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In honor of J. Jortner and R.D. Levine, on their being awarded the 1988 Wolf Prize

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Dynamic Behavior of Individual Rovibronic States in S_1 Benzene

ULRICH SCHUBERT,* EBERHARD RIEDLE, HANS J. NEUSSER AND EDWARD W. SCHLAG**
Institut für Physikalische und Theoretische Chemie,
Technische Universität München, Lichtenbergstr. 4, D-8046 Garching, FRG

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Abstract. Pulsed Doppler-free two-photon excitation of single rotational states of the 14_1^1 vibronic state of benzene with a resolution of 70 MHz is employed to investigate the influence of molecular rotation on the decay behavior of these states. The analysis of the completely resolved ($\Delta\nu = 15$ MHz) spectrum of the 14_0^1 band, measured with a CW laser, makes it possible to specify whether individual states are perturbed by other ("dark") S_1 states and allows the precise determination of the degree of admixture of these background states. The vibrational identity of the background states is known from emission spectra of single rovibronic states. Unperturbed rovibronic states were investigated up to $J_{K'} = 67_{61}$, and a pure exponential decay was found which does not depend on molecular rotation in accord with a nonradiative decay of S_1 benzene in the statistical limit. The decay of perturbed states, which was also found to be purely exponential, depends strongly on the degree of admixture of the background state and on its vibrational identity. Values of the decay time of two identified "dark" zero-order S_1 vibrational states, which cannot be directly excited by optical transitions, are determined by evaluation of the decay behavior of the perturbed states.

1. INTRODUCTION

The decay of the electronically excited prototype organic molecule benzene is dominated by nonradiative processes in the statistical limit.¹ Due to strict selection rules in molecules with high symmetry (e.g., D_{6h} for benzene) and to restrictive Frank-Condon factors, not all vibrational modes of the molecule can be excited by optical transitions² and a complete experimental investigation of the vibrational dependence of the nonradiative process has not been possible so far even for the prototype molecules. In addition, couplings between the optically excited "light" state and "dark" background states lead to a mixing of the different states which can further obscure the situation. These couplings lead to an intramolecular vibrational redistribution (IVR) of the energy, which is selectively deposited into the molecule by the optical excitation.³ Despite extensive investigations, it is still an important and open question whether redistribution at chemically relevant excess energies is complete or whether some selectivity is maintained.^{4,5}

We have shown in recent publications that the *onset*

of the coupling at low excess energies can be seen as perturbations in the spectrum.⁶⁻⁸ To analyze the perturbations, the rotational structure of the various vibronic bands has to be resolved. This was shown to be possible by Doppler-free excitation of the molecule.^{9,10} It was found that the couplings are caused not only by the well-known anharmonic resonances, but even more frequently by weak rotation-vibration couplings.¹¹ The rotation-vibration couplings lead to *isolated* perturbations in a particular band,⁶ and therefore transitions in a single vibronic band can be used to study both the influence of the rotation on the dynamic behavior of rovibronic states with pure vibrational identity *and* the dependence of the dynamic behavior on the degree of admixture of states with differing vibrational character. Such an investigation will be performed in this work for a very large range of rotational states. From the analysis of the decay behavior of mixed states, the decay be-

*Present address: TÜV Bayern e.V., Westendstr. 199, D-8000 München 21, FRG.

** Author to whom correspondence should be addressed.

havior of the pure "dark" states will be deduced. Since the "dark" states are combination states which contain quanta of normally not accessible vibrational modes, the dynamic behavior of these modes can be elucidated in this way. Furthermore, knowledge of the decay behavior of the "dark" states is of importance, as coupling to "dark" states is known to increase with their density; consequently, the vibrational excess energy and therefore the decay behavior of the "dark" states are believed to be dominant in the dynamic behavior of the molecule at high excess energy.

2. EXPERIMENTAL

To record rotationally resolved room temperature spectra of benzene vapor, Doppler-free two-photon spectroscopy¹² was employed. Basically, the absorption of two photons with opposite direction of propagation and equal frequency leads to the Doppler-free excitation from the S_0 electronic and vibrational ground state to the 14^1 vibrational state in the S_1 electronically excited state.⁹ The resolution in this experiment is mainly determined by the line width of the exciting tunable visible laser, i.e., an extremely narrow bandwidth laser has to be used to resolve individual rovibronic transitions. The experimental setup used has been described in previous publications^{8,13-15} and only the relevant features will be reviewed.

To record spectra with extremely high resolution, a CW experiment was performed.^{8,13} The tunable laser light is produced by a Kr^+ laser pumped ring dye laser (Coherent CR 699/21) with a frequency width of about 1 MHz and a maximum scan width of 30 GHz. To obtain high sensitivity, the light of the dye laser is coupled to an external resonator which contains the fluorescence cell with benzene vapor at a pressure of about 1 Torr. Two-photon excitation to the S_1 state is monitored by the UV one-photon emission from the excited state. For relative frequency calibration, the transmission spectrum of an evacuated and temperature-stabilized Fabry-Perot Interferometer (FPI) with a free spectral range of 150 MHz (known to better than 1 part in 10^5) is recorded simultaneously with the benzene spectrum.

For decay time measurements, the light of the CW dye laser is pulsed amplified in three amplifier stages pumped by the output of a XeCl excimer laser.^{14,15} In earlier experiments,¹⁴ an excimer laser with a pulse length of 10 ns was used, and the resulting light pulses had a nearly Fourier-transform limited bandwidth of 80 MHz. This was sufficient to resolve a large percentage of the rovibronic transitions, but did not allow us to investigate all rovibronic states of interest. Particularly, most perturbed states could not be cleanly excited, since the corresponding transitions are weaker than the ones leading to unperturbed states. To increase the spectral resolution, an excimer laser (EMG 1003 MSC) with a pulse length of 20 ns was used in the present investigation. This led to tunable light pulses of a considerable smaller bandwidth (50 MHz).¹⁵ The light was focused into a fluorescence cell containing benzene

vapor and refocused to a common focus with a spherical mirror to allow for Doppler-free absorption. To suppress undesirable Doppler-broadened background in the spectrum, two $\lambda/4$ delay plates were used on either side of the excitation cell to produce counterclockwise circularly polarized light and avoid the effective absorption of two photons from one laser beam leading to the Doppler-broadened background.¹⁰ To record spectra, the dye laser was scanned and the resulting UV fluorescence integrated in a boxcar integrator (PAR 164). To measure decay curves of single rovibronic states, the laser was scanned by the output of a computer-controlled 16-bit DA converter and stopped at the frequency of the selected excitation line. The decay curves were recorded with either the boxcar integrator or a wave form processing system (Tektronix WP 2221).

3. RESULTS AND DISCUSSION

3.1. Spectrum of the 14^1_0 Band

Fifty-four overlapping scans of the 14^1_0 band of benzene, C_6H_6 , of 24 GHz width each, were recorded with the CW laser setup. This resulted in a continuous spectrum from -45 cm^{-1} to $+24\text{ cm}^{-1}$ from the rotationless origin, i.e., the complete R branch and S branch and a large part of the much wider Q branch. The first 6 cm^{-1} of the Q-branch spectrum were shown in a previous publication.⁸ Isotopically pure $^{12}C_6H_6$ (MSD Isotopes No. 138; 99.9 atom % ^{12}C stated purity) was used as a sample to avoid spurious contributions to the spectrum due to the 6.7% abundance of $^{13}C^{12}C_5H_6$ present in natural benzene. The relative frequency scale obtained from the 150-MHz free spectral range FPI is believed to be accurate to ± 10 MHz. The spectrum consists of very sharp spectral features, most of which are single rovibronic transitions. About 50 to 100 lines are observed per cm^{-1} in the Q branch. This corresponds to an average line spacing of about 400 MHz. The measured width of unblended lines, 15 MHz, is mainly due to the pressure broadening at the sample pressure of about 1 Torr.^{8,13}

Assignment of the Q-branch spectrum according to a semirigid Hamiltonian is straightforward and unambiguous, since the average spacing of lines is much larger than the line width and the uncertainty in the frequency calibration. The energy formula used for the Q-branch lines is:¹⁶

$$\Delta E_{\text{rot}} = \Delta B J(J+1) + (\Delta C - \Delta B) K^2 - \Delta D_J J^2(J+1)^2 - \Delta D_{JK} J(J+1) K^2 - \Delta D_K K^2. \quad (1)$$

Only the differences in the rotational constants C and B and the quartic centrifugal distortion constants D_J , D_{JK} , and D_K between the electronically excited and the ground state are needed, since the rovibronic transi-

tions in the Q branch of the totally symmetric 14_0^1 two-photon band obey the selection rule $\Delta J = \Delta K = 0$. About 3400 Q-branch lines with J' and K' up to 101 were assigned in this way. Lines from the R and S branch, which are much weaker than the corresponding Q-branch lines,⁶ were only used to check uncertain assignments. Values of the spectroscopic constants obtained from a fit to the observed line positions have been recently reported.⁸

About 90% of the observed rotational lines can be interpreted with the model of the semirigid symmetric top. The remaining lines in the experimental spectrum are not found at the expected positions.⁶ This is due to the fact that the “light” rotational levels of the 14^1 vibronic state are coupled to rotational levels of other “dark” S_1 vibronic states, i.e., states which cannot be accessed in two-photon excitation.^{6,14} This coupling results in a splitting of the expected line into two components shifted to higher and lower energy. If we denote the energy of the “light” zero-order state $|1\rangle$ by E_1 and the energy of the “dark” zero-order state $|d\rangle$ by E_d , the energies E_a and E_b of the two eigenstates resulting from coupling with the coupling matrix element V can be calculated by first-order perturbation theory to be¹⁷

$$E_{a,b} = \frac{E_1 + E_d}{2} \pm \frac{1}{2} \sqrt{4V^2 + \delta^2}, \quad (2)$$

with $\delta = E_1 - E_d$. The state $|a\rangle$ is chosen to be the state with the higher energy. The transitions to the two eigenstates are both observed in the spectrum, since their wave functions are given by¹⁷

$$|a\rangle = \alpha |1\rangle - \beta |d\rangle \quad (3)$$

and

$$|b\rangle = \beta |1\rangle + \alpha |d\rangle \quad (4)$$

with

$$\alpha^2 = \frac{\sqrt{4V^2 + \delta^2} + \delta}{2\sqrt{4V^2 + \delta^2}} \quad (5)$$

and $\alpha^2 + \beta^2 = 1$, i.e., both contain a significant contribution from the “light” state $|1\rangle$ if the spacing δ of the zero-order states is not much larger than V and the “light” and “dark” rovibronic zero-order states are nearly degenerate. Due to the high signal-to-noise ratio in the spectrum,⁸ both lines resulting from the coupling can be observed even for a weak admixture of the “light” state, i.e., when $\delta > V$. If the residuals $E_1 - E_a$ and $E_1 - E_b$ are plotted against J' for constant K' , typical avoided crossing curves are found. E_1 is set equal to the expected energy of the “light” state according to Eq. (1). The typical shape of the avoided crossing curves is due to the fact that the rotational constant B' of the “dark” vibronic state is slightly larger than B' of the 14^1 state. For a certain value of J' , the “light” and the “dark” states are in exact resonance, but for smaller values of J' the energy of the “dark” state is slightly less than the energy of the “light” state, while for higher J' the order is reversed. The coupling of the two states leads to the observed repulsion, which is largest at the crossing point. Typical examples of this behavior are shown in Fig. 1 for $K' = 9$ and $K' = 14-17$. For $K' = 9$ even two crossings are seen, which are due to the coupling to two different “dark” states. The continuous shift of the crossing point in the curves for $K' = 14-17$ is due to additional differences in the K' dependence of

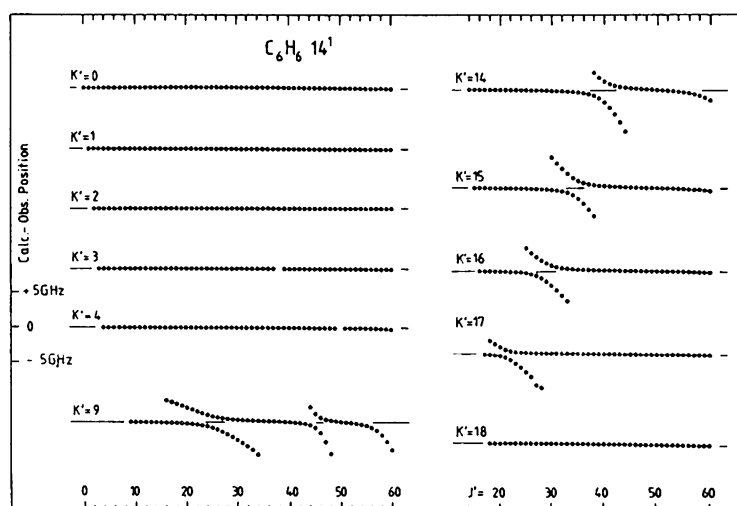


Fig. 1. Residuals (calculated – observed position) of rotational line frequencies in the 14_0^1 two-photon band of C_6H_6 as a function of the final-state quantum number J' for several K' . The avoided crossings are caused by the coupling of the “light” rotational states (labelled by the quantum numbers J' and K') in the 14^1 vibronic state to “dark” states in S_1 .

the energy of the "light" and "dark" states. For comparison, the residuals (calculated - observed position) are also shown for $K' = 0-4$ and $K' = 18$. Since these residuals are 0 within experimental accuracy, we can conclude that these states are unperturbed, i.e., they are pure rotational states of the 14^1 vibronic state. A number of additional avoided crossings have been found for K' values not shown in Fig. 1, but the majority of K' values do not show any shift and therefore are unperturbed. An exact spectroscopic model is presently developed to account for all the observed perturbations.

To find the value of the coupling matrix element, we deduce from Eq. (2) that

$$E_a + E_b = E_1 + E_d, \quad (6)$$

i.e., the average energy of the two coupled states is not changed by the coupling. Since E_1 can be calculated with good accuracy from Eq. (1) with the known rotational constants and E_a and E_b are the experimentally observed energies of the two eigenstates, E_d and δ can be easily derived. With E_a and E_b known experimentally and E_1 , E_d , and δ determined, Eq. (2) can be solved for the coupling matrix element V :

$$V = \sqrt{-(E_a - E_1)(E_b - E_1)} \quad (7)$$

and a value of V can be calculated for every pair of observed coupled states. The result is shown for the $K' = 9, 15,$ and 17 levels in Fig. 2. A strong dependence of the coupling matrix element on both the J and K rotational quantum numbers is found. This shows that the observed perturbations are *not* due to anharmonic coupling or parallel Coriolis coupling. Instead, the rotational dependence of V can be well represented by the one expected for a particular type of rotation-vibration coupling commonly referred to as x, y or perpendicular Coriolis coupling with the selection rule $\Delta K = \pm 1$. For perpendicular Coriolis coupling with $\Delta K = -1$, the coupling matrix element is known to be $V = V_0 \sqrt{(J+K)(J-K+1)}$.¹⁸ Values of V calculated according to this formula are included in Fig. 2 as lines. Different values for V_0 had to be used for $K' = 9$ on the one hand ($V_0 = 34.4$ MHz), and $K' = 15$ and $K' = 17$ on the other hand ($V_0 = 38.2$ MHz) to get reasonable agreement between the calculated and observed values of V . As the same value of V_0 can be used to reproduce the J dependence of the coupling elements found for $K' = 15$ and $K' = 17$ states, we can conclude that they are coupled to the same "dark" vibronic state, but to different rotational states of this "dark" state.

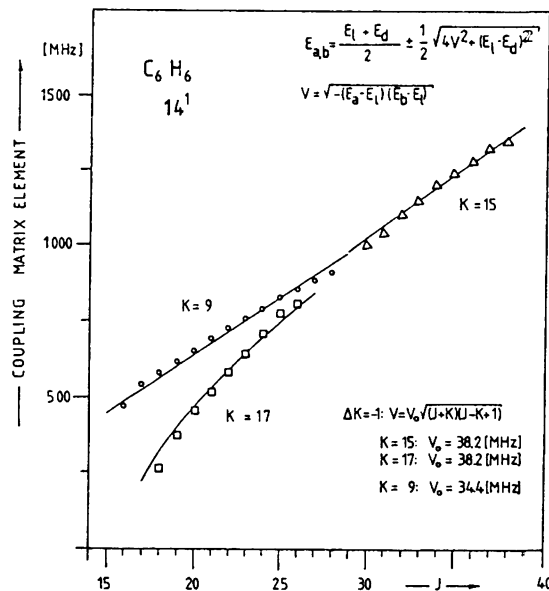


Fig. 2. Rotational dependence of the coupling matrix element V for the coupling between the "light" and "dark" states. The lines represent the result of a calculation for perpendicular Coriolis coupling.

To identify the "dark" states, emission spectra of both unperturbed and perturbed rovibronic states have been recently recorded.¹¹ The emission spectrum of an unperturbed state shows the structure expected for the 14^1 vibronic state. A detailed analysis of the spectrum has been given. For perturbed states, additional lines appear in the spectrum, which are due to the admixture of a "dark" state. The analysis showed that the "dark" state coupled to the $K' = 9$ states around $J' = 25$ is the e_{2u} vibrational angular momentum component $l_{10} = \pm 1, l_{16} = \mp 1$ of the state $5^1 10^1 16^1$,¹¹ while the emission spectra of the $K' = 15$ states around $J' = 35$, of the $K' = 17$ states around $J' = 22$, and of the $K' = 9$ states around $J' = 46$ show identical indications of coupling to the e_{2u} vibrational angular momentum component $l_6 = \pm 2$ of the state $6^2 11^1$ and/or the e_{2u} vibronic state $3^1 16^1$.¹¹ The fact that the "dark" state coupled to the $K' = 9$ states is different from the one coupled to the $K' = 15$ and $K' = 17$ states agrees well with the different values of V_0 observed for the respective crossings. A further indication of this difference will be seen in Section 3.2.2, where the decay behavior of the "dark" states is discussed.

The symmetry of all three "dark" vibrational states identified with the help of the emission spectra is e_{2u} . To confirm this determination, we can also use the result that the rotational dependence of the coupling

matrix element points to perpendicular Coriolis coupling as the coupling process. The symmetry selection rule¹⁸ for perpendicular Coriolis coupling in the point group D_{6h} of benzene,

$$\Gamma(|d\rangle) \otimes \Gamma(R_{x,y}) \otimes \Gamma(14^1) \supset a_{1g}, \quad (8)$$

determines the symmetry of the dark vibrational state $|d\rangle$ to be e_{2u} , since $\Gamma(14^1) = b_{2u}$ and $\Gamma(R_{x,y}) = e_{1g}$. Both arguments show that the "dark" vibrational states are of e_{2u} symmetry and therefore of different symmetry than the b_{2u} normal mode ν_{14} .

3.2. Decay Behavior of Single Rovibronic States

3.2.1. Unperturbed States

To investigate the decay behavior of single rovibronic states, the pulsed laser setup described in Section 2 is used. The spectral resolution of 70 MHz achieved in this experiment is still sufficient to resolve most of the rovibronic transitions. This is demonstrated in Fig. 3 for the region around -675 GHz from the rotationless origin. Comparison with the spectrum obtained by excitation with the CW laser (Fig. 3, bottom of right-hand box) allows us to detect which of the spectral features seen in the spectrum obtained by pulsed excitation is due to single rovibronic transitions. It should be noted that the region shown in Fig. 3 corresponds to a part of the Q branch with a comparatively dense structure of lines with very high J' and K' values. As an example, the line $J'_{K'} = 67_{61}$ is indicated. Lines with such high values of the rotational quantum numbers can only be observed under room temperature con-

ditions and not under jet conditions. Due to the Doppler width of 1.7 GHz, none of the single transitions in the shown part of the spectrum would be resolved in a Doppler-limited experiment. Since single rovibronic lines are resolved in the spectrum recorded with the pulsed light source, the corresponding excited rovibronic states can be selectively excited in our experiment. This allows us to record the decay curve for these states. It is important to note that in the Doppler-free two-photon experiment *all* molecules in the ground state belonging to a particular transition can be excited independent of their individual velocity component and that excitation of molecules whose transition frequency is also within the Doppler width does not occur. The spectral coherence width of the pulsed laser light is indicated in the CW spectrum as a hashed area around the $J'_{K'} = 67_{61}$ line, and we see that it is larger than the measured line width and consequently also larger than the homogeneous width of the line. Therefore, a coherent excitation of the particular rotational state is guaranteed.

As an example for the fluorescence decay behavior of a state which is found to be unperturbed from the analysis of the CW spectrum, the measured decay curve of the $J'_{K'} = 67_{61}$ state is shown in the left part of Fig. 3. This curve is seen to be single exponential within the experimental accuracy over more than three decay times. Decay curves were measured for a number of different unperturbed states with low J' and K' , high J' and K' , and high J' and low K' . The experiments were performed with sample pressures below 0.1 Torr to

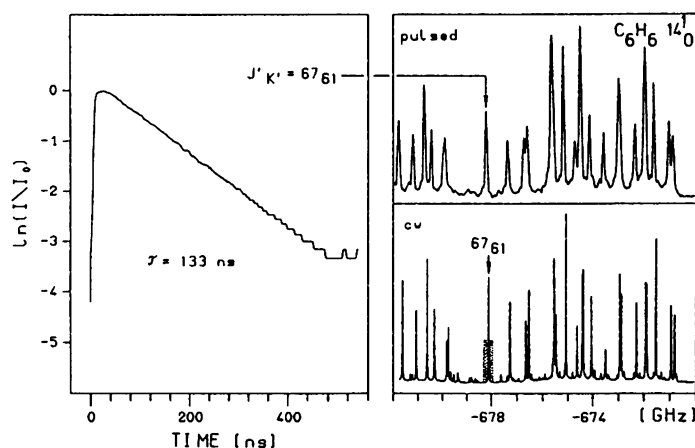


Fig. 3. Part of the Q branch of the Doppler-free two-photon excitation spectrum of the 14^1_0 band of C_6H_6 as recorded with the pulsed laser and the CW laser. The coherence width of the pulsed laser is indicated as a hashed area around the $J'_{K'} = 67_{61}$ transition in the spectrum obtained by CW excitation. In the left part of the figure, the fluorescence decay curve after pulsed excitation of the $J'_{K'} = 67_{61}$, 14^1 rovibronic state is shown on a semilogarithmic scale.

prevent any influence of collisional deactivation on the decay curves.¹⁴ All decays were found to be single exponential. The curves were evaluated according to $I(t)/I(0) = \exp\{-t/\tau\}$, and the resulting values of τ are summarized in Table 1. There is no rotational dependence of the decay time found even for this very large range of rotational quantum numbers. Lack of any rotational dependence of the decay time was already reported in our previous work,¹⁴ but in this earlier investigation the range of rotational quantum numbers was much smaller. The exponential character of the decay and the lack of any rotational dependence show that the decay of excited benzene molecules is determined by relaxation in the statistical limit. The main contribution to this relaxation is the electronic non-radiative decay,¹ which is believed to be due to ISC to

Table 1. Measured Decay Times for Several Selectively Excited Rotational Levels within the 14^1 Vibronic State of C_6H_6 , which Were Found To Be Unperturbed in the Analysis of the Spectrum

Quantum number values	Rotational state in $14^1, J'_K$	Decay time τ (ns)
Low J' , low K'	5_4	132
	7_7	135
	12_9	136
	14_4	135
	16_7 (B)	134 ± 4
	16_9	136
	17_{11} (B)	126 ± 5
	18_8	128
	18_{14} (B)	126 ± 5
	19_6	134
	19_6 (B)	129 ± 6
	High J' , high K'	25_{20} (B)
30_{27}		132
33_{31}		136
50_{37}		137
67_{61}		133
High J' , low K'	21_5 (B)	127 ± 4
	22_{15}	133
	27_7	134
	28_8	132
	28_{17}	136
	43_6	134
47_{15}	133	

Values marked by (B) were measured with the boxcar integrator and have the corresponding error indicated. All other values were measured with the wave form processing system to an accuracy of ± 3 ns.

the quasi-continuum of triplet states.¹⁹ Since any possible rotational dependence of the radiative decay was previously excluded,¹⁴ we can conclude that the non-radiative decay is completely independent of the particular rotational state excited.

From the values given in Table 1, an average decay time of $\langle\tau\rangle = 133$ ns is determined. This value is slightly longer than the value of $\langle\tau\rangle = 126$ ns reported in our previous work,¹⁴ but the present decay curves, which were mainly measured with the wave form processing system, are believed to be more accurate than the older ones. The value of 133 ns is significantly longer than the value of $\tau = 115$ ns found in our previous measurements²⁰ with broadband excitation and consequently without rotational selection. It will be shown in Section 3.2.2 that the decay of perturbed states is much faster and, since we know from the spectral analysis of the 14^1_0 band that about 10% of all lines are perturbed, averaging of the decay times of unresolved lines yields a smaller value for the decay time.

3.2.2. Perturbed States

After we have seen that the decay behavior of unperturbed states is independent of the particular rotational quantum numbers J and K , we want to investigate the decay behavior of perturbed states. In Fig. 4, part of the Q-branch spectrum of the 14^1_0 band around the perturbed $(21_{17})_a$ state is shown under the resolution of both the CW laser and the pulsed amplified light. It can be seen that both the $(21_{17})_a$ and the neighboring unperturbed 18_8 state are well resolved under pulsed excitation conditions. The decay curves obtained after selective excitation of both states are shown in the lower part of Fig. 4. Both curves represent single exponential decays in accordance with the statistical limit character of the nonradiative decay responsible for the total decay,¹ but the decay time of the perturbed state is found to be significantly shorter. The decay curves of a number of perturbed states with $K' = 9, 15,$ and 17 were measured, and the values of the decay times are summarized in Table 2. All decays of perturbed states are shorter than the value of $\langle\tau\rangle = 133$ ns found for the unperturbed states.

To discuss quantitatively the observed shortening of the decay time of perturbed states, we note that the width $\gamma_{a,b} = 1/(2\pi\tau)$ of the eigenstates $|a\rangle$ and $|b\rangle$ resulting from the coupling between the "light" and the "dark" states is given for the strong coupling limit ($V \gg \gamma_l, \gamma_d$) present in the investigated situation by^{21,22}

$$\gamma_{a,b} = c_1^2(\gamma_l - \gamma_d) + \gamma_d \quad (9)$$

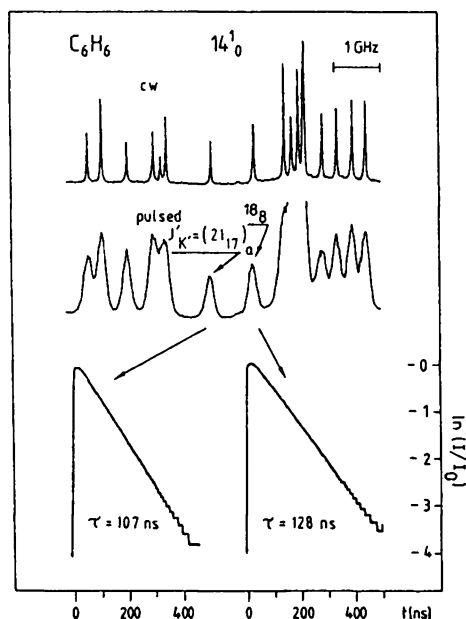


Fig. 4. Part of the Q branch of the Doppler-free two-photon excitation spectrum of the 14_0^1 band of C_6H_6 as recorded with the pulsed laser and the CW laser. In the lower part of the figure, the fluorescence decay curves after pulsed excitation of the perturbed $J_{K'} = (21_{17})_a$ and the neighboring unperturbed $J_{K'} = 18_8$ rovibronic states are shown on a semilogarithmic scale. Comparison between the CW and pulsed spectra shows that both excitation lines are well resolved even under the lower resolution of the pulsed experiment.

Table 2. Measured Decay Times for Several Selectively Excited Rotational Levels within the 14^1 Vibronic State of C_6H_6 , which Were Found To Be Perturbed in the Analysis of the Spectrum

Rotational state in $14^1, J_{K'}$	Decay time τ (ns)	Line width γ [MHz]	c_1^2
$(24_9)_b$	87	1.83	0.37
$(25_9)_a$	96	1.66	0.51
$(26_9)_b$	98	1.62	0.61
$(27_9)_b$	99	1.61	0.71
$(28_9)_b$	110	1.45	0.79
$(21_{17})_a$	107	1.49	0.62
$(22_{17})_a$	105	1.52	0.36
$(22_{17})_b$	111	1.43	0.64
$(35_{15})_a$	104	1.53	0.41

All values were measured with the wave form processing system to an accuracy of ± 5 ns. In addition to the decay time, the value of the line width calculated according to $\gamma = 1/(2\pi\tau)$ and the content c_1^2 of the “light” 14^1 state in each quasi-eigenstate are given.

with $\gamma_l = 1/(2\pi\tau_l)$ the width of the “light” state and $\gamma_d = 1/(2\pi\tau_d)$ the width of the “dark” state. c_1^2 is the content of the “light” zero-order state in the eigenstate $|a\rangle$ or $|b\rangle$, which is equal to α^2 or β^2 according to Eqs. (3) and (4). c_1^2 can be calculated from Eq. (5), since both V and δ can be obtained from measured quantities as has been discussed in Section 3.1. The values of c_1^2 are included in Table 2.

The experimental observation that the decay time of perturbed states is shorter than that of unperturbed ones means that the width γ_d of the “dark” states is larger than the width of the “light” rotational states of the 14^1 vibronic state of $\gamma_l = 1/(2\pi\tau) = 1.20$ MHz. Both γ_l and γ_d are determined by the nonradiative relaxation to the triplet manifold and possibly to the highly excited S_0 electronic state, and to a lesser degree by the radiative decay.¹⁹ It is important to note that this relaxation is already contained in the definition of the “light” and “dark” states as zero-order states, i.e., that they are not true Born–Oppenheimer states. Due to the different symmetry of the “light” and the “dark” states, the particular states to which radiative and nonradiative relaxation leads are different and it is justified to describe the width of the eigenstates $|a\rangle$ and $|b\rangle$ by Eq. (9).²² The resulting coupling scheme is shown schematically in Fig. 5. The width of the zero-order levels is due to coupling of the “light” and the “dark” states to separate quasi-continua and in addition there exists a coupling between the two states. The quasi-eigenstates are coupled to both continua with different strengths according to their content of “light” and “dark” states.

From the lack of rotational dependence of the decay of pure 14^1 rotational states we can conclude that the different rotational states of the “dark” zero-order vibronic states have also an equal width γ_d . If we use all perturbed states belonging to the same “dark” state to determine the width of this “dark” state according to Eq. (9), a common zero-order width should result. The measured dependence on c_1^2 of the width of all investigated quasi-eigenstates is shown in Fig. 6. The solid lines represent the result of a least-squares fit to the measured points according to the dependence proposed in Eq. (9). Since the $K' = 15$ and $K' = 17$ states are known to couple to the same “dark” state, they are used in one fit. As a result of this fit procedure, the following zero-order line widths are obtained: for $5^1 10^1 16^1$, $\gamma = 2.24$ MHz; $\tau = 71$ ns; for $6^2 11^1/3^1 16^1$, $\gamma = 1.77$ MHz; $\tau = 90$ ns.

While no value of the decay time of the $5^1 10^1 16^1$ state was reported previously, a value for the $6^2 11^1/3^1 16^1$ state which deviates somewhat from the present one was given in our previous work.¹⁴ This deviation is due

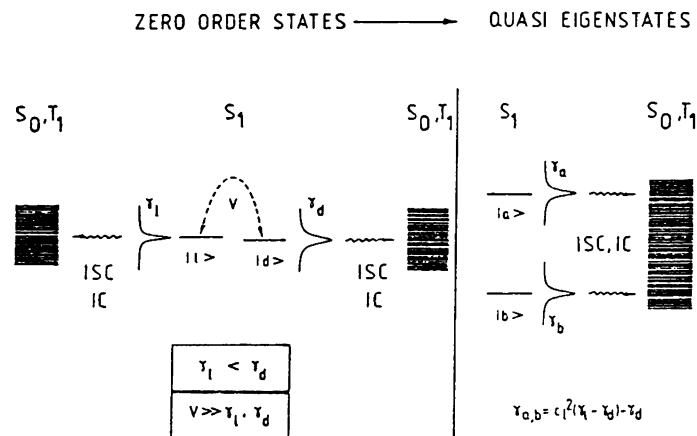


Fig. 5. Coupling scheme of the “light” zero-order state $|1\rangle$ and the “dark” zero-order state $|d\rangle$ in S_1 . Both zero-order states have different line widths due to a faster electronic nonradiative relaxation process of the “dark” state ($\gamma_l < \gamma_d$). The line widths of the resulting quasi-eigenstates are shown on the right side in the strong coupling limit.

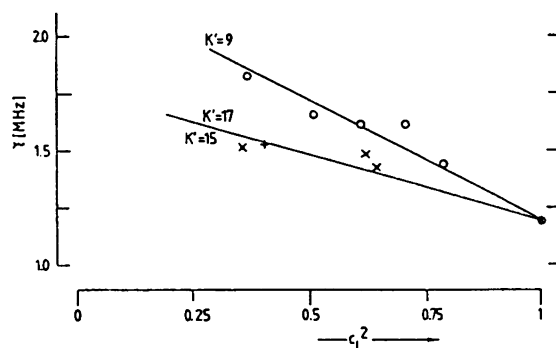


Fig. 6. Line widths γ of several perturbed rotational states in the 14^1 vibronic state of C_6H_6 as determined from the measured decay time τ according to $\gamma = 1/(2\pi\tau)$. Values for $K' = 9$ states are marked by \circ , for $K' = 15$ states by $+$, and for $K' = 17$ states by \times . The values of γ are displayed as a function of the content c_l^2 of the “light” state in each quasi-eigenstate. The straight lines are the result of a fit of the line width γ_d of the unperturbed “dark” state according to the model explained in the text.

to a number of reasons: (i) In the earlier investigation,¹⁴ decay curves were measured with the box car and not with the wave form processing system, which yields more accurate values. (ii) Only one perturbed state was investigated previously, while the improved spectral resolution of the present investigation allowed us to investigate a larger number of perturbed states (compare also Section 2). (iii) The “light” content c_l^2 of the $(21_{17})_a$ state was estimated to be 0.5, while it is now known to be 0.62.

The decay times of the zero-order “dark” states are indeed significantly shorter than that of the “light” 14^1 state, as already discussed qualitatively above. They are within the range reported recently for a number of different benzene S_1 states at similar vibrational excess energy.^{23,24} A strong variation of the decay behavior with the particular vibrational identity of the “dark” states is observed. In particular, the $5^1 10^1 16^1$ state, which solely comprises out-of-plane modes, decays quite fast in accordance with experimental observations²³ and theoretical considerations²⁵ showing that out-of-plane modes lead to a faster nonradiative decay.

4. SUMMARY AND CONCLUSION

Doppler-free two-photon fluorescence excitation spectra of the 14^1_0 band of benzene, C_6H_6 , at an experimental resolution of 15 MHz were analyzed to identify perturbed rotational states in the 14^1 vibronic state. The perturbations are due to rotation–vibration coupling of the “light” 14^1 state to “dark” background states within the S_1 electronic state. The vibrational identity of the “dark” states has recently been identified with the help of fluorescence emission spectra of single rovibronic states.¹¹ The observed shift of the perturbed states from the expected position of the “light” state was used to deduce the value of the coupling matrix element for every pair of quasi-eigenstates resulting from the coupling and the degree of admixture of the “dark” state. The rotational dependence of the coupling matrix element is found to agree with the one expected for perpendicular Coriolis coupling.

To study the dynamic behavior of single rovibronic states, the fluorescence decay curves after selective

pulsed excitation of the states were recorded. The decay was found to be single exponential for both perturbed and unperturbed states in accord with the statistical limit electronic nonradiative decay of S_1 benzene. For unperturbed states, the decay time was found to be independent of molecular rotation for the large range of rotational states investigated. This shows that the quasi-continuum of triplet and highly excited S_1 states responsible for nonradiative decay is very smooth and shows no sign of varying density of states. The decay time of perturbed states was found to be significantly shorter in accordance with the result of our previous work,¹⁴ and in addition we were able to show that it depends on the degree of admixture of the respective "dark" state. To account for this observation quantitatively, a model is presented which describes the investigated situation as a coupling in the strong coupling limit between two rovibronic states with varying energy mismatch and finite homogeneous width due to the additional coupling to different quasi-continua. The evaluation of the observed decay times according to this model rendered the decay times for the two "dark" vibronic states coupled to the 14^1 state. They are considerably shorter than the decay time of the 14^1 state.

The present investigation shows that the decay behavior of vibronic states which cannot be directly excited by optical transitions can be determined through the precise analysis of perturbations in the rotationally resolved spectrum and the measurement of the decay behavior of the quasi-eigenstates resulting from the coupling responsible for the perturbations. The precise analysis of the spectrum is only possible if a large number of lines are observed, i.e., if the spectrum is recorded at room temperature. For the large molecules of interest, Doppler-free techniques are needed to completely resolve the rotational structure.

The "dark" background states are typically combination states of various vibrational modes. The understanding of the dynamic behavior of such combination states is of particular importance for the understanding of the molecular decay at higher excess energy, since combination states present the majority of all vibrational states at higher vibrational excess energy, and couplings between the different vibrational states become very frequent at these energies. Extrapolation of the behavior found at low excess energy to the high energy range should allow a good understanding of the decay behavior at the chemically relevant high excess energy regime.

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