

RADIATIONLESS PROCESSES IN A MOLECULAR BEAM: TIME RESOLVED EMISSION FROM BENZOPHENONE

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In order to study the radiative properties of the isolated benzophenone molecule, a molecular beam of benzophenone is excited by a pulsed nitrogen laser or a pulsed tunable dye laser and the subsequent emission intensity is measured as a function of time. We find the decay to be exponential with a lifetime of about 0.5 μ s. This value is shorter than the radiative lifetime calculated from absorption measurements. As the background pressure in the molecular beam chamber is raised from 10^{-6} torr to 10^{-4} torr, the decay of the emission lengthens and becomes biexponential. An explanation involving giant self-collision-induced cross sections for intersystem crossing is advanced to reconcile these observations with results from previous studies of benzophenone emission decay.

1 Introduction

The time-resolved emission from benzophenone (ϕ_2 CO) has served as a model to test various theories of radiationless processes in large molecules. In 1967 Borisevitch and Gruzinskii [1] studied the emission spectrum and decay of benzophenone at a pressure of one torr. They reported two lifetimes, a short nanosecond component and a much longer ($\approx 30 \mu$ s) component. Later, Busch et al. [2,3] re-examined the radiative decay of benzophenone using several pulsed picosecond laser sources. The pressure of benzophenone was varied from 10^{-4} to 1 torr. They reported the following results:

- (a) the decay is biexponential,
- (b) the two emission lifetimes (10 μ s and 200 μ s) are both longer than the radiative lifetime calculated from absorption measurements to be 3.8 μ s [4],
- (c) the decay shows oscillations,
- (d) there is strong self-quenching,
- (e) the intensity ratio of the slow to the fast component increases as the pressure increases.

They explained these results according to a model that invokes strong coupling of some of the triplet vibronic levels with the initially excited singlet level [2–5]. This mixing “dilutes” the oscillator strength of the

singlet level, causing the relatively long decay times. According to this model the interference terms in the emission process produce quantum beats that appear as oscillations in the decay rate. The slower component is interpreted to be “hot phosphorescence,” i.e., emission from high vibrational levels of the triplet manifold.

In a subsequent study Hochstrasser and Wessel [4] reported that they observed biexponential decay, but that the quantum beats were absent. The measurements were performed in a 2.5 cm diameter bulb and the benzophenone pressure was reduced to as low as 10^{-4} torr.

The two lifetimes are 10–20 μ s for the fast component and about 130 μ s for the slow component, which was recognized to be affected by collisions with the walls. Hochstrasser and Wessel propose a model in which excitation is followed by very rapid intersystem crossing, based on the observation that in the condensed phase the build-up of triplet–triplet absorption occurs at the rate of about 10^{11} s^{-1} [6,7]. In this model the fast component is associated with hot phosphorescence and the slow component with relaxed phosphorescence.

In 1974 Bell et al. [8] studied the effects of temperature and pressure on the lifetime of benzophenone

emission in a 1 cm square cell. They indicated that wall effects were the significant factor in quenching the fluorescence in previous experiments. In fact the lifetimes observed by Busch et al. and by Hochstrasser and Wessel are in the ratio of the diameters of the vessels used.

In 1977 Zevenhuijzen and van der Werf [9] investigated again the electronic relaxation of benzophenone in the vapor phase. Using either a pulsed nitrogen laser or a nitrogen pumped dye laser, they observed a single exponential decay at 3.8×10^{-4} torr pressure of benzophenone contained in a 30 cm diameter cell. The emission lifetimes were measured to be $48 \mu\text{s}$ at 3371 \AA and $128 \mu\text{s}$ at 3650 \AA . Again these values are longer than the calculated radiative lifetime. By adding cyclohexane, they observed a second component with a lifetime of about a millisecond. They interpret this to be relaxed phosphorescence. They found that the emission was shifted to the blue with increasing pressure. Zevenhuijzen and van der Werf question the previous lifetime measurements because the work was carried out in much smaller cells.

They call their fast component long lived fluorescence; they claim it is caused by a mixing of the initially excited singlet level with all of the near-lying triplet levels. From this model they obtain the ratio of triplet to singlet density of levels to be in the range of 10^4 for an excess energy of 1197 cm^{-1} above the $^1n\pi^*$ origin.

Because the previous results seem contradictory and to be extremely sensitive to pressure and cell dimensions we decided to repeat these measurements on a molecular beam of benzophenone in the hope that this would better approximate the behavior of the isolated molecule. Following a description of the experimental procedure, we present time-resolved data that show single exponential decay of the isolated molecule which is *shorter* than the radiative lifetime. In the discussion we attempt to reconcile the different previous measurements and offer a unifying picture for the radiative behavior of benzophenone.

2. Experimental

Fig. 1 shows a schematic diagram of the experimental setup. A beam of benzophenone effuses from an oven into a long chamber. A pulsed laser excites the beam of benzophenone molecules and the subsequent

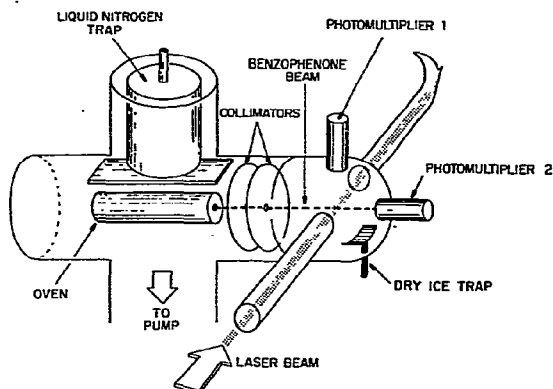


Fig. 1. Schematic of the experimental apparatus.

emission is viewed by a photomultiplier and recorded as a function of time.

The molecular beam machine consists of a stainless steel cross closed on one end by a long glass bell jar. The cross contains the beam source consisting of a stainless steel tube. The oven orifice is a 0.2 cm hole located in the middle of a stainless steel insert that plugs one end of the tube. The other end of the tube is crimped shut. The oven is heated resistively to $40\text{--}70^\circ\text{C}$ by passing AC current through its body.

The benzophenone (Baker Chemical Co.) is recrystallized once in a mixture of ethanol and water. Then the crystallized material is further purified by vacuum distillation. Despite these efforts the same results are obtained as with the untreated benzophenone.

The effusive beam of benzophenone is defined by two collimating holes (see fig. 1). A liquid-nitrogen-cooled trap is placed close to the collimation region to pump away the scattered benzophenone molecules.

Two different configurations are used to observe the emission. In the first, a photomultiplier is located perpendicular to the laser beam and to the molecular beam. The advantage of this configuration is that short lifetimes ($\leq 100 \mu\text{s}$) can be readily measured. In the second configuration, the photomultiplier is located with its face pointing into the beam direction some distance from the point where the laser beam crosses the molecular beam. This has the advantage that long lifetimes (up to a millisecond) can be measured. In this latter configuration a dry ice trap prevents the build-up of condensation of the benzophenone on the photo-

multiplier face. In both configurations we use a bell jar 20 cm in diameter and 40 cm long. The laser beam enters and exits through 50 cm long baffle arms to reduce scattered light.

With this bell jar it is difficult to maintain the background pressure at a constant level. To solve this problem and to search for very long lifetimes (≥ 1 ms) a second bell jar 20 cm in diameter and 100 cm long, is used. In this chamber the pressure fluctuates by no more than 5% during a run. The pressure is in the 10^{-6} torr region with the beam on. The pressure is measured by a vacuum ionization gauge that was calibrated against a capacitance manometer. The bell jar is evacuated by a 6" oil diffusion pump attached to the cross through a water-cooled baffle.

The excitation source is either a nitrogen laser (3371 Å) or a nitrogen-laser-pumped dye laser (3620–3690 Å). The nitrogen laser has a repetition rate of 5 pps, each pulse of which has a width of 15 ns and a power of 350 kW. It was constructed by Turner [10]. The dye laser is a Molelectron model DL 200. We use Molelectron dye PBD.

For broadband detection Corning cutoff filters (7-54 and 7-39) are placed in front of the EMI 6256S photomultiplier. The output of the photomultiplier is connected to a wide band preamplifier (Princeton Applied Research model 115) that feeds into a boxcar integrator (Princeton Applied Research model 162 mainframe with a model 164 plug-in). The aperture delay (window) ranges from 0.2 μ s to 10 ms with a gate width of 5 ns.

3. Results

Fig. 2 shows a typical trace of the emission intensity as a function of time. We observe a single exponential decay of the benzophenone emission under beam conditions at background pressures between 10^{-4} – 10^{-6} torr. The emission lifetime at the lowest pressure is about a factor of six less than the calculated radiative lifetime.

Table 1 lists the emission lifetime as a function of excitation energy measured from the $n\pi^*$ singlet origin (26250 ± 100 cm^{-1}). This value was determined by Hochstrasser and Wessel [4] for pure crystalline benzophenone, assuming a crystal–gas shift of about 2200 cm^{-1} . The lifetime decreases as the excitation

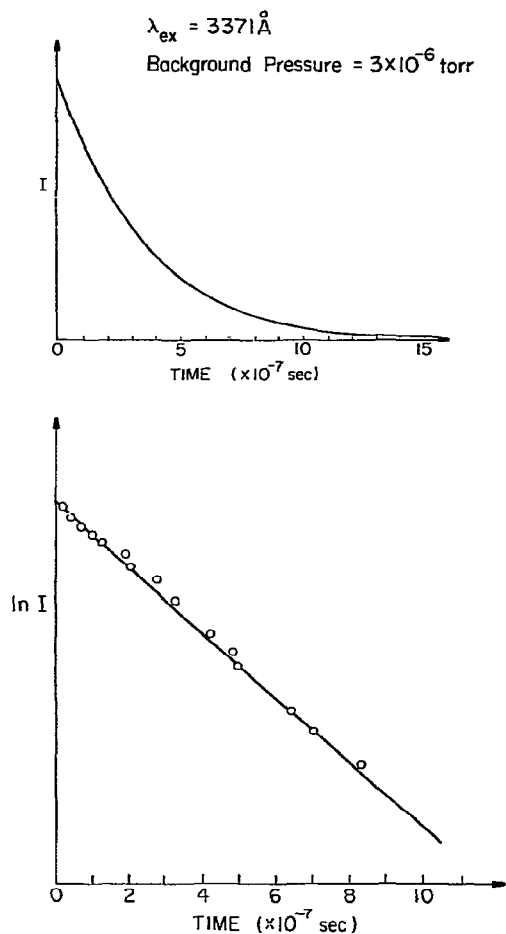


Fig. 2. Decay of benzophenone emission as a function of time. The laser excitation wavelength is 3371 Å; the background pressure in the molecular beam chamber is 3×10^{-6} torr.

energy increases. However, around 1000 cm^{-1} above the $n\pi^*$ singlet origin fluctuations in the lifetime appear.

Table 2 presents the variation of the benzophenone emission lifetime with pressure. A significant decrease in the emission lifetime and the relative emission intensity is apparent at the highest pressure. We were not able to extend these measurements to high pressures with the present experimental setup. At the same pressure in which the lifetime begins to decrease another longer but weaker lifetime component appears (fig. 3) having an emission lifetime of about 75 μ s at an exci-

Table 1
Radiative decay of benzophenone as a function of excitation wavelength (λ_{ex})

λ_{ex} (Å)	$E^a)$ (cm^{-1})	Pressure ^{b)} (μtorr)	Lifetime ^{c)} (μs)
3689	850	2.0	0.63
3675	953	7.2	0.69
3662	1050	7.0	0.62
3645	1177	9.0	0.66
3623	1344	7.8	0.56
3371	3406	3.2	0.47

a) Excess energy above the $n\pi^*$ singlet origin (26250 cm^{-1}).

b) Recorded using the 1 m ball jar so that the pressure fluctuation is no more than 5%.

c) The uncertainty of each lifetime is estimated to be $\pm 0.05 \mu\text{s}$, based on the maximum scatter in the data.

tation wavelength of 3645 Å. This longer component could only be measured at the highest pressures because of its low intensity. We believe that this component of the decay is probably the same component that Zevenhuijzen and van der Werf [9] observed. They measured a lifetime of 128 μs for excitation in the 3650 Å region at a benzophenone pressure of 3.8×10^{-4} torr.

4. Discussion

Our aim in measuring the time-resolved emission from benzophenone excited under beam conditions is to learn about the photophysical behavior of the isolated molecule. Molecular beam techniques have

Table 2
Radiative decay of benzophenone as a function of pressure for $\lambda_{\text{ex}} = 3645 \text{ Å}$

Pressure (torr)	Relative intensity ^{a)}	Lifetime ^{b)} (μs)
9×10^{-6}	1.0 ₀	0.66
2×10^{-5}	1.0 ₆	0.58
7×10^{-5}	0.8 ₃	0.60
1×10^{-4}	0.7 ₅	0.33 ^{c)}

a) The estimated uncertainty is ± 0.1 unit.

b) The estimated uncertainty is $0.05 \mu\text{s}$.

c) At this pressure a long component with a lifetime of about 75 μs is observed.

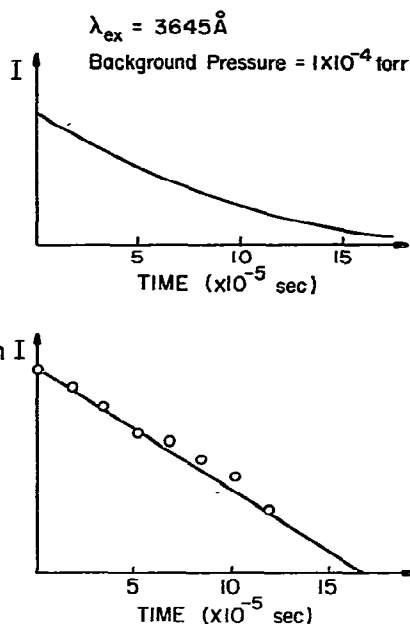


Fig. 3. Decay of benzophenone as a function of time. The laser excitation wavelength is 3645 Å; the background pressure in the molecular beam chamber is 1×10^{-4} torr. The recording of the emission decay trace is triggered 2 μs after the excitation pulse. Under these conditions, the presence of the fast component is suppressed.

the virtue that all the molecules in the beam move in the same direction; although there is a velocity distribution, the number of collisions in the beam is vastly reduced compared to that of a bulb. Under our operating conditions there is an average flux of benzophenone molecules of about 2×10^{15} molecules $\text{cm}^{-2} \text{ s}^{-1}$. A simple estimate of the average separation between nearest neighbors is 10^4 Å . From this calculation it seems that the isolated molecule condition can be easily met in molecular beam experiments.

The observed benzophenone decay can be classified according to the "large molecule" statistical limit [11]. The emission that is shorter than the calculated radiative lifetime is attributed to fluorescence from the initially excited levels of S_1 . Internal conversion ($S_1 \rightarrow S_0$) probably accounts for the shortening of the fluorescence lifetime compared to the radiative one. This may also explain why we fail to observe a second (longer) emission component in our beam experiments.

An increase in the benzophenone pressure causes

quenching of the fluorescence with high efficiency. The large self-quenching cross section is explained by collision-induced intersystem crossing ($S_1 \rightsquigarrow T$). Hence, "hot phosphorescence" occurs from the unrelaxed vibrational levels of the triplet manifold with a lifetime of about 75 μ s. As the total pressure is further increased, either by adding foreign gas or by increasing the benzophenone pressure, the population in the vibrational levels of T becomes relaxed; then an emission lifetime is obtained in the millisecond regime [4,9]. We rule out the slow component as delayed fluorescence because of the high density of levels in the triplet manifold and the long lifetime.

We believe the above model explains the shift in the emission to the red with increasing pressure, as seen in fig. 3 of Busch et al. [3] and as reported by Zevenhuijzen and van der Werf [9]. Let v denote the vibrational quantum numbers in S_0 and T. It is well known [12] that the $\langle v|v-1\rangle$ vibrational overlap integral will be larger than $\langle v-1|v-2\rangle$. At lower pressure, the high vibrational levels of T are populated; hence, the emission spectrum is shifted to the blue at lower pressures compared to higher ones where the vibrational population in T is relaxed to the origin. This explanation may also account for the blue shift with increasing temperature in condensed-phase benzophenone emission, reported by Jones and Calloway [13].

Previously, Hochstrasser and Wessel [4] also invoked hot phosphorescence emission to explain their emission decay rates for benzophenone in the 10^{-4} torr pressure range. However, their model was for an isolated molecule, rather than a molecule undergoing collision-induced intersystem crossing. Efficient self-collision-induced intersystem crossing was also detected in several other molecules, e.g. glyoxal [14] and propynal [15]. Naaman et al. [16] proposed that this phenomenon is caused by long range interactions such as dipole-dipole and dipole-induced-dipole forces. They obtained qualitative agreement between their calculations and the experimental results on benzophenone. The same model also explains the present results.

In order to interpret their data as fluorescence emission, Zevenhuijzen and van der Werf had to claim that the density of triplet to singlet levels is about 10^4 at an excess energy of 1200 cm^{-1} above the $n\pi^*$ singlet origin. This corresponds to more than 3000 cm^{-1}

above the $n\pi^*$ triplet origin [9], where the density of levels is about $(10^6 - 10^7)/\text{cm}^{-1}$, as calculated from the Haarhoff formula [17]. Thus, this implies a singlet density of $(10^2 - 10^3)/\text{cm}^{-1}$, which is much too large for such an energy in excess of the origin. Another problem raised by the interpretation of Zevenhuijzen and van der Werf of their results is that there should exist a subnanosecond emission lifetime. Although several experiments were done with picosecond excitation pulses [2-4], no such fast decay component was observed. Our conclusion that Zevenhuijzen and van der Werf observed instead hot phosphorescence emission removes these problems.

The present molecular beam study shows that the radiative decay of isolated benzophenone molecules is characterized by a single exponential. However, this result should not be misinterpreted to imply necessarily that other instances of biexponential decay in large molecules is only caused by collisions.

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