

# Lifetimes of single rotational states in the "channel three" region of C<sub>6</sub>H<sub>6</sub>

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Lifetimes of single rotational states in the  $14^1 1^2$  vibrational state of benzene, C<sub>6</sub>H<sub>6</sub>, at  $3412\text{ cm}^{-1}$  excess energy were measured. The lifetimes depend strongly on the rotational quantum number  $J$  and we find them to agree with our recent homogeneous linewidth measurements of the same states. We present a coupling scheme including the coupling of the excited narrow light zero order state with a broadened dark background state. The broadening is due to a fast electronic nonradiative relaxation process typical for a state containing quanta of out-of-plane modes. It is demonstrated that the observed  $J$  dependence is due to perpendicular Coriolis coupling in the weak coupling limit. The IVR process resulting from this coupling explains the onset of "channel three" in a natural way without any further mystery states in the model.

## I. INTRODUCTION

In previous work Wunsch *et al.*<sup>1</sup> have shown that the increase in nonradiative electronic relaxation rate of  $S_1$  benzene is by no means as strong as originally concluded by Callomon *et al.*<sup>2</sup> In addition recently Riedle *et al.*<sup>3</sup> were able to show that the total nonradiative relaxation depends strongly on the rotation of the molecule.

In our work<sup>3,4</sup> we were able to excite single rotational states in  $S_1$ . We found a strong influence of rotation on the nonradiative behavior of benzene, C<sub>6</sub>H<sub>6</sub>, in the channel three region at excess energies of more than  $3000\text{ cm}^{-1}$  in the  $S_1$  state. This was explained by a fast electronic decay of  $K' \neq 0$  states which is initiated by parallel Coriolis coupling within  $S_1$ . In ultrahighly resolved Doppler-free two-photon spectra we found a strong increase of homogeneous linewidths of individual rotational lines (with  $K' = 0$ ) upon the quantum number  $J$ .<sup>4</sup> The typical  $J$  dependence of the linewidth produced by intramolecular relaxation points to additional perpendicular Coriolis coupling within the  $S_1$  state as being responsible for the rotational dependence of the linewidth.

The influence of rotations on the intramolecular vibrational redistribution (IVR) has also been deduced from partly resolved emission spectra of pyrimidine under bulk and supersonic jet conditions.<sup>5</sup> There, however, no resolution of individual rotational states was possible, and influence of Coriolis coupling was concluded from the gross features of the rotational contour. Recently,  $K$  mixing due to Coriolis coupling in  $S_0$  has been concluded from stimulated emission pumping experiments for the smaller molecule formaldehyde.<sup>6</sup> An important consequence of this observation would be that vibration-rotation coupling and in particular Coriolis coupling of vibrations via the rotation could increase the density of coupled background states in the IVR process. This can be caused by  $K$  mixing via the  $\Delta K = \pm 1$  selection rule of perpendicular Coriolis coupling and provides an explanation for the frequently observed low energy thresholds of the IVR process with insufficient total density of vibrational states.<sup>7</sup>

In this work we present for the first time rotational selective lifetime measurements of the excited state of a large polyatomic molecule. The data constitute new direct timing

information on the IVR process for selected individual rotational states in benzene, C<sub>6</sub>H<sub>6</sub>, at vibrational excess energies above  $3000\text{ cm}^{-1}$ . These states investigated are the same one as were explored by the recent linewidth measurements.<sup>4</sup> The question asked is whether both techniques yield the same relaxation time or further processes produce a divergence between the two measurements.

Aside from examples in atomic spectroscopy only a few cases of small molecules are known where precise homogeneous linewidths as well as reliable lifetime measurements of the same defined states are available. This is mainly due to the fact that inhomogeneous Doppler broadening is present in a gas which prevents one from measuring the homogeneous linewidth. If on the other hand due to a rapid decay the homogeneous linewidth is much larger than the inhomogeneous Doppler broadening the line shapes of different states begin to overlap in the spectrum of polyatomic molecules and again the precise homogeneous linewidths as well as lifetimes of defined individual states can no longer be measured. In order to obtain reliable dynamic information from linewidth and lifetime measurements for larger molecules it is mandatory to eliminate the inhomogeneous Doppler broadening and proceed with the preparation of pure states.

For isolated small molecules in the absence of an intramolecular dephasing process there is no doubt that both techniques, i.e., measurements in the frequency domain, as well as those in the time domain must yield the same information,<sup>8</sup> namely the population relaxation time.

The situation is more complicated in a larger polyatomic molecule. Due to the high density of vibrational states for these systems, in addition to population decay of the excited electronic state a loss of coherence of vibrational phase within the excited electronic state may occur. Here a special situation exists where linewidth and lifetime measurements may lead to different results. If emission can only be observed from the  $S_1$  vibrational levels (triplet  $T_1$  and  $S_0$  are not deemed to emit) and if the emission probability is the same for all vibrational levels within  $S_1$ , spectrally unresolved emission directly monitors the total population within the  $S_1$  state. The fluorescence decay constant then reflects the population decay time of the  $S_1$  electronic state, i.e., the

decay rate due to radiative relaxation and to electronic non-radiative relaxation like intersystem crossing (ISC) or internal conversion (IC). On the other hand for such cases, a homogeneous linewidth is still due to both a loss of population in the  $S_1$  state as well as a possible dephasing of the originally prepared  $S_1$  state. Then the dephasing leading to an intramolecular vibrational redistribution within  $S_1$  can *not* be measured by observing the time behavior of the spectrally unresolved emission. In our previous work<sup>1</sup> we have shown that integrated fluorescence lifetime measurements and previous linewidth measurements of Callomon *et al.*<sup>2</sup> indeed yield different results for very high vibrational excess energies ( $E_{exc} > 4000 \text{ cm}^{-1}$ ) in benzene. Vibronic bands above  $4000 \text{ cm}^{-1}$  excess energy were very diffuse,<sup>2</sup> yielding lifetimes of  $10^{-12} \text{ s}$ ,<sup>2</sup> whereas from our recent fluorescence yield measurements<sup>1</sup> we found considerably longer lifetimes of  $10^{-10} \text{ s}$  for the same excess energy. It appears likely that in this excess energy range the IVR process is dissipative and much faster than the subsequent nonradiative electronic relaxation process and therefore linewidth and lifetime measurements lead to different results. If on the other hand fluorescence emission is spectrally resolved or if the emission probability is different for different vibrational levels within  $S_1$ , the decay of these states can be distinguished and time measurements are sensitive also to an IVR process within  $S_1$ . This has been demonstrated for selective interaction of two states (restricted IVR),<sup>9</sup> which leads to quantum beats, as well as for IVR in the intermediate case leading to biexponential behavior.<sup>10</sup> Finally, even in larger polyatomic molecules IVR might be completely absent if the density of vibrational states within  $S_1$  is small and their interaction is weak. This situation seems to be present for benzene,  $C_6H_6$ , at low excess energies within  $S_1$  as has been shown in our recent analysis of the highly resolved Doppler-free rotational line spectrum of the  $14_0^1$  band at an excess energy of  $1570 \text{ cm}^{-1}$ .<sup>11</sup> It has been found that 90% of all rotational lines are at the expected position and it was concluded that for these states no coupling, i.e., no static IVR to other states within  $S_1$  is present. Only 10% of the lines are perturbed due to a coupling of the excited zero order state to a dark background state. Obviously at this low excess energy of  $1570 \text{ cm}^{-1}$  the density of states within  $S_1$  is so small that coupling only accidentally exists for a few states and dynamic IVR within the statistical limit can be completely excluded. Therefore, our recent lifetime measurements<sup>12</sup> of single rotational states represent the interstate electronic nonradiative relaxation process and in the absence of a dephasing (IVR) the linewidth would be given simply by the nonradiative electronic relaxation process. Hence, at low excess energy of  $1570 \text{ cm}^{-1}$  the benzene,  $C_6H_6$ , molecule is similar to a small molecule without IVR and information from linewidth and lifetime measurements is expected to be identical.

In the present work lifetime results for the intermediate case of an excess energy of  $3412 \text{ cm}^{-1}$  will be given and in particular a comparison is made with our recent linewidth measurements of this band ( $14_0^1 1_0^2$ ). Finally, a coupling scheme is presented which explains the measured dependence of intramolecular relaxation on the rotational quantum number  $J$ .

## II. EXPERIMENTAL SETUP

The experimental setup used is similar to that described recently.<sup>12</sup> Individual rotational states within the  $14_0^1 1_0^2$  vibronic band of  $C_6H_6$  were populated by pulsed Doppler-free two-photon excitation. Pulsed excitation was achieved with the pulsed output of an amplifier system amplifying the cw light of a single-mode ring dye laser. Since short lifetimes below 10 ns are expected from the linewidth measurements the 7 ns pulse length of the narrow bandwidth laser light was decreased substantially in some measurements. This was achieved by depleting the inversion in one of the amplifiers with increased amplified spontaneous emission in a controlled way. A similar technique has been recently applied for the production of picosecond excimer-laser pulses.<sup>13</sup> We were able to decrease the pulse length to about 2.5 ns while maintaining a peak power of 400 kW. The longer lifetimes of more than 20 ns have been measured with the longer pulse of 7 ns and a peak power of 650 kW. Coumarin 102 was used for the excitation wavelength of  $4820 \text{ \AA}$ . The fluorescence from the populated states was monitored with a photomultiplier (VALVO DUVP 56) and in addition to the boxcar integrator used in our previous work<sup>12</sup> for shorter lifetimes a waveform processing system (Tektronix WP 2221) was used to record the time evolution of the fluorescence signal. The time response of the detection system is about 3 ns. Fluorescence decay curves were obtained after averaging over 200–1000 laser pulses. The pressure within the fluorescence cell was 0.1 Torr in order to guarantee nearly collision free conditions.

## III. EXPERIMENTAL RESULTS

Due to the shortened laser pulse with a length of about 2.5 ns (see Sec. II) the spectral resolution in this experiment is only 260 MHz. This resolution would not be sufficient for excitation of every individual rovibronic state if all rotational lines were present in the  $14_0^1 1_0^2$  band as is, e.g., the case in the  $14_0^1$  band at  $1570 \text{ cm}^{-1}$ . In the fluorescence excitation spectrum of the  $14_0^1 1_0^2$  band, however, most of the lines are missing and only lines with  $K' = 0$  are left at the blue edge of the  $Q$  branch for  $J' < 14$ . This we attributed to parallel Coriolis coupling to short-lived vibrational background states within  $S_1$ .<sup>3</sup> Due to the low fluorescence quantum yield of these background states, which is probably caused by a very fast electronic nonradiative process (IC), all lines with  $K' \neq 0$  are strongly broadened and disappear in the spectrum. Only lines with  $K' = 0$  are left. They are not affected by parallel Coriolis coupling since  $V^{\parallel} \propto K$ . Thus, even though  $K' = 0$  lines are broadened they are not seen to overlap with neighboring lines since the spacing of  $K' = 0$  lines is large and increasing with  $(B' - B'')2(J' + 1)$ . As a consequence, with the short pulse the coherent excitation of the broadened  $K' = 0$  Lorentzian lines observed in our previous work<sup>4</sup> is guaranteed while a simultaneous excitation of other rotational lines (i.e., rotational inhomogeneous broadening) can be neglected for the moment. This problem will be discussed in more detail below.

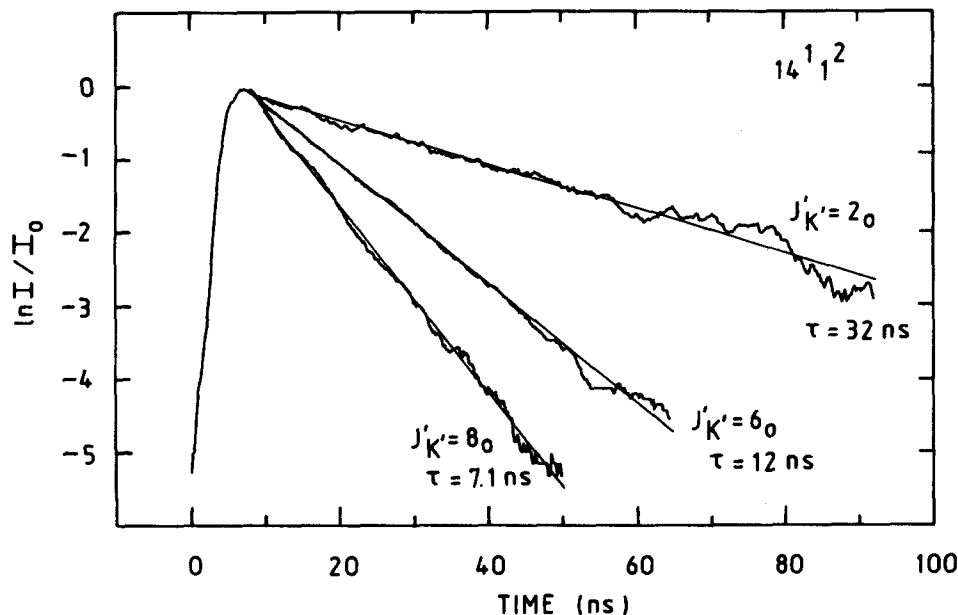


FIG. 1. Fluorescence decay curves measured after pulsed Doppler-free two-photon excitation of  $J'_{K'} = 2_0, 6_0, 8_0$  rotational states within the  $14^1_1^2$  vibrational state of  $C_6H_6$  at  $3412\text{ cm}^{-1}$  excess energy. Fluorescence intensity is plotted on a logarithmic scale with normalized peak intensity. The straight lines represent least square fits to a single exponential decay.

In Fig. 1 fluorescence decay curves for the three rotational states  $J'_{K'} = 2_0, 6_0,$  and  $8_0$  are shown on a semilogarithmic scale. It is obvious, that the measured decays are completely different for the three observed lines and strongly dependent on the  $J$  value. The solid line represents a least square fit to the measured decay curve. Within the experimental accuracy the decay is single exponential for these lines. From the slope of the solid line the lifetime  $\tau$  according to  $I(t)/I_0 = \exp\{-t/\tau\}$  is obtained. In a deconvolution procedure the finite laser pulse length (even though it was reduced to only 2.5 ns) and the time response of the detection system have been taken into account. It is found that even for the shortest decay the deconvolution yields a decay constant which deviates only by 5% from the decay constant found directly from the measured decay.

The experimentally determined lifetime of the three ro-

tational states shown in Fig. 1 is found to be very different. It decreases from 32 ns for the  $J'_{K'} = 2_0$  state to 12 ns for the  $J'_{K'} = 6_0$  to 7.1 ns for the  $J'_{K'} = 8_0$  state. In Fig. 2 the measured decay curve for the  $J'_{K'} = 3_0$  state is plotted. In this case  $J'$  is odd and the statistical weight is only 3/7 of the lines with  $J'$  even investigated above. For this reason, this line is smaller in intensity than the  $J'_{K'} = 2_0, 6_0, 8_0$  lines. The striking feature of the decay curve is its biexponential behavior. For the long component we find  $\tau = 26$  ns. We believe that this long component has to be compared to the decay curves of the  $J$  even states. The origin of the short component will be discussed in the next section.

All measured lifetimes are listed in Table I. The error is given by the uncertainty of the least square fit and the deviation of individual measurements. From the values in Table I a pronounced dependence of the measured lifetime on the

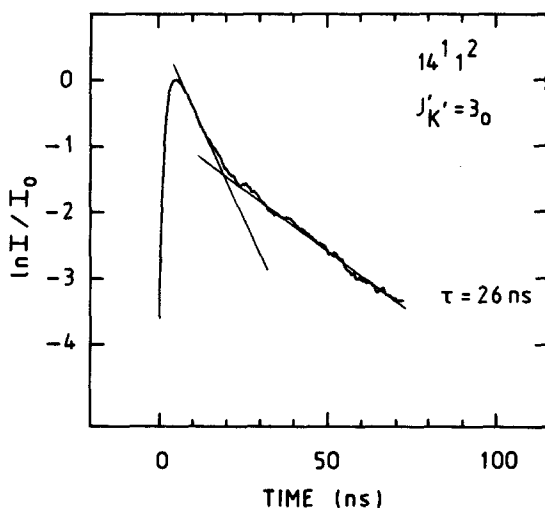


FIG. 2. Fluorescence decay after pulsed Doppler-free two-photon excitation of the  $J'_{K'} = 3_0$  state within the  $14^1_1^2$  vibrational state of  $C_6H_6$ . The two straight lines represent a fit to a biexponential decay behavior.

TABLE I. Measured lifetimes  $\tau$  for several selectively excited rotational states  $J'_{K'}$  with  $K' = 0$  within the  $14^1_1^2$  vibronic state of  $C_6H_6$ . The errors indicate the largest deviations of individual measurements and the uncertainty of the least square fits.  $K = 1/\tau$  is the corresponding relaxation rate and  $\gamma_r = 1/2\pi\tau$  the corresponding relaxation linewidth. For comparison also the relaxation linewidth  $\gamma_v$  found from our recent linewidth measurements (Ref. 4) is given.

Rotational state $J'_{K'}$	Lifetime $\tau$ ns	Rate $k \times 10^{-6} \text{ s}^{-1}$	Calculated linewidth $\gamma_r$ MHz $= 1/2\pi\tau$	Measured linewidth $\gamma_v$ MHz
$0_0$	$\geq 55$	$\leq 18$	$\leq 2.9$	1.3
$1_0$	$\geq 50$	$\leq 20$	$\leq 3.2$	1.9
$2_0$	$32 \pm 1$	31.3	5.0	4.0
$3_0$	$26 \pm 1.5$	38.5	6.1	6.8
$4_0$	$21.6 \pm 1$	46.3	7.4	9.5
$5_0$	$14.5 \pm 1.5$	69.0	11.0	12.8
$6_0$	$12.0 \pm 1$	83.3	13.3	18.7
$8_0$	$7.1 \pm 0.7$	141	22.4	25.4

rotational quantum number  $J'$  is found. For comparison the Lorentzian linewidths  $\gamma_r$ , obtained from a Fourier transformation of the exponential decay curve are also given in Table I. These linewidths can be directly compared with the collisionless relaxation linewidths  $\gamma_v$ , obtained from our recent very high resolution measurements of the same band<sup>4</sup> which are also listed in Table I. Both linewidth values agree well for the high  $J$  levels, however, they differ for lower  $J$  levels. These discrepancies can be understood in terms of the experimental uncertainties which are naturally high for the linewidth measurements due to the finite resolution in the two-photon experiment of our recent work.<sup>4</sup> In view of these difficulties the agreement of lifetime and linewidth measurements is very good. This is illustrated in Fig. 3. There the relaxation linewidths as found from recent linewidth measurements<sup>4</sup> ( $\circ$ ) ( $\gamma_v$  in Table I) are plotted together with the corresponding linewidths calculated from the present lifetime data ( $\blacksquare$ ) ( $\gamma_r$  in Table I) as a function of  $J'(J' + 1)$ . We find a linear dependence of both experimental results on  $J'(J' + 1)$  over the range  $0 \leq J' < 9$ .

#### IV. DISCUSSION

The most important result shown in Table I is the clear documentation of a rotational dependence of the measured lifetimes of single rovibronic states. Within the experimental accuracy the  $J$  dependence as well as the absolute value of the relaxation rates  $k$  found from linewidth measurements in our previous work<sup>4</sup> and from lifetime measurements ( $k = 1/\tau = 2\pi\gamma$ ) of this work are in good agreement. We have shown recently that the experimentally found

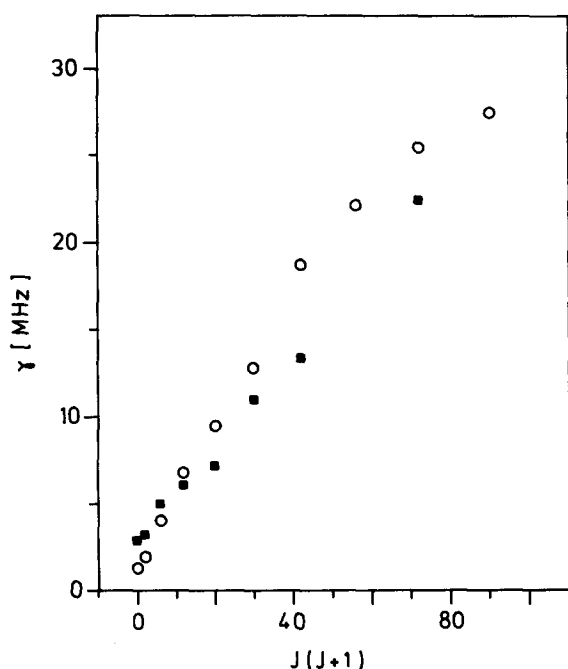


FIG. 3. Relaxation linewidth  $\gamma$  measured for various rotational states with  $K' = 0$  in the  $14^1_1 1^2$  vibrational states of C<sub>6</sub>H<sub>6</sub> as a function of  $J(J + 1)$ : ( $\circ$ ) Relaxation linewidth obtained from recent linewidth measurements (Ref. 4); ( $\blacksquare$ ) relaxation linewidth calculated from the lifetime data of this work.

linewidths and corresponding relaxation rates  $k$  are proportional to  $J'(J' + 1)$  for  $J' \leq 9$ . This result is now confirmed by the direct lifetime measurements of this work.

These results contrast strongly with our recent results for the low excess energy range.<sup>12</sup> No  $J$  dependence of the relaxation rate is found for unperturbed rotational states of the  $14^1$  state. Similarly we would not expect any  $J$  dependence for the purely electronic nonradiative component of the relaxation rate in the  $14^1 1^2$  state. Hence, the observed rotational dependence of lifetime found here for the channel three state  $14^1 1^2$  can only be attributed to an IVR process active in the vibrational band, which in fact is due to perpendicular Coriolis coupling.<sup>4</sup> Clearly this demonstrates the increased importance of IVR processes at higher excess energy of  $S_1$  benzene, i.e., in the mysterious channel three region. Since we observe single exponential decay and Lorentzian line shapes for the  $K' = 0$  states, we have to discuss two possible explanations: (a) Coupling to many vibrational modes within the same electronic state, i.e., IVR in the statistical limit; (b) coupling to one broadened background state. The broadening of this background state could be due to fast electronic nonradiative relaxation, i.e., interstate coupling. In principle the coupling could also be due to many broadened states. However, the  $J(J + 1)$  dependence of the relaxation rate of the  $K' = 0$  states as well as the high  $K$  selectivity in the spectrum of the  $14^1_0 1^2_0$  band point to a sparse number of such coupling states.

##### A. IVR in the statistical limit

In this case the IVR process within  $S_1$  is nearly irreversible and IVR can be described by a relaxation rate. Since a pronounced dependence of the relaxation rate on  $J$  is experimentally observed and on the other hand the electronic nonradiative relaxation has been shown to be independent of  $J$ <sup>12</sup> the observed linewidth would be determined predominantly by the IVR rate. In this case the IVR rate has to be much larger than the electronic nonradiative rate. In the statistical limit  $k_{\text{IVR}}$  can be approximated in first order by Fermi's Golden Rule:

$$k_{\text{IVR}} = 2\pi\gamma_{\text{IVR}} = 4\pi^2 V^2 \rho_{\text{eff}}. \quad (1)$$

Furthermore, the statistical limit is only given if

$$V \gg \rho_{\text{eff}}^{-1}, \quad (2)$$

i.e., the coupling encompasses several levels.

The total density of vibrational states at an excess energy of  $3412 \text{ cm}^{-1}$  ( $14^1 1^2$ ) is  $165 [1/\text{cm}^{-1}]$ . Due to the selection rule for perpendicular Coriolis coupling only states with the overall symmetry  $e_{2u}$  can be coupled. We have calculated the density of suitable states and found  $\rho_{\text{eff}} \approx 30 [1/\text{cm}^{-1}]$  or a state every 1000 MHz. It is easily seen that with this low effective density of states and for the measured rates  $k_{\text{IVR}}$  the condition in Eq. (2) for the statistical limit cannot be fulfilled. Hence, we conclude that IVR is not in the statistical limit and the second coupling scheme has to be discussed.

##### B. Coriolis coupling to a broadened level

This coupling scheme is illustrated in Fig. 4. On the left side the zero order state basis is shown, on the right side the

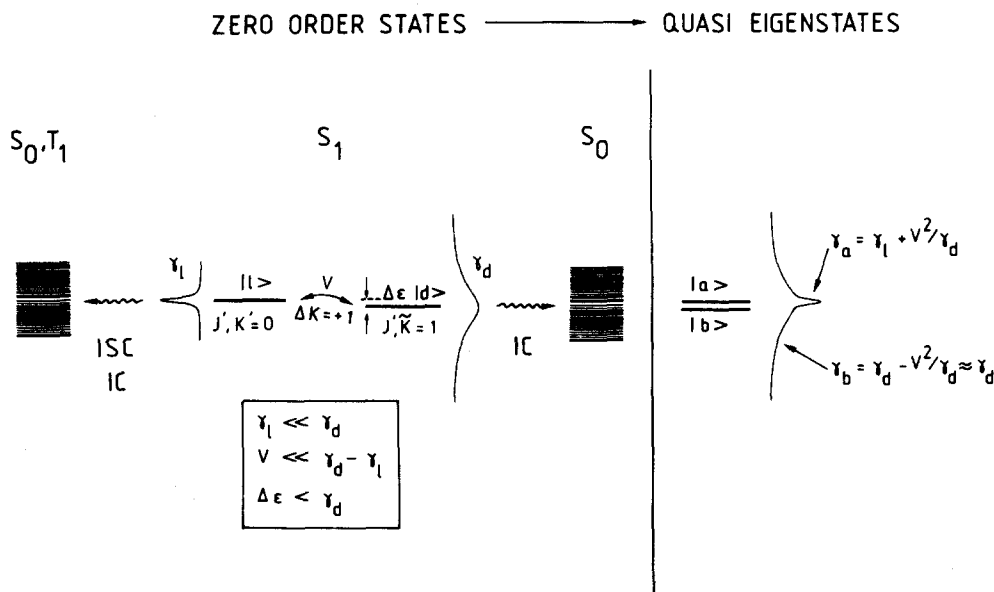


FIG. 4. Coupling of the light zero order state  $|l\rangle$  with narrow linewidth  $\gamma_l$  and the dark zero order state  $|d\rangle$  with broad linewidth  $\gamma_d$ . Both zero order states have strongly differing linewidths due to a faster electronic nonradiative relaxation process of the dark zero order state. The energy distance  $\Delta\epsilon$  of both zero order states is smaller than the linewidth  $\gamma_d$  of the dark background state. On the right side the line shape of the resulting quasieigenstates  $|a\rangle$  and  $|b\rangle$  is shown for the weak coupling limit.

quasieigenstates resulting from the coupling of the two zero order states within  $S_1$ . The interaction is produced by perpendicular Coriolis coupling with the coupling matrix element

$$V^+ \propto \sqrt{(J-K)(J+K+1)} \quad \text{with } \Delta K = +1. \quad (3)$$

Coupling with  $\Delta K = -1$  and the corresponding matrix element

$$V^- \propto \sqrt{(J+K)(J-K+1)} \quad (4)$$

need not to be considered since  $K' = 0$  for the excited zero order state. Hence the light zero order state  $J', K' = 0$  is coupled to the rotational state  $J', K' = 1$  within the dark vibrational background state. It is assumed in this model that the coupled background state is strongly broadened due to a fast electronic nonradiative relaxation process. The linewidth  $\gamma_l$  of the optically excited light zero order state  $|l\rangle$  is therefore much smaller than the linewidth  $\gamma_d$  of the dark coupled zero order state  $|d\rangle$  ( $\gamma_l \ll \gamma_d$ ). This background state probably is a combination state containing several quanta of out-of-plane modes, which are good accepting modes for IC and thus can strongly increase the IC rate.<sup>14</sup> Further arguments for the existence of the broadened background state will be discussed below. The IC rate for the light zero order state is smaller than that of the dark zero order state since the  $14^{12}$  state does not contain out-of-plane modes. Furthermore we know for the interaction matrix element (high order Coriolis coupling)

$$V \ll \gamma_d - \gamma_l \quad (5)$$

(weak coupling limit) and for the energy distance  $\Delta\epsilon$  of the zero order states

$$\Delta\epsilon < \gamma_d. \quad (6)$$

Under these assumptions (whose validity will be discussed below in more detail) the linewidth of the two resulting eigenstates  $|a\rangle$  and  $|b\rangle$  is given by<sup>15</sup>

$$\gamma_a = \gamma_l + V^2/\gamma_d, \quad (7)$$

$$\gamma_b = \gamma_d - V^2/\gamma_d. \quad (8)$$

Since

$$V^2 \ll \gamma_d^2$$

and

$$V^2/\gamma_d \ll \gamma_d,$$

$$\gamma_b \sim \gamma_d. \quad (9)$$

From Eq. (7) and Eq. (9) it is seen that two quasieigenstates with strongly differing linewidths  $\gamma_a$  and  $\gamma_b$  should appear in the spectrum. However, as it is illustrated in Fig. 4 the two quasieigenstates are not separated and their line shapes overlap. This is different from the strong coupling presented in our previous work.<sup>12</sup> There the separation of the two eigenstates is much larger than their linewidths and both eigenstates were observed in the spectrum. Here in the weak coupling limit the original line of the light zero order state with linewidth  $\gamma_l$  is broadened due to the term  $V^2/\gamma_d$  [Eq. (7)]. In addition a second broad line with linewidth  $\gamma_b$  should appear. This originates from the dark zero order state with linewidth  $\gamma_d$ . The linewidth  $\gamma_b$  is somewhat reduced by  $V^2/\gamma_d$ . Since  $V^2/\gamma_d \ll \gamma_d$  we may neglect  $V^2/\gamma_d$  as a good approximation.

As a result we predict a broad line with a sharp line on top of it to be seen in the spectrum. Conversely in the time picture this demands that we observe a biexponential decay with the narrow line leading to the slow component and the broad line leading to the fast decay component. This result has now to be compared with the experimental result which shows only a single Lorentzian line in the spectrum and basically a single exponential decay in time resolved measurements.

## C. Comparison with experimental results

### 1. Linewidth measurements

Theory here predicts the very broad ( $\gamma_b$ ) eigenstate  $|b\rangle$  which mainly reflects the characteristics of the dark zero order state  $|d\rangle$ . The second resulting eigenstate  $|a\rangle$  is superimposed since the energy splitting of the zero order states  $\Delta\epsilon \ll \gamma_d$  and the coupling matrix element  $V \ll \gamma_d$ . Hence from theory we expect a broad pedestal Lorentzian line with linewidth  $\gamma_a$  and a sharper line with linewidth  $\gamma_l + V^2/\gamma_d$  on top of it. When we compare this result with the single line found in the experiment we have to bear in mind that in a fluorescence excitation spectrum the broad pedestal is hard to detect due to the small fluorescence quantum yield of the dark zero order state  $|d\rangle$ . Generally, the broader component is harder to detect than the narrow line with  $\gamma_a$ , even in an absorption spectrum since oscillator strength distributes over the broad linewidth. Hence, it is reasonable that only the quasieigenstate  $|a\rangle$  is experimentally observed in the frequency domain. The observed strong rotational dependence of linewidth  $\gamma_a = \gamma_l + V^2/\gamma_d$  is then explained by the dependence of  $\gamma_a$  on the coupling matrix element  $V$  which itself is dependent on  $J$  for perpendicular Coriolis coupling according to Eq. (3). This will be discussed in more detail below.

### 2. Lifetime measurements

The situation is somewhat different in the time resolved measurements. If time resolution is sufficiently high, and the coherence width of the laser pulse is large enough to cover both the narrower line and the broad pedestal, the two contributions in the frequency domain correspond to a biexponential decay in the time domain. Even though the integrated signal of the short decay (which corresponds to the broad line) is much smaller than that of the slow decay (corresponding to the sharper line) due to the small fluorescence quantum yield it might be more easily detected in a time resolved experiment than in a time-integrated spectrum. As will be shown below for the present experiment the coherence width of the pulsed laser is not sufficient to excite the complete broad state coherently. This will make an observation of the short component even more difficult. Therefore it is not surprising that only the longer exponential decay is observed in Fig. 1.

At this point the appearance of the biexponential decay of the  $J'_{K'} = 3_0$  state shown in Fig. 2 has to be discussed. Even though theory predicts a biexponential decay with a short decay component it must be remembered that biexponential decay can also be observed if several states with differing lifetimes are excited at once. Hence, it is questionable whether the experimental result can be explained in terms of the model discussed. The  $J'_{K'} = 3_0$  line has a small statistical weight of only 3/7 as compared to states with  $J'$  even. For this reason the intensity of the narrow  $J'_{K'} = 3_0$  line is small. When we excite with a laser pulse length of 2.5 ns the coherence width of 260 MHz of the laser pulse is much larger than the Lorentzian linewidth (6.8 MHz) of the narrow component ( $\gamma_a$ ) of the  $3_0$  state. As a consequence, certainly part of the broad pedestal of the  $J'_{K'} = 3_0$  line is coherently excited

but even more neighboring overlapping  $J'_{K'} \neq 0$  lines which are strongly broadened.<sup>3</sup> The first would result in a true biexponential decay resulting from coherent excitation as described above whereas the latter yields a quasibiexponential decay after an incoherent excitation caused by inhomogeneous rotational broadening.<sup>16</sup> Since in our experiment biexponential behavior is observed only for the weak  $J'_{K'} = 3_0$  line we hesitate to identify the short component of the biexponential decay (in Fig. 2) as the one predicted by the coupling scheme discussed above. It is more likely that it is produced by the simultaneous excitation of a neighboring broadened line (e.g., the  $J'_{K'} = 4_4$ ). For the same reason quasibiexponential decays due to inhomogeneous rotational broadening are an even more severe and fundamental problem in picosecond excitation experiments, with an even larger coherence width of far more than 1 GHz. This fact severely limits the applicability of picosecond excitation for pure state preparation in large molecules. For a molecule as large as benzene several rotational transitions are simultaneously excited with high probability even in a cooled supersonic beam. Since decay behavior has been shown to depend so strongly on rotation it is hard to agree that the recently observed biexponential decay of benzene in the channel three region<sup>17</sup> (with a 10 cm<sup>-1</sup> resolution) can be directly interpreted as a coherent IVR process. In our work we demonstrate that a careful spectroscopic analysis of the rotational band structure must accompany any picosecond excitation experiment in the gas phase to judge the purity of the preparation.

In summary, the present results demonstrate that in both the frequency domain and time domain measurements only the eigenstate  $|b\rangle$  with  $\gamma_b = \gamma_l + V^2/\gamma_d$  is observed and linewidth and lifetime measurement yield the same result.

## D. Numerical results

### 1. Weak coupling limit and $J$ dependence

It is of interest to show that the assumptions made in our theoretical model for the weak coupling limit are in agreement with experimental results.

The smallest value for  $\gamma_a$  obtained from our linewidth and lifetime measurements is  $\gamma_a = 2.1 \times 10^6$  s<sup>-1</sup> for  $J' = 0$ ,  $K' = 0$ . In this case the Coriolis coupling matrix element  $V = 0$  and  $\gamma_a = \gamma_l$ ; i.e., there is no coupling and the linewidth is given by the electronic nonradiative relaxation of the light zero order state:  $\gamma_l = 2.1 \times 10^6$  s<sup>-1</sup>.

Next, a value of  $\gamma_a$  has to be found. This in principle could be obtained from the short component of the biexponential decay according to the model discussed above. Since, however, at present no decay measurements of single rotational states with the desired temporal resolution are available, we have to estimate  $\gamma_a$  from the fast decays seen in previous picosecond lifetime measurements<sup>17</sup> with no rotational resolution. The average decay rate of five vibrational states around 3500 cm<sup>-1</sup> excess energy is found to be  $5 \times 10^9$  s<sup>-1</sup>. This yields  $\gamma_a = 1/2\pi \times 5 \times 10^9$  s<sup>-1</sup> =  $8 \times 10^8$  s<sup>-1</sup>.

With the values for  $\gamma_l$  and  $\gamma_a$  we are able to calculate  $V$ . For example, with  $\gamma_a = 8.5 \times 10^6$  s<sup>-1</sup> measured for  $J' = 4$  we obtain from Eq. (7)  $V = 7.2 \times 10^7$  s<sup>-1</sup>. We see that these

values for  $\gamma_l$ ,  $\gamma_d$  and  $V$  agree well with the conditions for the weak coupling case  $\gamma_l \ll \gamma_d$  and  $V \ll \gamma_d - \gamma_l$ . The coupling matrix element  $V = 2.4 \times 10^{-3} \text{ cm}^{-1}$  for  $J' = 4$  corresponds to  $V = 0.8 \times 10^{-3} \text{ cm}^{-1}$  for  $J' = 1$ . This is a reasonably small coupling matrix element as expected for higher order Coriolis coupling to a background combination state. It is further seen that  $\gamma_l < V^2/\gamma_d$  and therefore  $\gamma_d \sim V^2/\gamma_l \propto J'(J' + 1)$ . This  $J$  dependence indeed has been experimentally verified for  $J' \leq 9$ .

## 2. Energy distance of zero order states

Another assumption in the theoretical model is that the energy spacing  $\Delta\epsilon$  between the light and dark zero order state is smaller than the linewidth  $\gamma_d$  of the dark zero order state ( $\Delta\epsilon < \gamma_d$ ). Otherwise the broad and the narrow line corresponding to the quasideigenstates resulting from the coupling would be separated. This assumption has to be verified for all zero order levels from  $J' = 0$  up to  $J' = 9$  which are studied in our experiment.

Since the coupling already occurs for low  $J$  levels this means that there exists a background combination state with a vibrational frequency close to that of the  $14^1 1^2$  state. Furthermore, the rotational term curves of the two vibrational levels have to be nearly parallel in order to guarantee an energy distance smaller than the linewidth of the dark background level ( $\Delta\epsilon < \gamma_d$ ) for each pair of interacting states from  $J' = 1$  to  $J' = 9$ . This would be easily achieved for a  $\Delta K = 0$  selection rule of the coupling, e.g., for a parallel Coriolis coupling. For the  $\Delta K = +1$  selection rule in the present case the situation is less transparent. For a symmetric top and  $\Delta K = +1$  the energy difference  $\Delta\epsilon$  of a light and a dark state is given by<sup>18</sup>

$$\Delta\epsilon = \delta B J'(J' + 1) + (\delta C - \delta B) K'^2 - 2(C_d - B_d) K' - C_d - B_d \quad (10)$$

if the pure vibrational energies are identical. Here  $\delta B = B_l - B_d$  and  $\delta C = C_l - C_d$  and  $B_l$  and  $C_l$  are the rotational constants of the light  $14^1 1^2$  state.  $B_d$ ,  $C_d$  are the rotational constants of the dark state, respectively.  $K' = 0$  since only lines with  $K' = 0$  are excited. From Eq. (10) it is clear that the vibrational energy of the rotationless dark and the light state have to differ by  $B_d - C_d \approx 0.1 \text{ cm}^{-1}$  in order to produce the degeneracy of the two coupled zero order states for low  $J$  levels. The energy mismatch is then given by  $\Delta\epsilon = \delta B J'(J' + 1)$ . When  $\Delta\epsilon < \gamma_d$  for  $0 \leq J' \leq 9$  it follows that  $\delta B < \gamma_d/90$ . For the value of  $\gamma_d = 8 \times 10^8 \text{ s}^{-1}$  assumed above this yields  $\delta B < 9 \times 10^6 \text{ s}^{-1} = 3 \times 10^{-4} \text{ cm}^{-1}$  which is a reasonable upper limit for change of rotational constants with vibration in a molecule-like benzene. Hence, we have shown that for the reasonable value of  $\gamma_d$  used above the two interacting zero order states can be nearly degenerate over the  $J$  range ( $0 \leq J' \leq 9$ ).

In summary it is shown that for the experimental values given above the conditions for weak coupling are fulfilled for the observed  $J$  range. This strongly points then to model (b) above and coupling of the excited zero order states to strong-

ly broadened background levels seems to be the mechanism responsible for IVR in the intermediate energy range.

## V. SUMMARY AND CONCLUSION

In this work we have presented lifetime measurements of individual rotational states of the vibrational state  $14^1 1^2$  in benzene, C<sub>6</sub>H<sub>6</sub>, just above the onset of channel three. The lifetimes are found to strongly vary with rotational quantum number  $J'$ . The measurements are in good agreement with our recent homogeneous linewidth measurements for the same states.

We demonstrate that lifetime and linewidth measurements yield identical information not only for the typical case of small molecules without intramolecular dephasing but also for larger molecules, in fact for IVR of benzene at intermediate level density. Time-resolved measurements are advantageous for detecting the short component of a biexponential decay but in principle this information is present in linewidth measurement, as well. The example discussed in this work shows that reliable information from time-resolved measurements is only obtained if a complete detailed rotational analysis of the excited part of the spectrum is available and care is taken to match the timing of the excitation source as close as possible to the molecular system. Otherwise, it is not clear whether the measured time behavior represents the dynamics of a defined quantum state of the molecule or is an artifact due to excitation of a mixture of several states. Particularly this is a problem in time-resolved measurements of larger polyatomic molecules with dense rotational line structure. Averaging the decay of several rotational lines does not yield meaningful results since, as has been shown in this work, dynamic behavior is strongly depending on rotation. Here a particular word of caution must be sounded for picosecond measurements, particularly for situations not in the statistical limit.

Finally, we would like to discuss our results in terms of the channel three problem in benzene. The original definition of channel three was a purely spectroscopic one. From a sudden diffuseness of absorption spectra at  $3000 \text{ cm}^{-1}$  excess energy the sudden onset of a new nonradiative channel called channel three was concluded.<sup>2</sup> This interpretation was supported by the breakoff of fluorescence at the same excess energy.<sup>19</sup> More recent measurements by Wunsch *et al.*<sup>1</sup> show that population depletion does not display such a sudden onset, but nevertheless a rather sudden decrease of lifetimes with excess energy is observed near  $3000 \text{ cm}^{-1}$  of excess energy. Even though these are low resolution results, the general conclusion of the abrupt change of rates is maintained under our conditions of sub-Doppler excitation.

Our results show the existence of very short-lived vibrational background states in  $S_1$ . Probably these are background states containing several quanta of out-of-plane modes which are the modes of lowest frequency in  $S_1$  benzene and therefore appear with increasing probability in combination states at higher excess energy. Out-of-plane modes are known to be good accepting modes for the IC<sup>14</sup> and ISC<sup>20,21</sup> process. The density of these states is strongly increasing with excess energy and coupling to optically

accessible light zero order states becomes more probable. The coupling is found to be Coriolis coupling which produces an intramolecular vibrational redistribution process (IVR). This turn on of the IVR process is responsible for the sudden increase of the observed electronic nonradiative relaxation rate and the consequent breakoff of fluorescence. It is not necessary to invoke a new relaxation channel (unidentified electronic state or photoisomerization) to explain the channel three behavior.

We have shown in this work that rotation plays an important role in the IVR coupling process and it turns out that the observed  $J$  dependence of linewidths<sup>4</sup> and lifetimes is what can be expected from Coriolis coupling responsible for coupling of a sharp light state to a broad dark state in the weak coupling limit. Around the onset of an efficient coupling the coupling scheme is dependent on the accidental spectral position of lines, the strength of the coupling matrix element, and on the selection rules for Coriolis coupling. This is probably the reason for the previously observed differences in spectral broadening for states of the same symmetry and similar excess energy (e.g., 7<sup>1</sup> as compared to 6<sup>1</sup>1<sup>3</sup>) around the onset of channel three. It seems reasonable, that at even higher vibrational excess energies than the one of the 14<sup>1</sup>1<sup>2</sup> state considered in this work, the density of broadened background states increases so much, that all light zero order rotational states are coupled effectively. This would then lead to the fast relaxation rate observed in low resolution experiments and no more dependence of the rate on the rotational state would be observed.

In summary our present results demonstrate that

- (1) Rotational effects in radiationless process can be quite strong. This is demonstrated for the channel three region of benzene.
- (2) The rotational effects observed are clearly demonstrated as being due to Coriolis coupling within  $S_1$ .
- (3) Coriolis coupling is an important part of the physics responsible for IVR in large molecules.
- (4) IVR becomes abundant around 3000 cm<sup>-1</sup> of excess energy, this being the onset of channel three in benzene.
- (5) The IVR process couples the light states to broad background states. These are broadened due to fast non-radiative electronic relaxation.

- (6) The onset of IVR naturally explains the onset of channel three since it now opens up the fast electronic nonradiative relaxation channel for most light states.

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