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The projective geometry of ambiguous surfaces

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Pathways for intramolecular relaxation in S_1 benzene

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Sub-Doppler spectra of various one- and two-photon vibronic bands of benzene are discussed and analysed to determine the pathways of intramolecular relaxation for S_1 benzene. New results are presented for the $14_0^1 1_0^1 16_2^2$ band of C_6H_6 and the $14_0^1 1_0^2$ band of $^{13}C_6H_6$. The decay behaviour depends strongly on the excess energy and the rotational quantum numbers rather than on the vibrational character and symmetry of the excited state. At low vibrational excess energy the pathway for intramolecular relaxation is a coupling in the strong limit between pairs of states in S_1 leading to shifts of lines, whereas at intermediate excess energy coupling in the weak limit to background states in S_1 is present. These background states are strongly broadened due to a fast electronic non-radiative process. The intramolecular relaxation is found to be initiated by the coupling to the broadened S_1 background states and energy can flow via these states to the T_1 or S_0 state. The rotationally selective disappearance of lines is believed to be due to an intricate interplay of the rotational dependence of the coupling matrix elements and accidental resonances, which lead to interference of possible decay channels.

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1. Introduction

Benzene has long been a prototype for the study of intramolecular energy relaxation in large molecules. Due to its high symmetry (D_{6h}), detailed spectroscopic studies are possible despite the large number of vibrational degrees of freedom (Ziegler & Hudson 1982). A fluorescence quantum yield of S_1 benzene smaller than unity was observed under collision free conditions (Anderson & Kistiakowski 1968; Douglas & Mathews 1968; Parmenter & White 1969) and it was concluded that a non-radiative electronic decay takes place which is irreversible on the timescale of fluorescence and occurs in the statistical limit (Robinson 1967; Jortner *et al.* 1969; Parmenter 1972). Much work has been done to identify the pathways leading to the non-radiative decay, but important questions still remain. In particular, the rapid increase of the non-radiative decay rate at about 3000 cm^{-1} vibrational excess energy in S_1, which was termed 'channel three' (Callomon *et al.* 1972), has attracted much attention (for a review see Riedle *et al.* 1990).

The concept behind our detailed investigation of intramolecular relaxation processes in benzene is to study first the spectroscopy and dynamics of states of various symmetries at low vibrational excess energy to achieve a thorough understanding of the coupling matrix elements of importance. Next we turn to vibronic states at intermediate excess energy (i.e. the onset of 'channel three'), where

[1]

sufficient selectivity for a precise investigation can still be expected. Finally, the results are generalized to interpret the situation at high excess energy, where detailed studies have not been possible.

The concept described above requires the selective excitation of single rovibronic quantum states and the investigation of their dynamical behaviour. We were able to show that Doppler-free two-photon fluorescence excitation spectroscopy can be used to resolve completely the rotational structure of two-photon states under room temperature conditions. cw excitation (Riedle *et al.* 1981; Riedle & Neusser 1984; Sieber *et al.* 1988) provides the highest spectral resolution ($\Delta\nu \approx 5$ MHz), while pulsed excitation ($\Delta\nu \approx 70$ MHz) makes possible decay-time measurements of single rovibronic states (Schubert *et al.* 1986 *a, b*). Single 'one-photon' states became accessible by combining a collimated molecular beam and a frequency-doubled narrow band-width laser ($\Delta\nu_{\mathrm{uv}} \approx 100$ MHz) as a probe yielding rotationally resolved one-photon spectra at moderate rotational cooling (Riedle *et al.* 1989, 1990). The experimental arrangements have been described previously (Riedle & Neusser 1984; Sieber *et al.* 1988; Riedle *et al.* 1989; Weber *et al.* 1990).

Here we present a brief summary of the state-selected spectroscopic and kinetic investigation of benzene at various excess energies in S_1. As typical for low excess energies the 14^1 state will be briefly discussed, but other states have also been studied (Riedle *et al.* 1984, 1989; Sieber *et al.* 1988). For intermediate excess energy a brief review of the previously analysed $14_0^1 1_0^2$ two-photon band and the $6_0^1 1_0^3$ one-photon band will be given. To broaden the experimental basis additional Doppler-free two-photon spectra of the $14_0^1 1_0^1 16_2^2 (l_2^2)$ band of C_6H_6 and the $14_0^1 1_0^2$ band of $^{13}C_6H_6$ are presented. Finally, theoretical models which can explain the spectroscopic and dynamic findings, particularly in the beginning of the 'channel three' region, will be discussed.

2. States at low excess energy (less than 2000 cm⁻¹): the 14¹ state of C₆H₆ as an example

The 14^1 state of C_6H_6 at 1571 cm^{-1} vibrational energy above the zero point of S_1 can be excited through the strong two-photon absorption 14_0^1. Doppler-free cw spectra with thousands of well separated rovibronic lines of 15 MHz width were recorded at room temperature. Individual transitions were assigned up to $J' = K' = 101$ (von Bargen 1989; Schubert *et al.* 1990) and the frequencies of 90% of these lines could be well fitted by a semirigid symmetric top model. The remaining lines are shifted from the expected position or split into two components separated by some GHz (Riedle *et al.* 1984). The appearance of these isolated perturbations is due to the fact that the 'light' 14^1 state is coupled locally to 'dark' states within S_1 through higher-order rotation–vibration couplings (Riedle *et al.* 1984). From emission spectra of the single eigenstates (Schubert *et al.* 1989) we were able to determine the identity of the three 'dark' states involved. An exact modelling of the coupling scheme is complicated by the fact that the 'dark' states are expected to couple among themselves by anharmonic or l-type resonances (von Bargen 1989). The importance of l-type resonances in the S_1 state of benzene was recently deduced from the analysis of bands involving multiply degenerate vibronic states (Riedle & Pliva 1990).

Pulsed excitation allowed the decay of single rotational states of the 14^1 vibronic state to be measured. The decay was found to be singly exponential in all cases investigated (Schubert *et al.* 1986 *a*, 1989). For states that are not perturbed by a

coupling within S_1 (unperturbed states) the decay time was found to be independent of the molecular rotation, while for perturbed states the decay times are shorter due to the admixture of the 'dark' states which decay faster. The fluorescence quantum-efficiency of all the states, including the 'unperturbed' ones, is much less than unity (Parmenter & White 1969), indicating an additional general background perturbation. The rotationally independent decay of the 'unperturbed' states points to an electronic non-radiative relaxation process to T_1, in the statistical limit.

To summarize, the rotationally resolved two-photon spectra at low vibrational excess energy show *isolated* perturbations which can be understood as rovibrational coupling in the strong limit to discrete background states in S_1. This coupling causes a mixing of the vibrational character of the resulting quasi-eigenstates and therefore a rotational dependence of the non-radiative decay, which otherwise would not depend on the rotation of the molecule. The behaviour of states excited through one-photon transitions (i.e. of differing symmetry and parity) is found to be qualitatively the same (Riedle *et al.* 1989).

3. States at intermediate vibrational excess energy (2000–3500 cm⁻¹)

For explanation of the 'channel three' phenomenon the intermediate excess energy range is of particular interest. In this section we present the results for four selected states (three in C_6H_6 of differing symmetry and parity and one in $^{13}C_6H_6$) to probe the influence of the slightly varying densities of states and differing accidental degeneracies.

(a) The $14^1 1^2$ state of C_6H_6

The first state at intermediate excess energy to be investigated with rotational resolution was the $14^1 1^2$ state of C_6H_6 at an excess energy of 3412 cm⁻¹ (Riedle *et al.* 1982). In the blue part (low rotational energy) of the ^qQ-branch of the $14^1_0 1^2_0$ band only (unshifted) $K = 0$ lines were seen, in the fluorescence excitation spectrum, while further to the red (higher rotational energy) the only observed structure seemed to be due only to lines with $K \approx J$. This finding was interpreted as due to predominant coupling in the weak limit of $14^1 1^2$ to a strongly diffusely broadened background state which allows only a minority of uncoupled (or weakly coupled) states to survive in the fluorescence excitation spectrum. The strong K-dependence of decay rates was supposed to be due to the rotational dependence of the coupling matrix element, i.e. parallel Coriolis coupling for the blue part and perpendicular Coriolis coupling for the red part of the band (Riedle & Neusser 1984).

It was also possible to measure the decay times and the homogeneous collisionless widths of the $K = 0$ lines in the blue part of the $14^1_0 1^2_0$ band. The decays were all found to be singly exponential within the experimental accuracy. The values of the decay rates determined from the time-resolved and frequency-resolved experiments agreed quite well, indicating that in our experiment single quantum states were observed. This was one of the first examples of a combined measurement of the dynamic behaviour of a large molecular system in both time and frequency domains.

(b) The $6^1 1^3$ state of C_6H_6

To test whether the strong rotational dependence of the non-radiative decay rates in the intermediate excess energy range is a specific property of the $14^1 1^2$ (B_{2u}) state or rather a property of all S_1 states at comparable energy, rotationally resolved

single-photon spectra of the $6_0^1 1_0^3$ band of C_6H_6 leading to the $6^1 1^3$ (E_{1u}) state at 3287 cm^{-1} excess energy were recorded (Riedle *et al.* 1990). The fluorescence excitation spectrum at a rotational temperature of 15 K showed fewer sharp lines than expected, with variations in line widths, deviations from expected line intensities and a broad background in the dense Q- and R-branches. This points again to a rotationally dependent decay behaviour of the individual rotational states, and strong variations were indeed found in measured decay times. Due to its heavily perturbed character the irregular $6_0^1 1_0^3$ fluorescence excitation spectrum could not be rotationally assigned.

To identify the longest-lived states in the spectrum as an aid to assignment, a delayed two-colour two-photon ionization (MPI) spectrum of the $6_0^1 1_0^3$ band was measured under identical beam conditions. This spectrum is greatly simplified and regular, and it could readily be assigned (Riedle *et al.* 1990). It was found to consist only of transitions leading to states with $K' \leqslant 3$ and states with $K' = 10$, $l'_6 = +1$ or $K' = 13$, $l'_6 = -1$. All the other states appear to decay rapidly due to coupling to broadened dark background states in S_1. The appearance of states with low values of K' is in line with the behaviour observed in the $14^1 1^2$ state, but for the $K' = 10$, $l'_6 = +1$ and $K' = 13$, $l'_6 = -1$ states a new situation arises and an extended model was invoked which incorporates interferences between the decay channels leading to different background states (Riedle *et al.* 1990) (see below).

(c) *The $14^1 1^1 16^2$ state of C_6H_6*

Due to the numerous selection rules of the highly symmetric benzene molecule and the restrictive Franck–Condon factors, only few vibronic states in the energy range of the onset of 'channel three' can be reached through either one- or two-photon transitions. A band which appears with reasonable strength in the vibrationally resolved two-photon spectrum is the $14_0^1 1_0^1 16_2^2$ sequence band. Since this transition leads to the $14^1 1^1 16^2$ state at 2963 cm^{-1} it is of particular interest, for this energy is close to the threshold of 'channel three'.

The rotationally resolved spectrum of the $14_0^1 1_0^1 16_2^2$ band was recorded in a cw two-photon experiment (Riedle & Neusser 1984; Sieber *et al.* 1988) at a vapour pressure of 1.6 Torr, corresponding to a pressure-broadened resolution of 25 MHz. The blue edge of the ^qQ-branch is shown in the lower trace of figure 1. It would be expected to display a rotational structure quite similar to that of the corresponding part of the 14_0^1 band (see, for example, figure 2 in Sieber *et al.* (1988)) since both bands involve totally symmetric transitions. The general increase of line intensities with increasing distance to the red from the rotationless origin is indeed observed, but in the $14_0^1 1_0^1 16_2^2$ band a much larger variation of intensities is seen than in the regularly behaved 14_0^1 band, or in the spectrum calculated with constants from the analysis of the experimental spectrum shown in the upper part of figure 1. The $14_0^1 1_0^1 16_2^2$ band leads from the triple degenerate 16_2 state to the triple degenerate $14^1 1^1 16^2$ state and complications due to these degeneracies might be invoked to explain the observed variations; but comparison with sequence bands of lower excess energy shows this not to be true. Therefore, the large variation of line intensities has to be an intrinsic property of the $14^1 1^1 16^2$ state, caused by a rotationally selective coupling process, rather than a property of the type of transition.

To obtain quantitative information on the observed variations in the line intensities the spectrum was assigned and some of the assignments are shown above the experimental spectrum in figure 1. It is evident that the line intensities decrease
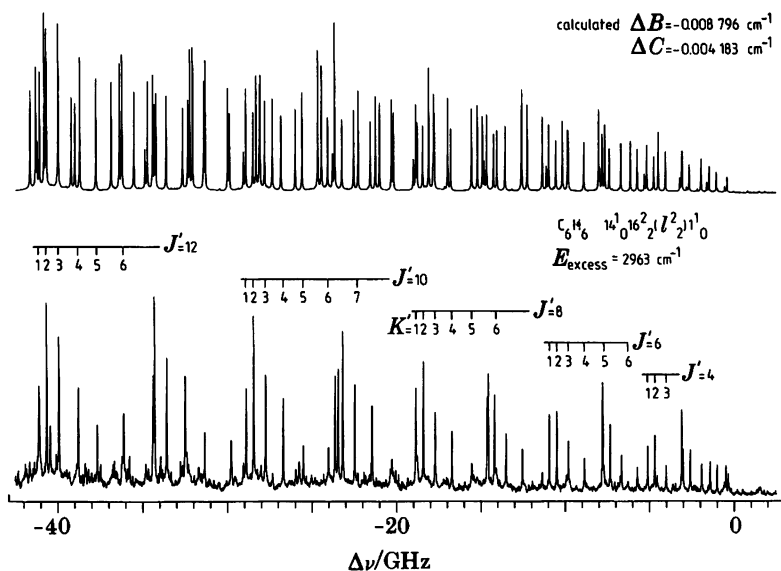
Figure 1. The lower trace shows part of the ^qQ-branch of the Doppler-free cw two-photon fluorescence-excitation spectrum of the $14^1_0 1^1_0 16^2_2 (l^2_2)$ band of C_6H_6 at an experimental resolution of 25 MHz. The $14^1 1^1 16^2$ state reached by this transition is of particular interest, because its vibrational excess energy of 2963 cm^{-1} is very close to the onset of 'channel three' at 3000 cm^{-1}. Some assignments are indicated above the spectrum. The upper trace shows the regular ^qQ-branch spectrum calculated with the values of the rotational constants determined from the analysis of the experimental spectrum. For a discussion of the differing intensities see text.

progressively with increasing K'. (An intensity alternation in the calculated spectrum reflects nuclear statistical weights.) The peak areas of the transitions were measured and divided by the theoretically expected intensities. The resulting normalized intensities scale as K'^{-2}. The line positions deviate only slightly from those expected. This situation is interpreted as coupling in the weak limit to a non-fluorescing quasi-continuum or a broadened background state with a matrix element that scales linearly with K'. The coupling also noticeably broadens lines with higher values of K' in addition to decreasing fluorescence quantum-yields. We therefore conclude that in the $14^1 1^1 16^2$ state the onset of rotationally dependent non-radiative decay with increasing K' is still slow enough to see lines over a range of K' values. This is in contrast to $14^1 1^2$ in which only the $K' = 0$ states decay slowly and are hence prominent in the fluorescence excitation spectrum, whereas lines with $K' \neq 0$ are already totally quenched. The $14^1 1^1 16^2$ level at 2963 cm^{-1} lies only 237 cm^{-1} above $14^1 1^1 16^1$ and 474 cm^{-1} above $14^1 1^1$. Fluorescence from both of these levels is rotationally complete and with the intensities expected.

The analysis of the $14^1_0 1^1_0 16^2_2$ band still contains a number of unsolved details, such as the total disappearance of the $K' = 0$ lines, a splitting of the $K' = 1$ lines for odd values of J' and the observation of an isolated perturbation for the $K' = 4$ states. These observations and the assignment of the particular vibrational angular momentum l-components observed in the spectrum will be discussed elsewhere (Somers *et al.* 1990).
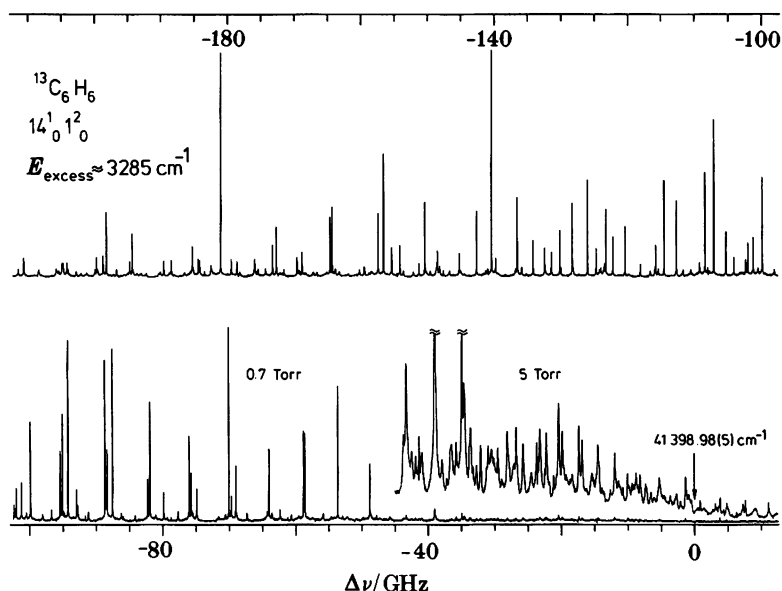
Figure 2. The main traces show part of the ^qQ-branch of the $14_0^1 1_0^2$ band of $^{13}C_6H_6$ as excited with the cw laser at a sample pressure of 0.7 Torr†. The typical band-edge seen in regular spectra of benzene cannot be seen, and the observed number of lines is much lower than expected. The insert shows part of the same spectral region at a sample pressure of 5 Torr. Under these conditions the typical rise of the signal strength with decreasing energy away from the band centre as expected for a Q-branch of a totally symmetric two-photon band is observed, and reveals the location of the rotationless origin at $\nu_{00} = 41\,398.98(5)$ cm^{-1}.

(d) The $14^1 1^2$ state of $^{13}C_6H_6$

Additional information on the electronic decay of S_1 benzene can be obtained from the spectra of other benzene isotopes of D_{6h} symmetry. These should display a similar selectivity of coupling due to the high symmetry, but the densities of states are different and differing accidental degeneracies with background states can occur. We were able to record the Doppler-free two-photon spectrum of the $14_0^1 1_0^2$ band of $^{13}C_6H_6$ in a cw experiment (Riedle & Neusser 1984; Sieber *et al.* 1988) at room temperature and to compare it with the previously measured and analysed spectrum of the 14_0^1 band at low excess energy. Part of the spectrum with tentative assignment was already shown in figure 4 of Dietz & Fischer (1987). The vibrational assignments agree with those of Nibu & Goodman (1986).

(i) Rotational assignment of the $14_0^1 1_0^2$ band

The main 25 cm^{-1} of the Doppler-free two-photon spectrum of the ^qQ-branch of the $14_0^1 1_0^2$ band of $^{13}C_6H_6$ were recorded at a sample pressure of 0.7 Torr and an experimental resolution of 15 MHz. Less than 10% of the expected number of rotational lines appeared. The part of the band that contains the highest density of lines is shown in figure 2. No strong lines were found further to the blue, but a few strong lines per cm^{-1} stand out in the 500 GHz part to the red. As in any Q-branch of a totally symmetric two-photon band of benzene (Sieber *et al.* 1988) the line intensities would normally be expected to increase smoothly at the blue edge of the
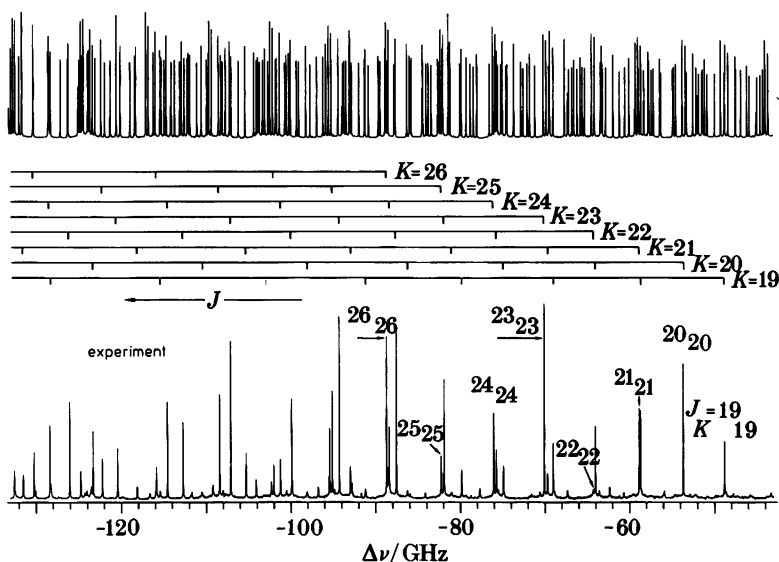
† 1 Torr ≈ 133.3 Pa.

Figure 3. The lower trace shows part of the experimental spectrum of the $14^1_0 1^2_0$ band of $^{13}C_6H_6$ shown in figure 2. The assigned values of $K = K' = K''$ are shown for most of the lines above the spectrum. The value of $J = J' = J'' \geqslant K$ increases by one for every mark from right to left. $J = K$ lines are marked separately for clarity. The upper trace shows a calculated (unperturbed) spectrum, for comparison. Note the lesser number of lines in the experimental spectrum and the strong variation in line intensities which is not seen in the calculated spectrum.

spectrum (compare, for instance, the spectra in figure 1). Since this is not what is found, the rotationless origin of the band cannot be located and the observed sparse line structure is not easily assigned.

To find the rotationless origin, part of the spectrum was rerecorded at a sample pressure of 5 Torr and with the highest available laser power. The resulting structured spectrum is shown as an insert in figure 2. At low pressures, transitions to slowly decaying states give rise to sharp lines in the fluorescence excitation spectrum, but transitions to states with a fast non-radiative decay are weakened and broadened, and are therefore not observed. At high pressures the pressure broadening washes out the differences in line widths and, in addition, increases the fluorescence quantum-yield by collisional vibrational deactivation to lower lying long-lived vibronic states. As a result some of the structure in the spectrum is recovered. The analysis of the high-pressure spectrum yields two results.

1. The rise of the signal with decreasing frequency allows us to determine the rotationless origin at nearly 50 GHz distance from the first strong line in the low pressure spectrum.

2. The high-pressure spectrum was coarse grained and a series of broad features with increasing spacing to the red was found. This structure could be well simulated if the line intensities in a coarse grained calculated spectrum were weighted by K'/J'. We therefore concluded that the remaining lines in the low-pressure spectrum are due to transitions with $K' \approx J'$.

These results finally made it possible to assign the spectrum. The part shown in figure 2 and the lower half of figure 3 consists of only a few regular branches of lines with smoothly increasing distance between the lines. This is quite similar to the situation in the $6^1_0 1^3_0$ band of C_6H_6 (Riedle *et al.* 1990). From the changes of the
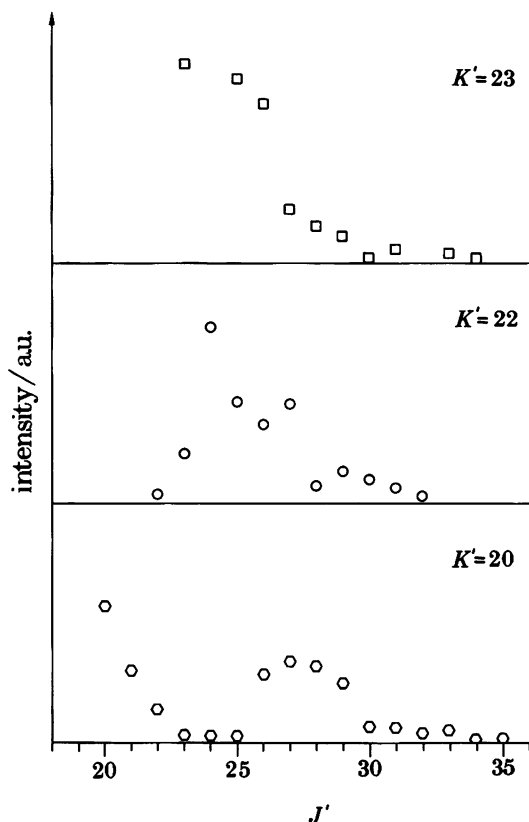
Figure 4. J' dependence of the intensity of lines with $K' = 20$, 22 and 23 in the Doppler-free spectrum of the $14_0^1 1_0^2$ band of $^{13}C_6H_6$. For discussion see text.

Table 1. *Values of the rotationless origin ν_{00} and the changes ΔB and ΔC of the rotational constants for the 14_0^1 and the $14_0^1 1_0^2$ transitions of $^{13}C_6H_6$ as determined from the analysis of the Doppler-free Q-branch spectra*

band	ν_{00}/cm^{-1}	$\Delta B/cm^{-1}$	$\Delta C/cm^{-1}$
14_0^1	39 618.66 (5)	-0.008008	-0.003938
$14_0^1 1_0^2$	41 398.98 (5)	-0.008231	-0.004058

distance between neighbouring lines it was concluded that each branch consists of lines with a constant value of $K = K' = K''$ ($\Delta K = 0$ and $\Delta J = 0$ for the observed ^qQ-branch) and increasing values of $J = J' = J''$. Hence the value of K could be determined from the absolute values of the distances. Furthermore, the planarity of benzene in the S_0 and S_1 state demands that $\Delta C \approx \Delta B/2$ and this allowed us to assign the first line in each branch unambiguously to a transition with $J = K$. Some of the assignments are shown in figure 3 above part of the experimental spectrum shown already in figure 2. No lines with $K' < 19$ could be identified.

With 101 lines assigned, ΔB and ΔC were fitted to the observed line positions with a standard deviation of 38 MHz. These values, and the extrapolated position ν_{00} of the rotationless origin of the band are summarized in table 1 together with the values for the 14_0^1 band. The observed change in ΔB between the two bands is quite

Table 2. *Measured decay times of selectively excited rotational levels in the* $14^1 1^2$ *vibronic state of* $^{13}C_6 H_6$

rotational state $J'_{K'}$	decay time τ/ns	rotational state $J'_{K'}$	decay time τ/ns
19_{19}	11.3	26_{23}	14.2
20_{20}	15.0	27_{23}	12.3
21_{20}	12.3	28_{23}	11.5
27_{20}	14.3	26_{24}	17.7
25_{21}	10.3	27_{24}	15.5
26_{21}	9.0	28_{24}	15.3
26_{22}	14.6	29_{24}	8.0
27_{22}	18.6	28_{25}	10.7
23_{23}	20.5	29_{26}	13.9
24_{23}	15.1	32_{31}	29.0

similar to the changes found for two quanta of the totally symmetric ring stretching mode ν_1 of $C_6 H_6$ (Riedle *et al.* 1982, 1990) and the change in the inertial defect $(\Delta B - 2\Delta C)$ is reasonable. This can be taken as strong additional evidence for the assignments.

A theoretical spectrum calculated with the newly determined values of ΔB and ΔC and the assumption of constant fluorescence quantum-yield is shown in the upper trace of figure 3. The line intensities in this spectrum vary only slowly, as observed in other bands. Yet in the experimental spectrum even the few lines observed show strongly varying intensities. This is demonstrated in figure 4, where the J-dependence of the intensities is displayed for a few K values. An analysis of all the spectral features in the whole of the total measured range of 25 cm^{-1} shows a distribution of monotonically decreasing line intensities, which is indicative of the heavily perturbed character of the band (Sieber *et al.* 1988). On the other hand, except for $K = 19$, all assigned lines are found to be unshifted. This is quite different from the situation at low excess energies where monotonically decreasing intensities are usually connected with large frequency shifts. The latter has been explained by coupling in the strong limit and we conclude that in the present case there is a coupling in the weak limit.

(ii) *Decay rates of single rotational states*

We measured the fluorescence decay of a number of the rotational states of the $14^1 1^2$ vibronic state of $^{13}C_6 H_6$ with the pulsed amplifier system described previously (Schubert *et al.* 1986 *a*, *b*). In all cases a single exponential decay was found, which shows that the fluorescence-quenching radiative decay is in the statistical limit (Parmenter 1972; Robinson 1967). The measured decay times are summarized in table 2. There is a variation between $\tau = 29$ ns and $\tau = 8$ ns even for the strong lines which had to be selected for the measurements. This is paralleled by the variation in line intensities discussed above. In particular, for the $K = 23$ states a monotonic decrease of both the decay times, as well as the line intensities (compare figure 4), is seen.

The variation in decay times τ corresponds to a variation of line widths γ ($\gamma = 1/2\pi\tau$) of between 5.4 MHz and 19.9 MHz. Decay times could only be measured for the strongest lines, and these are expected to have the smallest widths. In comparison, the widths of all observed spectral features in the total recorded range

of 25 cm^{-1} were evaluated and most of them were found to be far broader than the experimental resolution of 15 MHz. We could find lines with a width of as much as 150 MHz. But even inclusion of these broad and very weak lines did not yield the expected total number of lines. This means that there must be many further lines which are even broader and consequently extremely weak and not observable in our experiment. The distribution of decay rates of individual rotational states of the $14^1 1^2$ state of $^{13}C_6H_6$ therefore seems to vary over more than two orders of magnitude.

4. Discussion of the observed couplings and relaxation pathways

(a) General considerations

The analysis of the rotationally resolved spectrum of bands at low excess energy (e.g. the 14^1_0 band of C_6H_6) shows the importance of rotation–vibration (higher-order Coriolis) and l-type couplings in addition to the well-known anharmonic resonances. Coupling is in the strong coupling limit and causes the appearance of extra lines and relatively large shifts of lines. For intermediate excess energy and a strong coupling limit we might therefore expect an even larger number of observed lines and the loss of any regularity due to ubiquitous shifts. Instead, we generally observed a drastically reduced number of nearly unshifted lines. This can only be understood as rotationally selective coupling in the weak coupling limit to fast-decaying (broadened) background states. From the rotational dependence of the decay rate it can be concluded that even at intermediate excess energies, rotation–vibration coupling plays an important role. We see a K'-dependence of the decay rate in the $14^1_0 1^1_0 16^2_2$ and $14^1_0 1^2_0$ bands of C_6H_6 which could be generally interpreted as caused by some form of parallel Coriolis coupling. The observation of mainly low K'-values in the spectrum of the $6^1_0 1^3_0$ band would also be in line with such an interpretation, but then the isolated appearance of $K' = 10$, $l'_6 = +1$ and $K' = 13$, $l'_6 = -1$ lines deviates drastically from this model. This situation is even more pronounced in the $14^1_0 1^2_0$ band of $^{13}C_6H_6$ where only lines with $K' \geqslant 19$ were found. No single coupling operator can be thought of that would display the J- and K-dependence needed to explain the observed pattern of long-lived rotational states. The disappearance of a few lines could still be explained in terms of accidental resonances, which cause the fast decay of a few states, analogous to the isolated perturbations seen at low excess energies, but the disappearance of most but not all lines needs a different explanation. It will be shown in the next section that this can be found in terms of couplings to a number of background states and hence, in a few cases, as accidental interference between the resulting decay channels.

Recently we argued (Riedle et al. 1982, 1984; Riedle & Neusser 1984) that the broadened background states isoenergetic with the optically accessible ('light') S_1 states are other states in S_1. This was proven experimentally for states of low excess energy by the observation of emission spectra of single quasi-eigenstates (Schubert et al. 1989). The total density of these 'dark' S_1 states is about 100/cm^{-1} at intermediate excess energy and therefore sufficiently large to allow for close resonance and even overlap, but still sufficiently low for selectivity in perturbative couplings. A major proportion of the 'dark' states are combination states with vibrational characters quite different from all 'light' states. They could well be coupled much more strongly to the highly excited S_0 state than the 'light' states of S_1 (Hornburger & Brand 1982) and, contrary to the situation at low excess energies,

where they would rarely be admixed with the 'light' states, the more frequent couplings at intermediate or high excess energy would then make their admixture quite probable. Vibrational states with decay times much faster than the ones measured for the states observable in our spectra have indeed recently been claimed (Sumitani *et al.* 1985) at intermediate excess energy.

(b) *Interference of decay channels*

Polik *et al.* (1988) recently presented model calculations for coupling in the weak coupling limit of one optically accessible state $|\psi_0\rangle$ to a manifold of states $\{|\phi_k\rangle\}$, $k = 1, 2, 3, \ldots$, each of which is in turn coupled to a continuum. This coupling to the continuum gives each of the states $|\phi_k\rangle$ a finite width. In addition it is assumed that there is substantial coupling between the states $|\phi_k\rangle$. Prediagonalization of the manifold $\{|\phi_k\rangle\}$ of real basis functions together with the continuum yields a set of complex eigenfunctions $|\tilde{\psi}_k\rangle$ with complex coupling elements

$$\langle \psi_0 |H| \tilde{\psi}_k \rangle = \tilde{v}_{0k} = |\tilde{v}_{0k}| e^{i\theta_k}, \tag{1}$$

between the state $|\psi_0\rangle$ and each state $|\tilde{\psi}_k\rangle$. θ_k is the phase of the eigenfunction $|\tilde{\psi}_k\rangle$. These couplings between $|\psi_0\rangle$ and $|\tilde{\psi}_k\rangle$ give rise to a decay width Γ of the state $|\psi_0\rangle$ of

$$\Gamma = \Gamma_0 + \sum_k \left[\frac{|\tilde{v}_{0k}|^2 (\tilde{\Gamma}_k - \Gamma_0)}{(\tilde{E}_k - E_0)^2 + \frac{1}{4}(\tilde{\Gamma}_k - \Gamma_0)^2} \cos 2\theta_k + \frac{2|\tilde{v}_{0k}|^2 (\tilde{E}_k - E_0)}{(\tilde{E}_k - E_0)^2 + \frac{1}{4}(\tilde{\Gamma}_k - \Gamma_0)^2} \sin 2\theta_k \right] \tag{2}$$

Γ_0 is the width of the zero order state $|\psi_0\rangle$, $\tilde{\Gamma}_k$ the width of each prediagonalized state $|\tilde{\psi}_k\rangle$, and E_0 and $\tilde{E}_k$ are the respective energies.

Originally this model was developed to describe asymmetric line shapes in Stark level-crossing spectra of S_0 formaldehyde, but it can be used for the description of the decay of single rovibronic states of benzene, if we associate the state $|\psi_0\rangle$ with such a 'light' zero-order state, the states $|\phi_k\rangle$ with broadened background states, and the continuum with the dense manifold of highly excited T_1 or S_0 states, or both. New interference effects are therewith introduced which could give an explanation for the observed non-monotonic appearance of lines.

Equation (2) reduces to the well-known formula for coupling in the weak limit to one broad state (Nitzan *et al.* 1972; Tric 1973), since for a single coupled state the phase (i.e. θ_1) will be zero. In this case the rotational dependence of the decay rate follows solely from the rotational dependence of the coupling matrix element rather than from a contribution of the phases θ_k. For more than one state $|\phi_k\rangle$ even non-vanishing values of θ_k will in most cases still lead to an increase in the width Γ, but for particular combinations of the various parameters the sine and cosine terms in (2) together with the dispersive dependence on $\tilde{E}_k$ (third term in equation (2)) will lead to significant cancellation of the contributions from the $|\phi_k\rangle$ states and Γ will not be much greater than Γ_0. In other words, there exists a destructive interference between the decay channels caused by the different background states.

5. Summary and conclusions

We have reviewed the situation of coupling and rotationally selective decay behaviours at both low and intermediate vibrational excess energies in the S_1 state of benzene. New evidence in the analyses of the rotationally resolved spectra of the $14_0^1 1_0^1 16_2^2$ band of C_6H_6 and the $14_0^1 1_0^2$ band of $^{13}C_6H_6$ is presented. All investigations

have shown the intricate involvement of molecular rotation in the intramolecular relaxation of S_1 benzene. No dependence of the general behaviour on the symmetries of the vibronic states nor on the slight variations of state densities and state energies for different isotopes of benzene is observed at a given excess energy. The pathways for intramolecular relaxation in S_1 benzene are found to be a primary coupling of the 'light' states to 'dark' states in S_1 due to rotation–vibration and anharmonic coupling and l-type resonances, and electronic non-radiative decay to the T_1 or S_0 state, or both. The decay behaviour at intermediate excess energies ('channel three' (Callomon *et al.* 1972) régime) is found to involve close interplay between the rotational dependence of the coupling matrix elements and accidental resonances of the various rovibronic states. These resonances may cause interference between the various possible decay channels and hence give rise to the observation of a few strong lines in the fluorescence excitation spectra with nearly unshifted frequencies, while most of the excited states decay very fast and are not observed. The broad background states in the 'channel three' region responsible for the rotationally selective decay of S_1 benzene are thought to be 'dark' states within S_1 which are strongly coupled to the highly excited S_0 state due to their vibrational nature.

At even higher excess energies, coupling of the 'light' states to the dark background states is leading to broadened states becoming so frequent that no sharp structure can any longer be observed in the spectra. We still expect large fluctuations, however, in the fast decay rates of the individual states due to the remaining interferences. Since the individual lines are broad and overlap these interferences may no longer be apparent in the spectra, which then appear to be diffuse and unstructured as was thought to be typical for 'channel three'. To observe these proposed decay-rate fluctuations, double resonance spectroscopy would be needed to separate inhomogeneous contributions to the spectra from the homogeneous effects under consideration.

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