Fluorescence from High Vibronically Excited Benzene: a "Channel Three" Problem

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Gas phase benzene is excited by two-photon absorption at various pressures between 4 and 80 torr. Fluorescence is observed even from states located at excess energies of 3000 cm^{-1}— 7000 cm^{-1}, i.e. well above the onset of "channel three". The nonradiative decay rates as estimated from this fluorescence intensity continue the well known shortening of lifetime with excess energy in a monotone fashion and do not show a drastic cut-off as often concluded from previous line-width measurements.

I. Introduction

One of the most puzzling problems in the field of radiationless transitions is a sudden break-off of fluorescence, i.e. increase in radiationless rates in the S_1 state of benzene when the vibrational excess energy exceeds about 3000 cm^{-1} [1]. High resolution absorption spectra in gas phase benzene revealed a diffuseness in the rotational contours of vibronic bands in the region of increased radiationless rates [2]. From the broadening in the spectrum a decay rate of more than 10^{11} (sec^{-1}) was concluded. The new radiationless decay rate above 3000 cm^{-1} is much faster than the radiative fluorescence decay which therefore cannot compete with radiationless deactivation. As a consequence this is made responsible for the "cut off" of the fluorescence. Recently there have been several other molecules for which broadening of high lying vibronic states has been experimentally observed [3]. We here wish to report data of Wunsch [4] which bear on the "channel three" problem. Vibrational states at excess energies up to 6000 cm^{-1} are excited by two-photon absorption. In contrast to previous experiments the two-photon excitation at these high energies results in a weak fluorescence which was detected in our experiments.

II. Experimental Set Up

The experimental set up is similar to that described in an earlier paper [5]. For two-photon excitation the light from a tunable dye laser (Molectron DL 200) is focussed into a fluorescence cell containing benzene vapour under different pressures. The light peak power between 4500 and 5100 Å is in excess of 100 kW at a band width less than 0.2 Å. The simultaneous absorption of two photons by the molecules results in a very weak UV-emission which can be detected by a 56 DUVP multiplier. Special filters block the strong visible stray light and enable one to detect the weak UV-emission with high sensitivity. For time-resolved measurements of the fluorescence the very noisy decay curves have to be averaged over many (~ 100) laser shots. This is achieved by digitizing each individual fluorescence decay curve in a 7912 transient digitizer of the wave processing system WP 2221 (Tektronix) and by processing the information during the measurement in batch transfer to a standby computer.

Benzene from Merck and Co. with a purity of 99.9% was used and destilled from liquid nitrogen into the vacuum line. The vapor pressure of benzene and the buffer gas in the region from 1 to 100 torr was monitored with a Baratron pressure gauge.

III. Experimental Results

Contrary to typical one-photon spectroscopy we are able to detect fluorescence from levels as high

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as 6000 cm^{-1} in excess energy in S_1 when benzene is excited by two-photon absorption. The bands of the two-photon excitation spectrum in this energy range have been assigned previously [3].

Here we are interested in the time behaviour of the fluorescence. For this we tuned the laser wavelength to transitions at different excess energies and measured the decay curves of the emitted fluorescence. In Fig. 1 as an example the decay of fluorescence from the $14^1 1^2$ state with an excess energy of 3414 cm^{-1} is shown. The striking feature in Fig. 1 is the biexponential behaviour. The biexponential decay is also observed when states at higher excess energy are excited. The short component in Fig. 1 has a decay time ($1/e$) of 3.5 nsec which is close to 3 nsec, the time response of our detection system. Several tests were performed to assure that the short component is not stray light from the intense visible laser light (additional block filters for discrimination of visible light, nonlinear intensity dependence, etc.).

Thus, it is clear that the short component is really UV fluorescence of the molecule.

The long component has a lifetime of about 70 nsec which is close to the well known lifetime of 75 ± 10 nsec of the thermalized S_1 state in benzene vapour [1].

With the progression number n and thus with increasing excess energy the long component of the bands $14_0^1 1_0^n$ decreases in intensity more rapidly than the short component. This demonstrates that collisional deactivation from levels with higher excess energy is less efficient.

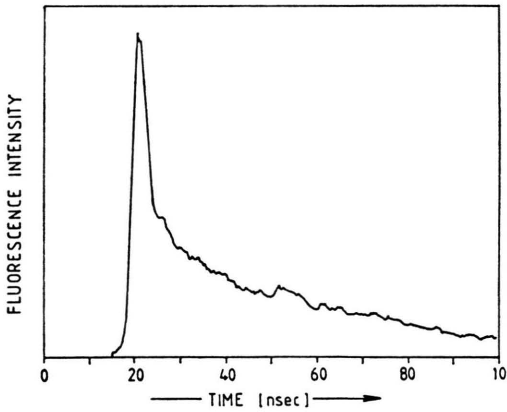

Fig. 1. Time-resolved decay of fluorescence from the $14^1 1^2$ state excited by two-photon absorption.

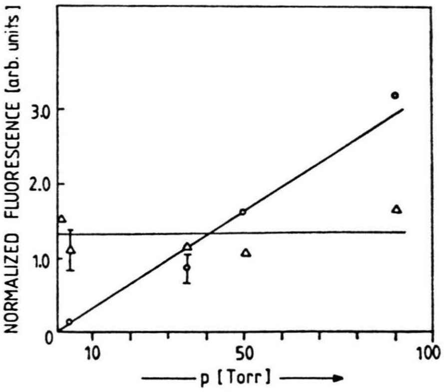

Fig. 2. Time-integrated intensity of the short (△) and the long (○) component of the fluorescence from the $14^1 1^3$ state as a function of pressure.

In order to clarify the origin of the two components observed in Fig. 1 we performed some additional experiments. Firstly we investigated the spectral range of both components. For this we added combinations of additional cut-off filters (Corning 9-54, 0-52, 0-54) in front of the multiplier. By this method we found that most of the long-lived fluorescence is emitted in the spectral range between 2500 and 3200 Å, whereas the spectral range of the short component is extended by about 300 Å to the red. For a further test we measured the pressure dependence of the time integrated, density normalized intensity of both components. The result for the band $14_0^1 1_0^3$ is shown in Figure 2. Here the benzene pressure is varied between 4 torr and 90 torr. 4 torr is the lowest pressure for which a long component could be detected by our device. Even at the highest pressure self absorption of the UV fluorescence can be neglected since the thermalized emission is redshifted from the absorption spectrum. Within the experimental errors the long decay shows a linear dependence on benzene pressure.

Contrary to the behaviour of the long component the density normalized intensity of the short decay shows no pressure dependence within the error limits of the experiment. The pronounced difference in these pressure dependences will be discussed in the next section.

IV. Discussion

From the various experimental results presented in the preceding section we may draw the following conclusions on the origin of the two decay components.

The slow component most likely originates from thermalized fluorescence of the molecule. This is in line with the reported lifetime data [1] as well as with the pronounced pressure dependence in Figure 2.

The short component may be interpreted as a direct fluorescence from the excited levels at high excess energies. This would explain the weak pressure dependence of this type of fluorescence since the collisional rate of about 10^9 (sec^{-1}) at the highest pressure is still much smaller than the nonradiative rate, which is expected to be larger by at least two orders of magnitude from previous linewidth measurements [2].

Another argument for the interpretation is the measured red shift of the fluorescence, which is known to be typical for fluorescence from states with high excess energies due to the Franck-Condon-principle.

For a further test of this interpretation we now compare the integrated intensity of the short (I_s) and the thermalized fluorescence (I_{th}) component.

$$I_s = n_s K_{rad}/(K_{nr} + K_{coll}), \tag{1a}$$

$$I_{th} = n_s \Phi_0 K_{eff}/(K_{coll} + K_{rad} + K_{nr}); \tag{1b}$$

$\Phi_0 = 0.18$ [6] is the fluorescence quantum yield of the thermalized level and n_s is the population of the excited level.

Here K_{rad} is the radiative rate of the excited level, which is known to be similar to the radiative rate of the vibrationless S_1 state ($K_{rad} = 3 \cdot 10^6$ sec^{-1} [7]).

K_{coll} is the collision rate for the excited molecule. K_{eff} is the effective collision rate according to a step ladder model [8]. For the excited level $14_0^1 1_0^5$ at an excess energy of about 6000 cm^{-1} we assume 5 collisions for thermalization.

Neglecting K_{rad} in (1b) we are able to calculate a value for K_{eff} from (1a, b). Since it is measured that $I_s/I_{th} \approx 1$ for the $14_0^1 1_0^5$ level at 80 torr we obtain a value for $K_{eff} = 2.1 \cdot 10^5$ (torr^{-1} sec^{-1}) and thus a value of $K_{coll} = 10^6$ (torr^{-1} sec^{-1}).

This is close to the range of expected collision frequencies ($3 \cdot 10^7 < K_{coll} < 3 \cdot 10^6$ (torr^{-1} sec^{-1})) [7, 9].

The reasonable result for the collision frequency found from the measured intensity value of the long and the short fluorescence components is thus a strong argument for the interpretation as thermalized fluorescence and direct fluorescence from the excited level.

From the time integrated intensity of the short component we are now able to estimate the non-radiative rate of the excited two-photon levels. Collisional deactivation may be neglected in a first approximation since i) non-radiative rates are expected to produce the fastest deactivation channel of the excited state and ii) no pressure dependence is experimentally found for the short component (Figure 2).

The non-radiative rate is found from a comparison of the short fluorescence component with the SVL fluorescence from the 14^1 level at the low excess energy of 1570 cm^{-1}. For this level the lifetime has been found from direct decay measurements [5] to be 154 nsec.

The procedure is divided into two steps. First the integrated SVL fluorescence from the 14^1 and the $14^1 1^2$ levels are compared at the low pressure of 0.55 torr where collisions may be neglected even for the long-lived 14^1 level. Then the integrated SVL fluorescence of the $14^1 1^2$ level is compared with $14^1 1^n$ levels up to $n = 5$ at high excess energies at somewhat higher pressures. The non-radiative rates K_{nr} are obtained according to

$$K_{nr}(n) = I_s(2)\,\mathrm{FC}(n)/I_s(n)\,\mathrm{FC}(2). \tag{2}$$

Here $I_s(n)$ is the measured time integrated intensity of the short component of the fluorescence from the n^{th} progression member, FC(n) is the Franck-Condon-factor for the n^{th} progression member of the totally symmetric ν_1 vibration. The Franck-Condon-factors for the progression members 1_0^n are known from [10].

The results for the non-radiative rates (□) according to (2) are given in Fig. 3 together with the integrated intensity of the short component (○) which is normalized to the fluorescence from the 14^1 level. For comparison also the results from direct lifetime measurements of one-photon levels [7] as well as of two-photon levels [5] in the low excess energy range are plotted (△). Finally in the upper part of Fig. 3 the decay rates are shown as concluded in Ref. [2] from linewidth measurements (△).

There is some discrepancy between the non-radiative rate of 10^9 (sec^{-1}) of the $14^1 1^2$ vibronic

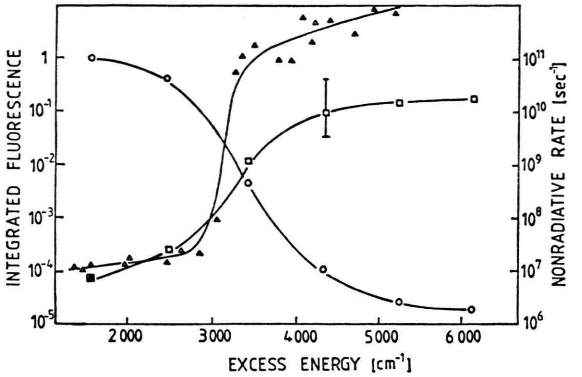

Fig. 3. Time-integrated short fluorescence for the $14^1 1^n$ states up to $n = 5$ (○). Nonradiative rates for various vibrational levels in S_1 as a function of excess energy. The values have been obtained in different experiments from (△) direct time-resolved decay measurements of states at low excess energies ($\leqq 3000$ cm^{-1}) excited by one-photon [7] and by two-photon absorption [5], (△) linewidth measurements of one-photon transitions to states at high excess energies ($\geqq 3000$ cm^{-1}) [2], (□) as estimated in this work for $14^1 1^n$ states from the observed time-integrated fluorescence.

state found by this procedure and our earlier lifetime measurements [5] yielding a value of $8 \cdot 10^{-9}$ sec. The lifetime value of $8 \cdot 10^{-9}$ sec most probably reflects the time resolution of our earlier experimental system rather than an accurate lifetime value of the excited $14^1 1^2$ state. The time resolution of the detection system used in this work is improved so that we find a value of 3.5 nsec (see Fig. 1) for the decay time of the short component from the $14^1 1^2$ level and a somewhat shorter value of 3 nsec for the higher levels. From this we conclude that the value of 3.5 nsec for the $14^1 1^2$ level is mainly due to the time resolution of the detection system and the true lifetime is much shorter, in agreement with the results from the integrated short component of this work.

Both, one and two-photon lifetimes agree well in the low excess energy range. One observes a general trend of increasing rates with excess energy for "gerade" as well as for "ungerade" vibrational states. Recent linewidth measurements of the $14_0^1 1_0^n$ two-photon transitions performed with the multi-photon ionization method [11] show a remarkable broadening (3—10 cm^{-1}) for states with $n \geqq 3$. This is of the same magnitude as the broadening observed for one-photon states at the same excess energy. From this we may conclude that the symmetry of the excited state is of minor importance for the radiationless channel in the low as well as in the high excess energy range. Hence we may directly compare the results of this work with the former results from one-photon linewidth measurements [2]. From our results in Fig. 3 it is seen that the increase of radiationless decay around 3000 cm^{-1} excess energy is neither as steep as found in Ref. [2] nor leads to such faster rates as concluded from the linewidth measurements of [2, 11]. The highest non-radiative rates are some 10^{10} (sec^{-1}) compared to rates of 10^{12} (sec^{-1}) from the linewidth measurements. Generally, our result points to a normal non-radiative behaviour rather than to a symptomatic "channel three" behaviour.

Finally, the reason for this discrepancy should be discussed. To our knowledge it is questionable whether the linewidth measurement performed in Refs. [2, 11] yields direct information about the kinetic T_1 population relaxation time of vibronic levels. There may well exist fast phase erosion effects, even in the isolated molecule, that produce a broad linewidth for relatively long-lived levels.

Our results then lead to the conclusion that the non-radiative decay of S_1 increases with excess energy in a way typical of large molecules. If a new very fast "channel three" is confirmed as turning on at excess energies of 3000 cm^{-1} then this new channel apparently does not lead to an additional depopulation of S_1, but rather must be viewed as a process within S_1.

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