25°C. The fluorescence spectrum is weak and extends from 450 to 500 nm(11). Phosphorescence, on the other hand, is strong and extends from 500 nm to greater than 610 nm with broad maxima occurring at 510, 560 and 610 nm(48,51). The fluorescence and phosphorescence quantum yields in gas phase at room temperature are 2.5 × 10^{-3} and 0.15 ± 0.03 respectively when excited with 436, 405 or 365 nm(52). Okabe and Noyes(53) found that the ratio of fluorescence to phosphorescence is independent of exciting wave length and of the pressure of the diketone, which suggests that the intersystem crossing and fluorescence occur from closely similar vibrational levels of the excited singlet state. Also, from lower vibrational levels the efficiency of cross-over to the triplet state is almost unity(54,55). Further, the emission spectrum is independent of pressure and exciting wavelength which suggests that the emission originates from the lowest vibrational levels of the excited states.

Both fluorescence and phosphorescence decrease as temperature increases(56) although the latter decreases much more rapidly than the former. The processes competing with the radiative processes must have a considerable activation energy since at 200°C the phosphorescence is completely quenched.

Oxygen quenches the phosphorescence but not the fluorescence of biacetyl. The quenching obeys a Stern-Volmer mechanism up to a pressure of 350 microns of oxygen but above 3 torr the emission yield is constant, corresponding to fluorescence(34,56). No emission is observed when the excitation is between 238 and 313 nm(11). This is understandable, because at shorter wave lengths the excitation is to a different excited state that can photo-decompose more efficiently.

Halogenated Ketones:

The halogenated ketones and aldehydes have attracted interest as radical sources, although in recent years photochemical studies, particularly of hexafluoroacetone, have been directed toward understanding of basic mechanisms. The substitution of halogen atoms leads to an increase in the molecular extinction coefficient and shifts the absorption maxima toward red. Ketones containing both chlorine and fluorine atoms show some structure in their absorption spectra(57).

Hexafluoroacetone:

Hexafluoroacetone is one of the most extensively investigated carbonyl compounds. The primary photochemical processes for this ketone are fairly well understood. The hexafluoroacetone ultraviolet absorption spectrum extends from 245 to 355 nm(23,58) with the maximum occuring at about 302 nm. Thus, there is a red shift of about 20 nm compared with acetone.

Okabe and Steacie(59) first observed the luminescence from hexafluoroacetone excited with 313 nm. They found the emission profile to be independent of the ketone pressure at room temperature. The emission spectrum is a broad structureless band extending from 347 to 600 nm with the maximum at 420 nm and the spectrum is independent of the exciting wavelength. These authors also reported fluorescence enhancement with increasing pressure of the ketone of an added gas due to vibrational deactivation of the excited state.

Bowers and Porter(60) and Gandini and Kutschke(61) later showed that the emission from hexafluoroacetone consists of both fluorescence and phosphorescence. The phosphorescence of hexafluoroacetone increases as the temperature decreases because at lower temperatures thermal dissociation is inhibited(60) The absence of phosphorescence in earlier investigations was attributed to the quenching by some olefinic impurity present in the sample(61). Thus, the presence of both singlet and triplet states in gas phase at room temperature is established.

The phosphorescence lifetime of hexafluoroacetone at room temperature is 3.4 m sec(58). Kutschke and co-workers(62,63) first reported an efficient quenching of the phosphorescence of hexafluoroacetone by mercury [$k_{Hg} = 3 \times 10^{10}$ M^{-1} sec^{-1}]. Quenching of the hexafluoroacetone phosphorescence by olefins, benzene, perfluorobutane, oxygen and isobutane(61) and by biacetyl(60,64) has also been studied. Kutschke and co-workers(58,64,65-67) have carried out very interesting and extensive studies on primary photochemical processes of hexafluoroacetone. Their investigations included variations in exciting wavelength, temperature and pressure of the ketone and the added gas. The quantum yields of the fluorescence and phosphorescence (limiting values at high pressure) are 0.018_5 and 0.11_3 respectively. Thus it is evident that the phosphorescence is one of the important primary processes in the photochemistry of hexafluoroacetone. Cook and Landrum(68) and later Knipe and Gordon(69) found that the triplet state hexafluoroacetone plays an important role in the oxetane formation.

The fluorescence-enhancement with increasing pressure of the ketone or an added gas was also observed by Ware and Dutton(70). These authors determined the fluorescence lifetime as 78 ± 2 nsec and it decreased as temperature increased. Studies on the fluorescence of hexafluoroacetone were later extended(71) to include quenching by olefins, oxygen and benzene. Among the quenchers studied piperylene was most efficient ($k_{pip} = 8.0 \times 10^{10}\ M^{-1}\ sec^{-1}$ at 25°C) and perfluoropropylene does not quench. Kutschke et al(65,66) confirmed the fluorescence enhancement due to vibrational deactivation and observed the quenching of the singlet state of hexafluoroacetone by butenes and biacetyl at higher concentrations.

McIntosh and Porter(72) studied the energy transfer from the excited state of hexafluoroacetone to ground state hexafluorobiacetyl. At lower pressures of hexafluorobiacetyl only phosphorescence is quenched and at higher pressures of hexafluorobiacetyl both phosphorescence and fluorescence are quenched. The rate constants for the singlet-singlet and the triplet-triplet energy transfer are $6.0 \times 10^{9}\ M^{-1}\ sec^{-1}$ and $8.5 \times 10^{8}\ M^{-1}\ sec^{-1}$ respectively.

Very recently Halpern and Ware(73) reinvestigated the fluorescence lifetime of hexafluoroacetone as a function of exciting wave length and the ketone pressure. At pressures greater than 15 torr the fluorescence decay was exponential and independent of the exciting wavelength and pressure yielding the fluorescence lifetime 84×10^{-9} sec. At very low pressures, < 0.5 torr, the decay curve is again exponential but the lifetime is a function of exciting wavelength, i.e. the lifetime decreases as the energy increases. In the intermediate pressure range the decay curve does not exhibit exponential behaviour and the departure from the exponential behavior is a function of the pressure and the exciting wavelength. Relevant data will be discussed later in more detail.

Present Work:

Luminescence studies have been most important in explaining the primary photochemical processes in ketones in gas phase. The fluorescence and phosphorescence of acetone(38), biacetyl(11) and hexafluoroacetone(58) have been correlated with the photodecomposition processes of these ketones. However, the photochemistry of the chlorinated ketones in the gas phase has been concerned mainly with photodecomposition studies and investigations of radical reactions e.g. chloroacetone(74), chlorobutanone(75), hexachloroacetone(77), 1, 3-dichlorotetrafluoroacetone(78), 1,1,3-trichlorotrifluoroacetone(77) and 1,1,3,3-tetrafluoroacetone(10). Little interpretation of the photophysical processes has been presented.

While the present investigations were in progress the photolysis of chloropentafluoroacetone was reported(80). The photolysis products formed are CO, CF_3Cl,CF_2Cl_2, C_2F_6, C_2F_5Cl, $C_2F_4Cl_2$, C_3F_8, C_3F_7Cl, $C_3F_6Cl_2$ and octafluorobut-3-one. The following reaction scheme was proposed to explain the experimental data:

$$CF_3COCF_2Cl + h\nu \rightarrow CF_3^{\bullet} + CO + \dot{C}F_2Cl \tag{1.16}$$

$$\rightarrow CF_3CO\dot{C}F_2 + Cl^{\bullet} \tag{1.17}$$

$$2CF_3^{\bullet} \rightarrow C_2F_6 \tag{1.18}$$

$$CF_3^{\bullet} + \dot{C}F_2Cl \rightarrow C_2F_5Cl \tag{1.19}$$

$$2\dot{C}F_2Cl \rightarrow C_2F_4Cl_2 \tag{1.20}$$

$$\dot{C}F_3 + \dot{C}F_2Cl \rightarrow CF_3Cl + :CF_2 \tag{1.21}$$

$$2\dot{C}F_2Cl \rightarrow CF_2Cl_2 + :CF_2 \tag{1.22}$$

$$:CF_2 + 2\dot{C}F_3 \rightarrow C_3F_8 \tag{1.23}$$

$$:CF_2 + \dot{C}F_3 + \dot{C}F_2Cl \rightarrow C_3F_7Cl \tag{1.24}$$

$$:CF_2 + 2\dot{C}F_2Cl \rightarrow C_3F_6Cl_2 \tag{1.25}$$

$$\dot{C}F_3 + C\dot{l} \rightarrow CF_3Cl \tag{1.26}$$

$$\dot{C}F_2Cl + C\dot{l} \rightarrow CF_2Cl_2 \tag{1.27}$$

$$CF_3CO\dot{F}_2 + \dot{C}F_3 \rightarrow CF_3COC_2F_5 \tag{1.28}$$

$$CF_3CO\dot{C}F_2 + \dot{C}F_2Cl \rightarrow CF_3COCF_2CF_2Cl \tag{1.29}$$

As expected reaction (1.17) becomes more significant at shorter wavelengths. On the basis of their data the authors suggest that some excited state whose mean lifetime is expected to be shorter than that of hexafluoroacetone but longer than that of acetone, is involved in the photochemistry of chloropentafluoroacetone. However, they do not identify the excited state.

Chloropentafluoroacetone was chosen for the present investigation as it can shed some light on the general applicability of the photochemical mechanism given earlier. By comparing the relevant data on chloropentafluoroacetone with those of the related ketones one can determine the effect of the chlorine atom on the photochemistry of the ketones and the interaction with quenching molecules. This molecule is especially interesting as the effect of the heavy atom on the radiative and radiationless processes from both the excited singlet and triplet states can be evaluated.

CHAPTER 2

EXPERIMENTAL

Vacuum equipment

The vacuum rack was a conventional pyrex system divided into low vacuum and high vacuum sections. The low vacuum section was evacuated by a single stage rotary pump while the high vacuum section was evacuated by a mercury diffusion pump backed by a two stage rotary pump. A liquid nitrogen trap was used to protect the high vacuum mechanical pump.

The high vacuum system was grease-free and subdivided into two sections: (i) purification and general storage section and (ii) cell section with a limited storage-arrangement. Mercury float valves (Delmar) were used in the purification section. Thus the purification section was saturated with mercury vapor. The cell-section was connected to the other section by Delmar teflon valves. The contamination of the cell-section by mercury vapor was minimized by maintaining two U-traps in series at -78°C, during the process of transferring gases from the purification section to the cell-section or at -196°C at other times. The pressure-measurements were done on a pyrex Bourdon gauge attached to the cell-section.

Reaction cells:

Two types of cells were used in the present studies: (a) 1-cm cubical cell for work at high ketone pressures and (b) 10-cm cell for work at low ketone pressures. Two different cells had to be used because of intensity problems. At low pressures the emission signal from a 1-cm cell became very noisy due to scattered light. Therefore, a 10-cm cylindrical cell was used to get a better signal. The 1-cm suprasil cubical cells (Hellma) were polished on all four sides and were 1 cm square in cross-section (suprasil is a high quality quartz that does not fluoresce). The 10-cm cylindrical cell was T-shaped and had suprasil windows attached to it. The diameters of the end windows and side window were 5.4 and 3.3 cm respectively. The 1-cm and 10-cm cells transmitted over 92% of the incident radiation. The cells were attached to the vacuum system via metal valves with kovar-pyrex seals.

Absorption studies:

The absorption spectra of the samples were taken on Cary-14 (dual beam) recording spectrophotometer in the 1-cm and 10-cm cells. The absorption spectra of the interference filters and filter solutions were also measured; these are shown in figures 2.1, 2.2 and 2.3.

Emission studies with wavelength resolution:

Preliminary measurements of the luminescence of chloropentafluoroacetone were made on an Aminco Bowman spectro-

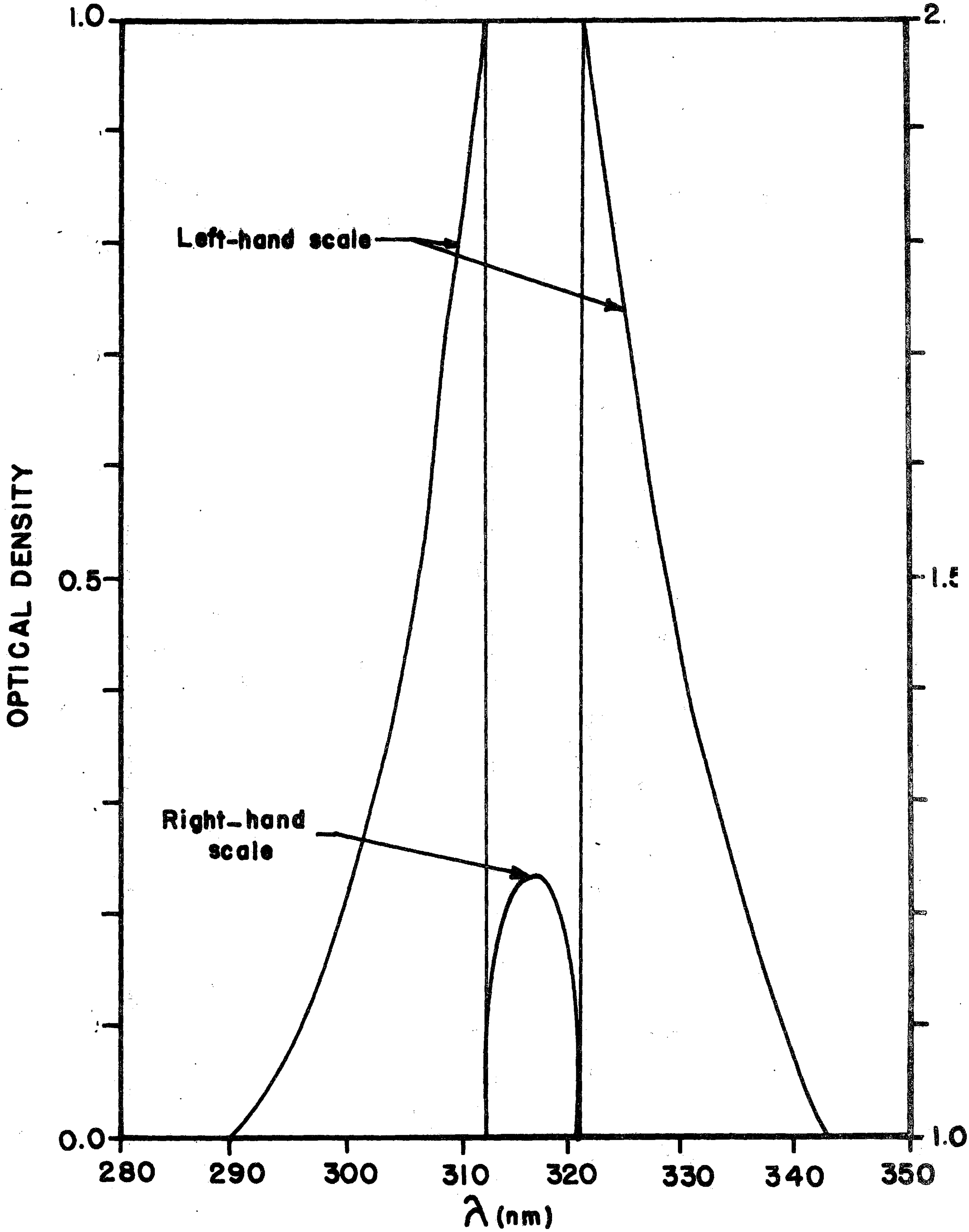


Figure 2.1 Absorption spectrum of 313 nm interference filter

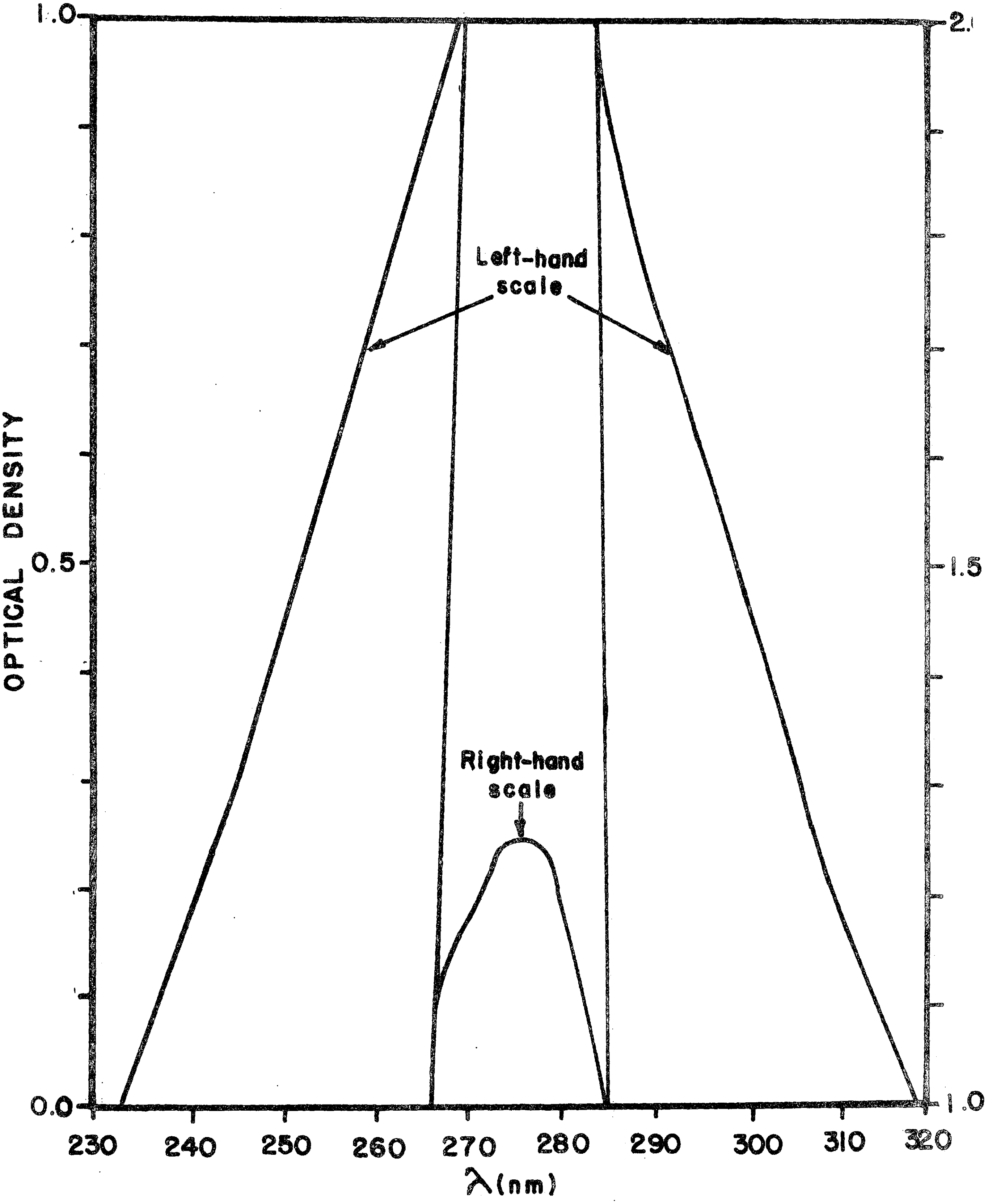


Figure 2.2 Absorption spectrum of "290" nm interference filter

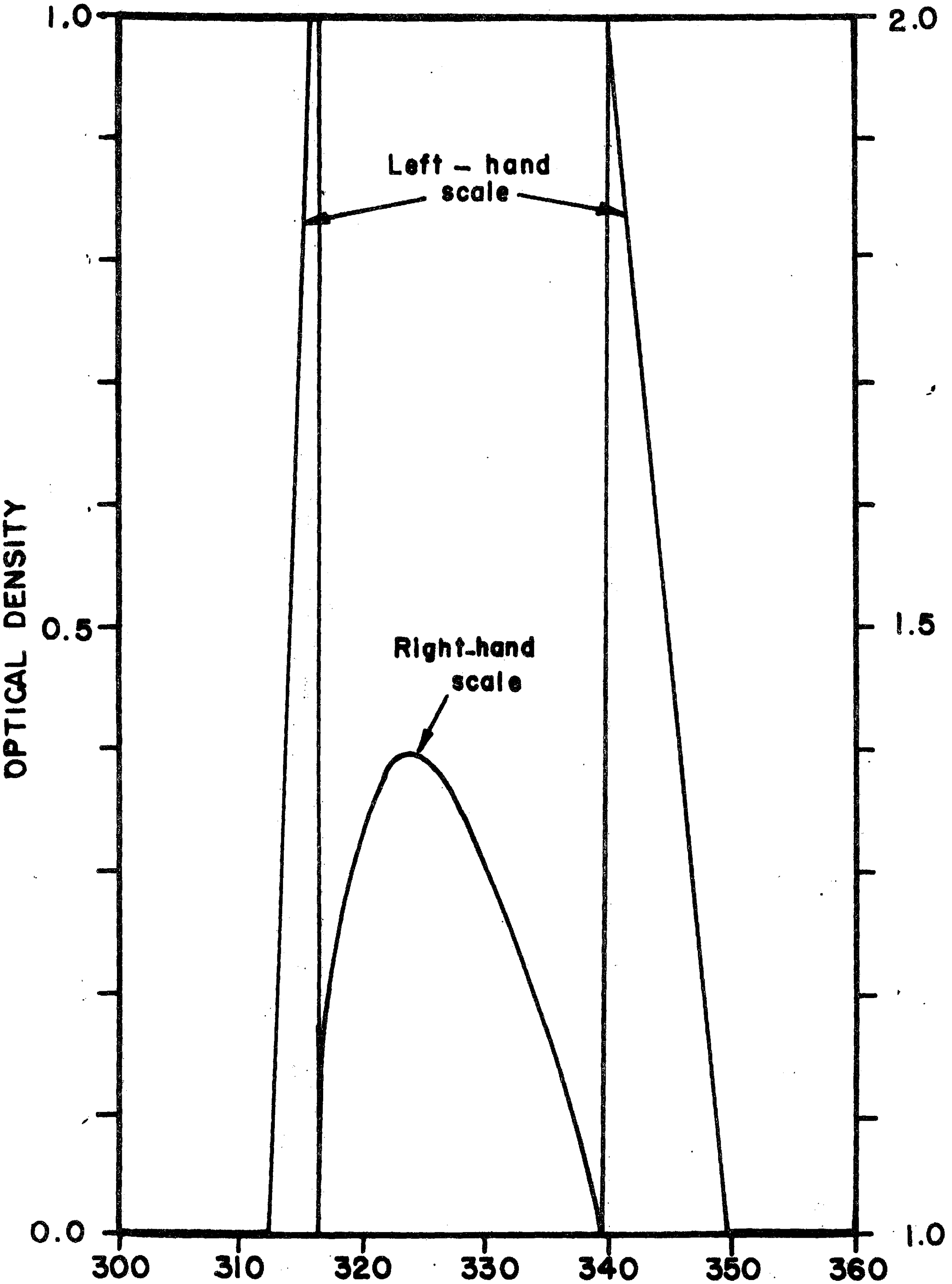


Figure 2.3 Absorption spectrum of chemical filter for 334 nm

fluorometer fitted with a phosphoroscope attachment. Detailed studies of the luminescence were done using a different apparatus. The excitation source was either a 1000 WHg/Xe lamp or 450 W Xe lamp. The monochromator used for the excitation radiation was a small Bausch and Lomb monochromator with a 1200 grooves/mm grating blazed at 400 nm. The emitted light at right angles to the incident beam was analyzed using a 0.5 m Ebert Jarrell-Ash monochromator with 1180 grooves/mm grating blazed at 400 nm, fitted with an RCA8575 photomultiplier cooled to -78°C. The output was measured by a Keithley electrometer (model 610B or 610C) and the emission spectrum recorded by a pen recorder.

Absolute quantum yield determinations:

The absolute quantum yield of emission can be calculated from a true spectrum. Since the sensitivity of photomultiplier is a function of wavelength, the spectrum presented on the recorder is not a true spectrum of the sample. In order to get a true spectrum, one can correct the above spectrum by comparing it with the spectrum of a standard substance taken under identical conditions. During the present investigations quinine sulfate(81,82) was selected as standard for the following reasons:

(i) the fluorescence of quinine sulfate extends from 390 to 580 nm, therefore is suitable for calibrating spectrophotometers in the visible region ,

(ii) it is reasonably stable to visible and near ultraviolet radiation ,

(iii) there is very little self-quenching,

(iv) fluorescence of quinine sulfate is not quenched by dissolved air,

(v) fluorescence quantum yield is high,

(vi) the emission profile is independent of quinine sulfate concentration, and

(vii) change in acid concentration does not change the fluorescence spectrum.

Two matched one-cm suprasil cells were taken. One was filled with the appropriate amount of chloropentafluoroacetone and the other with quinine sulfate solution in sulfuric acid. The cell holder along the optical bench was in a fixed position so that the cell positions were the same in both the cases. The spectra were then recorded. Although the sample was in the gaseous state and the standard was a solution the data were not corrected for reflections at the windows. These corrections are within 5% in both cases and tend to cancel. Thus the overall effect of these corrections is negligible.

By comparing the absolute (81,82) and relative (present) fluorescence spectra of quinine sulfate a sensitivity scale was derived. This sensitivity scale was used to correct the fluorescence spectrum of the sample. The absolute quantum yield of fluorescence of chloropentafluoroacetone excited at 313 nm was obtained by comparing areas under the corrected spectra (plotted as intensity versus wave number) of the ketone and quinine sulfate.

Emission studies without wave length resolution:

The total chloroketone luminescence, without wave length resolution,was also measured. The experimental arrangement for this study is shown in figure 2.4.

The excitation source was a medium pressure mercury lamp (Hanovia # 673A). The lamp housing was water-cooled and the flow of water was adjusted to give the maximum stable intensity. The lamp was always warmed up for at least half an hour before being used. The radiation from the medium pressure mercury lamp consists of a number of wave lengths with different intensities. Table 2.1 gives the relative energy distribution of this lamp(83).

Excitation wave lengths were isolated by using appropriate filters. 334 nm radiation was obtained using filter-solutions(84) as described below:

	(1)	(2)	(3)
Components	$NiSO_4.6H_2O$ 10.0 gm/100 c.c. aqueous solution	Corning glass filter 6-71 (5970)	Naphthalene in isooctane 1.28 gm/10 c.c.
Path length	5.0 cm	0.5 cm	1.0 cm

Since the transmittance of the filter-solution varies

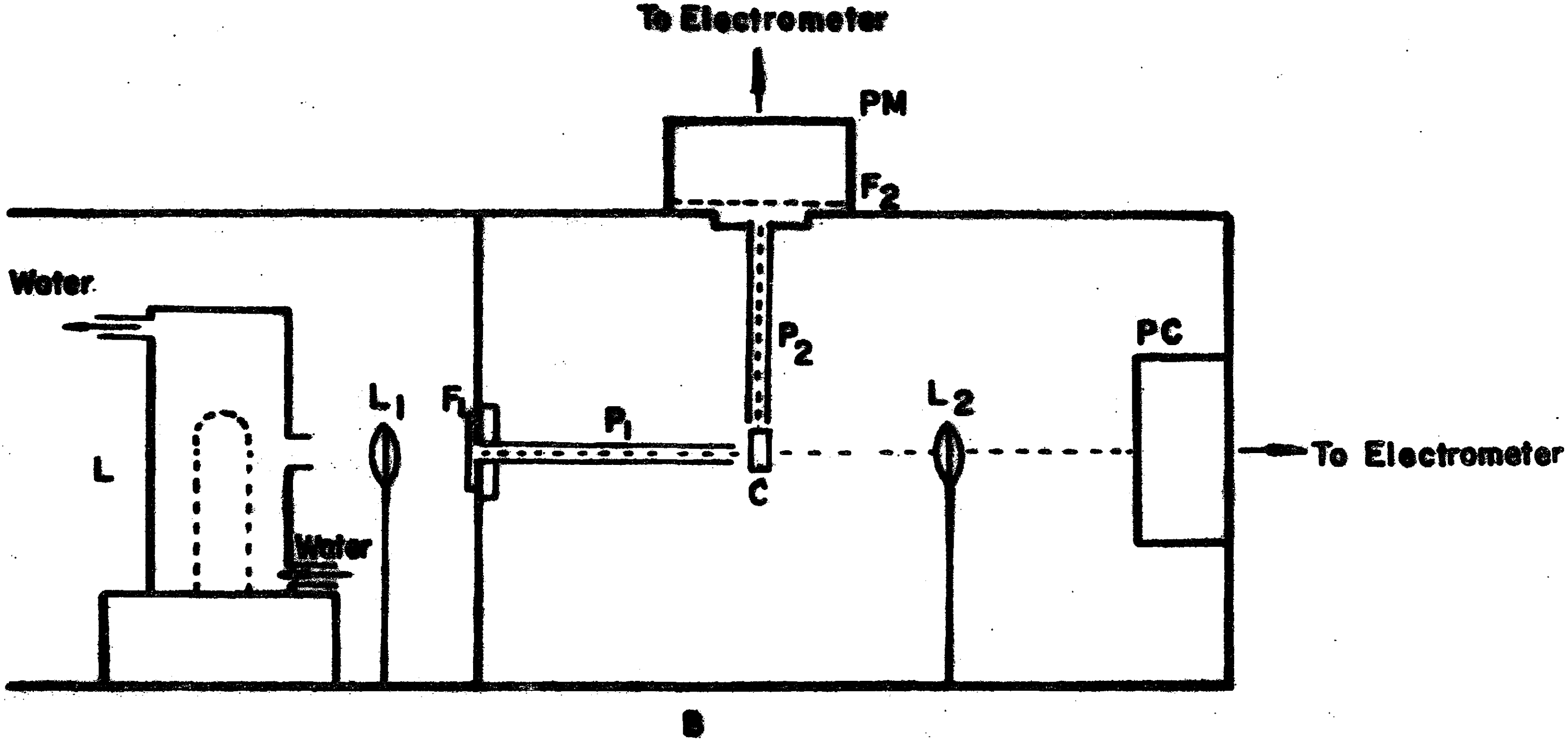


Figure 2.4 Optical arrangement for steady state studies
Legend: L, lamp; L_1 and L_2, lenses; P_1 and P_2, light pipes; F_1 and F_2, filters; PM, photomultiplier; P.C., photocell; c, cell; and B, light proof wooden box.

Table 2.1

Energy Distribution in Medium Pressure Mercury Lamp

Wave length (nm)	Relative Intensity
1367	15.3
1129	12.6
1014	40.6
577-579	76.5
546	93.0
436	77.5
405-408	42.2
365-366	100.0
334	9.3
313	49.9
302-303	23.9
297	16.6
289	6.0
280	9.3
275	2.7
270	4.0
265-266	15.3
257	6.0
254	16.6
248	8.6
240	7.3
238	8.6
236	6.0
232	8.0
222	14.0

to some extent when fresh solutions are used, the compact assembly of filter-solutions was irradiated for about 10 hours before being used in the emission experiments.

The 313 nm line was selected using a third order interference filter (Baird Atomic). The radiation classed as "290" nm group was isolated by an interference filter (Optics Technology #2700). This group consisted mainly of 289 and 297 nm radiation. The lamp,filters and the cell were housed in separate light-proof compartments of a wooden box.

The excitation radiation, which was collimated by a quartz lens, passed through the cell as a parallel beam and was condensed by a quartz lens onto a photocell (RCA 935). The emitted light observed at right angles to the incident beam was collimated by a stainless steel tube. The emitted light passed through a Corning 0-52 glass filter which removed radiation below about 350 nm, was detected by a 1P28 photomultiplier and measured on the electrometer. The dark current plus the scattered light signal was approximately 3×10^{-9} amperes in the above equipment.

Singlet quenching studies:

The singlet quenching studies were done on an improved version of the earlier equipment used for total emission studies without wavelength resolution. This equipment is shown in figure 2.5. The fluctuations in the lamp intensity were monitored by reflecting a fraction of radiation (313 nm) from

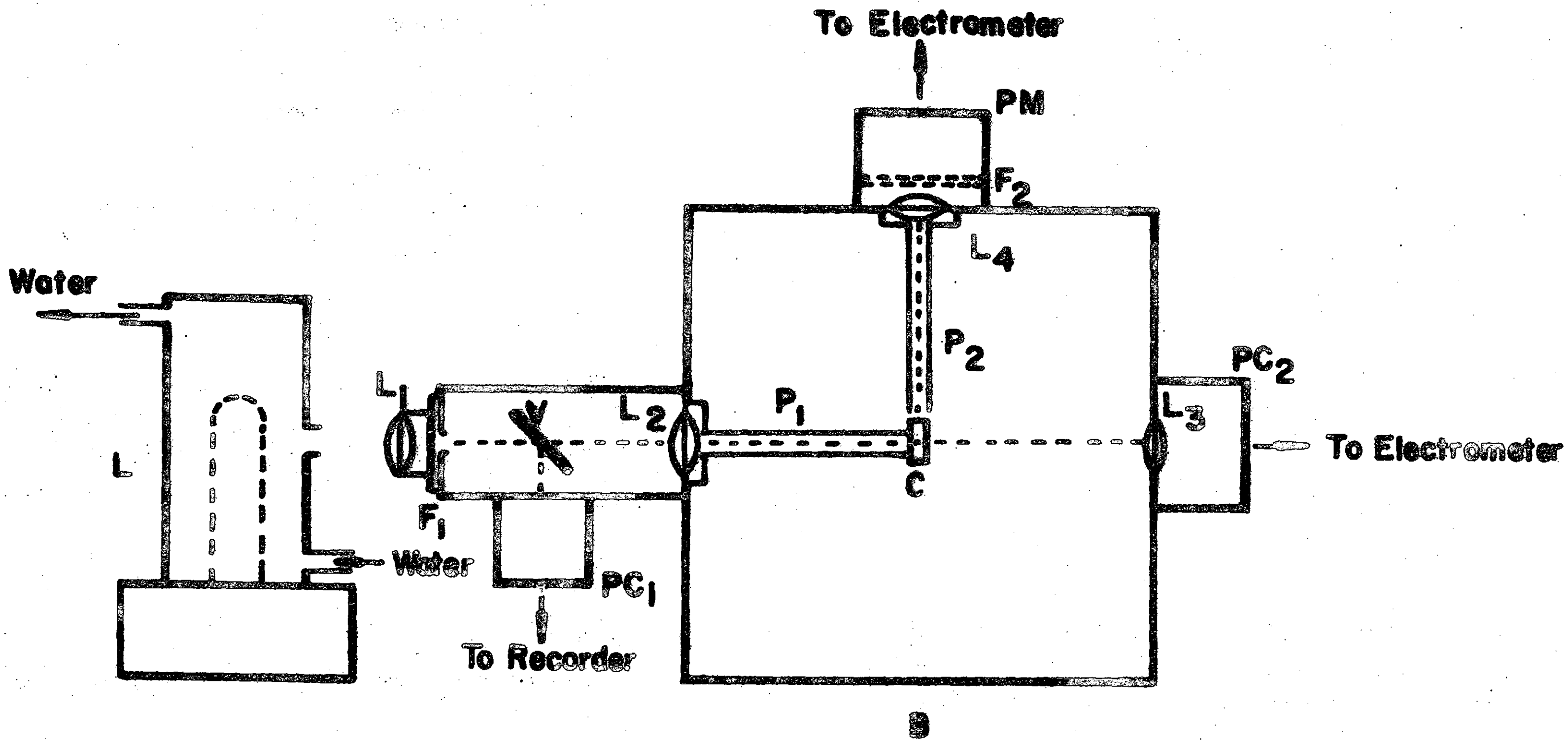


Figure 2.5 Optical arrangement for singlet quenching studies. Legend: L, lamp; L_1,L_2,L_3 and L_4 lenses; F_1 and F_2 filters; V, Vycor reflecting plate; PC_1 and PC_2, photocells; PM, photomultiplier; P_1 and P_2, light pipes, C, cell and B

a vycor 7910 plate to a photocell (RCA 935) and registering the current on a recorder. This technique was useful for correcting the data for the small variations in the lamp intensity. The light source was the medium pressure mercury lamp in a water cooled housing described earlier.

The vacuum rack used for the singlet-quenching-studies was grease-free but saturated with mercury vapor. The pressure measurements were done using a McLeod gauge and mercury manometer. Since the ketone pressure was in the high pressure region for these studies the reaction cell used was the 1-cm suprasil cell. The equilibrium between the ketone sample and the quencher was usually attained within a few hours of the mixing. The equilibrium was checked frequently by taking readings at different intervals of time.

Relative quantum yields:

For the total emission without wavelength resolution and the singlet quenching studies the relative fluorescence quantum yield, Q, was measured. Q is defined by the following expression

$$Q = \frac{I_f - I_f^o}{(I_t^o - I_t)g} \quad . \qquad (2.1)$$

Here I_f and I_f^o are the emission signals and I_t and I_t^o the intensities of the transmitted light. Superscript 'O' refers to the absence of the ketone sample. g is a factor which takes into account the fact that the emission is observed at a distance from the entrance window of the cell. For a 1-cm cell g is assumed to be unity and for a 10-cm cell g is given by the following expression:

$$g = \frac{\sinh(\varepsilon c \delta/2)}{\sinh(\varepsilon c \ell/2)} \qquad (2.2)$$

where $\varepsilon = 2.303\alpha$, α being the decadic molar extinction coefficient, c is the concentration, δ the length of the cell viewed by photomultiplier and ℓ is the total length of the cell. The data were not corrected for reflections since the corrections are only of the magnitude of the experimental error.

The absolute quantum yield of the fluorescence, ϕ_f, can be related to the relative quantum yield, Q by the following equation:

$$Q = \beta\ \phi_f\ . \qquad (2.3)$$

Here β is a constant provided the following conditions are fulfilled:

(1) The geometry of the arrangement of the apparatus remains unchanged.

(2) The high voltage applied to the photomultiplier is kept constant.

(3) Response of the photocell does not change.

(4) The exciting wave length is not altered. If the exciting wavelength is changed appropriate sensitivity corrections are applied to the Q-values.

Fluorescence lifetime measurements:

The fluorescence lifetime, τ_f, was measured using a TRW nanosecond spectral source system. This apparatus consists of a TRW model 31A power supply, model 32A decay time computer plug-in unit, model 33A photomultiplier unit and a dual beam oscilloscope such as type 556 (Tetronix).

The basic principle involved in this technique is that the sample is excited with repetitive pulses of short duration (n sec). These pulses are displayed on channel 1 of the oscilloscope. Emission from the sample is observed at right angles to the incident beam, detected by a photomultiplier and displayed on channel 2 of the scope. These signals are not true representations of the n sec light pulses because of inherent delays involved in the system. Therefore, the signal displayed on channel 1 is simulated by computer on a millisecond range and then displayed on channel 3. The signal on channel 4 is the signal of channel 3 plus an added exponential decay chosen so that the final channel 4 and channel 2 signal match. The exponential decay corresponds to the fluorescence decay of the sample. The decay time after matching the signals of channel 2 and 4 is directly read from the computer.

The lifetime measurements were done for samples in 1-cm cell at room temperature in the gaseous state. The exciting wave length 316 nm from the pulsed nitrogen lamp was isolated by the interference filter. The emitted light passed through a Corning glass filter (3-75), at right angles to the incident beam, to minimize the scattered light and was detected by a 1P28 photomultiplier.

The applicability of the technique was verified by measuring the fluorescence lifetimes of hexafluoroacetone and quinine sulfate.

Sensitized emission studies at room temperature:

The sensitized emission studies were carried out by exciting mercury-free mixtures of the chloroketone and biacetyl with 313 nm radiation from 1000W Hg/Xe lamp or 450W Xe lamp. At this wavelength there is little direct excitation of biacetyl luminescence. The cell was filled with the appropriate amounts of the chloroketone and biacetyl and the emission spectra recorded by Jarrell-Ash spectrophotometer in conjunction with the Bausch and Lomb monochromator. The procedure followed was similar to that described earlier.

Triplet lifetime of chloropentafluoroacetone at room temperature:

After recording the sensitized emission spectra of the mixture of the ketone and biacetyl attempts were made to estimate the lifetime of the triplet of the chloroketone at room temperature in gas phase by observing the rise of the sensitized emission of biacetyl. The excitation source was either a xenon flash lamp (25 J with $\frac{1}{e}$ lifetime 6×10^{-6} seconds) or spectroscopic flash (100 J and $\frac{1}{e}$ lifetime 6×10^{-6} seconds).

Phosphorescence at liquid nitrogen temperature:

The samples were collected in the quartz tubes (2 mm, internal diameter) and thoroughly degassed by freeze-pump thaw technique. The tubes were then sealed. The samples were kept at liquid nitrogen temperature for at least an hour before measurements to ensure complete thermal equilibrium.

The phosphorescence spectra of chloropentafluoroacetone and hexafluoroacetone were then taken using the Aminco-Bowman spectrofluorometer with rotating shutter operating. The time resolution of the phosphorometer was about 10^{-4} seconds.

After taking the phosphorescence spectra the triplet lifetimes of these samples were measured using the xenon flash lamp described earlier. The phosphorescence was analyzed by the Ebert grating monochromator and the emission in 460 nm region was detected by the RCA8575 photomultiplier (at -78°C). The signal was displayed on an oscilloscope and photographed. The lifetimes were calculated from log intensity versus time plots.

Phosphorescence lifetime at 113°K:

The phosphorescence lifetime measurements were also carried out at 113°K. The sample tubes (2 mm quartz tube) were filled with the ketone and cooled to 113°K for at least an hour in a quartz dewar containing isopentane slush (solid and liquid in equilibrium). The temperature of the isopentane slush was measured by copper-constantan thermocouple. The procedure for the triplet-lifetime-measurements has been described earlier.

Materials:

The chloropentafluoroacetone (Allied Chemicals Co.) was purified by trap to trap distillation at temperatures of -78°, -95° and -112°C. The -95°C fraction was retained after large head and tail fractions were discarded. This technique removed small traces of an unidentified impurity which was detected in the initial ketone by gas chromatography. The samples purified by distillation had similar properties to those of small quantities of the ketone purified by gas chromatography. The purity of the chloroketone was also verified by mass-spectrometry. The purified chloroketone was stored at 77°K in the dark and thoroughly degassed before use.

Hexafluoroacetone (Pierce Chemical Co.) was also purified by a trap to trap distillation similar to the one used for the chloroketone. The -112°C fraction was retained after large head and tail portions were discarded. No impurity was detected in the -112°C fraction by gas chromatography and mass-spectrometry. The purified ketone was stored at 77°K in the dark.

Sulfurhexafluoride (Matheson) was of 98% minimum purity. This gas was further purified by a trap to trap distillation. After discarding the large head and tail fractions, the -112°C fraction was retained for the use in the experiments.

Carbon dioxide (Matheson, bone dry grade) was of 99.8% minimum purity. The gas was distilled from -105°C and collected at 77°K. The retained fraction was thoroughly degassed. No impurities were detected by gas chromatography in this fraction.

Isobutane (Matheson, instrument grade, minimum purity 99.5 mole %) according to the suppliers, had only n-butane as an impurity. The gas was distilled from -105°C and collected at 77°K. The fraction retained was thoroughly degassed. The purity of isobutane was verified both by gas chromatography and mass spectrometry. In particular no olefins or dienes were detected in the sample.

Ethylene (Matheson, C. P. grade) according to the suppliers was of minimum purity of 99.5 mole % and had the following impurities:

propylene (0.05 mole %) , propane (0.07 mole %),
methane (0.01 mole %) , butanes (0.07 mole %) and
ethane (0.08 mole %).

Further purification of ethylene was achieved by trap to trap distillation at -130°, -161° and -196°C. The -161°C fraction was retained and no impurities were detected in this fraction by gas chromatography.

Propylene (Matheson, C.P. grade) had a minimum purity of 99 mole %. The suppliers cited the impurities present as propane (0.3 mole %), ethane (0.2 mole %) and carbon dioxide (trace). The propylene was collected in the storage bulb through a trap at -104°C and the retained fraction was pumped off at -161°C for a few minutes to remove more volatile components.

1-Butene (Matheson, C.P. grade, minimum purity 99 mole %) was further purified by trap to trap distillation at -78°, -104° and -196°C. The -104°C fraction was retained after large head and tail discards. Gas chromatographic and mass-spectrometric analysis did not show any significant amount of impurities.

Cis-2-butene (Matheson, C.P. grade, minimum purity of 99 mole %) was collected at -95°C, discarding large head and tail fractions at -78° and -196°C respectively. No detectable amount of impurities could be found by gas chromatography and mass-spectrometry.

Isobutylene (Matheson, C.P. grade) had minimum purity of 99 mole % and was collected at -98°C, discarding large fractions at -78°C and -196°C. No significant amounts of impurities could be detected by gas chromatography and mass-spectrometry.

Vinylchloride (Matheson, minimum purity 99%) according to the suppliers had 50-500 p.p.m. (maximum) of the inhibitor (phenol). The fraction collected was -104° after discarding

-78° and -106°C fractions. The purified fraction was stored at -196°C.

1,1-difluorethylene (Matheson, minimum purity of 99%) was distilled from -126°C and collected at -196°C. The fraction collected at -196°C was degassed for a few minutes at -161°C to remove more volatile impurities. This process also removed a significant amount of 1,1-difluoroethylene. The distilled fraction was stored at -196°C.

Perfluorobutene (Matheson, 95% minimum purity) was distilled from -78°C and the retained fraction was thoroughly degassed at -196°C. Further degassing was done by pumping off the retained fraction for a few minutes at -130°C.

Tetrachloroethylene (Eastman) was of spectroquality and it was stabilized by thymol. This compound was purified first by passing the liquid through an alumina column and then distilling (boiling point 120°C) the filtrate from the column. Only the middle fraction was collected for use in the experiments. The purified sample was stored at 77°K.

Benzene (Baker analyzed reagent) was of spectrophotometric purity. It was stored in the storage bulbs and degassed before being used. No further purification of benzene was thought necessary.

Quinine sulfate (Fisher) was NF grade. There was an excellent agreement between the absorption spectrum of this sample and the one reported in the literature for quinine sulfate(85). Therefore, no further purification of quinine sulfate was done. The standard quinine sulfate solutions (made in 0.25 N H_2SO_4) were kept in the dark.

2,3-Butanedione, also known as biacetyl, (Matheson, Coleman and Bell) was of 99+ mole % minimum purity (as quoted by the suppliers). This was confirmed by the gas chromatographic and mass-spectrometric analyses. The compound was always kept in the dark at -196°C.

1,3-Pentadiene or piperylene (Matheson, Coleman and Bell) was re-distilled (boiling point 42°C) and used without further purification.

Cyclohexene (Eastman) was first passed through an alumina column and the filtrate was then distilled (boiling point 83°C) under nitrogen and the middle fraction collected.

1-Hexene (Aldrich Chemicals) was also purified by passing it through an alumina column followed by distillation (boiling point 63°C) under nitrogen. The middle fraction was stored and used in the experiments.

The following chemicals were used for making solution filters.

Nickel sulfate was from British Drug House (Analar quality). Potassium-chromate (Reagent grade) was supplied by Shawinigan Chemical Co.Potassium biphthalate (Matheson, Coleman and Bell) was Reagent A.C.S. quality and had a minimum purity of 99.9%. In one set of experiments potassium biphthalate was used was from Allied Chemicals (Reagent ACS quality,minimum purity 99.5--100.05% as quoted by the suppliers). Naphthalene (Allied Chemical was resublimed. Isooctane (Fisher) was of spectranalyzed quality. Isopentane was from Phillips (pure grade 99 mole %). These chemicals were used without further purification.

Gas chromatographic analysis:

The gas chromatographic equipment used for the analysis consisted of a Gow-Mac model TRII-B, W-2X temperature regulated thermal conductivity cell, a Gow-Mac regulated DC power supply 9999-D, a suitable column and a recorder. The following conditions were employed for the gas chromatographic analysis:

(1) cell-current 150-200 ma

(2) detector box temperature about 180°C, and

(3) carrier gas, He ; flow rate 40-50 ml/min

The columns used for the analysis are shown in Table 2.2.

Table 2.2

Columns for chromatographic analysis

S.No.	Column	Length of column (meter)	Compounds analyzed
1	Porapak P	2	Chloropentafluoroacetone, hexafluoroacetone, isobutane, ethylenes, propylene and butenes.
2	Porapak Q	2	Chloropentafluoroacetone, hexafluoroacetone, isobutane, ethylenes, propylene and butenes.
3	25% DC-703 on chromoporb	3	Chloropentafluoroacetone, hexafluoroacetone and biacetyl.
4	Silica gel	3	Carbon dioxide.
5	10% SE-30 on chromosorb	6	Biacetyl.

CHAPTER 3

THE ABSORPTION SPECTRUM OF CHLOROPENTAFLUOROACETONE AND THE NATURAL RADIATIVE LIFETIMES OF THE EXCITED SPECIES

RESULTS

A number of ultraviolet absorption spectra of the chloroketone were taken under different experimental conditions using a Cary model 14 spectrometer. The ketone pressure varied from 28 torr to 221 torr. The gas phase absorption spectra at room temperature were reproducible under the conditions studied. A typical ultraviolet absorption spectrum of chloropentafluoroacetone in gas phase at room temperature is shown in figure 3.1. The figure also shows the spectrum of the empty cell. The spectrum extends from below 250 nm to greater than 356 nm with a maximum at 303 nm(ε=48). The spectrum is quite asymmetric and shows structure. The structure is evident especially at larger wave lengths. There are at least five bands at the wave lengths 339, 325, 314, 303 and 293 nm. There may be a sixth band at 283 nm. The average spacing of these bands is about 1200 cm^{-1}.

An absorption spectrum can be used for estimating the natural radiative lifetime of the excited species. The natural radiative lifetime or the true lifetime (τ_o) is defined as the reciprocal of the rate constant for the disappearance of

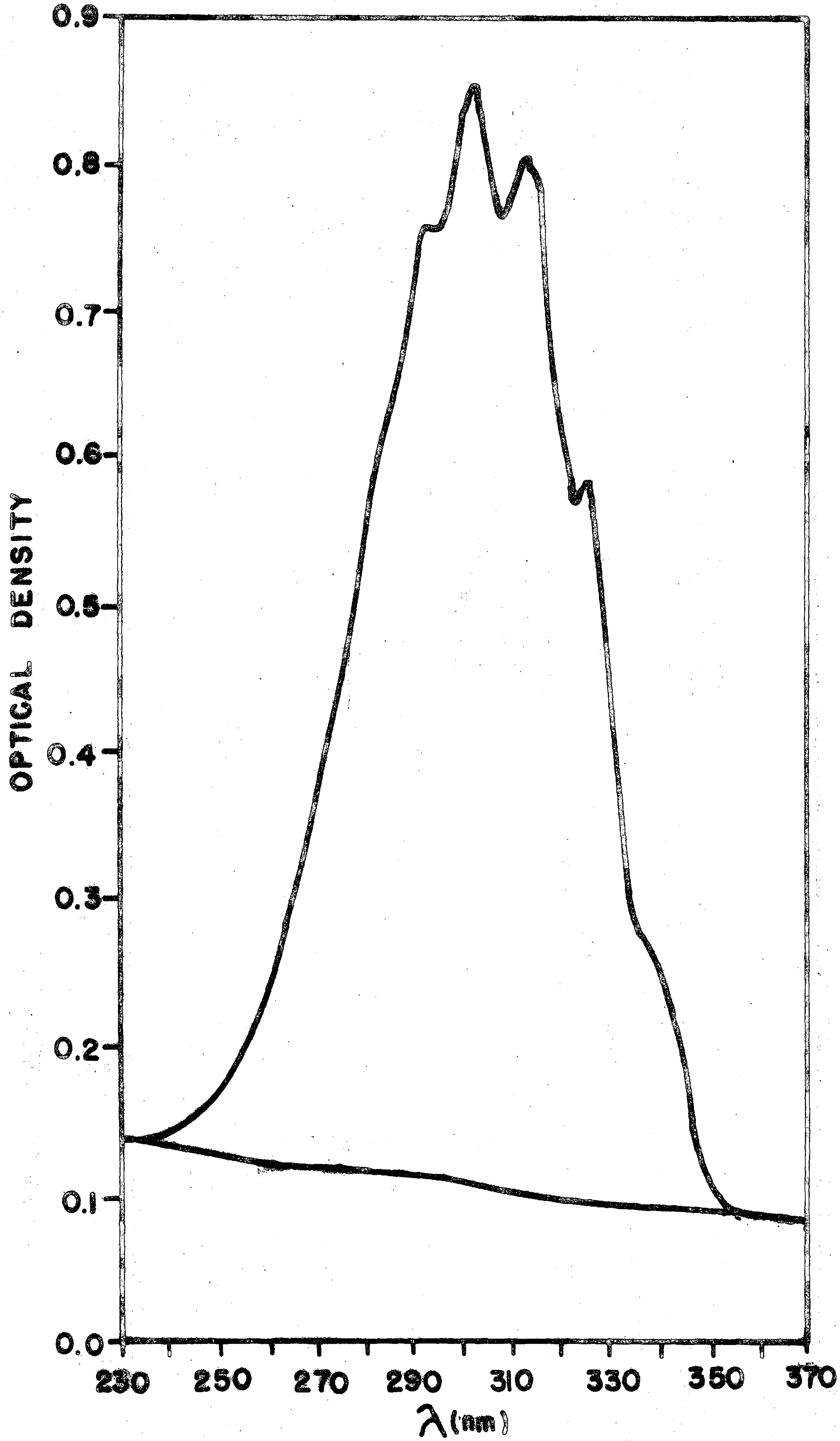


Figure 3.1 Absorption spectra of chloropentafluoroacetone, pressure 28 Torr (upper curve) and empty cell (lower curve)

a species which decays only by fluorescence or phosphorescence. τ_o for the fluorescence of the chloroketone is estimated below using its absorption spectrum.

The molar extinction coefficients (ε) of the chloroketone at different wavelengths are calculated from the absorption spectrum and are shown in table 1 in the appendix.

The true fluorescence lifetime (τ_o) can be estimated from a relationship between τ_o and the oscillator strength. The final relationship between τ_o and the experimental quantities is as follows$^{(86)}$:

$$\tau_o = \frac{3.5 \times 10^8\ G_2}{G_1\ \bar{\nu}^2 \int \varepsilon\ d\bar{\nu}} . \qquad (3.1)$$

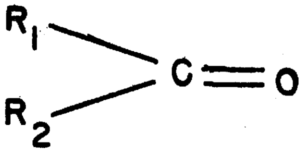
Here $\bar{\nu}$ is the wave number, G_2/G_1 is a statistical factor which is equal to one for singlet-singlet and three for singlet-triplet transitions. $\int \varepsilon\ d\bar{\nu}$ is the integrated absorption band. In the present case (singlet-singlet transition) $\frac{G_2}{G_1} = 1$, therefore,

$$\tau_o = \frac{3.5 \times 10^8}{\bar{\nu}^2 \int \varepsilon\ d\bar{\nu}} . \qquad (3.2)$$

From the present results the natural radiative lifetime of the fluorescence of the chloroketone is estimated to be 1.1×10^{-6} sec.

DISCUSSION

In the carbonyl group in addition to σ-bonding electrons there are two electrons in the c=O π bond and two "lone pairs" on the oxygen atom, one localized in the s orbital and the other in the n orbital of oxygen. However, the s orbital electrons usually are not of interest in studies of electronic transitions observed in the ultraviolet region and only an n orbital electron is promoted to the π* orbital in the longest wave length transition . Thus, a symmetry "forbidden" n → π* transition plays an important role in the photochemistry of a carbonyl compound, for which this transition typically occurs around 300 nm, e.g. 270 nm for formaldehyde(87) and 280 nm for acetone(27). However, the position of this transition depends on the substituents, R_1 and R_2



The electronic spectra of aliphatic carbonyl compounds have been considered both experimentally and theoretically by Csizmadia et al.(88) . They found very large red shifts of the n → π* frequencies on replacing the α-carbon by either α-silicon or α-germanium in R_3 X COR' (where X = C, Si or Ge). However, there was little effect on the frequencies when the substituents attached to the α-atom were varied.

In a more recent study Csizmadia et al.(89) have investigated the absorption spectra of CH_3CHO and PhCOX in detail. They point out that changing the atom or group attached directly to the carbonyl carbon produces striking effects on n → π* transitions and there is no significant change in the frequencies when the atoms or groups attached to the α-carbon atom are changed from hydrogen to methyl or phenyl or even halogen. Thus the authors conclude that the largest effects on the transition energies of R CO X system arise principally from the nature of the first atom in the group X. Except where the α-atom is capable of strong π-interaction through the filled p-type orbitals it is the σ-donor or σ-acceptor ability of this atom relative to the carbon atom which produces the most striking variations in transition energy. The σ-donor or σ acceptor ability of the β-atoms in the group X is of secondary importance, particularly with β-halogen substituents, i.e. when X is a halomethyl substituent there are only very small shifts in the n → π* bonds relative to the standard methyl derivatives.

The ultraviolet absorption spectrum of chloropentafluoroacetone in the gas phase at room temperature (figure 3.1) extends from about 250 to 356 nm with a maximum at 303 nm. The general region of the absorption is similar to that of hexafluoroacetone(58). As expected, the absorption coefficient is higher for the chloroketone than for hexafluoroacetone. The oscillator strength of the chloroketone absorption is about 10^{-3}. The spectrum is thus consistent with an $n \rightarrow \pi^*$ transition. Unlike the absorption spectrum of hexafluoroacetone(58), the chloroketone absorption spectrum contains structure. There are five, possibly six, bands with an average separation of about 1200 cm^{-1}. The structure is also evident in the spectrum of chloropentafluoroacetone reported by Majer et al.(80). This structure can perhaps be assigned to a vibrational progression in the excited state of C = 0 stretching frequency. The 1200 cm^{-1} stretching frequency of the CO—group of the chloroketone may be the analogue of the stretching vibrations at 1182.6 cm^{-1} in the $^1A''$ state of formaldehyde(90) and at 1460 cm^{-1} in ^1A_u state of oxalylchloride(91).

As reported earlier the $\frac{1}{\tau_o}$ value for chloropentafluoroacetone is 9.1×10^5 sec^{-1}. This probably is a valid estimate of the natural radiative lifetime of the excited singlet state of the chloroketone, although there are approximations made in applying the formula to large molecules. Strictly, the equation 3.2 for the natural radiative lifetime is applicable to sharp atomic transitions and resonance fluorescence. In molecular transitions this relationship will be only approximate(92). O'Sullivan and Testa(33) have determined $\frac{1}{\tau_o}$ values for a number of ketones and the values for some simple ketones are tabulated below:

Table 3.1

<u>Ketone</u>	$\frac{1}{\tau_o}$ (sec^{-1})
$CH_3-CO-CH_3$	4.0×10^5
$CD_3-CO-CD_3$	4.0×10^5
$CH_3-CO-C_2H_5$	4.4×10^5
$C_2H_5-CO-C_2H_5$	5.3×10^5
$(CH_3)_3C-CO-C(CH_3)_3$	5.9×10^5

Halpern and Ware(73) report the $\frac{1}{\tau_o}$ value 2.1×10^5 sec^{-1} for hexafluoroacetone. Thus, the observation of O'Sullivan and Testa(33) that the natural radiative singlet lifetimes of simple aliphatic ketones in the gas phase are not greatly changed by substitution is approximately true even when the substituent is a chlorine atom.

CHAPTER 4

EMISSION AT ROOM TEMPERATURE

RESULTS

Preliminary investigations showed that when chloropentafluoroacetone in the gaseous state at room temperature is excited in the region 280 to 334 nm luminescence is observed. These observations were made using an Aminco-Bowman spectrofluorometer (with phosphoroscope attachments) and using a steady state apparatus shown in figure 2.4.

On the basis of these preliminary observations a more detailed study was undertaken with a view of identifying the emission, i.e. fluorescence,phosphorescence or both, and establishing the mechanism of the primary processes involved.

313 nm Exciting wave length:

These studies were carried out on the 0.5 meter Ebert scanning spectrometer (Jarrell-Ash) described earlier. The emission spectra of chloropentafluoroacetone were taken in a 1-cm quartz cell at room temperature in the gas phase. The samples were mercury free. Figure 4.1 shows a typical emission spectrum of the chloroketone (pressure = 109.0 torr) not corrected for the detector and monochromator sensitivity. The uncorrected spectrum extends from about 337 nm to greater than 560 nm with maximum around 408 nm.

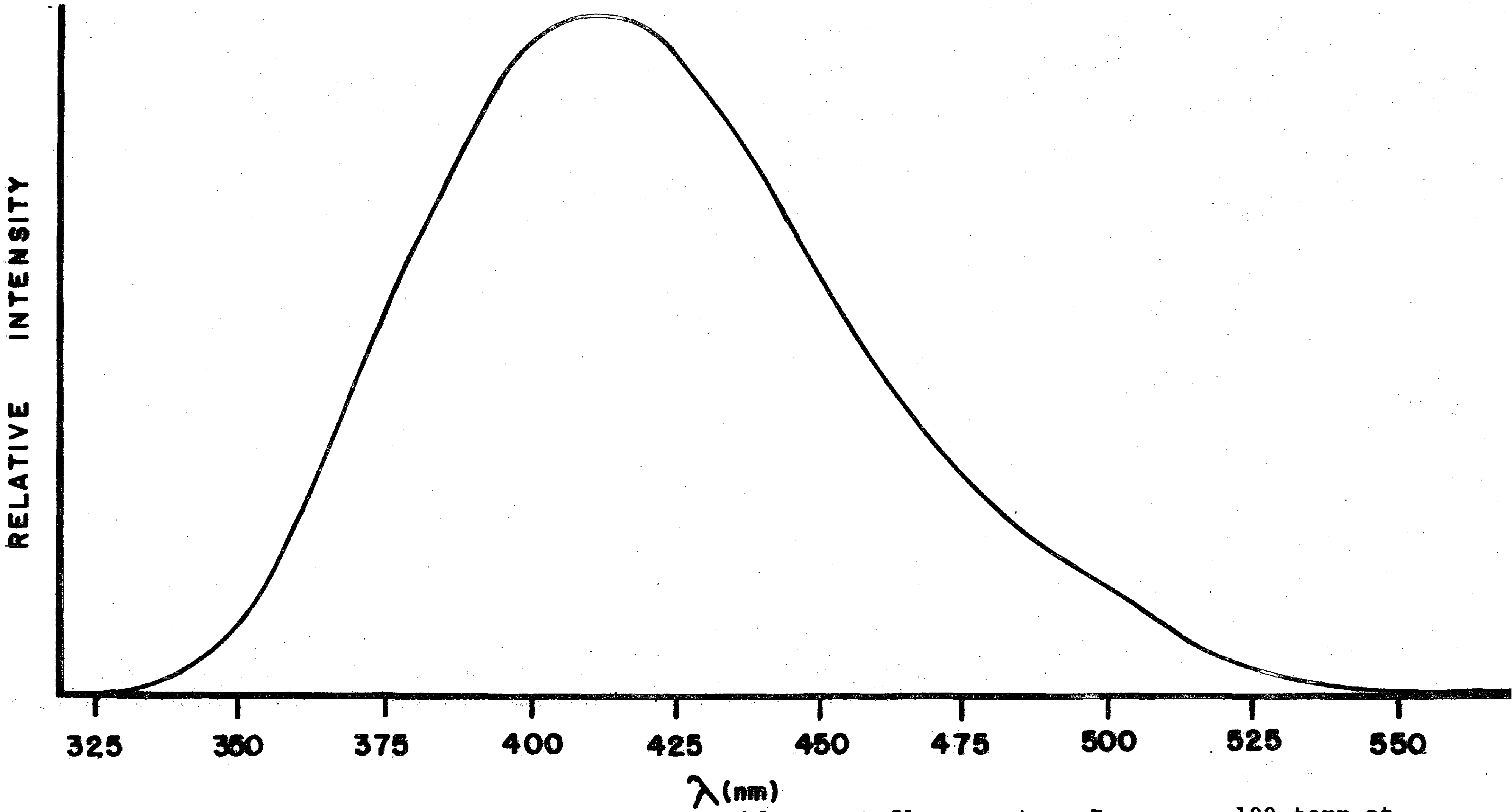


Figure 4.1 Uncorrected emission spectrum of chloropentafluoroacetone P_{ketone} = 109 torr at room temperature; λ_{ex} = 313 nm

In order to attach any quantitative significance to the emission spectrum it should be corrected for the sensitivity of the detector and the monochromator(93) using a standard substance of known emission characteristics as reference. Kutschke et al.(58) have used quinine sulfate as standard for correcting the fluorescence spectrum of hexafluoroacetone. These authors also checked the validity of quinine sulfate as a standard substance for correcting the spectra by determining the phosphorescence quantum yield of biacetyl excited at 436 nm. Their value of the phosphorescence quantum yield of biacetyl was well within experimental error of that obtained by Almy and Gillette(52). Therefore, in the present study quinine sulfate was selected as reference for correcting the emission spectra of chloropentafluoroacetone. However, this calibration technique is somewhat limited in its application to the chloroketone luminescence. The quinine sulfate emission starts at 390 nm whereas the chloroketone emission has its short wave limit at about 337 nm. Therefore, the sensitivity factors used to correct the chloroketone spectra at shorter wavelengths were obtained by extrapolation. At longer wavelengths because of the decreasing sensitivity of the photomultiplier (1P28) the calibration is again subject to large errors. Fortunately, the contribution to the total emission from either the short or long wave length region is small. As a result, the calibration is probably valid to within 20%.

The emission spectra of quinine sulfate were re-plotted as intensity versus wave-number. The maxima in all cases were made equal to the same arbitrary unit for normalization purposes. The absolute emission spectrum (quanta sec^{-1} cm^{-2} nm^{-1}) of quinine sulfate (81,82) was also re-plotted on the same scale. By comparing the experimental emission spectrum with the absolute emission spectrum of quinine sulfate a sensitivity curve for the detector and monochromator was obtained. Figure 4.2 shows the sensitivity factor as a function of wave-number. This sensitivity curve was used in correcting the emission spectra of chloropentafluoroacetone. The sensitivity curve so obtained is valid only for one particular experimental arrangement, e.g. slit-width of monochromator, etc. Therefore, the experimental arrangement was not changed during these experiments.

Figure 4.3 shows the corrected emission spectrum of the chloroketone with 109 torr of the ketone at room temperature in the gas phase excited at 313 nm. The corrected spectrum is asymmetric, extends from about 337 nm to greater than 560 nm and has a maximum at 420 nm. The spectrum does not have structure even though the resolution of the spectrofluorophotometer was better than 0.5 nm.

In order to investigate the effect of the ketone concentration on the emission profile, spectra for 3.4, 11.5, 33.6, 96.1, 109 and 209 torr of the ketone sample were recorded in separate experiments. In all the cases the luminescence of

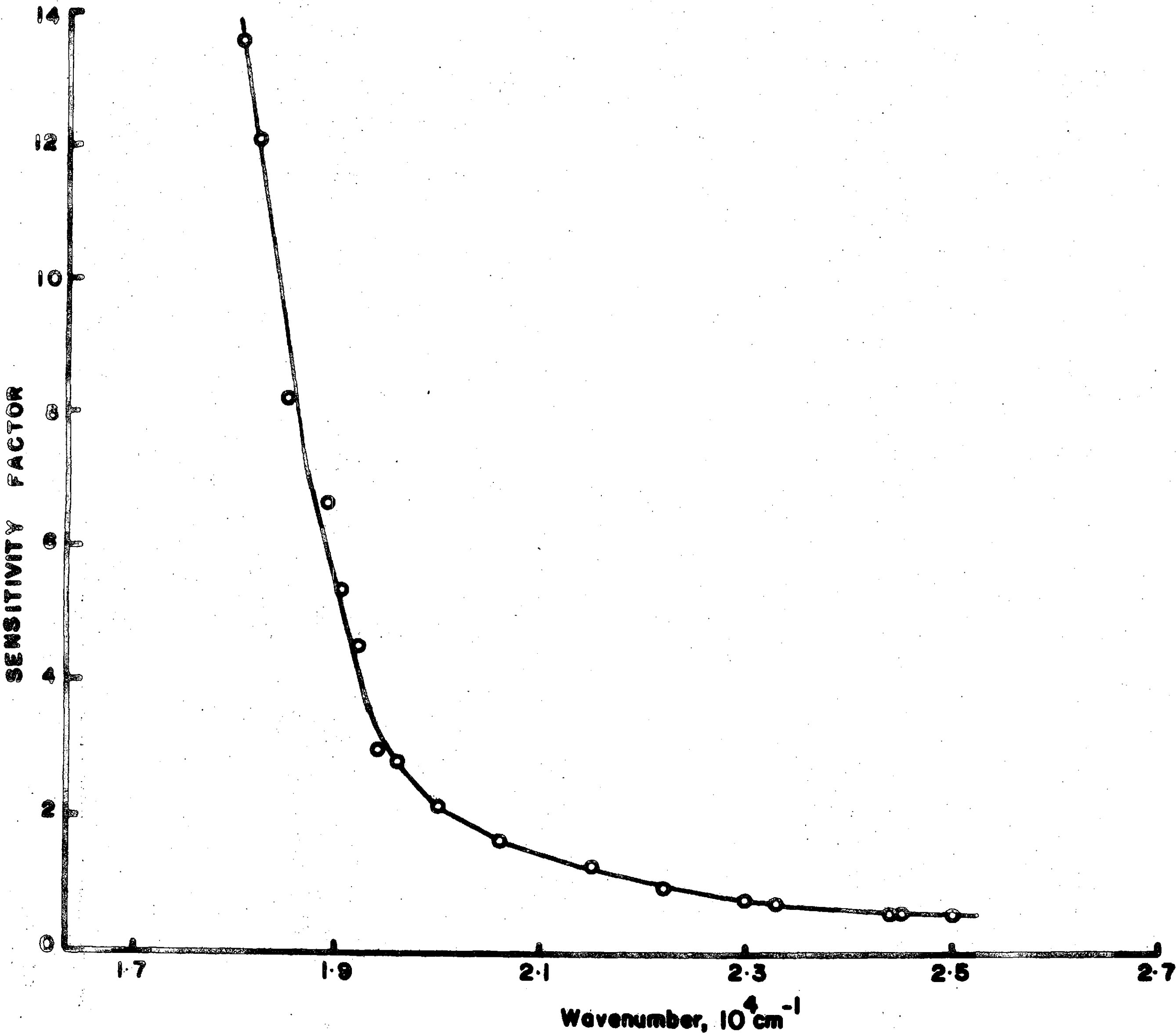


Figure 4.2 Sensitivity curve for correcting emission spectra.

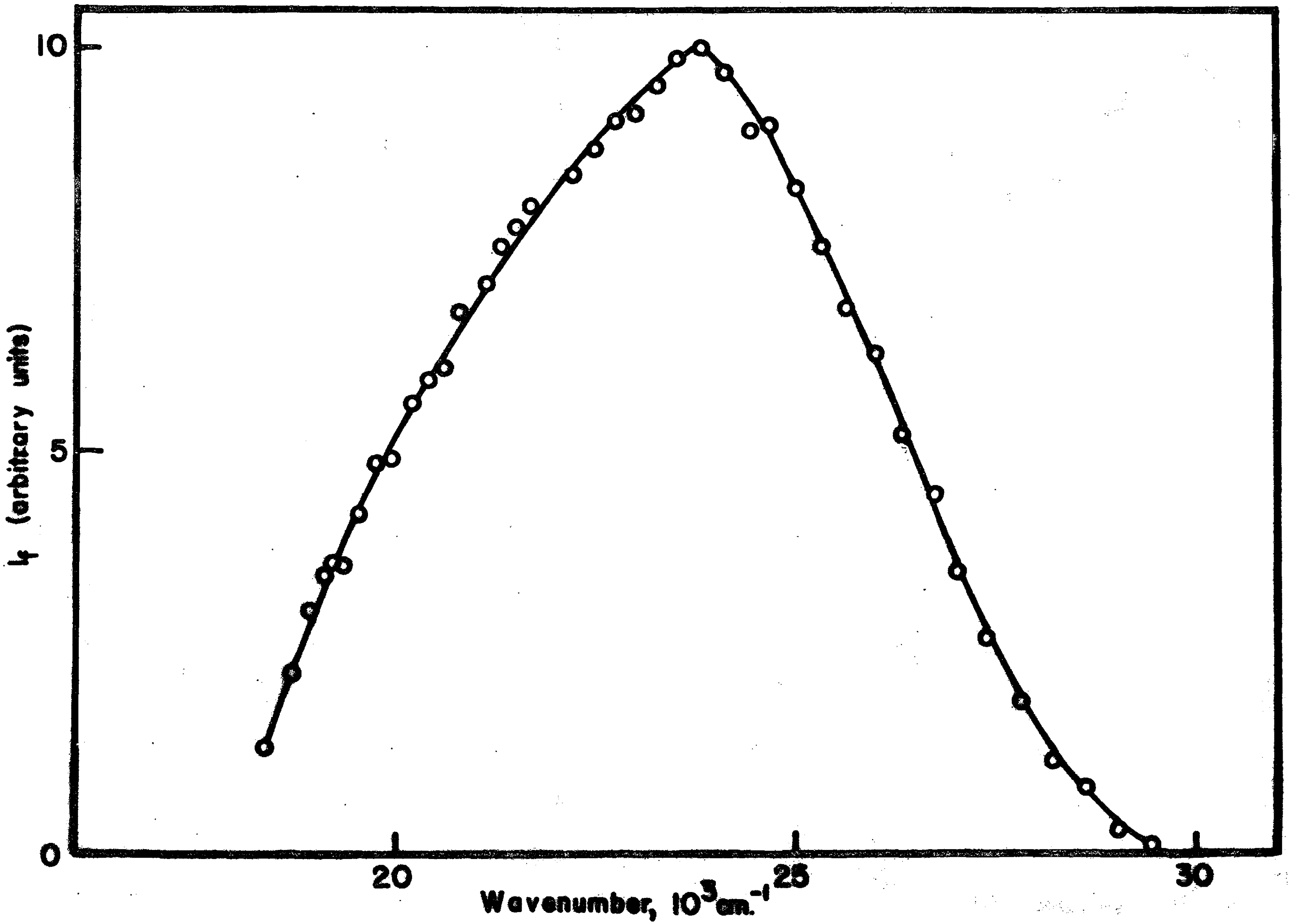


Figure 4.3 Corrected emission spectrum of chloropentafluoroacetone (P_{ketone} = 109 torr) as a function of wave number λ_{ex} = 313 nm

the chloroketone extends from about 337 to greater than 560 nm with the maximum at 420 nm. A more precise limit of the emission at higher wavelengths cannot be given because the sensitivity of the photomultiplier decreases rapidly toward longer wave lengths.

In a separate experiment addition of 24 torr of oxygen to 109 torr of the ketone sample did not decrease the intensity of the emission spectrum. A few experiments were also performed in the presence of mercury vapor in the ketone sample. No decrease was observed in the intensity of the spectra of the chloroketone when the spectra of mercury-free samples were compared with those of samples containing mercury vapor. Thus, the emission is unaffected by mercury vapor.

Attempts were also made to observe long-lived emissions using the Aminco-Bowman spectrofluorometer with rotating shutter operating (time resolution being $\sim 10^{-4}$ sec). Under these conditions only delayed emission, if any, would be observed. But with the chloroketone in the gas phase at room temperature no long-lived emission could be observed even at the maximum sensitivity of the instrument. Check runs were carried out with hexafluoroacetone in the gas phase at room temperature. The long-lived emission (phosphorescence) from hexafluoroacetone was observed under these conditions. Since the emission from hexafluoroacetone consists of both fluorescence and phosphorescence special care was taken in the attempts to observe any long-lived emission from chloropentafluoroacetone.

"290" and 334 nm exciting wavelengths:

Several experiments were performed to investigate the emission profile as a function of the exciting wavelength. The identical emission profiles were obtained when 30 torr of the chloroketone were excited with 334, 313 and "290" nm radiation in separate experiments. Similar results were also obtained in the high pressure region of the ketone (209 torr) with 334, 313 and "290" exciting wavelengths.

Pressure effects on the fluorescence

Exciting radiation 313 nm:

A number of experiments were performed using the steady state apparatus (figure 2.4) in order to study the effect of the ketone pressure on the fluorescence at room temperature in gaseous state with 313 nm excitation wavelength. The results are summarized in table 4.1.

Table 4.1

Effect of the Ketone Pressure on the Fluorescence Excitation Radiation 313 nm

Run number	Ketone pressure (torr)	Q
25	20.8	1.85
26	37.8	2.12
27	55.3	2.17
28	79.9	2.37
29	106.	2.45
30	157.	2.53
31	251.	2.55
32	9.30	1.42
33	31.1	2.12

Figure 4.4 shows the plot of Q versus the ketone pressure. It may be seen from these data that the fluorescence yields are low at lower pressures and increase to a limiting value at high pressures of the ketone. In preliminary investigations it was also found that the Q value increases linearly at very low pressures of the ketone. However, the data were

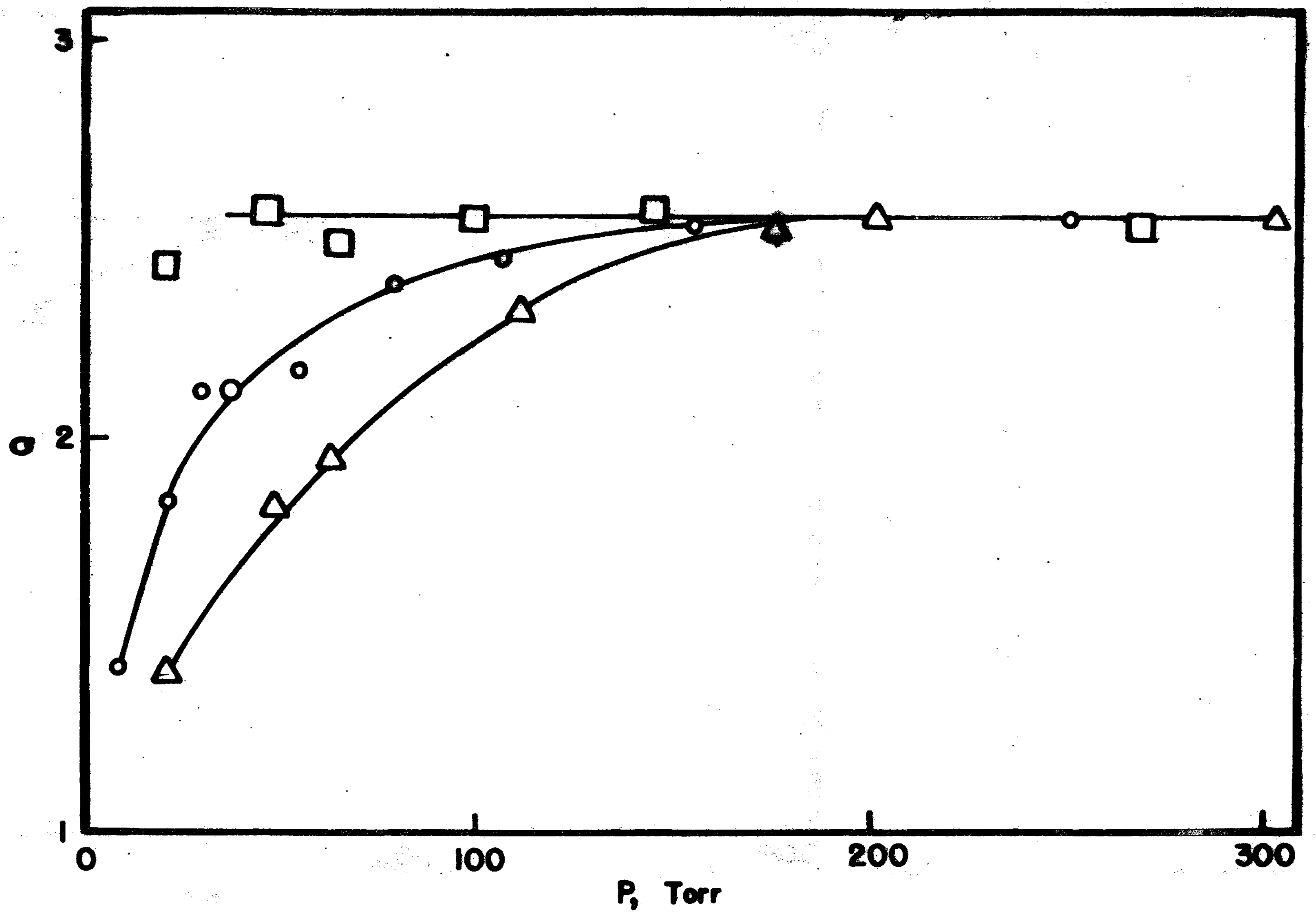


Figure 4.4. Variation of the relative fluorescence yield, Q, with pressure of chloroketone, □, λ_{ex} = 334 nm; O, λ_{ex} = 313 nm; Δ, λ_{ex} = "290" nm.

not reliable at very low pressures because the emission intensity was very small.

Effect of inert gases on the emission

Since the emission signal reaches a limiting value at high pressures of the ketone it would be of some interest to see how added gases affect the emission. Therefore, carbon-dioxide, perfluorobutene and sulfurhexafluoride were selected as inert addends.

Effect of carbon dioxide

In this series of experiments carbon dioxide was added to a fixed amount of the chloroketone (20.4 torr). The relevant data are summarized in table 4.2, and figure 4.5 gives the Φ versus total pressure plot. It is clear that the effect of carbon dioxide is to increase the fluorescence yield with increasing pressure. At high pressures the fluorescence quantum yield reaches the same limiting value as that reached in the case of the pure ketone. However, the pressure required to approach the plateau value is higher than the pressure required in case of the pure ketone.

Effect of sulfurhexafluoride:

Again the ketone pressure was kept constant (12.3 torr), the sulfurhexafluoride pressure varied, and the relative fluorescence yield measured in the steady state apparatus. Table 4.3 shows the Φ-values as a function of

Table 4.2

Effect of CO_2 on the emission

Excitation wavelength 313 nm.
Ketone pressure = 20.4 torr

Run number	Total pressure (torr)	Q
48	31.0	1.82
49	38.8	2.00
50	59.9	2.24
51	93.4	2.38
52	147.	2.43
53	206.	2.53
54	280.	2.48
55	354.	2.51
56	394.	2.53

Table 4.3

Effect of SF_6 on the emission

Excitation wavelength 313 nm.
The ketone pressure = 12.3 torr

	Run number	Total Pressure (torr)	Q
A:	35	25.2	1.70
	36	35.8	1.92
	37	54.0	2.13
	38	86.1	2.24
	39	145.	2.36
	40	261.	2.51
B:	42	24.3	1.69
	43	60.9	2.13
	44	109.	2.39
	45	182.	2.54
	46	297.	2.51
	47	45.3	1.98

the total pressure in the cell. Relative fluorescence yields are plotted as a function of the total pressure in figure 4.6. The effect of the sulfurhexafluoride on the emission is similar to that of the carbondioxide and the pure ketone. The pressure of sulfur hexafluoride required to approach the plateau value of the fluorescence is higher than that of the pure ketone.

The data shown in the table (table 4.3) represents two sets of experiments performed at different times (the same steady state apparatus was used). The reproducibility of the technique is verified by the agreement between these two sets of experiments.

Effect of perfluorobutene:

The effect of olefins on the emission was planned for a later part of the investigation. However, the effect of perfluorobutene in the emission is of considerable interest. The perfluorobutene was added in varying amounts to a fixed pressure (32.3 torr) of the ketone. Table 4.4 gives the results of the perfluorobutene experiments. The appropriate data are plotted in figure 4.7. It is evident from the figure that the perfluorobutene also enhances the emission of the ketone and reaches the same limiting value, within experimental error.

Exciting wavelengths "290" and 334 nm

The effect of exciting wavelength on the fluorescence

Table 4.4

The effect of perfluorobutene on the emission

Excitation wavelength 313 nm.
Ketone pressure = 32.3 torr

Run number	Total pressure (torr)	Q
108	50.0	2.28
109	86.6	2.40
110	143.	2.47
111	215.	2.50
112	344.	2.54
113	562	2.54

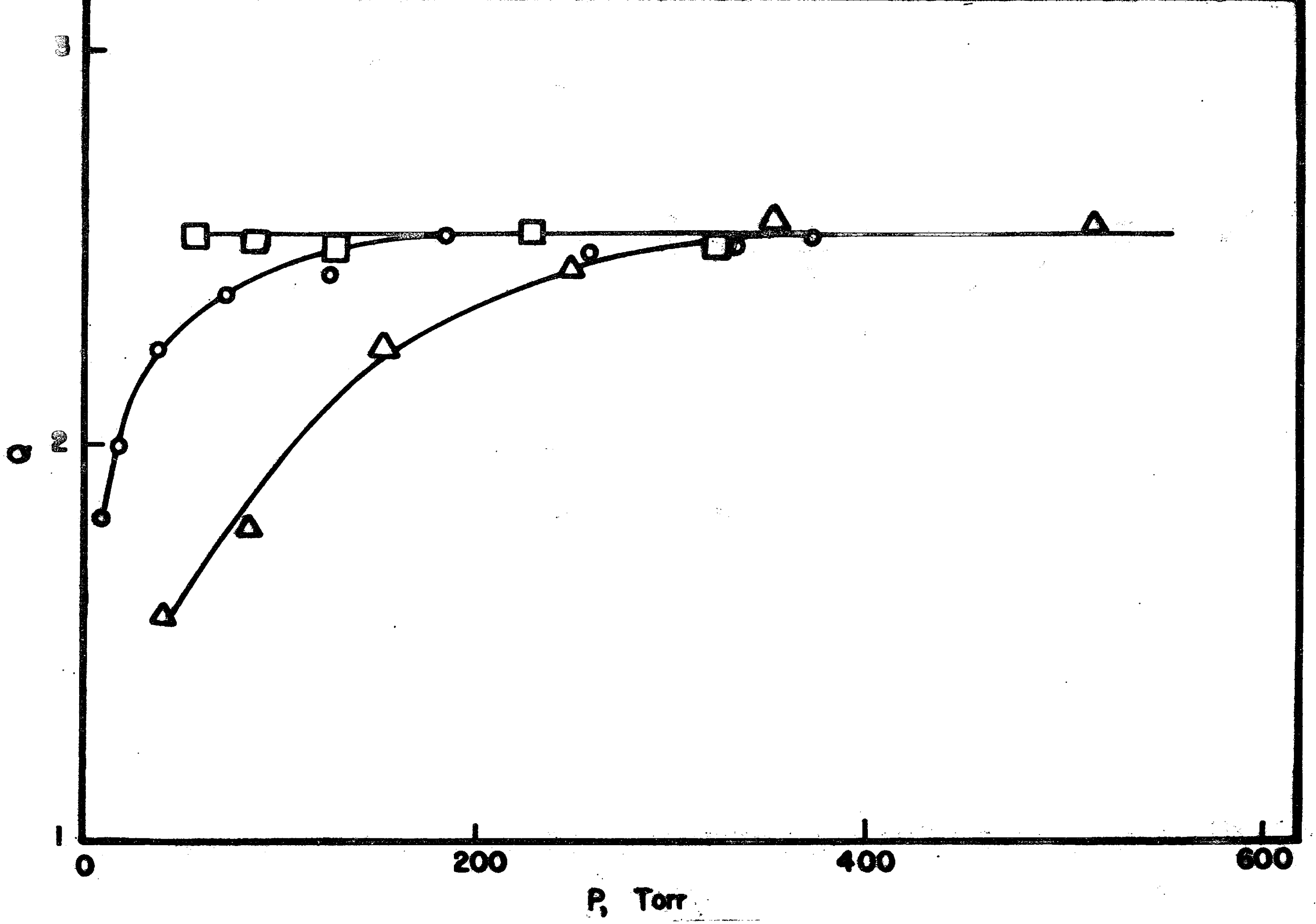


Figure 4.5 Variation of the relative fluorescence yield, Q, of chloroketone with pressure of carbondioxide. □ λ_{ex}= 334 nm; P_{ketone} = 38.1 torr O, λ_{ex} = 313 nm; P_{ketone} = 20.4 torr. Δ, λ_{ex} = "290" nm; P_{ketone} = 22.0 torr.

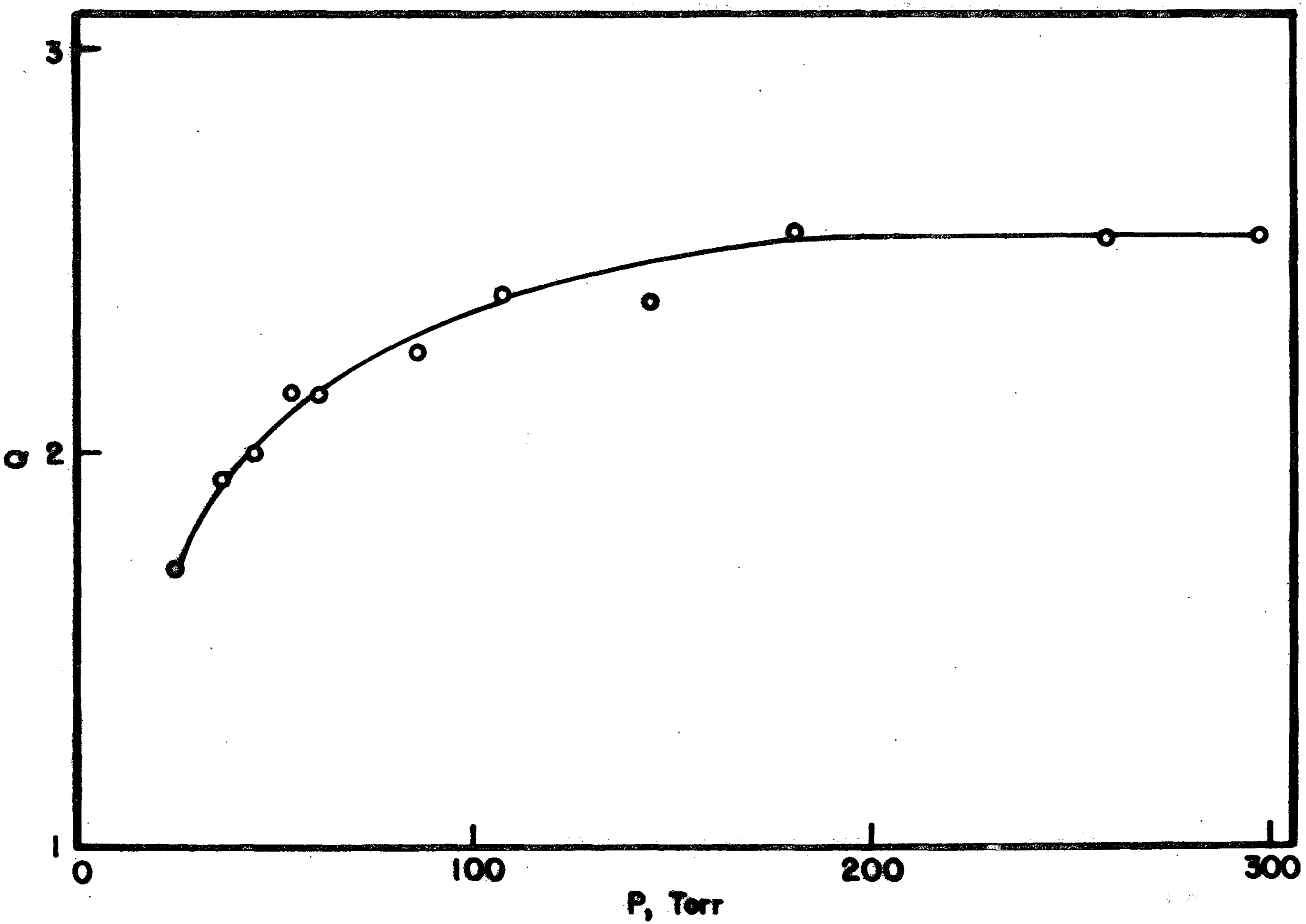


Figure 4.6 Relative fluorescence yield, Q, of chloroketone (P_{ketone} = 12.3 torr with pressure of sulfurhexafluoride.

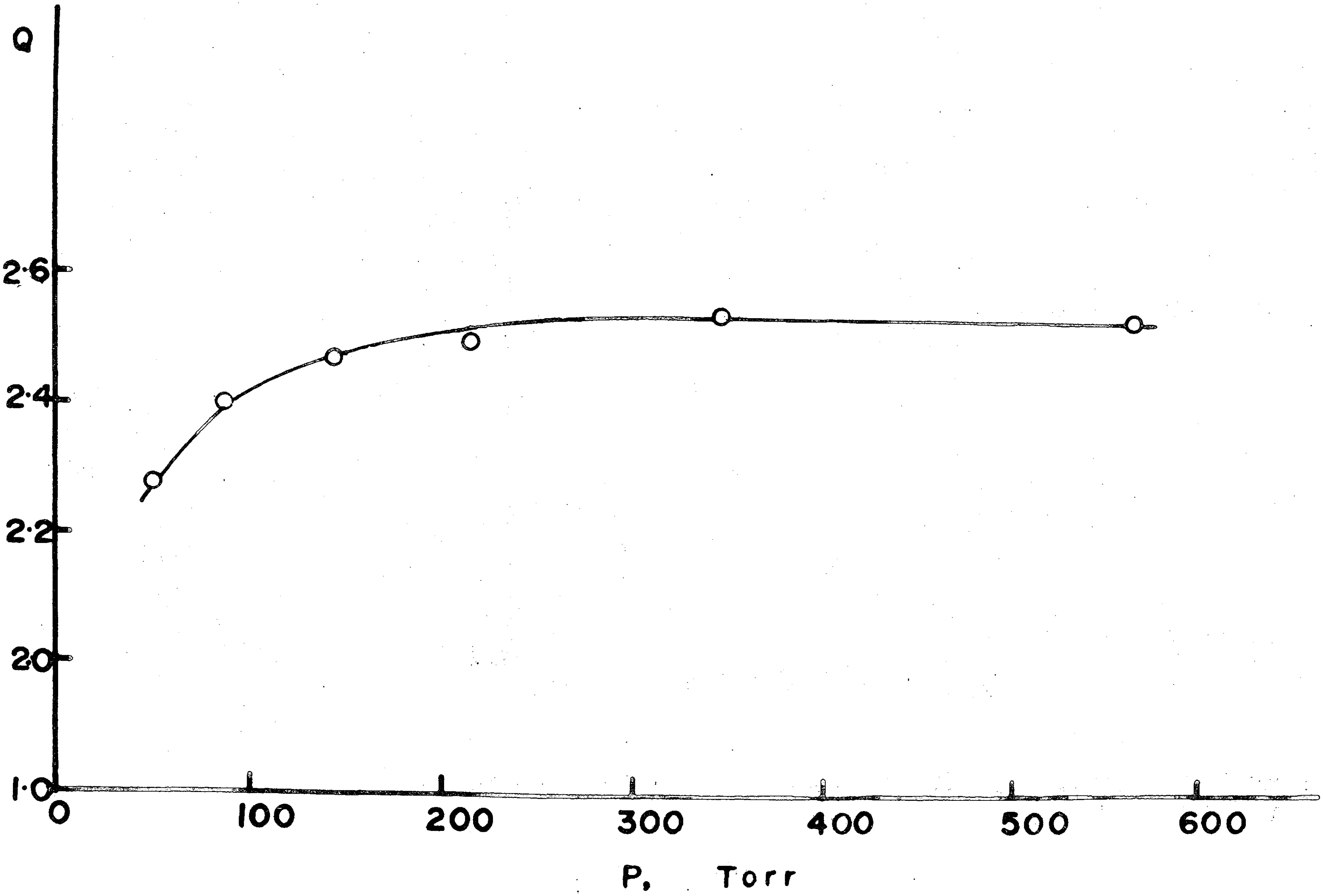


Figure 4.7 Variation of relative fluorescence yield, Q, of chloroketone with perfluorobutene pressure; p_{ketone} = 32.3 torr, λ_{ex} = 313 nm.

of the chloroketone was investigated by selecting two additional wavelengths "290" and 334 nm for excitation. These studies were carried out in the steady state apparatus and the results are described in the following sections.

Excitation wavelength "290" nm:

Fluorescence enhancement was more striking with "290" nm excitation than with 313 nm excitation. Table 4.5 shows the effect of the ketone pressure on the emission with "290" nm excitation.

The Q versus pressure plot is shown in figure 4.4 . Again the fluorescence quantum yields are low at lower pressures and increase to the same plateau value at higher pressures of the ketone within experimental error . It should also be noted that higher pressures of the ketone is required to approach the plateau for "290" nm excitation than for 313 nm excitation.

Table 4.6 gives the data for the effect of CO_2 on the emission with "290" nm exciting radiation, and figure 4.5 gives the plot of relative fluorescence quantum yield as a function of the pressure of CO_2.

Since the radiation classed as "290" nm contains both 289 nm and 297 nm radiations no quantitative significance is to be attached to the data shown above.

Table 4.5

Effect of the ketone pressure on the emission

Excitation radiation "290" nm.

Run number	Pressure of the ketone (torr)	Q
79	21.2	1.41
80	48.6	1.84
81	63.6	1.95
82	112.	2.33
83	177.	2.54
84	201.	2.56
85	305.	2.56

Table 4.6

Effect of CO_2 on the emission

Excitation radiation "290" nm.
Ketone pressure = 21.9 torr.

Run number	Total pressure torr	Q
87	42.5	1.57
88	87.0	1.80
89	15.3	2.02
90	252.	2.25
91	354.	2.58
92	516.	2.57

334 nm Excitation Radiation

The observations with 313 nm and "290" nm excitation radiation are further confirmed when 334 nm is chosen as the exciting wavelength. The ketone pressure in this study ranged from 21 to 270 torr. Still lower pressure of the ketone could not be investigated as the signal/noise ratio decreased and was subject to large errors. Table 4.7 summarizes the data for the effect of the ketone pressure on the emission when the exciting wavelength is chosen as 334 nm, and the Q versus pressure plot is shown in figure 4.4.

Table 4.7

Effect of the ketone pressure on the emission

Excitation wavelength 334 nm.

Run number	Ketone pressure torr	Q
93	21.0	2.43
94	46.6	2.57
95	64.5	2.49
96	99.6	2.54
97	145.	2.57
98	270	2.52

Table 4.8 shows the effect of carbondioxide on the emission of the ketone for 334 excitation radiation and the

Table 4.8

The effect of CO_2 on the emission of the ketone

Excitation wavelength 334 nm.
Ketone pressure = 38.4 torr.

Run number	Total pressure torr	Q
100	57.5	2.54
101	86.9	2.52
102	131.	2.49
103	229.	2.54
104	323.	2.50

data are plotted in figure 4.5.

In these sets of the experiments also (both the effect of the ketone and effect of the carbondioxide on the emission) the same pattern is followed as at shorter excitation wavelengths. The limiting value of Q in this case is also the same as obtained earlier within the experimental error.

The mean lifetime of the fluorescence

In Chapter 3 the true (or natural radiative lifetime) of the fluorescence was estimated from the ultraviolet absorption spectrum of the chloropentafluoroacetone. The actual mean lifetime of the fluorescence of the chloroketone was also obtained. The actual lifetime of the emission is the reciprocal of an observed first order rate constant for decay of an excited state which may be removed by several competing first order processes.

The fluorescence lifetimes were measured using the TRW nanosecond spectral source system in the pressure range from 9 to 392 torr of the ketone. All these measurements were done at room temperature in the gas phase in a mercury free system. Table 3.9 gives the actual mean lifetimes of the fluorescence of the chloroketone at different pressures. The average lifetime of the fluorescence of the chloroketone at 25°C is 35.1 ± 0.3 nanoseconds. The mean lifetime at any one pressure of the chloroketone is the average of several

Table 4.9

Actual mean lifetime of the fluorescence of the chloroketone as a function of pressure

Run number	Ketone pressure torr	τ_f (nanoseconds)
1	9.	34.7
2	43.	34.8
3	63.	35.1
4	74.	34.9
5	84.	35.4
6	179.	35.1
7	217.	35.1
8	278.	35.4
9	392.	35.4

readings of lifetime. Some of the readings were also taken with intervals of many hours to check the reproducibility. Thus the mean lifetime is independent of the ketone pressure under the range studied and the mercury also does not quench the actual lifetime of the fluorescence. The decay of the light intensity appears to be exponential, although it would be difficult to detect nonexponential decay using this nanosecond technique. In particular no systematic variation in the lifetime was observed in the five experiments of ketone pressures below 100 torr.

It may also be added here that small amounts of oxygen (10-20 torr) also did not affect the mean lifetime of the fluorescence.

Absolute quantum yield of fluorescence of the chloropentafluoroacetone at room temperature in gas phase:

The determinations of the absolute quantum yield of the fluorescence of the chloroketone used quinine sulfate (solution in 0.25N H_2SO_4) as a standard. The emission spectra of the chloroketone and the quinine sulfate were taken under identical conditions. The spectra were then corrected (as reported before). The quantum yield of the fluorescence of the chloroketone was calculated using the following relationship$^{(94)}$:

$$\phi_u = \phi_s \times \frac{\text{Area}_u}{\text{Area}_s} \times \frac{1-10^{-A_s}}{1-10^{-A_u}} \qquad (4.1)$$

Here ϕ_u and ϕ_s are the quantum yields of the unknown and the standard respectively. A_u is the absorbance of the unknown and A_s that of the standard. Areas refer to the areas under the emission spectra.

Quantum yield determinations were done with the ketone pressures of 113, 168 and 221 torr and the quinine sulfate concentrations were 1.0 μg/ml, 1.5 μg/ml and 2.0 μg/ml. The quantum yields obtained from these runs were 0.024, 0.021 and 0.025. The average fluorescence quantum yield of the chloroketone ($\phi_{f,\infty}$) is therefore 0.023 ± 0.002.

A further check on the absolute quantum yield of the fluorescence of the chloroketone was also made in the steady state apparatus (without wavelength resolution). The standard used here was hexafluoroacetone,as the quantum yield of fluorescence of hexafluoroacetone at high pressures is known(58). The fluorescence spectra of the chloroketone and hexafluoroacetone are almost identical (as reported elsewhere) and the quantum yield of the chloroketone is calculated using

$$\phi_C = \frac{Q_C}{Q_H} \times \phi_H \qquad (4.2)$$

Q_C and Q_H refer to the Q-values of the chloroketone and hexafluoroacetone respectively. ϕ_C and ϕ_H are the quantum yields of the chloroketone and hexafluoroacetone fluorescence respectively. In these check runs the absorbance of the chloroketone and hexafluoroacetone was kept the same.

The limiting Q-value (average of three runs) for hexafluoroacetone was found to be 2.15 where as Q_C was found to be 2.55. Thus, ϕ_C according to this method is 0.022. This value is in excellent agreement with that obtained using quinine sulfate as standard.

DISCUSSION

The corrected emission spectrum of chloropentafluoroacetone shown in figure 4.3 is the first report of luminescence from a chlorinated carbonyl compound in gas phase at room temperature. The spectrum extends from 337 nm to greater than 560 nm. The exact limit in the longer wavelength region is hard to establish, because of the limited sensitivity of the available photomultiplier at the longer wave lengths. The maximum in the spectrum occurs at about 420 nm. Like the emission spectrum of hexafluoroacetone the emission spectrum of the chloroketone is devoid of structure.

The emission could be either fluorescence or phosphorescence or both. The quenching of the triplet state of carbonyl compounds by oxygen has been reported by a number of authors. For example, relatively small amounts (about a few torr) of oxygen quench the phosphorescence but not the fluorescence of acetone(37), biacetyl(34,56) and hexafluoroacetone(61). It is usually assumed that low pressures of oxygen quench only the triplet states of carbonyl compounds in the gas phase and the emission in the presence of a few torr of oxygen is generally assigned to the fluorescence from the excited singlet state. However, Ware et al.(71) recently studied the fluorescence of hexafluoroacetone in the gas phase. They investigated the effect of a number of gases including oxygen on the fluorescence of hexafluoroacetone and found that high pressures of oxygen (of the order of 1 atmosphere) also quench the fluorescence of hexafluoroacetone. The quenching is rather inefficient and the quenching rate constant for oxygen was found to be 7.6 × 10^7 M^{-1} sec^{-1} at 25°C.

In the present investigation of the luminescence of chloropentafluoroacetone in the gas phase at room temperature it is found that a few torr of oxygen neither decrease the luminescence intensity nor alter the emission profile as a function of wavelength. Therefore, the luminescence is considered to be only fluorescence, i.e., the emission from the singlet state. These observations on the emission intensities are based on studies both with and without wavelength resolution. This assignment of emission is consistent with the observation that no long-lived emission (from the triplet state) is observed when the pure chloroketone emission is investigated using a rotating shutter with a time resolution of the order of 10^{-4} seconds. This technique would remove the short-lived emission (fluorescence) and permit only the long-lived emission (phosphorescence) to be observed. Since the triplet lifetime may be very short, the lack of phosphorescence of the chloroketone in the gas phase at room temperature does not imply that the triplet state molecules are absent.

From a knowledge of the absorption and fluorescence spectra the energy of the first excited singlet state relative to the ground state can be estimated provided there is an overlap between the two spectra. In the case of chloropentafluoroacetone the overlap between the absorption and fluorescence is at about 345 nm, which corresponds to about 83 K cal per mole as the O-O band of the singlet-singlet transition. This energy separation between the first excited and ground singlet states is about the value expected for a carbonyl compound. For example, the O-O splittings in the singlet states of acetone(95) and hexafluoroacetone(58) are about 80 Kcal and 83 Kcal per mole respectively.

If the structure in the absorption spectrum of the chloroketone is due to the C=0 stretching vibrational frequency at about 1200 cm^{-1} then 313 nm excitation would form the excited state in the higher vibrational levels. These excited molecules will have about three quanta of the vibrational energy in the C=0 stretch.

The excited singlet state molecules of the chloroketone that are formed in the higher vibrational levels should be capable of deactivation via vibrational relaxation at higher pressures. The fluorescence-enhancement should occur because some of the molecules which would otherwise be removed by other processes, e.g. dissociation, would now contribute to the fluorescence. The data of figures 4.4 to 4.7 show that the fluorescence increases with increasing pressure of the ketone or an inert gas and approaches a plateau value at still higher pressures when excited at "290" and 313 nm. In the case of 334 nm excitation radiation, in the pressure range studied, only the plateau region is observed. Thus, from these observations it is clear that the fluorescence enhancement does occur in the present system as a result of collisional deactivation. The plateau-value of the fluorescence corresponds to the near-zero vibrational level in the excited singlet state and under these high pressure conditions all the emission will be from the low lying vibrational level (probably the zeroth level). Evidence for collisional deactivation of an excited state was also found by Majer et al.(80) in their study of the photolysis of chloropentafluoroacetone although they did not attempt to identify the excited state being deactivated or decomposing. Independent studies by White(96) in our laboratory on the photolysis of the chloroketone also suggest that the excited state subject to collisional deactivation is the singlet state. The data show that the CO-yield decreases initially with increasing ketone pressure. This decrease may be ascribed to the collisional deactivation of the excited singlet state from higher vibrational levels. At still higher pressure of the ketone the CO-yield levels off and eventually reaches a limiting value. The residual dissociation probably occurs from a different electronic state which will be discussed later.

If the fluorescence can occur from the vibrationally excited levels of the excited singlet state, the emission profile as a function of wavelength might change with the exciting wavelength or the concentration of the ketone. As is evident from the data presented earlier the fluorescence is independent of the excitation wavelength and the concentration of the ketone within experimental error. The constant emission profile in the present system (as a function of the exciting wavelength and the ketone pressure) tentatively suggests that the majority of the emission is from the lower vibrational levels. If the higher vibrational levels in the excited singlet state molecules make a measurable contribution to the fluorescence, then change in the emission profile, especially at shorter wavelengths and lower pressures of the ketone, would be expected. Thus, at present, there is no evidence of a significant amount of the fluorescence being originated in the higher vibrational levels of the excited singlet state of chloropentafluoroacetone. However, in the case of hexafluoroacetone, Boyd and Kutschke(97) suggested that the higher vibrational levels also contribute to the fluorescence from the ground vibrational level of the excited singlet state. More precise and detailed measurements later(58) confirmed this contribution.

It may be pointed out here that the present equipment was not suitable for studies in the low pressure region. The precise emission data in the low pressure region are necessary for making a complete assignment of the fluorescence.

Since the fluorescence yield at room temperature is small ($\phi = 0.023$) other primary photochemical processes must play an important role in the photochemistry of chloropentafluoroacetone. Various modes of dissipation of the excitation energy are incorporated in the following mechanism which is adequate to correlate all the experimental data reported here on chloropentafluoroacetone:

$$A + h\nu \xrightarrow{I_a} {}^1A^n \quad (4.3)$$

$$ {}^1A^n + A \xrightarrow{k_2} {}^1A^0 + A \quad (4.4)$$

$$ {}^1A^n \xrightarrow{k_3} \text{Removal} \quad (4.5)$$

$$ {}^1A^0 \xrightarrow{k_4} A + h\nu_f \quad (4.6)$$

$$ {}^1A^0 \xrightarrow{k_5} \text{Removal} \quad (4.7)$$

Here A refers to the ketone molecule in its ground electronic state and ${}^1A^n$ represents the electronically excited singlet state ketone molecule in its higher vibrational level. ${}^1A^0$ is the electronically excited ketone molecule in its low lying vibrational level responsible for emission. The collisional deactivation of the vibrationally excited singlet state ketone molecule has a rate constant k_2. k_3 is the rate constant for all processes that remove ${}^1A^n$, e.g. intersysystem crossing or decomposition. ${}^1A^0$ is removed by fluorescence (rate constant

k_4) or by processes such as decomposition or intersystem crossing to the triplet state (combined rate constant k_5). The mechanism implies that the vibrational deactivation is by strong collisions and a steady state analysis yields:

$$\frac{1}{\phi_f} = \frac{k_4+k_5}{k_4} + \frac{k_3}{k_2} \cdot \frac{k_4+k_5}{k_4} \cdot \frac{1}{[A]} \cdot \qquad (4.8)$$

Thus a Stern-Volmer plot of $\frac{1}{\phi_f}$ or $\frac{1}{Q}$ versus $\frac{1}{[A]}$ would be linear, if the mechanism proposed is adequate. Figure 4.8 gives such a plot for 313 nm excitation of the pure ketone. The plot is linear within experimental error. The value of the slope to intercept ratio of this straight line is 4.5×10^{-4} mole/liter. This ratio is a measure of k_3/k_2 according to the above mechanism. If it is assumed that k_2 is 2×10^{11} M^{-1} sec^{-1},(100) on the basis of strong collision mechanism for bimolecular collisions at room temperature, then k_3 becomes 9×10^7 sec^{-1}. This may be compared with 4.2×10^7 sec^{-1} corresponding value for hexafluoroacetone.

Porter et al(98) concluded that strong collisions deactivated the vibrational levels of the upper state of hexafluoroacetone and were supported by the data acquired by Ware and Dutton(70). However, Strachan, Boyd and Kutschke(99) reinterpreted results of the photolysis of hexafluoroacetone and showed that a series of graphical tests could indicate whether the deactivation of the upper state is via weak collisions. Later, Kutschke and co-workers(67) in a more extensive study of the photolysis and emissions of hexafluoroacetone applied these

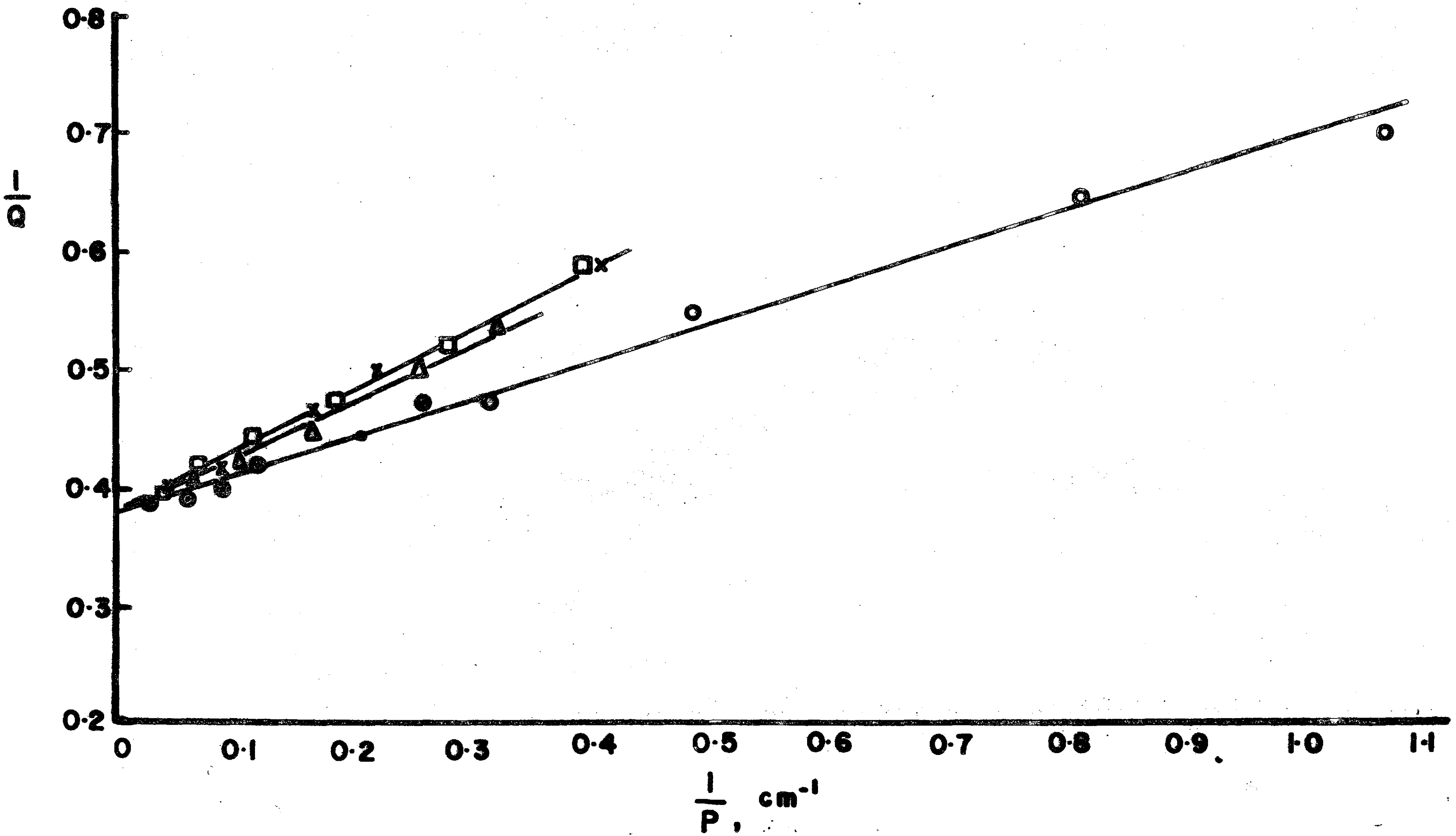


Figure 4.8. Plot of $\frac{1}{Q}$ vs $\frac{1}{P}$. o, chloroketone; ●, perfluorobutene; Δ, carbondioxide; □, X, sulfurhexafluoride

tests to their data. One of the more rigorous tests applied by these authors is based on the following equations (notations are according to Kutschke et al$^{(67)}$):

$$\phi+\phi^f = 1 - [1 - (\phi_\infty+\phi_\infty^f)]\pi \ . \qquad (4.9)$$

The plots of $\frac{1}{(\phi+\phi^f)}$ and $[1 - (\phi+\phi^f)]/[A]$ versus [A] support the weak collisional deactivations of the vibrational levels.

Thus, Kutschke and co-workers$^{(61)}$ consider that deactivation of the upper state of hexafluoroacetone involves a multi-step cascade via a small number of vibrational levels and their mechanism invokes intersystem crossing only from the ground vibrational level of the first excited singlet state. Very recently Halpern and Ware$^{(73)}$ have studied the fluorescence lifetime of hexafluoroacetone as a function of the exciting wavelength over a pressure-range from 0.1 to 700 torr. Their data are best explained by a four-level model (three emitting states and the ground state) and support the weak collision mechanism of vibrational deactivation. Their data also require that intersystem crossing occur from higher vibrational levels as well as from the lowest vibrational level.

The problem of a weak collisional deactivation of higher vibrational levels can be solved with techniques employed by Halpern and Ware$^{(71)}$ and Kutschke and co-workers$^{(61)}$. For the present investigation, the type of equipment used by Ware or Kutschke was not available. Therefore, the data reported here cannot decide whether collisions are weak or strong. However, in the case of a weak collision mechanism there is no simple interpretation of the slope of a plot of $\frac{1}{\Phi}$ or $\frac{1}{Q}$ versus $\frac{1}{[A]}$. Qualitatively the data on chloropentafluoroacetone are compatible with a strong collision-mechanism.

As expected the ketone is more efficient in deactivating the higher vibrational levels of the excited singlet state than carbon dioxide and sulfur hexafluoride. The efficiency of perfluorobutene is about the same as that of the ketone. The limiting value of the fluorescence is reached at a lower pressure when only the ketone is present than when an inert gas is used to increase the pressure (at a fixed pressure of the ketone). This is so for all the exciting wavelengths studied ("290", 313 and 334 nm). From the plots of $\frac{1}{Q}$ vs $\frac{1}{[A]}$ shown in figure 4.8 at 313 excitation the efficiencies of perfluorobutene, carbon dioxide and sulfurhexafluoride relative to the ketone are estimated as ∿ 1.0, 0.94 and 0.92 respectively based on a strong collision mechanism.

The role of the vibrationally excited state is further displayed in figure 4.4. The Q-value at the high pressure limit is independent of the excitation energy, as required by the mechanism (when appropriate corrections for the sensitivity of the detector for different wavelengths are made). However, the limiting value of Q is reached at progressively greater pressure as the excitation energy increases. This is again consistent with the formation of excited singlet states in higher vibrational levels at the shorter wavelengths. If the mechanism is extended to include vibrational deactivation by an added gas M then the mechanism is in agreement with the observations that the same value of Q is obtained when high pressure limit is attained by increasing the pressure of the added gas.

Regardless of the type of vibrational deactivation assumed for the system the quantum yield of the fluorescence, in the high pressure limit, $\phi_{f,\infty}$ is equal to $\frac{k_4}{k_4+k_5}$ according to the present mechanism. The reciprocal of (k_4+k_5) is the actual singlet state lifetime of the chloroketone (3.5×10^{-8} seconds) and since

$$\phi_{f,\infty} = 0.023$$

then k_4 is 6.6×10^5 sec^{-1} and k_5 is 2.8×10^7 sec^{-1}. This value of k_4 can be compared with that obtained from the integrated area under the absorption curve, 8.8×10^5 sec^{-1}. This is in excellent agreement considering the approximations inherent in the use of the formula for the $\frac{1}{\tau_0}$. If one assumes that there is no decomposition from the excited singlet state in the ground vibrational level, and that the internal conversion to the ground state is negligible, then the rate constant k_5 corresponds to that for intersystem crossing to a triplet state.

A comparison of k_4 and k_5 for chloropentafluoroacetone and the corresponding rate constants for hexafluoroacetone is of interest since it might show the effect of the chlorine atom as an intramolecular heavy atom on the excited singlet state of an $n \rightarrow \pi^*$ transition of carbonyl compound. Ware et al(70,73) have measured the fluorescence lifetime of hexafluoroacetone. The actual lifetime of the singlet hexafluoroacetone at room temperature in gas phase (ketone pressure > 15 torr) is found to be 8.4×10^{-8} seconds. Ware and Dutton(70) used the value of Porter(60) for $\phi_{f,\infty}$ to calculate the rate constants which are equivalent of k_4 and k_5. Kutschke(58) has redetermined $\phi_{f,\infty}$ for hexafluoroacetone fluorescence as 0.0185. Thus

$$k_{4_{\text{HFA}}} \text{ is } 2.2 \times 10^5 \text{ sec}^{-1}$$

and

$$k_{5_{\text{HFA}}} \text{ is } 1.2 \times 10^7 \text{ sec}^{-1}.$$

A comparison of these rate constants for hexafluoroacetone with the equivalent rate constants for chloropentafluoroacetone shows that the presence of chlorine atom has increased the rate constants of the radiative ($S_1 \rightarrow S_0$) and radiationless ($S_1 \rightarrow T_1$) in the gas phase at room temperature by factors of only about 3.0 and 2.3 respectively. Thus the radiative process $S_1 \rightarrow S_0$ is affected more than the radiationless process $S_1 \rightsquigarrow T_1$. This suggests that the spin-orbit coupling effect of the chlorine atom, as an internal heavy atom, on the ($n \rightarrow \pi^*$) singlet state transition is small. It may be pointed out here that the rate constants equivalent to k_4 and k_5 for acetone and other aliphatic ketones are of the order of 4×10^5 sec^{-1} and 4×10^7 sec^{-1} respectively(33).

In general the heavy atom substitution can affect the following transitions:

(1) Radiative (a) $S_1 \rightarrow S_0$
(b) $T_1 \rightarrow S_0$
(2) Radiationless (a) $S_1 \rightsquigarrow T_1$
(b) $T_1 \rightsquigarrow S_0$

The intramolecular (internal) and intermolecular (external) heavy atom effects on the singlet-triplet transitions of many organic molecules have been studied and it has been shown that the heavy atom substitution increases the singlet-triplet transition in most of the cases. For example, McClure(18) found that the phosphorescence lifetime of benzene is 7 sec and that of chlorobenzene 4×10^{-3} sec in rigid glasses at liquid nitrogen temperature. Thus, the substitution of a chlorine atom in benzene decreases the $T_1 \rightarrow S_0$ radiative lifetime by a factor of about two thousand.

At present the transitions of interest are radiative $S_1 \rightarrow S_0$ and radiationless $S_1 \rightsquigarrow T_1$. However, in aliphatic carbonyl compounds the intermolecular and intramolecular heavy atom effects reported in the literature are concerned mainly with the radiative and radiationless processes involving triplet state, i.e., $T_1 \rightarrow S_0$, $S_1 \rightsquigarrow T_1$, particularly the former. Thus El-Sayed(100) predicted negligible internal heavy atom effect on the phosphorescence ($T_1 \rightarrow S_0$) of the carbonyl compounds, especially X_2CO. His calculations were based on complete localization of the "lone pair" electrons on the oxygen atom. It is pointed out that the spin-orbit coupling with oxygen atom in the parent molecule, H_2CO, is relatively large as a result of which the heavy atom substitution does not increase this interaction significantly. On the other hand, McGlynn et al.(101) have calculated the intramolecular effect of halogen substitution on the natural radiative lifetime of formaldehyde triplet-state(30). Their calculations show that spin-orbit coupling in H_2CO is small and becomes increasingly important for heavy atom substitutions on formaldehyde and the phosphorescence lifetimes should vary from 10^{-2} sec for H_2CO to about 10^{-5} sec for I_2CO. Shimada and Kanda(102) have considered the intramolecular effects on the forbidden singlet-triplet absorption in glyoxal, oxalyl chloride and oxalyl-bromide. They find that singlet→triplet absorption ($S_0 \rightarrow T_1$) intensities increase with an increase in the atomic number of the halogen atom and this increase is attributed to the change in the transition energies and the spin-orbit interaction.

In addition to intramolecular heavy atom effects intermolecular heavy atom effects also have been investigated. For example, intermolecular heavy atom effect on the first excited singlet state has been investigated by Wagner(103). According to his observations there is no effect of propyl bromide on the intersystem crossing from the excited singlet to the triplet state ($S_1 \rightsquigarrow T_1$) in 2-hexanone, 2-heptanone and 2-octanone. As reported earlier no effect of the mercury vapor was observed either on the fluorescence yield or the fluorescence lifetime of chloropentafluoroacetone. This is in agreement with the observations of Kutschke et al.(63) who report that mercury does not affect the fluorescence of hexafluoroacetone. Since the singlet lifetime is short and the mercury concentration is low, this is the expected behavior. Porter and McIntosh(104) have suggested that the singlet state of hexafluoroacetone can transfer energy to bromine without a chemical change although there is no direct evidence for this transfer.

The chlorine atom in chloropentafluoroacetone is not attached directly to the carbonyl group and the size of the intramolecular heavy atom effect is, therefore, understandable, in the light of above discussion. The small heavy atom effect in chloropentafluoroacetone suggests that other chlorinated aliphatic carbonyl compounds may luminesce and this could be a useful tool in elucidating the photochemistry of halogenated compounds.

CHAPTER 5

QUENCHING OF THE CHLOROKETONE SINGLET STATE

RESULTS

The interaction of the excited states of carbonyl compounds with quenching molecules is of great interest, and extensive studies have been undertaken of olefin quenching of triplet states in solution. More recently, it has been recognized that excited singlet, (n,π^*), states can also be deactivated, but gas phase studies of singlet quenching are rare and the quenching ability of only a few molecules for the excited singlet state of hexafluoroacetone has been reported. Thus, the object of the present investigation was to study the effect of structure, substitution, conjugation and cyclization on the quenching efficiency. To ensure that the excited singlet state molecules are at lower vibrational levels, quenching studies were carried out with high pressures of the ketone (corresponding to $\phi_{f,\infty}$).

The quenchers studied during the present investigations are 1, 3-pentadiene (piperylene), ethylene, vinyl chloride, 1,1-difluoroethylene, tetrachloroethylene, propylene, 1-butene, cis-butene-2, isobutylene, 1-hexene, cyclohexene, benzene, and isobutane. All the quenching data are presented in tables 5.1

to 5.13. Note that the value of Q reported at any given pressure is the mean of several readings taken at time intervals of a few hours. Q_o in these tables refers to the relative fluorescence yield in the absence of the quencher whereas Q is the relative fluorescence when the quencher is present. For these studies plots of Q_o/Q vs pressure are shown in figures 5.1 to 5.5. The reproducibility of the technique was checked by performing two different series of the quenching experiments with propylene. The data are reported in tables 5.5A and B. The agreement between these two sets of data is excellent (see figure 5.4). The error in quenching rate constants is about 5%.

Table 5.1

Effect of ethylene on the emission

Ketone = 107 × 10^{-4} mole/liter

S. No.	Ethylene Concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	4.48	1.07
3	0.55	1.14
4	15.3	1.16
5	23.6	1.24
6	34.3	1.31

Table 5.2

Effect of vinyl chloride on the emission

Ketone = 106 × 10^{-4} mole/liter

S. No.	Vinyl chloride concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	1.68	1.10
3	3.95	1.09
4	10.5	1.24
5	21.5	1.49
6	39.6	1.75

Table 5.3

Effect of 1,1-difluoroethylene on the emission

Ketone = 118 × 10^{-4} mole.liter

S. No.	1,1-Difluoroethylene concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	2.40	1.09
3	5.83	1.16
4	11.6	1.26
5	22.2	1.47

Table 5.4

Effect of tetrachloroethylene on the emission

Ketone = 107 × 10^{-4} mole/liter

S. No.	Tetrachloroethylene concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	1.91	0.99
3	4.67	1.07
4	7.46	1.10

Note: Higher concentration of the tetrachloroethylene could not be used due to its relatively low vapor pressure at room temperature.

Table 5.5

Effect of propylene on the emission

A. Ketone = 107×10^{-4} mole/liter

S. No.	Propylene concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	2.48	1.28
3	4.45	1.40
4	8.51	1.76
5	12.7	2.04

B. Ketone = 107×10^{-4} mole/liter

1	0.00	1.00
2	1.10	1.08
3	3.22	1.35
4	5.57	1.62

Table 5.6

Effect of 1-butene on the emission

Ketone = 104 × 10^{-4} mole/liter

S. No.	1-Butene concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	2.61	1.26
3	7.67	1.71
4	13.6	2.15

Table 5.7

Effect of cis-butene-2 on the emission

Ketone = 107 × 10^{-4} mole/liter

S. No.	cis-Butene-2 concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	0.76	1.11
3	2.22	1.45
4	4.17	1.86
5	6.32	2.22
6	10.8	3.10

Table 5.8

Effect of isobutylene on the emission

Ketone = 100 × 10^{-4} mole/liter

S. No.	Isobutylene concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	0.97	1.19
3	3.64	1.66
4	5.55	1.10
5	9.85	2.62
6	11.9	3.06

Table 5.9

Effect of 1-hexene on the emission

Ketone = 105 × 10^{-4} mole/liter

S. No.	1-Hexene concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	1.29	1.19
3	2.81	1.29
4	4.08	1.42
5	8.23	1.84
6	14.8	2.53

Table 5.10

Effect of cyclohexene on the emission

Ketone = 106 × 10^{-4} mole/liter

S. No.	Cyclohexene concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	0.94	1.30
3	1.89	1.51
4	4.20	2.18
5	6.38	2.59
6	9.30	3.34

Table 5.11

Effect of piperylene on the emission

Ketone = 107 × 10^{-4} mole/liter

S. No.	Piperylene concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	0.08	1.03
3	0.50	1.13
4	2.32	1.92
5	13.1	5.80
6	17.2	6.60

Table 5.12

Effect of benzene on the emission

Ketone = 107 × 10^{-4} mole/liter

S. No.	Benzene concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	0.89	1.09
3	4.08	1.38
4	8.95	1.81
5	16.1	2.52
6	22.5	3.17

Table 5.13

Effect of isobutane on the emission

Ketone = 108 × 10^{-4} mole/liter

S. No.	Isobutane concentration 10^{-4} mole/liter	Q_o/Q
1	0.00	1.00
2	4.82	1.01
3	24.4	1.10
4	89.2	1.29

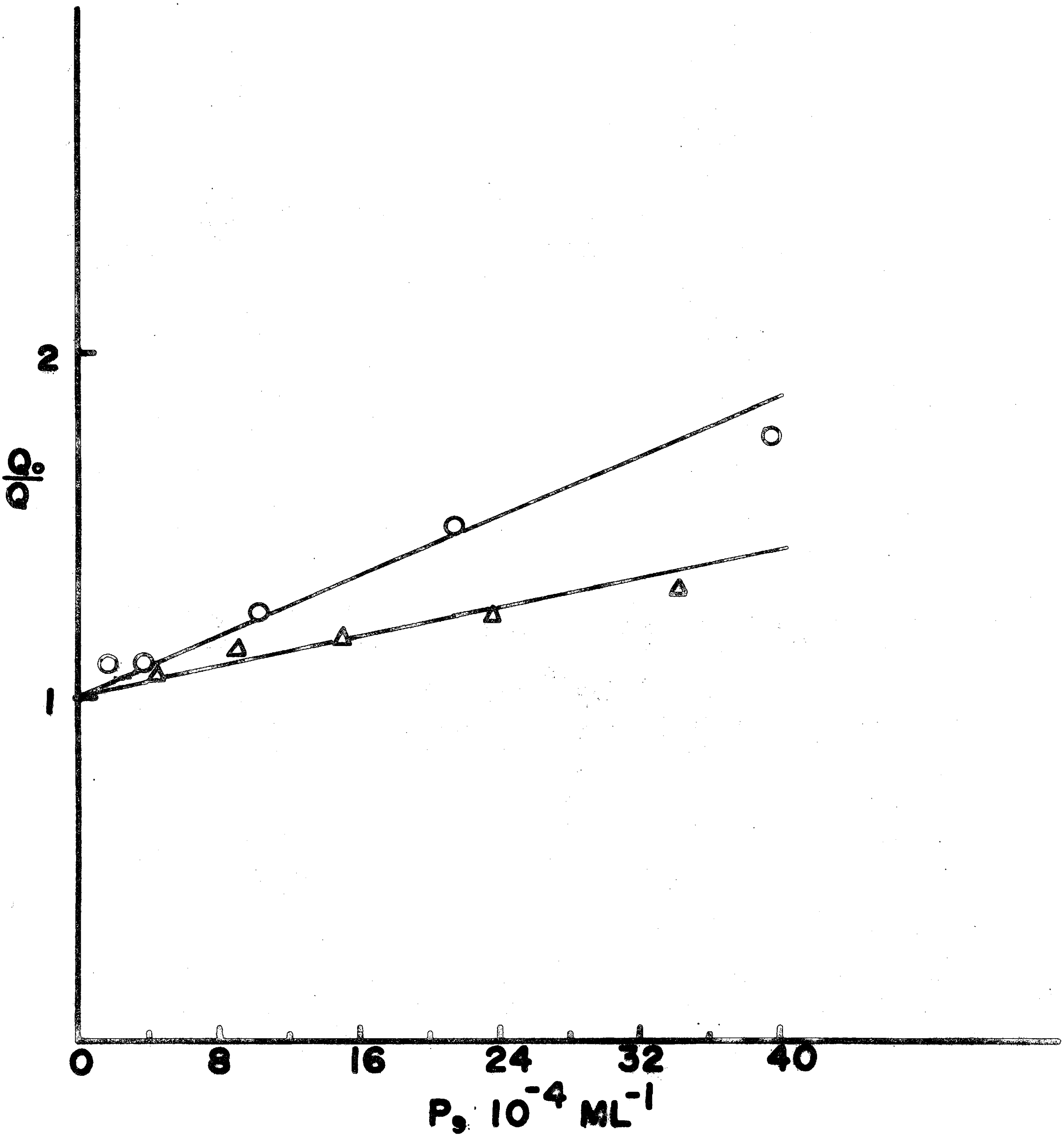


Figure 5.1 Effect of ethylene (Δ) and vinyl chloride (O) on chloropenta fluoroacetone-fluorescence ; λ_{ex} = 313 nm.

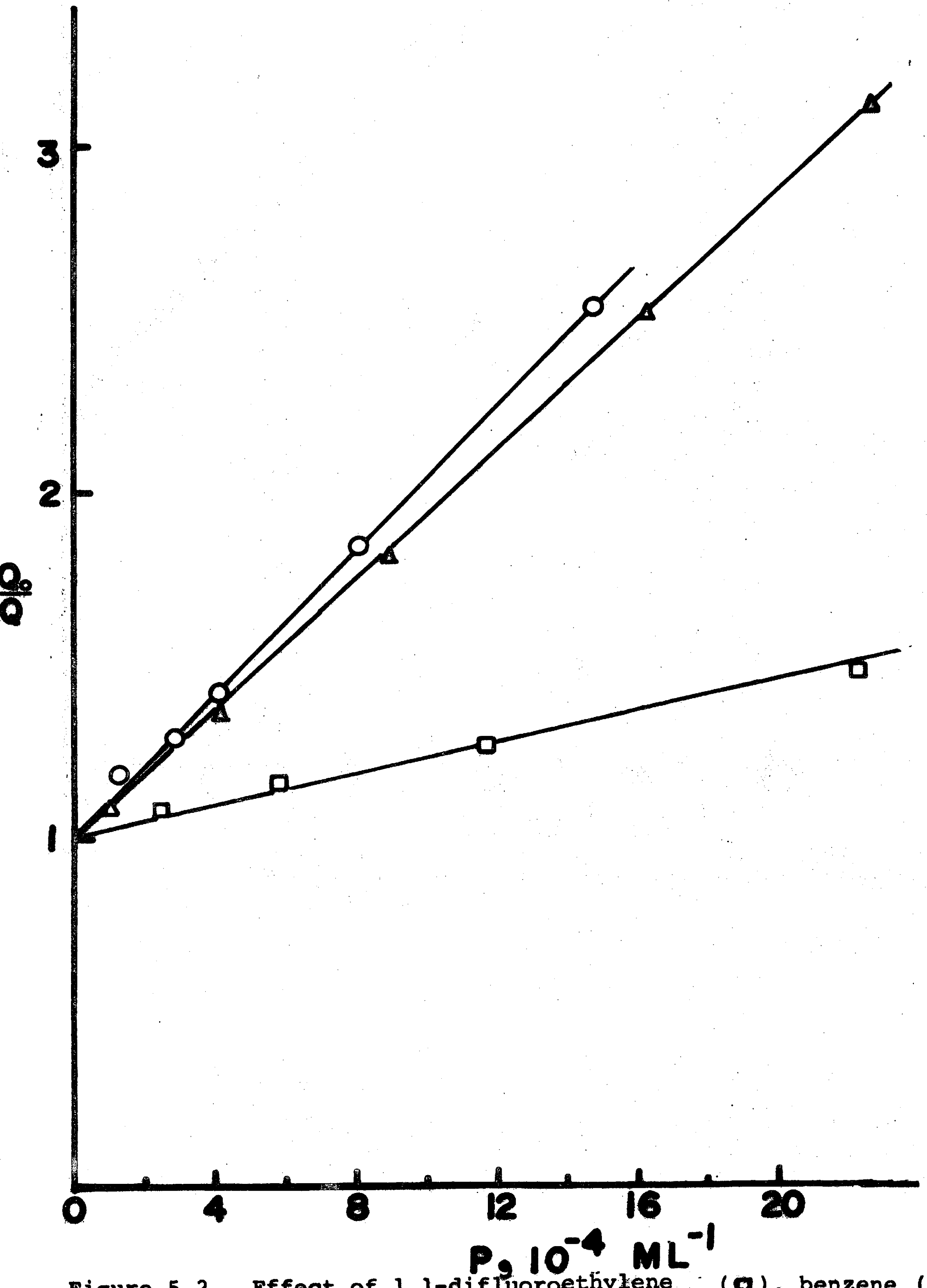


Figure 5.2. Effect of 1,1-difluoroethylene (□), benzene (Δ) and 1-hexene (O) on chloropentafluoroacetone-fluorescence; λ_{ex} = 313 nm.

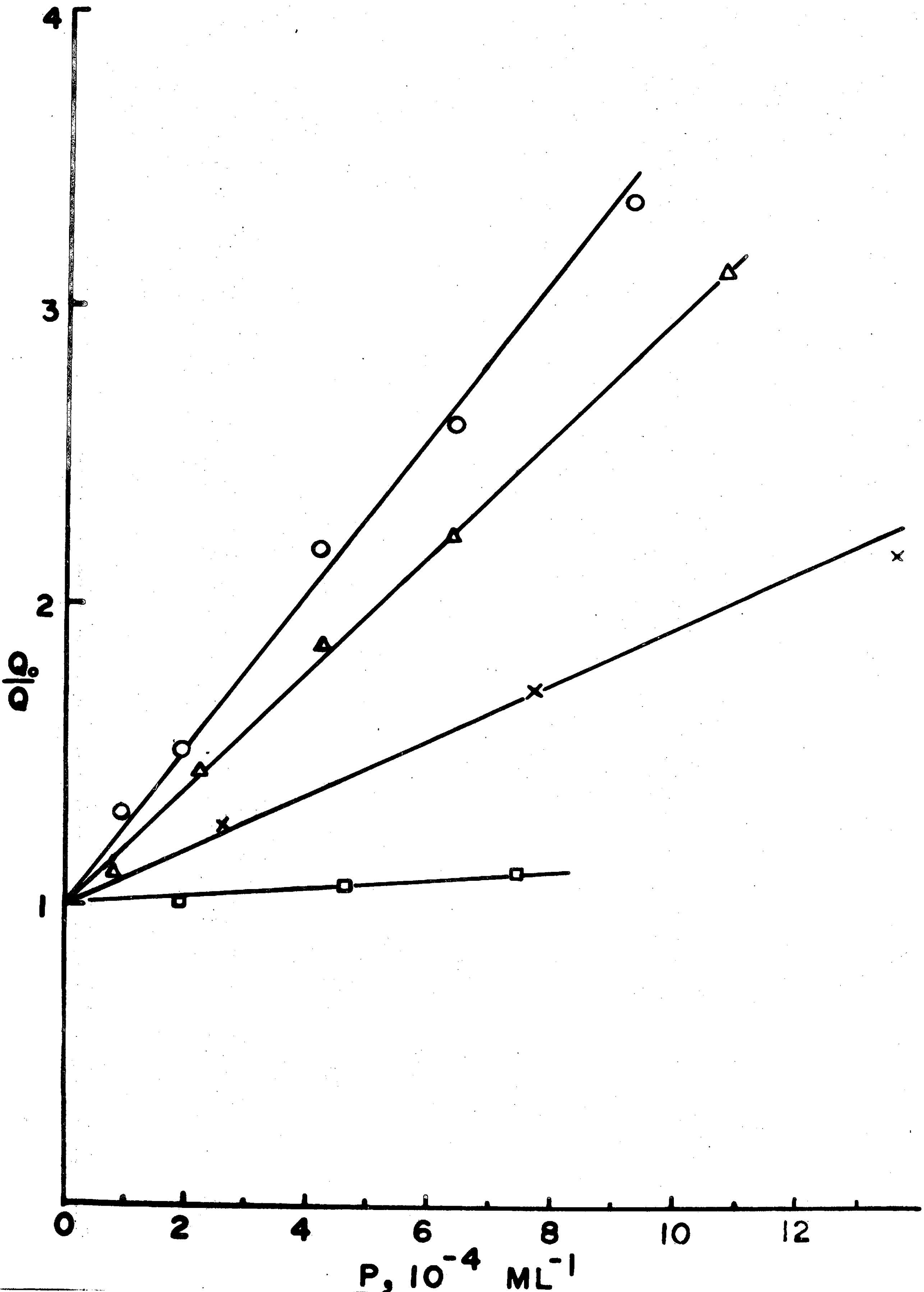


Figure 5.3. Effect of tetrachloroethylene (□), 1-butene (X), cis-butene-2 (Δ) and cyclohexene (O) on chloropentafluoroacetone fluorescence : λ = 313 nm.

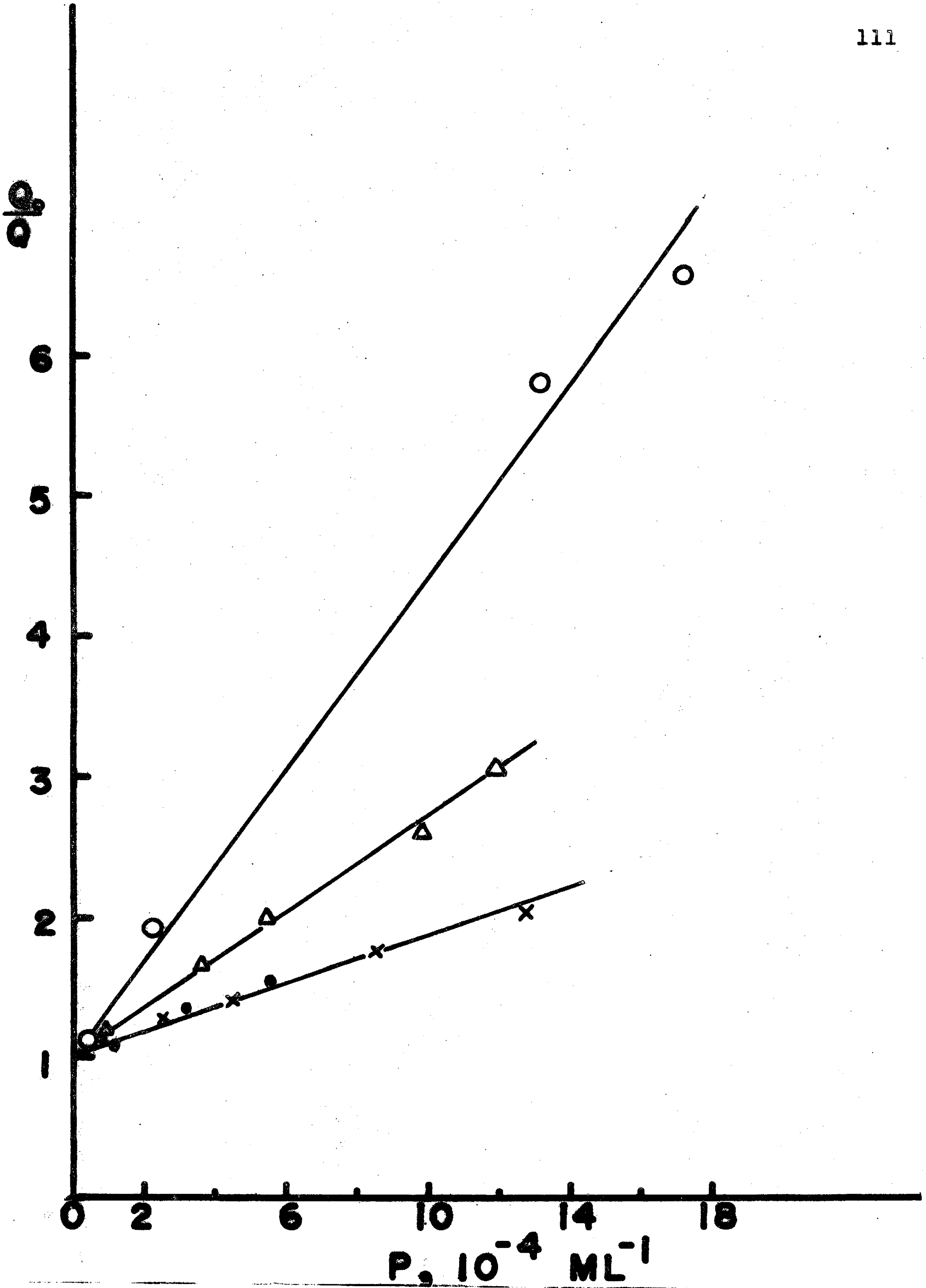


Figure 5.4 Effect of propylene (●,X), isobutylene (Δ) and 1,3-pentadiene (O) on chloropentafluoroacetone-fluorescence; λ_{ex} = 313 nm.

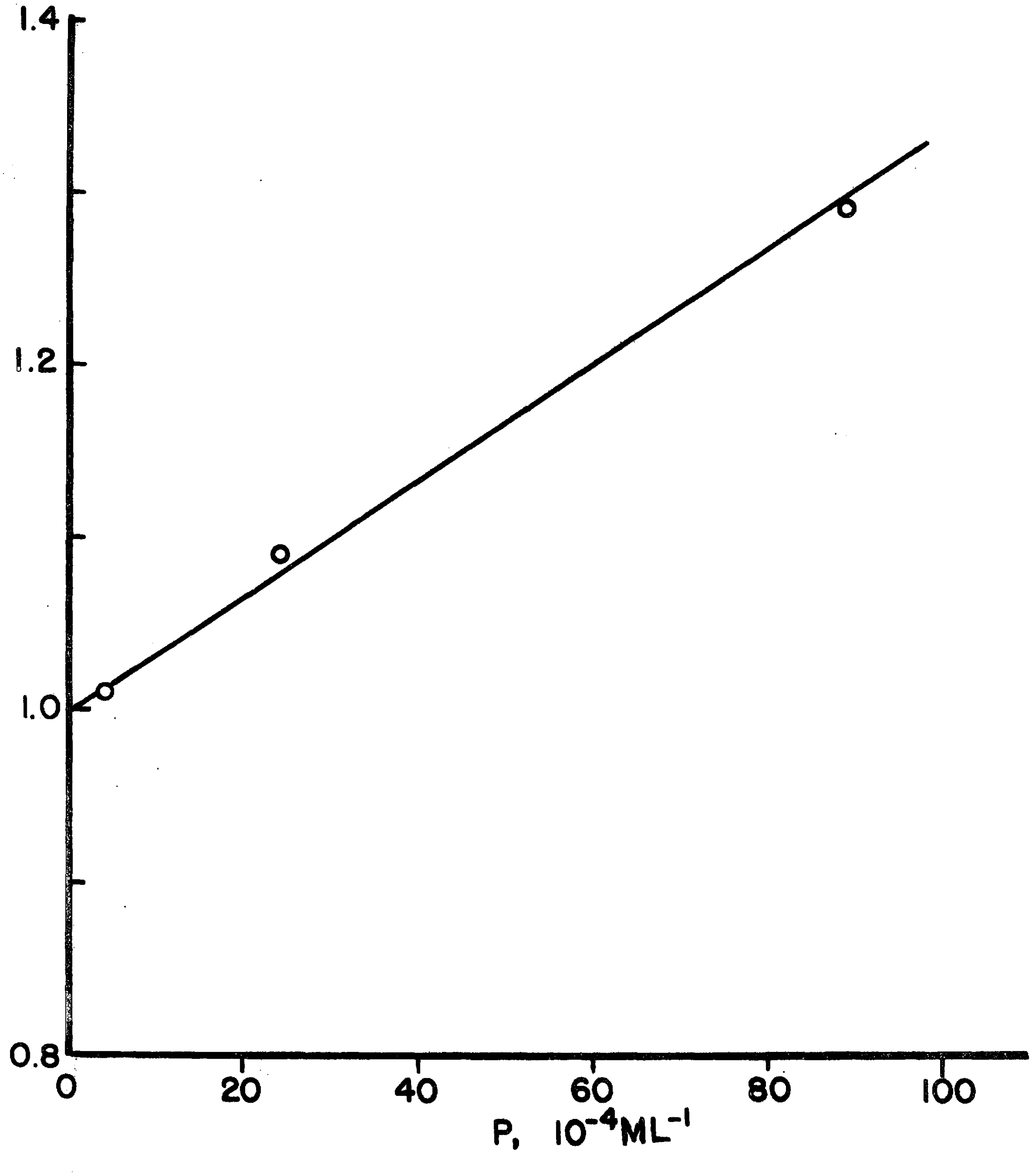


Figure 5.5 Effect of isobutane on chloropentafluoroacetone fluorescence; λ_{ex} = 313 nm

DISCUSSION

Although the research reported in the literature on the quenching of single states of carbonyl compounds in the gas phase is limited to a few ketones and quenching molecules, a considerable amount of work has been reported on the quenching of the singlet states of aromatic hydrocarbons, mostly in the condensed phase. For example Hammond and coworkers(105,106) found that the conjugated dienes quench the fluorescence of aromatic hydrocarbons without any significant amount of chemical reaction. With the view of extending the singlet-quenching-studies of the carbonyl compounds, the effect of a number of quenching molecules on the $^1(n,\pi^*)$ state of chloropentafluoroacetone has been studied during the present investigation.To ensure that the excited singlet state is in its lowest vibrational level, high ketone pressure was employed during these studies, i.e. the emission yield corresponds to the limiting value of the fluorescence ($\phi_{f,\infty}$).

The following mechanism, which explains the experimental observations, is proposed in presence of a singlet-quencher.

$$A + h\nu \rightarrow {}^1A^n \qquad (5.1)$$
$${}^1A^n + A \rightarrow {}^1A^0 + A \qquad (5.2)$$
$${}^1A^n \rightarrow \text{Removal} \qquad (5.3)$$
$${}^1A^0 \rightarrow A + h\nu_f \qquad (5.4)$$
$${}^1A^0 \rightarrow \text{Removal} \qquad (5.5)$$
$${}^1A^0 + Q \rightarrow \text{Removal} \qquad (5.6)$$

Here Q is a singlet quencher. All other steps have been explained earlier. If $\phi_{f,\infty}$ is the quantum yield of the fluorescence of the chloroketone in the absence of the added gas and $\phi_{f,Q}$, that in the presence of a quencher, then from the steady state approximation it can be shown that

$$\frac{\phi_{f,\infty}}{\phi_{f,Q}} = 1 + \frac{k_6}{k_4+k_5}[Q] \ . \qquad (5.7)$$

Therefore, a plot of $\frac{\phi_{f,\infty}}{\phi_{f,Q}}$ or $\frac{Q_o}{Q_Q}$ versus the concentration of the quencher, [Q], should yield a straight line with a slope of $(\frac{k_6}{k_4+k_5})$, if the proposed mechanism is consistent with the experimental data. Q_o and Q_Q refer to the relative fluorescence yields in the absence and presence of the quencher respectively. As can be seen from figures 5.1 to 5.5 which show linear behavior, the proposed mechanism is in excellent agreement with the experimental data. (k_4+k_5) represents the reciprocal of the actual singlet lifetime, 3.51 × 10^{-8} sec. Therefore, from the slope of the quenching rate constant, k_6 can be calculated for each quencher studied.

The singlet quenching rate constants of these quenchers are given in table 5.14. This table also contains the ionization potentials of the quenching molecules reported in the literature. Table 5.15 similarly shows the rate constants for the singlet and triplet quenching of hexafluoroacetone. It can be seen from table 5.14 that the most effective quenching

Table 5.14

Chloropentafluoroacetone singlet-quenching rate constants at room temperature

Quenching molecule	Rate constant (k_q, $M^{-1}sec^{-1}$)	Ionization potential of quencher (eV)
Ethylene	2.9×10^9	10.51*
Vinyl chloride	6.3×10^9	10.00*
1,1-Difluoroethylene	6.0×10^9	10.31*
Tetrachloroethylene	4.6×10^9	9.34*
Propylene	2.3×10^{10}	9.70†
1-Butene	2.4×10^{10}	9.65†
Cis-Butene-2	5.6×10^{10}	9.24†
Isobutylene	4.8×10^{10}	8.95†
1-Hexene	2.9×10^{10}	9.46††
Cyclohexene	7.1×10^{10}	9.20‡
1,3-Pentadiene	9.7×10^{10}	8.68††
Benzene	2.7×10^{10}	9.24†
Isobutane	8.6×10^8	10.34†
Perfluorobutene	$<10^7$	-

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*Reference (107)

†Reference (108)

‡Reference (109)

††Reference (110)

Table 5.15

Hexafluoroacetone singlet and triplet quenching rate constants at room temperature

Quenching molecule	Singlet quenching rate constant ($k_q, M^{-1}sec^{-1}$	Triplet quenching rate constant ($k_q, M^{-1}sec^{-1}$)
Ethylene	4.1×10^{9}[†]	5.9×10^{8}[*]
Propylene	1.6×10^{10}[†]	7.2×10^{9}[*]
1-Butene		
Cis-Butene-2	3.5×10^{10}[†] (2.4×10^{10})[‡]	
Isobutylene	(2.7×10^{10})[‡]	2.1×10[*]
1,3-Pentadiene	8.0×10^{10}[†]	
Benzene	8.2×10^{9}[†]	1.6×10^{9}[*]
Isobutane	-	1.2×10^{8}[*]

[†] Reference (71)

[‡] Reference (66)

[*] Reference (61)

molecule is 1,3-pentadiene ($k_q = 9.7 \times 10^{10}\ M^{-1}\ sec^{-1}$) and that the least efficient isobutane ($k_q = 8.6 \times 10^{8}\ M^{-1}\ sec^{-1}$). In the case of isobutane one in four hundred collisions results in deactivation of the excited singlet chloropentafluoroacetone.

Before considering the nature of the quenching of chloropentafluoroacetone involved in individual cases, it may be of advantage to summarize the salient features of the singlet-quenching studies of acetone and hexafluoroacetone. Considering first the research on acetone, Turro and Wriede(46) studied the photo-cycloaddition in solution of acetone to 1-methoxy-1-butene to form an oxetane via intermediate singlet and triplet biradicals. The mode of attack is electrophilic in nature, i.e., "the attack of the half-filled n-orbital of the ketone, (n,π*) state, on the π-system of the olefin results in a biradical that can cyclize to form an oxetane". They suggest this mechanism for quenching by the "electron-rich" olefins. On the other hand, Dalton, Wriede and Turro(47) suggest a different mechanism for the photocycloaddition of acetone to "electron-poor" olefins. These authors propose that there is an "electron-rich" system above and below the plane of the carbonyl group in the n,π* excited state of ketones. Therefore the attack of this nucleophilic system on the "electron-deficient" π-system of the olefin (1,2-dicyanoethylene) results in the inefficient stereospecific product formation. Both these photocycloadditions are examples of chemical quenching of both singlet and triplet n,π* states by the olefins.

Considering now the work on hexafluoroacetone, the quenching of the fluorescence of hexafluoroacetone was studied by Ware and Lee(71). They found that dienes, olefins, oxygen, nitric oxide and benzene all quench the hexafluoroacetone-fluorescence with varying efficiencies. Oxygen is a very poor quencher of the fluorescence of hexafluoroacetone ($k_q = 7.6 \times 10^7\ M^{-1}\ sec^{-1}$ at 25°C) and is in contrast with the high quenching efficiency of oxygen for the triplet state ($k_q = 4.5 \times 10^8\ M^{-1}\ sec^{-1}$). The mechanism proposed is the formation of an intermediate complex without a final chemical reaction. The complex may have some charge-transfer character. Their data show that the quenching efficiency is approximately in order of increasing molecular complexity and decreasing ionization potential. These authors also found that perfluoropropylene has no effect on the hexafluoroacetone fluorescence.

The quenching of the hexafluoroacetone triplet molecules has also been investigated. Knipe and Gordon(69) found that almost all oxetane is formed via triplet state by photocycloaddition of hexafluoroacetone to perfluoropropylene. Kutschke and coworkers(61-63) studied the quenching of the hexafluoroacetone triplets by a number of quenching molecules. They also concluded that, except in the case of mercury, the quenching of triplet state is a result of a chemical interaction between the excited ketone molecules and the ground state quencher molecules. The quenching by mercury is ascribed to an intermediate complex formation possibly with some charge-transfer character. On the basis of relative quenching efficiencies of different quenching molecules Ware and Lee(71) suggest that the same intermediate complex is involved in the quenching of both singlet and triplet states of hexafluoroacetone.

Present data on the quenching of the fluorescence of chloropentafluoroacetone are in general , consistent with the fluorescence quenching data on hexafluoroacetone(66,71) although these authors studied only a few quenching molecules. As in hexafluoroacetone-fluorescence quenching studies, there is a strong correlation between the quenching efficiency and the ionization potential of a quencher in the fluorescence-quenching of the chloroketone, i.e. the quenching efficiency increases as the ionization potential decreases (see table (5.14).

Quenching by mono-olefins, dienes, cyclic olefins and benzene:

The following possibilities, similar to those considered by Kutschke et al.(61) for triplet quenching of hexafluoroacetone, exist as mechanisms for the quenching of the fluorescence of the chloroketone by mono-olefins, dienes, cyclic olefins and benzene:

(1) Direct energy transfer between the excited ketone molecules and the ground state quenching molecules to form an

excited singlet state of the quencher and the ground electronic state of the ketone molecules.

(2) Collisional deactivation of the excited molecules to the ground state.

(3) External heavy atom-induced internal conversion or intersystem crossing.

(4) Deactivation by formation of an intermediate complex or radical from the excited singlet state ketone and the ground state quencher with or without an overall chemical change.

Among the possibilities described above the direct energy-transfer involving the singlet states of the ketone and the quenching molecules is not probable on the basis of energy considerations. The $^1S_0$ energy of the chloroketone is about 83 Kcal/mole and the singlet energy levels of the quenchers studied are much higher, e.g., the first excited singlet state of ethylene lies around 150 Kcal per mole above the ground state(111). The energy-transfer yielding the triplet state quencher is "spin-forbidden".

The collisional deactivation of the excited ketone molecules by the quenching molecules may be ruled out on the grounds that not all compounds, although of comparable size, quench the fluorescence of the chloroketone. The mechanism that involves an external heavy-atom effect to induce the intersystem crossing is also improbable.

Molecules containing a heavy atom should be more efficient quenchers than those containing light atoms which is not consistent with present data. Further, the magnitude of the external heavy atom effect is generally smaller than the internal heavy atom effect. In the present system the internal heavy atom effect itself is small and only a very small external heavy atom effect would be expected.

The mechanism involving the formation of an intermediate complex between the excited ketone molecule and the ground state quenching molecule seems more probable. The following steps, similar to those suggested by Ware et al., elucidate the formation and decomposition of such a complex:

$$^1A^0 + Q \rightarrow (^1A^0 \ldots\ldots Q) \qquad (5.8)$$

$$(^1A^0 \ldots\ldots Q) \rightarrow {}^1A^0 + Q \qquad (5.9)$$

$$(^1A^0 \ldots\ldots Q) \rightarrow A + Q \qquad (5.10)$$

$$(^1A^0 \ldots\ldots Q) \rightarrow \text{Product} \qquad (5.11)$$

$$^1A^0 \rightarrow A + h\nu_f \qquad (5.12)$$

The complex may decompose giving the ground states of the ketone and quencher molecules. Alternatively the formation of the complex may be reversible, giving the electronically excited ketone molecule and the quencher molecule in the ground state. It is also possible that the complex formation may be followed by an over-all chemical change giving a product, e.g. oxetane. Gordon and Knipe(69) found a small amount of residual oxetane from the photolysis of hexafluoroacetone-perfluoropropylene mixture in presence of piperylene which quenches the triplet ketone molecules. This residual oxetane might have resulted from the photocycloaddition of perfluoropropene to the excited singlet state molecules of the ketone. The mode of formation of the intermediate complex, particularly in the case of the olefins containing "electron-rich" π-band, is perhaps the electrophilic attack by the half-filled n orbital of the carbonyl group on the "electron-rich" π-system of the olefin. This model explains the chloroketone fluorescence-quenching by ethylene, propylene, butenes, piperylene, hexenes and benzene. The position of the alkyl group has some effect on the efficiency of the quencher. The close proximity of the "electron-donating" group to the carbon-carbon double bond increases the quenching efficiency as can be seen from table 5.14. This observation is consistent with the above model involving an electrophilic attack on the π-system. The model also explains the fact that perfluorobutene, which has an "electron-deficient" carbon-carbon double bond, does not quench the chloroketone fluorescence. Ware and Lee(71) also reported that perfluoropropylene does not quench the fluorescence of hexafluoroacetone. These observations, along with the relation between rate constants of the different quenching molecules (see tables 5.14 and 5.15) suggest that the fluorescence quenching mechanism in both systems (hexafluoroacetone and chloropentafluoroacetone) is similar. It may be pointed out here that according to the above mechanism the acetone-fluorescence should be less susceptible to the quenching by olefins. Indeed, Turro et al.(46) find that the photocycloaddition of the acetone singlets to the ground state olefins is not efficient. e.g. $k_q \simeq 3 \times 10^8$ M^{-1} sec^{-1} for 1-methoxyl-1 butene.

However, the quenching of the chloroketone fluorescence by vinyl chloride, 1,1-difluoroethylene and tetrachloroethylene is more difficult to explain with this model. Considering the inductive effects these halo-ethylenes should have "electron-deficient" carbon-carbon double bonds, therefore, should be less efficient quenchers than ethylene. Contrary to this, all three halo-ethylenes are more efficient quenchers than ethylene, e.g., $k_{q,C_2H_4} = 2.9 \times 10^9$ $M^{-1}sec^{-1}$, $k_{q,C_2H_3Cl} = 6.3 \times 10^9$ M^{-1} sec^{-1}, $k_{q,C_2F_2H_2} = 6.0 \times 10^9$ M^{-1} sec^{-1} and $k_{q,C_2C\ell_4} = 4.6 \times 10^9$ M^{-1} sec^{-1}.

In the light of these quenching efficiencies the possibility of nucleophilic attack on the electron deficient carbon-carbon double bond should be considered (suggested by Turro et al.(47) for the photocycloaddition of acetone to 1, 2-dicyanoethylene). This explanation is not valid in the present case since perfluorobutene or perfluoropropylene would be expected to significantly quench the fluorescence of chloropentafluoroacetone or hexafluoroacetone. This is contrary to observations in both cases. Also, tetrachloroethylene would be expected to be a better quencher than vinyl chloride or 1, 1-difluoroethylene which is not the case. However, the quenching efficiencies of ethylenes are generally consistent with their ionization potentials. The inductive effect described here may perhaps be more than offset by the conjugative effect of the "lone pair" electrons on halogen atoms, thereby increasing the quenching efficiency. Pople and Beveridge(112) suggest that "fluorine is a strong attractor of σ electrons and a weak π electron donor".

The present data show a distinct correlation between the quenching efficiency and the ionization potential of the quenching molecule. The efficiency increases as the ionization potential decreases. Figure 5.6 shows k_q as a function of the ionization potential of the quenching molecule. Thus the intermediate complex probably has some charge-transfer character,

$$({}^1A^{0^-} \;\ldots\ldots\; M^+)$$

The relatively low quenching efficiency of tetrachloroethylene can be ascribed to steric effects.

Very recently a charge-transfer mechanism has also been suggested by Davis and Cohen(113) for fluorenone-triplet-quenching by amines. Their observations on the triplet quenching are similar to the present data on the fluorescence-quenching, i.e., electron-donating alkyl groups when substituted in a quencher increase its quenching efficiency, and the quenching efficiency is a function of the ionization potential of the

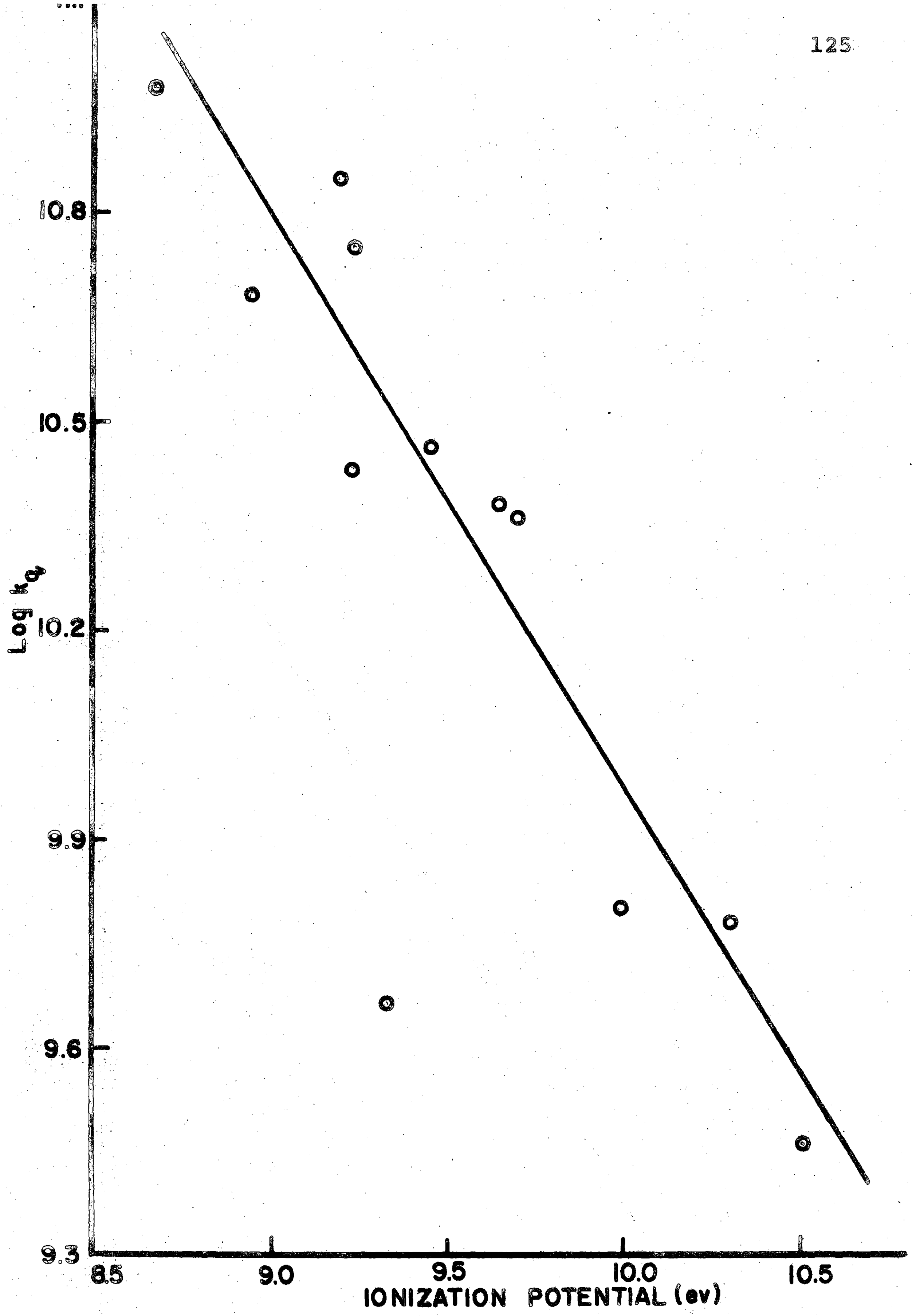

Figure 5.6 Quenching rate constant as a function of ionization potential of quenching molecules.

quencher. This suggests that the quenching mechanism for the singlet state is similar to that for the triplet state. A similar suggestion was also made by Ware and Lee(71) for the quenching of the singlet and triplet states of hexafluoroacetone.

Quenching by isobutane

The quenching of the chloroketone fluorescence by isobutane is not very efficient ($k_q = 8.6 \times 10^8 \; M^{-1} \; sec^{-1}$) in comparison with the quenching by olefins ($k_q \sim 10^{10} \; M^{-1} \; sec^{-1}$, see table 5.14) but it is significant that it quenches at all. This is the first report of quenching of the $^1(n,\pi^*)$ state of a carbonyl compound by an aliphatic hydrocarbon. Since the quenching by isobutane is inefficient one may suspect it to be due to some impurity. However, care was taken to ensure that the isobutane used was of high purity, especially that there were no olefins or dienes present. These results were later confirmed by experiments with research grade isobutane. In this case, too, the quenching by direct energy-transfer, collisional deactivation and external heavy atom effect can be safely ruled out on the grounds mentioned earlier. The quenching may be a function of chemical interaction between the excited ketone molecules and ground state quencher molecules. The intermediate complex formed may dissociate without a chemical change or result in an overall chemical change yielding product. The quenching of the fluorescence of the chloroketone by isobutane may be due to an overall chemical change, as has been suggested by Kutschke and coworkers[(61)] for the quenching of the phosphorescence by hydrocarbons.

Summary of the Singlet-quenching Studies

From an examination of the singlet quenching data the following conclusions may be drawn:

(1) Dienes are better quenchers than mono-olefins.

(2) The quenching efficiency in a homologuous series increases with increasing order in the series, e.g.,

ethylene < propylene < butenes.

(3) Aliphatic olefins are more efficient quenchers than aromatic compounds, e.g. cyclohexene is a better quencher than benzene.

(4) The quenching efficiency is also a function of the position of an alkyl group in an olefin (vide butenes).

(5) Acyclic molecules appear to be less efficient quenchers of the singlet state of the ketone than the corresponding cyclic ones.

(6) Perfluorobutene does not quench the fluorescence of the chloroketone.

(7) A hydrocarbon, such as isobutane, quenches the fluorescence of the chloroketone but the quenching is not very efficient.

CHAPTER 6

TRIPLET STATE OF CHLOROPENTAFLUOROACETONE RESULTS

Studies at room temperature in the gas phase:

As reported earlier, no phosphorescence could be detected in the emission from the chloroketone at room temperature in the gas phase. This was tested in a number of ways, e.g., (a) by observing the emission spectrum of the chloroketone (at a fixed pressure) in the absence and presence of oxygen and noting that there was no decrease in the intensity of the emission in the presence of oxygen, (b) by noticing that in the steady state apparatus there was no decrease in the emission when a few torr of oxygen were added to the ketone and (c) by the fact that no emission was detected using the Aminco-Bowman spectrofluorometer with the rotating can operating.

However, these observations do not preclude the presence of the triplet excited state of the chloroketone in the gas phase at room temperature. The triplet state might have a very short lifetime and thus a very low quantum yield of emission. Since there is no detectable long-lived emission from the excited chloroketone molecules, the presence of triplet states can only be determined by indirect methods.

Two simple methods, among others, for testing the presence of triplet states are:

(1) Sensitization of a suitable molecule under conditions where singlet→singlet energy-transfer is insignificant and the triplet-sensitized molecule can be monitored, and

(2) a comparison of the quantum yields of a photolysis product in the presence and absence of a molecule which can quench triplet states, e.g. oxygen. Oxygen, when present in small quantities, is supposed to quench the triplet state but not the singlet state. Thus, in the presence of oxygen a decrease in the product-formation is expected, provided the product in question is formed from the triplet state.

Of these two methods the former (sensitization) is simpler and can be applied to the present investigation. The molecule to be monitored should satisfy the following criteria:

(a) It should be an efficient quencher of the triplet state.

(b) The triplet-quenching should result either in a chemical change or sensitized emission which can be monitored.

(c) At least under certain specific conditions it should not quench the singlet state.

The object of the sensitization work was to identify and estimate the quantum yield of the triplet state of chloropentafluoroacetone at room temperature in the gas phase. For the present investigation biacetyl is a suitable substance to be sensitized and meets the requirements.

The preliminary investigations confirmed that the direct excitation of biacetyl by 313 nm does not produce significant emission. When the pressure of biacetyl added is below 1 torr there is no quenching of the singlets of the chloroketone.

In the case of the sensitized emission a number of spectra were taken for the following mixtures:

(a) Ketone pressure = 160 torr
    Biacetyl pressure = 0.4 torr
(b) Ketone pressure = 116 torr
    Biacetyl pressure = 0.9 torr.

The spectra were also recorded for (a) and (b) in the absence of the biacetyl under experimental conditions identical to those used for the sensitized spectra. The quantum yields were determined by correcting the spectra taking quinine sulfate as a standard. All spectra were taken under identical conditions. There was no decrease in the quantum yield of the fluorescence of the chloroketone in (a) and (b). The quantum yield of fluorescence of the chloroketone was again calculated from these spectra and found to be 0.021. The quantum yield of the sensitized biacetyl emission was obtained by subtracting the chloroketone fluorescence yields from the total emission yield and found to be 0.08.

Estimates of the triplet lifetime of the chloroketone:

The sensitized emission technique of Parmenter and Ring(114) was applied to the present system in an attempt to estimate the triplet lifetime of the chloroketone at room temperature in the gaseous state. The ketone pressure was varied from 20 to 120 torr and the biacetyl pressure from 50 microns to 2 torr. However, a signal, corresponding to the rise of the biacetyl triplets, could not be detected. The flash had a mean life of about 6 microsec.

It may be pointed out here that the sensitized emission (in the flash technique) from the diketone was observed and the mean lifetime of this emission was found to be about 1.6 milli-sec which is in good agreement with the literature value of 1.8 milli-sec(50) for the biacetyl phosphorescence. This again confirms the earlier observations showing the presence of the triplet state in the chloroketone at room temperature in the gas phase. At these concentrations of biacetyl there was no quenching of the singlets of the chloroketone and there is insignificant direct excitation of biacetyl at 313 nm.

Phosphorescence of the chloroketone at 77°K

As has been reported in the preceding sections there are triplet states of the chloroketone present at room temperature in the gas phase but there is no phosphorescence detectable under these conditions. However, phosphorescence from the chloroketone was observed at 77°K when the sample was excited with 313 nm. Phosphorescence was observed in pure crystals or in 3-methyl pentane matrix (0.02 M solution) at 77°K. A typical uncorrected phosphorescence spectrum is shown in figure 6.1 (taken by Aminco-Bowman spectrofluorometer with rotating can operating). The profile of the phosphorescence spectrum was the same whether the spectrum was taken with pure chloroketone crystals or with the chloroketone solution in 3-methyl pentane matrix at 77°K. As is evident from figure 6.1 the spectrum (uncorrected) extends from about 380 nm to a maximum at about 460 nm and has a long wavelength limit of about 610 nm. The actual longer wavelength limit probably lies at still longer wavelengths since the sensitivity of the detection system decreases very rapidly at higher wavelengths. Similar emission profiles were observed for the chloroketone solutions in ethylether,-iso-pentane - ethyl alcohol (EPA) at 77°K.

Relative quantum yields of the chloroketone and hexafluoroacetone:

From the preliminary investigations in the Aminco-Bowman spectrofluorometer it was found that the profile of the phosphorescence spectra of the chloroketone and hexafluoroacetone are almost exactly identical. Therefore, the relative quantum yields of the phosphorescence at 77°K of these two compounds were measured.

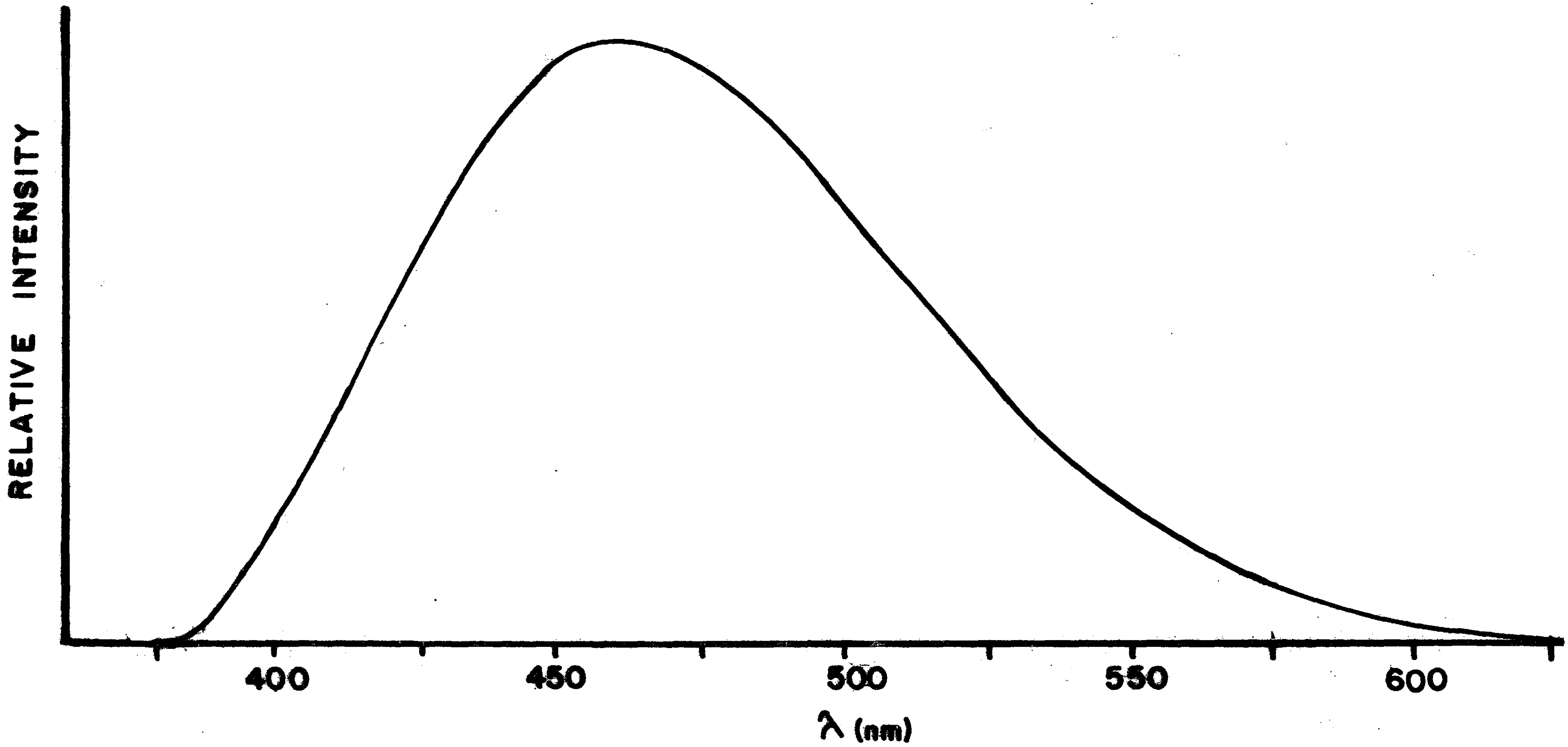

Figure 6.1 Phosphorescence spectrum of chloroketone (uncorrected) at 77°K.

The phosphorescence spectra of chloropentafluoroacetone (0.02 M in 3-methylpentane) and hexafluoroacetone (0.14 M in 3-methyl pentane) were taken in two identical quartz-phosphorescence-tubes. The concentrations of the ketones were chosen such that the amount of light absorbed in both cases was the same. Three sets of the spectra were taken. The relevant data are shown in table 6.1 below.

Table 6.1

Relative triplet quantum yields of chloropentafluoroacetone and hexafluoroacetone at 77°K (not corrected for phosphoroscope factor)

Set No.	Relative yield (P^C/P^H)*	Average P^C/P^H
1	0.63	0.67
2	0.67	
3	0.71	

---

*P is the phosphorescence yield and superscripts C and H refer to chloropentafluoroacetone and hexafluoroacetone respectively.

Phosphorescence lifetime measurements at 77°K:

The excitation wavelength for all lifetime measurements was 313 nm. The triplet state lifetimes of the following samples were measured at 77°K.

A. (1) Pure chloropentafluoroacetone crystals.

(2) 0.02 M solution of the chloroketone in 3-methylpentane matrix.

(3) 0.02 M solution of the chloroketone in EPA matrix.

B. (1) Pure crystals of hexafluoroacetone.

(2) 0.06 M solution of hexafluoroacetone in 3-methyl pentane.

(3) 0.14 M solution of hexafluoroacetone in 3-methyl pentane.

In the determination of these phosphorescence lifetimes of the chloroketone and hexafluoroacetone good exponential decays were observed at the times when the scattered light from the flash was negligible. As reported earlier the lifetimes were calculated from log intensity versus time plots. Typical plots for different samples are shown in figures 1 and 2 in the appendix.

The phosphorescence lifetimes of chloropentafluoroacetone and hexafluoroacetone reported here are based on several sets of photographs. The agreement between different sets of photographs for a sample was within 10%.

Table 6.2 collects the relevant data for chloropentafluoroacetone and hexafluoroacetone obtained during the present investigation. The triplet lifetimes of acetone reported in the literature are also shown in the table for a comparison.

Table 6.2

Triplet lifetimes at 77°K

S.No.	Ketone	Solvent	Lifetime, m sec.
1.	0.02 M chloropentafluoroacetone	3-methyl pentane	3.1
2.	0.02 M chloropentafluoroacetone	EPA	4.7
3.	Pure chloropentafluoroacetone crystals	-	7.8
4.	0.06 M hexafluoroacetone	3-methyl pentane	6.6
5.	0.14 M hexafluoroacetone	3-methyl pentane	6.6
6.	Pure hexafluoroacetone crystals	-	10.8
7.	Acetone	EPA	0.6*
8.	Acetone	EPA	0.33†
9.	0.2 M acetone	ether-isopropanol	0.40††
10.	0.2 M acetone	glycerine	0.30††
11.	Pure acetone crystal	-	1.0††

*Reference (18)

†Reference (33)

††Reference (95)

Phosphorescence and triplet lifetime of chloropentafluoroacetone at 113°K:

The investigations at 113°K were of an exploratory nature to investigate the effect of temperature on the phosphorescence lifetime.

The usual phosphorescence spectrum of the chloroketone (pure crystals) was observed at 113°K (isopentane slush). The mean life of the phosphorescence at this temperature was found to be 5.7 msec.

DISCUSSION

It has been stated earlier that the emission from chloropentafluoroacetone at room temperature in the gas phase consists of only fluorescence. However, from the results reported here on the phosphorescence and phosphorescence lifetimes at 77°K or 113°K (pure ketone or ketone in solvent matrices) it is evident that the triplet state of the chloroketone is populated under those conditions. The absence of the phosphorescence at room temperature in the gaseous state does not imply that the triplet state of the chloroketone is not formed. The biacetyl-sensitization technique to diagnose the presence of the triplet state of molecules, whose triplet state energy is greater than that of biacetyl, is well established. For example, in acetone(39) the triplet monoketone transfers energy to form the triplet biacetyl which emits the well-known green phosphorescence. Pressures of biacetyl below 1 torr do not alter the fluorescence yield of the chloroketone. Therefore, there is no significant quenching of the excited singlet state of the chloroketone at low pressures of biacetyl, i.e., singlet-singlet energy transfer is absent at low pressures of biacetyl. However, under the conditions where absorption of light is almost entirely by chloropentafluoroacetone, it is seen that the addition of small amounts of biacetyl results in significant phosphorescence from the latter. There is an energy transfer from an excited state of the chloroketone to ground state biacetyl to form triplet state biacetyl. This energy transfer from the chloroketone occurs from an excited state which is not the state that fluoresces but most probably is the triplet state.

Since the quantum yield of the sensitized emission of biacetyl is about 0.08, the quantum yield of the triplet state of the chloroketone is estimated to be about 0.54. This estimate of the triplet quantum yield is based on the fact that only about 15% of the triplet biacetyl molecules emit[52,58]. However the triplet quantum yield data must be interpreted cautiously. It is known that the emission from biacetyl is very sensitive to quenching by one of the products formed in the direct photolysis. If this quenching product is formed in sensitized reaction then it could modify the values of the apparent quantum yield of the sensitized emission. The value reported here (0.54) probably represents an estimate of the lower limit and the true quantum yield of the triplet state may be close to unity. Notwithstanding the approximate value for the triplet quantum yield, it is clear that the triplet state plays a major role in the photochemistry of chloropentafluoroacetone in the gas phase at room temperature. However, only a limit of < 10 microsec for the triplet lifetime of the chloropentafluoroacetone in the gas phase at room temperature could be obtained using the sensitization emission technique of

Parmenter and Ring(114)

Since there is no phosphorescence from the chloroketone in the gas phase at room temperature, the phosphorescence studies at 77°K are of special value. The phosphorescence from the pure ketone or ketone in the solvent matrices at 77°K extends from about 380 nm to greater than 610 nm with a maximum at about 460 nm. The actual long wave limit is difficult to establish since the sensitivity of the detection system decreases rapidly at longer wavelengths.

The triplet lifetime of the pure chloroketone decreases by about 27% upon warming from 77°K to 113°K. This indicates a definite temperature effect on the triplet lifetime. This effect may be due to change in both radiative (k_r) and non-radiative (k_{nr}) rate constants, although the change in the phosphorescence lifetime with temperature is generally governed by the change in k_{nr}. Jones and Siegel(115) during their investigations of temperature effects on the phosphorescence lifetimes of aromatic hydrocarbons and benzophenone found that the temperature effects are smaller for the hydrocarbons than for benzophenone. They suggest that the larger temperature effect is because of the n,π^* character of the benzophenone triplets. Thus, the relatively large temperature effect on the phosphorescence lifetime of chloropentafluoroacetone appears to be in agreement with the above suggestion. However, Hatch et al.(116) report large temperature effects on the phosphorescence lifetime of benzenes. These complicated effects are difficult to explain by the current theories of radiationless transitions.

From Table 6.2 it is evident that the lifetime of the chloroketones depends on the environment. The triplet lifetimes in the pure solids at 77°K are about 1.7 times as long as those in polar solvents for chloropentafluoroacetone and hexafluoroacetone. This is expected because the interactions would be more important in the polar than in the non-polar solvents or pure solids. Similar observations have been made on the phosphorescence lifetimes of acetone$^{(95)}$.

The energy difference between the first excited singlet state and the lowest triplet state of chloropentafluoroacetone can be estimated from a comparison of the onset of the phosphorescence (380 nm) and the fluorescence (337 nm) as about 9 K calories per mole. A further estimate of 8 K calories per mole for the singlet-triplet splitting may be made from the comparison of the maximum in the phosphorescence and fluorescence (460 nm and 408 nm respectively to the uncorrected spectra). Since the energy of the first excited singlet state of the chloropentafluoroacetone is about 83 K calores per mole, the triplet state energy should therefore be about 74 K calories per mole above the ground state.

The singlet and triplet-state energies of the chloropentafluoroacetone can be compared with those of hexafluoroacetone and contrasted with those of acetone. The energy of the singlet state of acetone was estimated as about 80 ± 4 K calories per mole above the ground state from the absorption and fluorescence spectra(95), which do not overlap in the gas phase. The triplet state of acetone is considered to be at about 77 K calories per mole from phosphorescence studies(11) and 80 K calories per mole from kinetic data(38) above the ground state. The energies of the singlet and triplet states of hexafluoroacetone are about 83 K calories per mole and 74 K calories per mole respectively(58). Thus the triplet states of chloropentafluoroacetone and hexafluoroacetone are about 9 K calories lower than the singlet states where as the triplet-singlet splitting in acetone is probably smaller. The photochemistry of chloropentafluoroacetone is, therefore, expected to be similar to that of hexafluoroacetone. For example, electronically excited hexafluoroacetone reacts with fluorinated olefins in the gas phase to form oxetanes(68,69) and the chloroketone might be expected to form oxetanes under similar conditions.

The emission spectra as a function of wavelength of chloropentafluoroacetone and hexafluoroacetone are almost identical. Therefore, the relative quantum yields of phosphorescence can be simply determined from the relative intensities of the emission of two ketones. Since the rotating can technique was employed for recording the emission spectra and since the triplet lifetimes of two ketones are different

(τ_p^C = 3.1 msec. and τ_p^H = 6.6 msec) the two emission intensities cannot be compared directly without appropriate corrections for phosphorimeter factor. The following expression, which is a slightly modified version of Parker's formula(117), is used for the correction term.

$$\frac{P_o}{P} = \frac{\tau}{t_1} \left[\frac{1-e^{-t_1/\tau}}{1-e^{-t_c/\tau}}\right] \left[e^{-(t_2-t_1)/2\tau} \quad e^{-(t_2+t_1)/2\tau}\right] \tag{6.1}$$

where P_o = observed intensity of the long-lived emission

P = total rate of emission

t_c = time taken for one complete cycle

t_1 = illumination time

t_2 = dark period

and τ = lifetime of the long-lived species.

After these corrections the ratio of the phosphorescence quantum yield of chloroketone, ϕ_p^C, to that of hexafluoroacetone, ϕ_p^H, is found to be 0.82 at 77°K.

The quantum yield of phosphorescence would be given by:

$$\phi_p = k_r \, \phi_{isc}/(k_r+k_{nr}) \tag{6.2}$$

where ϕ_{isc} is the efficiency of the intersystem crossing from the first excited singlet state to the triplet state, k_r is the rate constant for the radiative triplet to singlet process and k_{nr} is the sum of the rate constants for the nonradiative processes from the triplet state. The internal heavy atom effect on k_r and k_{nr} for the triplet state of the fluorinated ketones is an important feature of the system and the experimental data can be compared with the theoretical predictions of the behavior(100-102) of aliphatic carbonyl compounds.

In principle k_r may be estimated from

$$f = 1.5\, g_u\, k_r / g_\ell \bar{\nu}^2 \qquad (6.3)$$

where f is the oscillator strength, $\bar{\nu}$, the wave number of the forbidden transition and g the degeneracy of the upper (u) and lower (l) states. However, for aliphatic ketones the singlet-triplet absorption is usually hidden under the long wavelength tail of the singlet-singlet n→π* transition. Experimentally, k_r, can be determined from

$$k_r = \phi_p / \phi_{isc}\, \tau_p \qquad (6.4)$$

where τ_p is the actual phosphorescence lifetime. The ratio

$$\frac{k_r^C}{k_r^H} = \frac{\phi_p^C}{\phi_p^H} \cdot \frac{\phi_{isc}^H}{\phi_{isc}^C} \cdot \frac{\tau_p^H}{\tau_p^C} \qquad (6.5)$$

can be estimated if $\phi_{isc}^C/\phi_{isc}^H$ is assumed to be unity. This is reasonable since in acetone and acetone-d_6 ϕ_{isc} is 1.0 ± 0.1(44,95). The superscripts C and H refer to chloropentafluoroacetone and hexafluoroacetone respectively. The corrected ratio of the phosphorescence quantum yield of chloropentafluoroacetone, ϕ_p^C, to that of hexafluoroacetone, ϕ_p^H, is 0.82 in 3-methyl pentane at 77°K. Thus

$$\frac{k_r^C}{k_r^H} = 1.7 .$$

The effect of substituting chlorine atom in hexafluoroacetone is to increase the radiative rate from the triplet state by a factor of about 1.7. This effect on the radiative rate constant from the triplet state can be compared with that from the singlet state of the chloroketone, where the radiative rate constant is increased by a factor of about 2.7.

As reported earlier, the theoretical calculations of Carroll, Vanquickenborne, and McGlynn(101) on the internal heavy atom effect show that the radiative rate constants from the triplet state should be greater for Br_2CO and I_2CO than for H_2CO, F_2CO, and Cl_2CO. El-Sayed(100), on the other hand, predicts a small heavy atom effect on the radiative rate constant from the triplet state of aliphatic ketones, when the substitution is not directly on the carbonyl group. There are experimental observations on the external heavy atom effect on the biacetyl phosphorescence(118) and on the biacetyl singlet→ triplet absorption intensity in ethyl iodide solution(119). There is also a report on the triplet lifetime data of halogenated acetones(18). Those experiments are not in agreement with the prediction of El-Sayed(100). However, the present experimental data on the fluorinated ketones support the proposal of El-Sayed(100). Further, in a very recent re-investigation of external heavy atom effect, it has been shown that the effect of xenon on the biacetyl triplet lifetime is negligible(120). This suggests that the triplet lifetimes of halogenated acetones should be re-investigated.

The value of k_r^H has been determined as 37 sec^{-1} from gas phase measurements at room temperature(67). If there is a negligible effect of temperature and phase on k_r^H then from the ratio of $\frac{k_r^C}{k_r^H}$, k_r^C is found to be 65 sec^{-1}. These values for the fluorinated acetones can be compared with the data obtained recently by O'Sullivan and Testa(33) on alkyl substituted acetones in EPA at 77°K. They showed that the radiative rate constants from the triplet state only varied between 70 and 120 sec^{-1} in the alkyl substituted ketones including the cyclic ketones.

From the actual phosphorescence lifetimes, the non-radiative rate constants from the triplet state of the chloroketone and hexafluoroacetone in 3-methyl pentane matrix at 77°K can be obtained using the following relations,

$$\tau_p^H = \frac{1}{k_r^H + k_{nr}^H} \qquad (6.6)$$

and

$$\tau_p^C = \frac{1}{k_r^C + k_{nr}^C} \qquad (6.7)$$

On substituting the appropriate values, k_{nr}^H and k_{nr}^C are estimated as 115 sec^{-1} and 260 sec^{-1} respectively. The substitution of a chlorine atom in the fluorinated ketone has increased the non-radiative rate constant by a factor of about 2.3. In contrast, when bromine and iodine were substituted in acetone the triplet lifetimes at 77°K were found too small to measure, although the shortest lifetime the authors could measure was greater than 10^{-4} sec(18). In the light of the present investigations it is surprising that the substitution of a bromine or an iodine atom in acetone could have a large internal heavy atom effect. From the results reported here, it is seen that the internal heavy atom effect is similar on both radiative and nonradiative processes from the triplet state.

O'Sullivan and Testa(33) found that the spectral distribution remained constant for all the ketones investigated. However, the phosphorescence quantum yields at 77°K increased and the radiationless rate constants decreased on replacing the α-hydrogens by alkyl groups. They tentatively proposed that a major feature governing the radiationless rate constant is the energy of the C-H stretching vibration. Thus, in acetone the energy dissipation can occur via C-H stretch. In alkyl substituted acetones the probability of the emission increases because C-C stretch involves a smaller quantum of energy (600-1500 cm^{-1}) than C-H stretch (2900-3000 cm^{-1})(121). This explanation appears to be consistent with the data on hexafluoroacetone and chloropentafluoroacetone since the energies of the C-F vibration (1100 cm^{-1}) and the C-Cl vibration (650 cm^{-1})(121)

are much lower than the energy of the C-H vibration.

Although the phosphorescence of chloropentafluoroacetone is prominent at 77°K no phosphorescence was observed in the gas phase at room temperature. However, as pointed out earlier, the triplet state plays a major role in the photochemistry of chloropentafluoroacetone even in the gas phase at room temperature. Similar behavior is exhibited by many other molecules, e.g., cyclopentanone(122) and benzene(18,123) and indicates that there is a large increase in the non-radiative processes with the change in the environment and the temperature.

CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

CONCLUSIONS

When chloropentafluoroacetone in the gas phase at room temperature absorbs ultraviolet light (corresponding to n,π^* excitation) fluorescence is observed. This is the first report of light emission from a simple chlorinated carbonyl compound in the gas phase at room temperature. The energy of the first excited singlet state is about 83 K cal per mole above the ground state. Excitation at short wavelengths populates higher vibrational levels of the upper state. This feature is demonstrated by enhancement of the emission with increasing pressure of the ketone or an added gas. The emission profile is independent of the pressure and the exciting wavelength. Further, the fluorescence lifetime in the gas phase at room temperature is independent of the ketone-pressure in the pressure range investigated. The internal heavy atom effect of the chlorine atom on the radiative and radiationless transitions from the singlet state is relatively small. The radiative and radiationless rate constants are increased by factors of 3 and 2.3 respectively as compared with hexafluoroacetone.

The quenching of chloropentafluoroacetone molecules in the zeroth level of the first excited singlet state has been examined by fluorescence quenching studies. The quenching efficiency of the olefins investigated increases as the ionization potential of the quenching molecule decreases. Both "electron-rich" and "electron-deficient" olefins with the exception of perfluorobutene, can quench the fluorescence.

Phosphorescence is observed from chloroketone triplet molecules in a matrix at 77°K. The internal heavy atom effect on the radiative and radiationless transitions from the triplet state at 77°K has been estimated. The radiative and radiationless rate constants increase by factors of about 1.7 and 2.3 respectively in this case.

The triplet state energy of the chloroketone is estimated as 74 Kcal per mole above the ground state. The energy levels of the excited singlet and triplet states of the chloropentafluoroacetone and hexafluoroacetone are similar and the fluorescence spectra in the gas phase at room temperature and phosphorescence spectra in matrices at 77°K are almost identical in both cases. A significant difference between the photochemistry of chloropentafluoroacetone and hexafluoroacetone is the lack of phosphorescence of chloropentafluoroacetone in the gas phase at room temperature. This indicates a rapid radiationless process in the gas phase.

SUGGESTIONS FOR FUTURE RESEARCH

This research has concentrated on the process involving the excited singlet state in the gas phase at room temperature and the triplet state in a matrix at low temperatures. The research on the triplet state in the gas phase has been of an exploratory nature. A fuller understanding of the photochemistry of chloropentafluoroacetone requires research along the following lines:

A.

1. Singlet State:
   - (a) Studies of emission from vibrationally excited levels and mode of deactivation require fluorescence lifetime measurements at low ketone pressures.
   - (b) Identification of modes of decomposition of the singlet state would require an analysis of the products formed and their dependence on the pressure, temperature and the exciting wavelength.
   - (c) Extension of the quenching studies including product-analysis and temperature effect should be carried out.

2. Triplet State:
   - (a) Role of triplet state in the gas phase and characterization of the process that dominates phosphorescence should be investigated.
   - (b) Identification of modes of decomposition of the triplet state requires analysis of the products formed and their

dependence on the pressure, temperature and the exciting wavelength.

B. Similar photochemical studies on other halogenated ketones should be carried out to determine the factors that control the rate processes in photoexcited molecules.

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APPENDIX

Table 1

Wavelength λ (nm)	Molar extinction Coefficient, ε	Wavelength λ (nm)	Molar extinction Coefficient εε
240	< 1	310	44
245	1	313	48
250	3	315	47
255	5	320	34
260	8	325	32
265	11	330	26
270	16	334	16
275	21	335	14
280	27	340	12
285	33	345	7
290	35	350	2
295	43	355	3
300	47	360	∿ 0
305	49		

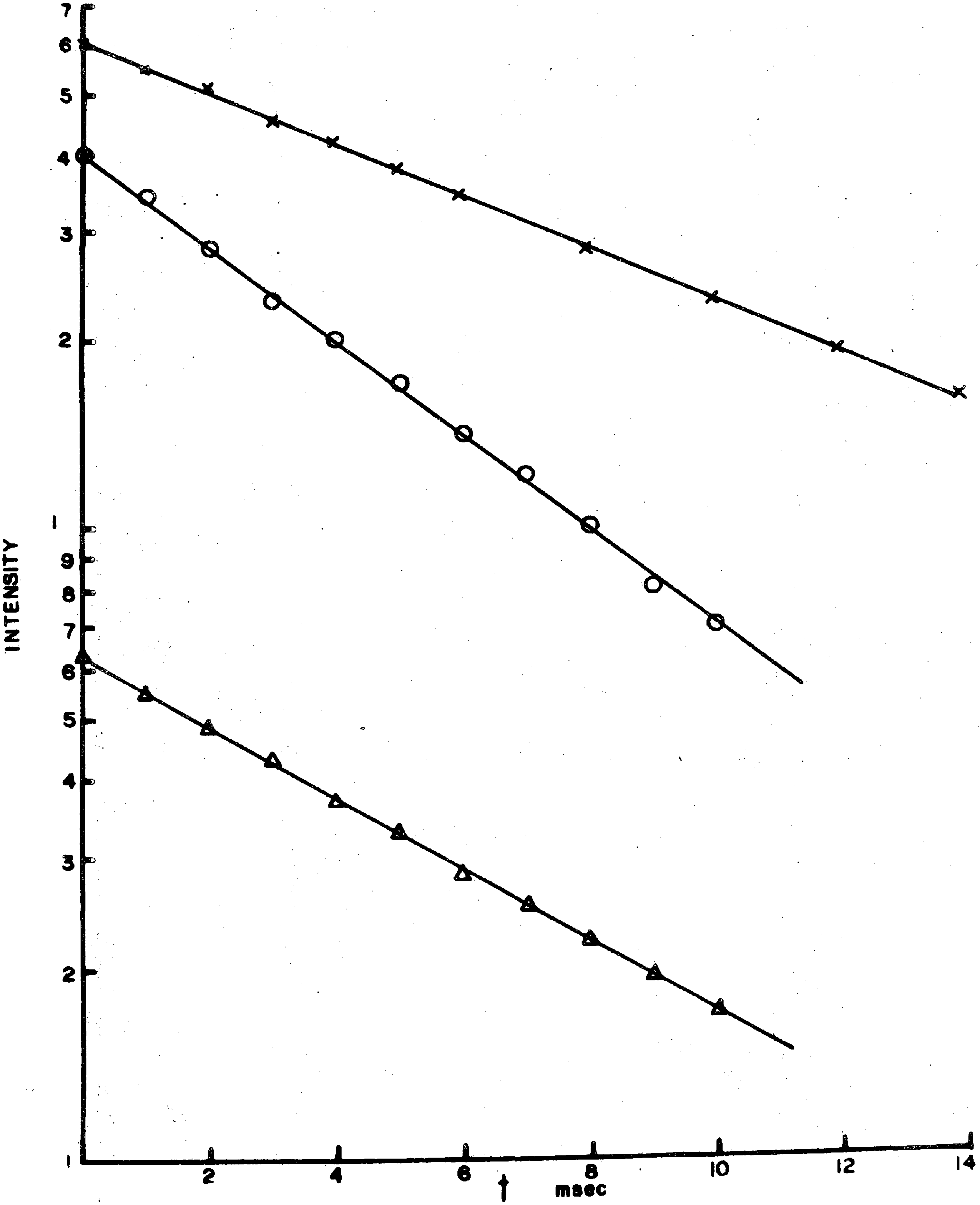

Figure A1. Log intensity vs time. Chloropentafluoroacetone crystals at 77°K (Δ) and at 113°K (O) and hexafluoroacetone crystals at 77°K. (X).

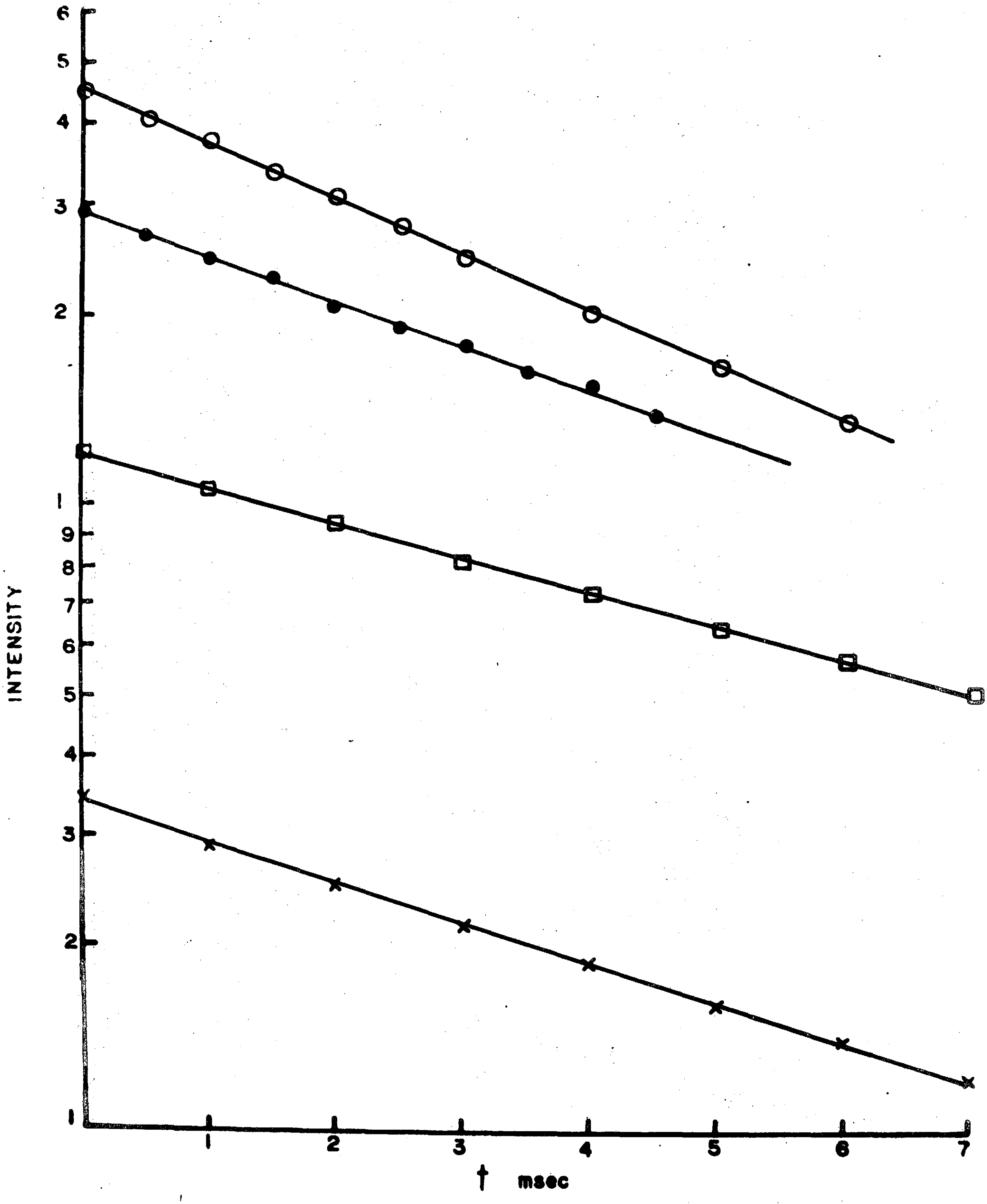

Figure A2. Log intensity vs time. .06 M (X) and .14 M (□) hexafluoroacetone in 3-methylpentane; .02M chloropentafluoroacetone in 3-methyl pentane ( ) and .02 M (O) chloropentafluoroacetone in EPA at 77°K.