Time evolution of individual rotational states after pulsed Doppler-free two-photon excitation: Influence of perturbations in S_1 benzene

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Single rovibronic level excitation has been demonstrated for a molecule representing the statistical limit of a nonradiative electronic relaxation process. Resolution of the complex 14_0^1 two-photon band of benzene was possible after elimination of the Doppler broadening in a Doppler-free two-photon absorption process with narrow bandwidth pulsed laser light and allowed for selective excitation of individual rotational states. Fluorescence decay measurements of these states under low pressure conditions display a pure exponential behavior and reveal that the nonradiative rate is independent of the rotational quantum numbers J, K for an electronic nonradiative relaxation process in the statistical limit. The decrease in lifetime found for perturbed states is attributed to the mixing with a background state containing quanta of an accepting mode.

I. INTRODUCTION

One of the currently discussed problems in intramolecular dynamics is the dependence of radiationless transitions on the rotation of the molecule. Experimental tests of this phenomenon turn out to be very demanding and require extremely selective excitation and sensitive detection methods under collision free conditions.

In our recent work[1] we were able to measure the homogeneous collision free linewidths of individual rotational transitions in the large polyatomic molecule benzene. The resolution of individual rotational lines was made possible by Doppler-free two-photon spectroscopy within the standing wave field of an external cavity. We found that the homogeneous linewidth of transitions at vibrational energies in excess of 3000 cm^{-1} is strongly dependent on the rotational quantum number of the molecule. This points to a rotationally dependent relaxation process. The rotational dependence was attributed to an intramolecular vibrational relaxation process (IVR) due to Coriolis coupling within the S_1 manifold rather than to an electronic relaxation process leading to a decrease of fluorescence from the excited state.[2]

Electronic relaxation of S_1-benzene can either proceed radiatively to low vibrational levels of S_0 or nonradiatively to isoenergetic levels of vibrationally highly excited levels in S_0 (IC) or the triplet manifold (ISC). From the small fluorescence quantum yield observed under low spectral resolution and collision free conditions[3] it was concluded, that the decay in the isolated molecule is dominated by the nonradiative channels. Due to the large energy gap to the S_1 state, the density of vibrational levels in benzene in both S_0 and T_1, that are isoenergetic to S_1 levels, is extremely large. This fact, together with the fluorescence quantum yield measurements[3] and low spectral resolution lifetime measurements[4] under low pressure conditions, has led to the conclusion, that the *electronic nonradiative* decay of S_1 benzene is in the statistical limit.[5] Recent multiphoton ionization experiments by Otis *et al.*[6] have shown that this nonradiative process is ISC at the low excess energy in S_1 studied in this work.

Even though rotationally selective excitation was not possible in previous experiments, attempts have been performed to obtain information whether the nonradiative electronic decay is dependent on the rotation of the molecule. Parmenter and Schuh[7] measured the dependence of the fluorescence quantum yield on the excitation position within the vibronic band with a resolution of 4 cm^{-1}. This resolution averages many rotational transitions so that, if at all, only extremely strong rotational effects could have been detected. No dependence of the fluorescence quantum yield on the excitation position within the vibronic band was found. In summary, up to now no experiments are known which are in contradiction with the existence of an electronic nonradiative process in the isolated benzene molecule which is in the statistical limit.

Contrary to the electronic nonradiative relaxation, *intrastate coupling* in S_1 benzene (IVR) can not even be close to the statistical limit at the excess energy of 1570 cm^{-1} considered here. This is due to the low density of vibrational levels. Hence the rotational dependence of the relaxation linewidth observed in our recent work[1] was attributed to an IVR process within S_1 rather than to the nonradiative electronic relaxation process.

Evidence for rotationally dependent IVR has also been found from rotationally averaged band contour measurements for pyrimidine[8] which has intermediate level structure in S_1.

The investigation of rotational dependence of population lifetime so far has been restricted to a few cases of small and intermediate case molecules. Strongly rotationally dependent decay behavior was found for formaldehyde,[9] pyrazine[10] and propynal.[11] None of these molecules is, however, in the statistical limit with regard to the electronic nonradiative relaxation process under consideration and a true resolution of individual rotational transitions was only possible in the case of the small molecules formaldehyde and propynal.

In this work the population lifetime of individual rotational states is investigated in a large polyatomic molecule

(benzene) whose electronic relaxation processes ISC and IC are believed to be in the statistical limit (see above). We measured population lifetimes of individual rovibronic states in the 14^1, $S_1(^1B_{2u})$ state of benzene C_6H_6 at an excess energy of 1570 cm^{-1}. While the electronic nonradiative process is assumed to be in the statistical limit at this low excess energy no dynamic IVR process is expected and lifetime measurements should reflect the electronic (nonradiative) relaxation process leading to the depopulation of S_1. The necessary selective excitation is possible in a Doppler-free two-photon experiment with extremely narrow bandwidth pulsed laser light.[12] The population lifetime is then measured by observation of the decay of fluorescence from the excited state. In this way precise information can be obtained about the possibility that an electronic nonradiative relaxation process could be influenced by the rotation of the molecule even in the statistical limit.

II. EXPERIMENTAL

The scheme of the experimental setup used in this work is shown in Fig. 1. The high resolution and the possibility for a precise linear scan is provided by a single-mode cw ring dye laser system (Coherent 699-21) pumped by a Kr$^+$ ion laser (CR 3000 KUV). The output power at 5043 Å with a Coumarin 102 dye is some 200 mW. For lifetime measurements of individual rotational levels the laser wavelength has to be tuned to the position of the different rotational lines under consideration. This is performed in the following way: The laser is scanned with a homemade computer interfaced 16 bit D/A converter and the Doppler-free two-photon spectrum is recorded simultaneously until the peak of the rotational line is reached. Then the laser scan is stopped. The laser frequency was found to be stable ($\pm$ 10 MHz) within a period of 10 min required for the lifetime measurement of a rotational state. This stability is sufficient to keep the time-integrated fluorescence intensity constant to within 5%. The stability of the cw-laser light is permanently controlled with a temperature-stabilized evacuated confocal interferometer with 150 MHz free spectral range (reference cavity in Fig. 1). For frequency calibration the signal of the transmitted light is simultaneously stored in a DCS data processing system and plotted together with the Doppler-free two-photon

spectrum. The laser wavelength is measured with a wavemeter (Burleigh WA 20).

For decay time measurements the cw-laser light is amplified in a pulsed amplifier setup similar to our previous work.[12] Here, however, we use an additional third amplifier setup, as an excimer pump laser (Lambda Physik EMG 150, XeCl) is used which provides light pulses with an energy as high as 60 mJ at a repetition rate of 16 2/3 Hz. For shortening of the pump pulse He is used as a buffer gas and light pulses with a half-width of about 9 ns are produced. 25% of the pulse energy is focused into amplifier I and II each and the remaining 50% of energy is used in amplifier III. Coumarin 307 is used in all amplifier stages. The output peak power after amplification in amplifier stage I is 50 W with a broadband amplified spontaneous emission (ASE) background of only 10^{-3}. Amplifier stages I and II are optically decoupled by an interference filter and a polarizer. Between the amplifiers I and II, and II and III, pin holes are used as spatial filters for suppression of the ASE. In amplifier stage II the light pulse is amplified to a peak power of 10 kW with an ASE background of 5×10^{-3} and finally with amplifier III a peak power as high as 300 kW is obtained. Typically, the broadband amplified spontaneous background is less than 3×10^{-2} or 10 kW. The pulse length is 6 ns (FWHM) and the pulse shape is somewhat asymmetric with a decay time twice as long as the rise time. The frequency width of the amplified light is estimated to be 80 MHz which roughly corresponds to the Fourier transform limited value of the light pulse. Since the amplified spontaneous emission is nearly unpolarized it can be reduced by a factor of 3 to about 10^{-2} of the narrow bandwidth amplified light with a second polarizer. The complete amplifier system is decoupled from the cw ring laser with an optical isolator consisting of a Faraday rotator and two polarizers.

The suppression of broadband emission due to ASE is of particular importance in fluorescence decay time measurements since nonselective excitation could contribute additional fluorescence and thus produce unreliable decay curves. For the same reason it is also important to suppress the Doppler-broadened background that results from the absorption of two photons from either the incoming or the reflected laser beam. This Doppler-broadened background is a problem particularly in the present measurements under
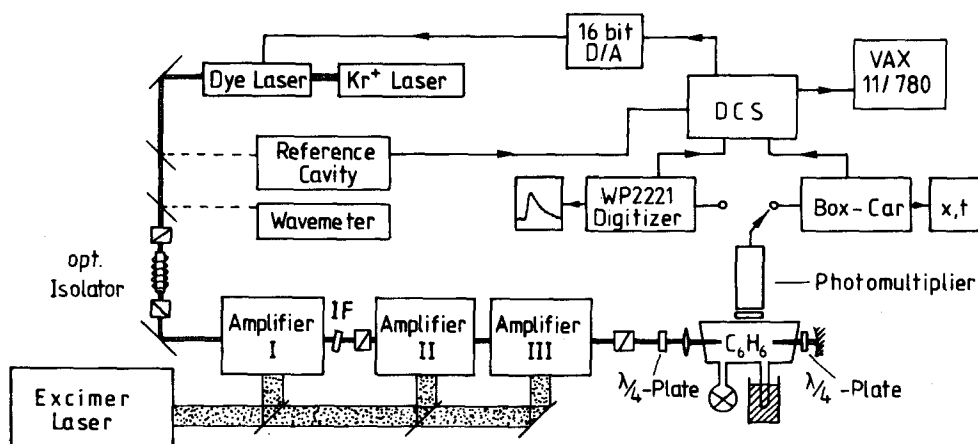

FIG. 1. Experimental setup for lifetime measurements of individual rotational levels in the 14^1 vibrational state of benzene. Fluorescence decay is observed after pulsed Doppler-free two-photon excitation with the amplified light of a cw dye laser.

a resolution of typically one-tenth of the Doppler width. In a large molecule—like benzene—several rotational lines are located within the Doppler width and two-photon absorption from one laser beam would result in a nonselective excitation of several rotational states. We have shown in our previous work[12] that as in the case of atoms[13] counter-circularly polarized light leads to a substantial suppression of the Doppler-limited excitation. For circular polarization a $\lambda/4$ retardation plate is inserted into the light beam before it is focused into the fluorescence cell containing the molecular gas under a low pressure of some 0.1 Torr. The divergent light beam is then refocused with an adjustable spherical mirror so that a complete overlap of the incoming and the reflected light beams is obtained. The sense of circular polarization (within the molecular frame) of the reflected laser beam is changed by inserting a second $\lambda/4$ retardation plate. Under these polarization conditions the fluorescence signal from nonselective Doppler-limited excitation is suppressed by nearly two orders of magnitude.

It is worth noting that in this way Doppler broadening is eliminated for *all* excited molecules independent of their individual velocity component. Under these conditions molecules are brought to a defined rotational state with $E = 2\,h\nu$. Excitation to other rotational states whose transition frequencies are located within the Doppler width with $E \neq 2\,h\nu$ is not possible in two-photon absorption. This is quite different from the situation present in saturation or polarization spectroscopy. Here the incoming light beam excites molecules to all rotational states available due to overlapping Doppler widths of the transition. The Doppler-free spectrum is then obtained by probing molecules with zero velocity and observing the resulting nonlinear signal either in absorption or emission.[14] Fluorescence lifetime measurements of defined rotational states are not readily possible with these techniques since fluorescence from all (nonselectively) excited states within the Doppler width is observed.

The fluorescence is monitored with a 56 DUVP photomultiplier and visible stray light is blocked with suitable filters in front of the photomultiplier tube. The fluorescence decay curve is measured with a boxcar integrator (PAR). The signal of the integrator is transferred to the DCS data processing system after every laser shot. The scan velocity of the gate has been chosen so that for a repetition rate of 16 2/3 Hz about seven laser pulses are integrated within the gate width of 5 ns. Under these conditions the complete decay curve is measured within 4 min. For a fast preliminary measurement of the decay curve, a waveform processing system (Tektronix WP 2221) can be used instead of the boxcar.

III. EXPERIMENTAL RESULTS

A. Doppler-free two-photon spectrum of the 14_0^1 band

Recently, we have investigated the spectrum of the 14_0^1 two-photon band of benzene C_6H_6 in detail.[15] A rotational analysis of the symmetric rotor spectrum was performed. We succeeded in assigning 320 rotational lines up to 120 GHz from the rotational origin.[16] The high resolution of about 17 MHz in the two-photon spectrum measured with cw-laser light allowed for the separation and identification

of every rotational transition in the observed region of the Q branch.

For lifetime measurements pulsed two-photon excitation of the rovibronic states is necessary. For accurate lifetime measurements the pulse duration should be considerably shorter than the decay time of the excited state. Naturally, owing to the increased coherence width of the pulsed source, this leads to a reduced resolution and not every rotational line is resolved. At the bottom of Fig. 2, part of the Q branch of the 14_0^1 band is shown as obtained with the pulsed amplifier setup of this work. It is immediately seen that many of the lines are not completely separated from neighboring ones. In these cases a completely selective excitation of a single rotational state is not possible. The highly resolved two-photon spectrum obtained for the cw laser excitation (17 MHz resolution) allows to select rotational lines which can well be resolved also with the pulsed laser setup of this work. Selected parts of the high resolution spectrum are shown at the top of Fig. 2 on an extended frequency scale. From a comparison of both spectra it is seen that selective excitation is possible for the rotational lines with $J'_{K'} = 7_3, 11_8, 10_4, 18_{14}, 17_{11}, 16_7, 19_{16}, 18_8, (21_{17})_a, 25_{20}, 21_5$. These lines have been chosen so that states with (low J, low K), (high J, low K), and (high J, high K) are included. The half-width of these lines in the spectrum recorded with pulsed excitation is about 160 MHz. This is close to the value expected if the bandwidth of the laser light is only limited by the Fourier transform of the laser pulse and the two-photon process is taken into account. The state with $J'_{K'} = 21_{17}$ is of particular importance. In recent work[16] we have shown that this state is coupled to a dark background state within S_1. This coupling results in a repulsion of the two zero-order states and, due to the mixing of the zero-order wave functions, both eigenstates $(21_{17})_a$ and $(21_{17})_b$ become visible in the spectrum. However, only the $(21_{17})_a$ component of the two eigenstates can be resolved with pulsed excitation. The other one $(21_{17})_b$ is hidden under the envelope of the neighboring $J'_{K'} = 18_7$ and $J'_{K'} = 19_{11}$ peaks. A closer analysis of the highly resolved spectrum[17] shows that none of the other peaks marked in the spectrum of Fig. 2 is perturbed.

B. Lifetimes of individual rotational states

Fluorescence decay curves after pulsed excitation were measured according to the procedure described in Sec. II for the 12 rotational states marked in Fig. 2. Typical results are shown in Fig. 3 for the unperturbed states $J'_{K'} = 7_3$, $J'_{K'} = 18_8$, and $J'_{K'} = 21_5$. In the lower traces the exponential decay curves are shown on linear scale, in the upper part fluorescence intensity is plotted on a logarithmic scale (natural logarithm) as a function of time. Fluorescence was observed down to a stray light and noise level of $e^{-5} \sim 10^{-2.17}$ of the maximum fluorescence intensity at the end of the laser pulse. The laser power was chosen so that saturation of the photomultiplier signal was avoided. Within the experimental accuracy a pure single exponential decay is observed. This single exponential decay of the excited defined single quantum state yields further evidence that the *electronic* relaxation of benzene (which is certainly far from that of a small molecule and dominated by the nonradiative relaxa-
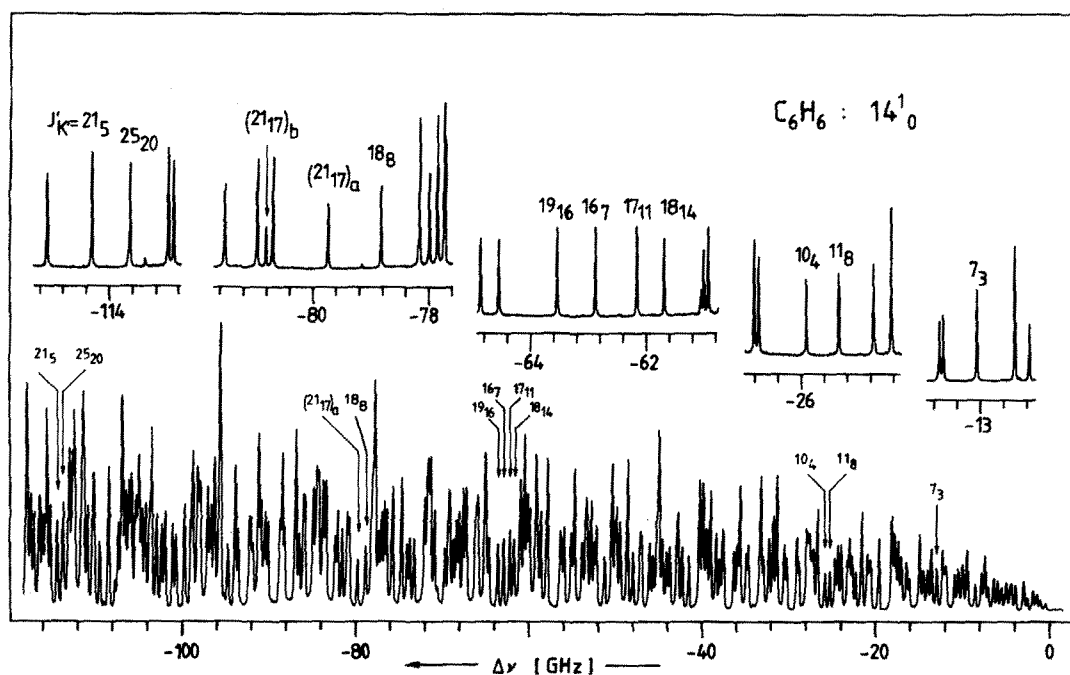
FIG. 2. Blue part of the Q branch in the 14^1_0 two-photon band of C_6H_6 as measured with the pulsed amplifier setup shown in Fig. 1 (bottom). Five sections of the spectrum are shown on an extended frequency scale at the top as obtained using the high resolution cw laser. These demonstrate that the rotational lines marked by an arrow in the lower resolution spectrum (bottom) correspond to completely resolved single rotational transitions.
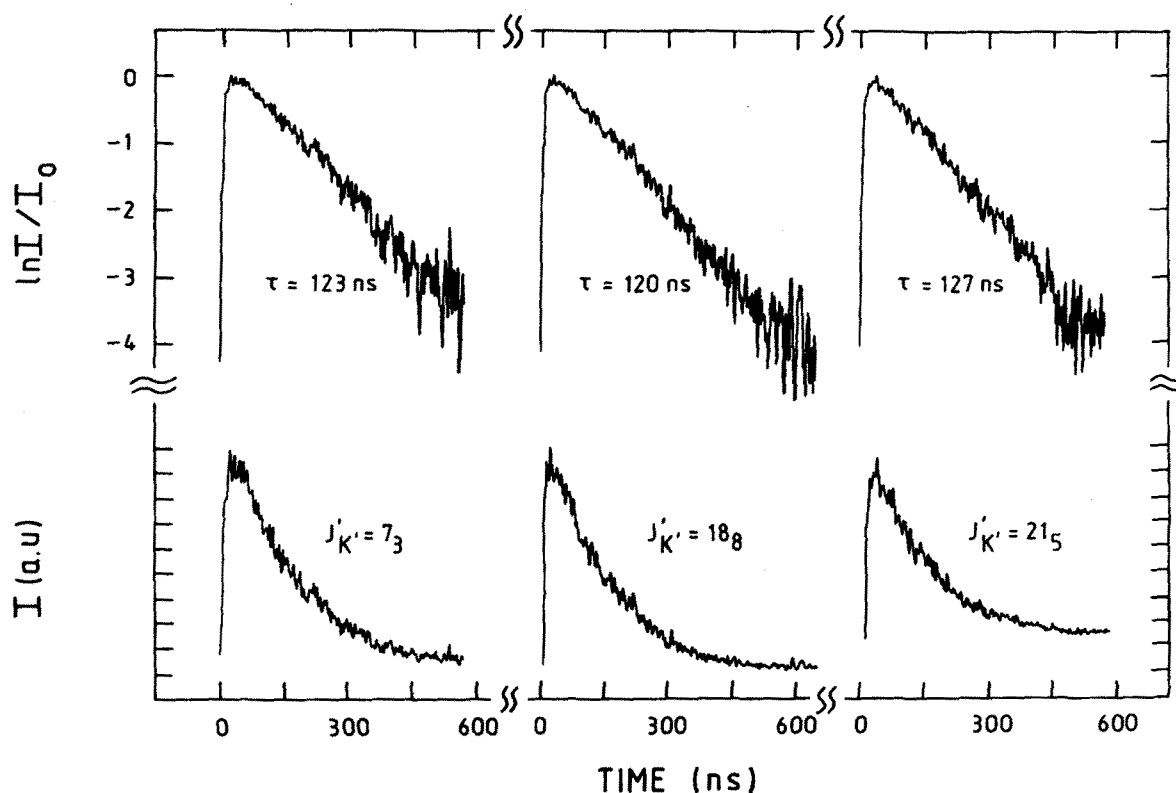

FIG. 3. Decay behavior of the fluorescence as measured for three unperturbed rotational states within the 14^1 state of benzene, C_6H_6. Fluorescence intensity is plotted on a linear scale (bottom) and on a logarithmic scale (top).

tion process) is actually in the statistical limit[18] on the time scale of our experiment. It is also seen from Fig. 3 that the finite pulse duration of 6 ns (FWHM) does not affect the accuracy of the decay time measurement. Deviations from the exponential decay are observed only for the first 15 ns which is in line with the measured pulse duration. This means that a coherent excitation within the (Lorentzian) line shape of the rotational states is guaranteed, since for a pulse length of 6 ns the coherence width is at least 100 MHz. This is already larger by more than one order of magnitude than the half-width of 10 MHz measured with the high resolution cw laser setup. The measured linewidth represents an upper limit for the homogeneous linewidth as it is given mainly by the finite resolution of the cw laser and by transit time broadening within the small laser focus.[1]

From a least square fit of a straight line to the half-logarithmic plot of the decay curve the lifetime τ is determined according to $I(t)/I(0) = \exp\{-t/\tau\}$. We find that the lifetime of $\tau = 123 \pm 3$ ns for the $J'_{K'} = 7_3$ state, the lifetime of $\tau = 120 \pm 2$ ns for the $J'_{K'} = 18_8$ state, and the lifetime of $\tau = 127 \pm 4$ ns for the $J'_{K'} = 21_5$ state are identical within experimental error.

In Fig. 4 the small section of the 14^1_0 band with the previously analyzed[16] perturbation is shown under high resolution (upper trace) and the lower resolution of the pulsed setup (lower trace). At the bottom the decay curves of the perturbed state $J'_{K'} = (21_{17})_a$ and the unperturbed $J'_{K'} = 18_8$ state are plotted on a half-logarithmic scale. Both curves represent single exponential decays. In contrast to the constant lifetimes of the states shown in Fig. 3, here we find differing lifetimes of the unperturbed $J'_{K'} = 18_8$ and the perturbed $J'_{K'} = (21_{17})_a$ state.

All lifetimes measured are listed in Table I for the 12 rotational states under investigation. The error represents the maximum deviation of individual fluorescence decay curve measurements of the same state. We see that the measured lifetimes of all rotational states are the same to within $\pm 5\%$. Only one exception can be found. This is the $J'_{K'} = (21_{17})_a$ state. Its lifetime of 91 ns is smaller than that of all the other measured states by 30%.

IV. DISCUSSION

A. Unperturbed rotational states

The main result seen from Table I is that the lifetimes of all unperturbed rotational states (except the state $J'_{K'} = 21_{17}$ which is perturbed and will be discussed below) are the same within the accuracy of the measurement. Furthermore, no deviation from an exponential decay is observed. This means that the population of the excited rovibronic states is found to decay single exponentially. Four contributions to the relaxation of the excited states have to be discussed: (i) For the pressure of 0.1 Torr in our experiment collisional deactivation can be neglected. In a separate experiment we checked that, indeed at this low pressure, no pressure dependence of the measured lifetime can be observed. This result is in line with previous collisional rate measurements[4,19]; (ii) a dynamic IVR process within the electronic S_1 state can be excluded at this excess energy since
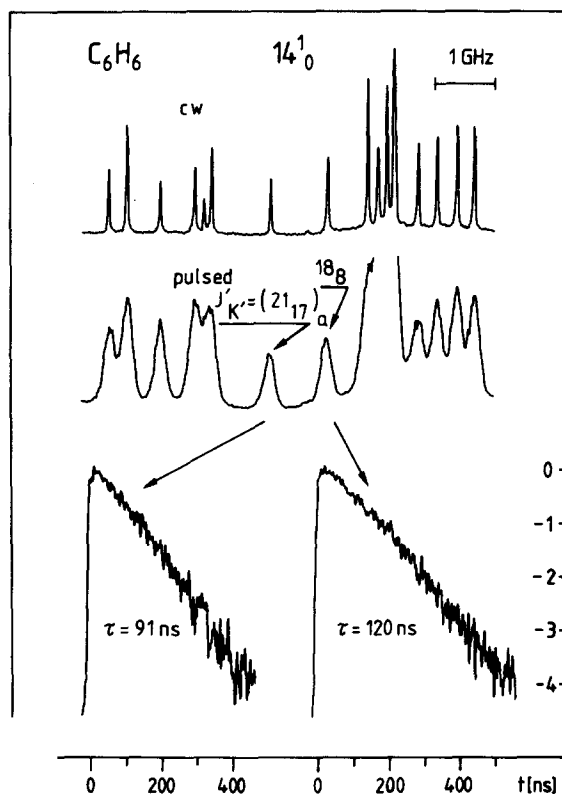

FIG. 4. Part of the Q branch of the 14^1_0 two-photon band of C_6H_6 under the high resolution of the cw laser (top) and the lower resolution of the pulsed laser (middle trace). At the bottom the fluorescence decay curves measured for the two neighboring lines ($J'_{K'} = 21_{17}$)_a and $J'_{K'} = 18_8$ are shown on a half-logarithmic scale. Both lines are well resolved, even with the pulsed laser. $J'_{K'} = (21_{17})_a$ is one component of the perturbed zero-order state $J'_{K'} = 21_{17}$, whereas $J'_{K'} = 18_8$ is an unperturbed state.

the small density ($\rho = 1.2$ 1/cm^{-1}) of background states does not permit a dissipative relaxation within S_1. On the other hand, the low density of states at this excess energy in some cases leads to a coupling of zero-order states within S_1 which has indeed been detected as perturbation of but a few lines in the rotational spectrum[16]; (iii) radiative relaxation contributes little to the measured decay. This has been found for all one-photon states of S_1 benzene from quantum yield

TABLE I. Measured lifetimes for several selectively excited rotational levels within the 14^1 vibronic state of C_6H_6. The errors indicate the largest deviations of a single individual decay curve from the average value.

Rotational state in 14^1 $J'_{K'}$	Lifetime τ [ns]
7_3	123 ± 3
10_4	121 ± 3
11_8	120 ± 5
16_7	134 ± 4
17_{11}	126 ± 5
18_8	120 ± 2
18_{14}	126 ± 5
19_{16}	129 ± 6
21_5	127 ± 4
$(21_{17})_a$	91 ± 2
25_{20}	134 ± 4

measurements.[5] In our previous work[20] we concluded from Franck–Condon arguments that the radiative lifetime of the vibrational state 14^1 (two-photon state) is close to the radiative lifetime of the vibrationless S_1 state which has been found to be 455 ns from low spectral resolution quantum yield and lifetime measurements.[4] From this it is clear that also for two-photon states radiative relaxation is not the predominant relaxation process; (iv) therefore the main contribution to the measured decay originates from the electronic nonradiative relaxation process which has been found to be ISC at the low vibrational excess energy of 1570 cm^{-1}.[6]

Hence at this point we assume that the measured decay time can be interpreted in terms of the electronic relaxation processes, exclusively. The average lifetime value of all rotational state lifetimes listed in Table I [except the perturbed $J'_{K'} = (21_{17})_a$ value] is $\langle \tau \rangle = 126$ ns. This value is in reasonable agreement with the value of $\tau = 115$ ns found in our previous measurements with a broadband excitation of 1 cm^{-1}.[20] In this previous experiment a selective excitation of individual rotational states was not possible. The measured lifetime value represents the average over about 80 rotational states, some of which probably are perturbed. In view of the lifetime shortening found for perturbed states (see below), the agreement of both measurements is surprisingly good.

The most important result of our experiment is that the lifetime does not change for different rotational levels within the 14^1 vibrational state. Even though the radiative relaxation contributes by only 28% to the measured total relaxation rate of the rotational state, first a possible dependence of radiative relaxation on rotation will be briefly discussed. From the unperturbed nature of the rotational states considered, we know the Born–Oppenheimer approximation to hold for these states. Since these states all belong to the same vibronic state, this means that changes in radiative transition probability could be due only to the different Hönl–London factors[21] for the different rotational transitions to the ground state. Since the radiative decay rate, however, is given by the sum of the probabilities of all six possible transitions ($\Delta K = \pm 1$, $\Delta J = 0$, ± 1 for $J'_{K'} \geqslant 1$[22]), the sum rule for the Hönl–London factors applies and the total radiative transition probability is constant for different J, K.

After having excluded a rotational dependence of the radiative rate it is concluded from the experimental result in Table I that also the nonradiative rate (which probably is determined by ISC) is independent of the rotational quantum number. This result is expected for an ISC nonradiative decay in the statistical limit.[23] It is further evidence that the electronic nonradiative decay in benzene is indeed in the statistical limit.

B. Perturbed rotational states

There is only one lifetime value in Table I which considerably deviates from all other values. This is the lifetime of $\tau = 91$ ns of the $J'_{K'} = (21_{17})_a$ rotational state. In our recent work[16] we have shown that this state is strongly perturbed by a dark vibrational background state within S_1 via perpendicular Coriolis coupling. As a consequence of the perturbation the two resulting quasieigenstates $(21_{17})_a$ and

$(21_{17})_b$ are split by about 1.1 GHz. An in depth rotational analysis[17] showed that the two observed lines are close to the crossing point of the term curves of both interacting states. For energetically degenerate zero-order states, both the dark and the light zero-order state are mixed into the quasieigenstates with 50% probability and both resulting lines have equal intensity. The coherent excitation of both eigenstates with a short pulse would lead to oscillations (quantum beats) on the exponential decay with a frequency of 0.55 GHz. A similar phenomenon was recently reported for anthracene, however, without spectral information about the nature of the excited state.[24] In the present experiment the coherence width of the laser pulse is only about 100 MHz and therefore only one quasieigenstate component $J'_{K'} = (21_{17})_a$ is excited. Thus no beating can be observed and a pure exponential decay is seen (compare Fig. 4). This exponential decay at the crossing point is an average mixture of the decay of the "light" zero-order state $J'_{K'} = 21_{17}$ and the "dark," still unknown background state. In the strong coupling limit ($V \gg \gamma_l, \gamma_d$) it holds that[25]

$$\gamma_a = \gamma_b = (\gamma_d + \gamma_l)/2. \tag{1}$$

Here γ_l and γ_d are the linewidths of the light and dark zero-order states coupled by the Coriolis interaction matrix element V. γ_a and γ_b are the linewidths of the quasieigenstates, respectively. The coupling scheme is illustrated in Fig. 5. If we choose for the linewidth of the light zero-order state the average value $\langle \gamma_l \rangle = 1/2\pi\langle \tau \rangle$ of all unperturbed rotational states shown in Table I we obtain $\langle \gamma_l \rangle = 1.26 \times 10^6$ s^{-1}. It is seen that the condition for the strong-coupling limit is fulfilled as $V = 0.55 \times 10^9$ s^{-1} in our case.[16] According to Eq. (1) and for the measured value $\gamma_a = 1/2\pi\tau_a = 1/(2\pi \, 9.1 \times 10^{-8}) = 1.75 \times 10^6$ s^{-1} we calculate for the relaxation rate γ_d of the unknown dark background state $\gamma_d = 2.24 \times 10^6$ s^{-1}. This corresponds to a lifetime of the dark zero-order background state of $\tau_d = 1/2\pi\gamma_d = 44.6$ ns. The above discussion is valid for the crossing point of the term curves. From Fig. 2 it is, however, seen that the peak $J'_{K'} = (21_{17})_a$ is somewhat larger than $J'_{K'} = (21_{17})_b$. Therefore, it has to be concluded that the interaction of the light $J_K = 21_{17}$ state and the dark zero-order state is not directly at the crossing point and the $(21_{17})_a$ state reflects the nature of the light zero-order state 21_{17} to a somewhat larger degree. Hence the lifetime τ_d estimated above for the dark zero-order state is an upper limit and $\tau_d < 44.6$ ns or $\gamma_d > 2.2 \times 10^6$ s^{-1}.

From the above discussion it is seen that the zero-order state $J'_{K'} = 21_{17}$ is coupled to a vibrational background state whose relaxation is at least three times faster than the relaxation of the zero-order 14^1 vibrational state. As discussed above, this difference in relaxation rate principally can be due either to the radiative or the nonradiative electronic relaxation rate of the dark background state. Since, however, radiative relaxation is known to be smaller than 3×10^6 s^{-1} in C_6H_6,[4] it is impossible that the threefold increase in total relaxation rate is due to an increase of the radiative rate of the background state. Hence, it is clear that the isoenergetic dark zero-order background state has a three times faster nonradiative electronic relaxation rate. This has to be attri-
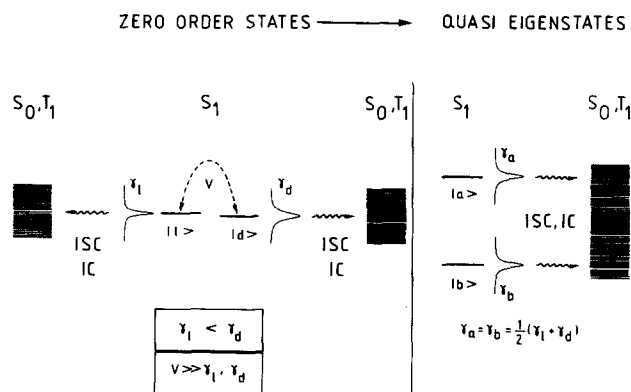
FIG. 5. Coupling scheme of the light zero-order state $|l\rangle$ with the dark zero-order state $|d\rangle$. Both zero-order states have different linewidths due to a faster electronic nonradiative relaxation process of the dark zero-order state $(\gamma_d > \gamma_l)$. The linewidths γ_a and γ_b of the resulting quasieigenstates are shown on the right side in the strong coupling limit.

buted to the different vibrational nature of this state. The existence of a short-lived vibrational background state is an important result in terms of our recent work on fast relaxation in the "channel three" region of benzene above 3000 cm^{-1} excess energy.[2] There we found that lines with $K \neq 0$ have disappeared in the Doppler-free two-photon spectrum of the $14_0^1 1_0^2$ band at 3412 cm^{-1} excess energy, whereas lines with $K = 0$ are nearly unaffected. This highly rotationally dependent nonradiative process was attributed to Coriolis coupling between the excited states and dark background states causing energy redistribution (IVR) within S_1. The strong disappearance of fluorescence was explained by a fast electronic nonradiative relaxation process typical for the dark background states. The key assumption in this model is that Coriolis coupling is possible to good acceptor modes for the nonradiative ISC or IC relaxation process. Once these acceptor modes are populated due to a mixing or after a dynamic IVR process, fast nonradiative electronic relaxation occurs leading to a disappearance of fluorescence. A detailed discussion is given in the accompanying paper.[26] In the low excess energy range studied in this work we are able to investigate a defined mixing between two individual isoenergetic vibrational states due to Coriolis coupling. As we have shown above we are able to explicitly measure the nonradiative relaxation rate of the coupled dark state even though it is not directly accessible. Indeed we found a threefold increase of nonradiative electronic relaxation rate. This explicitly shows that good accepting modes do exist and that indeed they are coupled to the optically excited ν_{14} mode. At present time the nature of the coupled vibration is not known, even though from symmetry selection rules it is clear that the total symmetry of the coupled state has to be e_{2u}.[16] A detailed analysis of the spectral perturbations is under way in order to identify this short-lived state. Good candidates for accepting modes are out-of-plane modes of low frequency. It is of particular interest to compare our spectral results with recent theoretical predictions on the nature of accepting modes.[27]

V. SUMMARY AND CONCLUSION

In this work lifetimes of individual rotational states up to $J = 25$ and for various K numbers within the 14^1 vibrational state of benzene, C_6H_6, have been measured. The necessary highly selective excitation was made possible by Doppler-free two-photon absorption of the light of a pulsed amplifier setup. We found pure exponential decay for all rotational states under consideration. Furthermore the lifetimes of all unperturbed rotational states were found to be identical within experimental error. However, the lifetime of the perturbed $J'_{K'} = (21_{17})_a$ state shows a pronounced difference from the other lifetime values.

The highly selective excitation of Doppler-free two-photon absorption enables us to study the rotational dependence of an electronic nonradiative relaxation rate within the statistical limit. It is found that the nonradiative rate for a fixed vibrational state does not depend on the rotational quantum number J, K of the molecule. The observed change in lifetime of a perturbed level is due to the mixing with another vibrational state in S_1 with different electronic nonradiative relaxation behavior rather than due to a rotational effect in the electronic nonradiative relaxation rate.

In conclusion it is now possible to excite single rovibronic states at variable J, K levels even in large polyatomic molecules whose electronic nonradiative relaxation process is in the statistical limit. This has become feasible after elimination of Doppler broadening in Doppler-free two-photon absorption. Single rovibronic level lifetime measurements are of great importance for the understanding of the mechanism of electronic nonradiative relaxation. It turns out that single rovibronic level excitation on the basis of a detailed spectroscopic analysis enables us to study the decay of those vibrational levels that are normally not accessible either in one- or two-photon excitation. This is possible when perturbations due to a state mixing are present in the spectrum. This method will complete our knowledge about electronic nonradiative relaxation processes and elucidate the role of vibrations in promoting ISC and IC processes.

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