

Back to the roots of "channel three": Rotationally resolved spectra of the $6_0^1 1_0^3$ band of C_6H_6

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Rotationally resolved fluorescence excitation and resonance enhanced multiphoton ionization (MPI) spectra of the $6_0^1 1_0^3$ one-photon band of benzene at the onset of "channel three" are reported. The fluorescence decay is monitored after rotationally selected excitation and a large variation of the nonradiative decay time (< 1 to 6.8 ns) is found for the different rotational states at the vibrational excess energy of 3287 cm^{-1} in S_1 . The rotational structure of the fluorescence excitation spectrum and the MPI spectrum measured with delayed laser pulses differ considerably. All observed lines of the MPI spectrum were assigned and the rotational line structure can only be understood with a model which incorporates interference between different decay channels. Due to this interference, particular rotational states decay fairly slowly and give rise to lines in the spectrum while states with neighboring rotational quantum numbers decay rapidly and are therefore not found in the spectrum. The previously reported drastic increase of the electronic, nonradiative decay of benzene in this region of excess energy, which led to the postulation of "channel three," cannot be confirmed. Instead, the optically excited rovibronic states are thought to be coupled to background states within S_1 which are themselves broadened due to strong coupling to the highly excited S_0 electronic state rather than due to an unknown ("channel three") or isomerization process.

I. INTRODUCTION

From the rotational contour analysis of vibronic bands of benzene¹ Callomon *et al.* concluded that the bands are more or less diffuse above 3000 cm^{-1} vibrational excess energy in S_1 .² The lowest band found to be diffuse was the $6_0^1 1_0^3$ band leading to the $6^1 1^3$ state at 3287 cm^{-1} excess energy with an estimated "linewidth" of 0.3 cm^{-1} . Comparison of the nonradiative decay rate determined from these "linewidths" with the directly measured fluorescence decay rate of states with excess energy below 3000 cm^{-1} ³ showed an increase by more than 4 orders of magnitude in the nonradiative decay rate over a very narrow range of excess energies. This is paralleled by a drastic decrease in fluorescence quantum yield seen before at the same range of excess energies.⁴ Since none of the known decay processes could explain these observations, a hitherto unknown "channel three" was invoked as an explanation.²

In the 20 years since this initial investigation, numerous experimental investigations were performed to clarify the fascinating problem of "channel three," i.e., the nonradiative decay of S_1 benzene. Aron *et al.*⁵ measured the width of the rotational contour of the two-photon $14_0^1 1_0^2$ bands at extreme rotational cooling in a supersonic jet. The increased width for $n \geq 3$ was interpreted as an increase in the homogeneous width of the $14^1 1^n$ states and found in good agreement with the above-mentioned "linewidth" of the one-photon states at the same excess energy. In contrast to that, Wunsch *et al.*⁶ measured the pressure dependence of the fluorescence decay curves after two-photon excitation of the same $14^1 1^n$ states at room temperature. From these experiments, they

concluded decay rates which were about 2 orders of magnitude lower than the values of Aron *et al.*⁵ In an attempt to identify the final electronic state of the "channel three" decay, Duncan *et al.*⁷ and Otis *et al.*⁸ used two-color resonant two-photon ionization with a variable delay between the two laser pulses. From the decay curves obtained in this way they concluded that at low excess energy in S_1 the dominant decay channel is intersystem crossing (in accord with earlier investigations by sensitized phosphorescence⁹), while at excess energies above 3000 cm^{-1} internal conversion becomes the dominant process. This result was confirmed by Yoshihara and co-workers¹⁰ by transient absorption measurements after excitation to high S_1 levels. However, no coupling mechanism could be identified to explain these findings.

The availability of ps light sources in the UV and streak camera detection allowed Sumitani *et al.*¹¹ to measure fluorescence decay curves of a number of one-photon vibronic states below and above 3000 cm^{-1} excess energy. The two prominent findings were that biexponential decay curves were observed around 3000 cm^{-1} excess energy and that the measured nonradiative decay rates of the very states previously considered by Callomon *et al.*² were considerably lower. They were, indeed, quite similar to the values found by Wunsch *et al.*⁶ for two-photon states at the same energy. This showed that comparison of "linewidth" and decay time measurements at this level of spectral resolution is critical.

All of the investigations discussed so far were only able to resolve the vibronic structure of the spectrum and therefore the decay times found in these measurements represent an average over the unresolved rotational structure. Riedle *et al.*¹² were the first to resolve single rotational lines in the electronic spectrum of benzene. Later they reported Doppler-free, two-photon spectra of the $14_0^1 1_0^2$ band¹³ and

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showed that the nonradiative decay of the $14^1 1^2$ state at 3412 cm^{-1} excess energy depends strongly on the rotation of the molecule. It was found that the decay time of $K = 0$ states is as long as tens of ns¹⁴ and agrees well with the homogeneous linewidth of typically 0.001 cm^{-1} .¹⁵ This result was in striking contrast to the decay behavior of rotational states in the 14^1 vibronic state at 1570 cm^{-1} excess energy reported by Schubert *et al.*^{16,17} There, no rotational dependence of the decay rate was measured after excitation of unperturbed rotational states, i.e., states without coupling in S_1 . This points to an electronic, nonradiative relaxation process in the statistical limit. From the high rotational selectivity in the $14^1 1^2$ state it was concluded that in the "channel three" regime of S_1 benzene an intricate, intramolecular vibrational redistribution (IVR) process serves as the primary relaxation process before the rapid rotationally independent nonradiative electronic decay.

The presence of IVR was also confirmed by Achiba *et al.*¹⁸ by multiphoton ionization photoelectron spectroscopy. Parmenter and co-workers¹⁹ used the method of "chemical timing," i.e., the investigation of the O₂ pressure dependence on the emission spectrum, to determine the IVR rate in various vibronic states after one-photon excitation. Their values for "IVR dephasing rates," which they equate to the nonradiative decay rates of Callomon *et al.*,² were in good agreement for excess energies above 3000 cm^{-1} with these earlier values and they also confirmed the finding of substantial IVR by Riedle *et al.*¹³⁻¹⁵ However, for the $6^1 1^2$ state at 2370 cm^{-1} they found a value of the IVR rate which is larger by more than 2 orders of magnitude than all previous decay time measurements.^{3,11,20} The large amount of unstructured emission seen by Parmenter and co-workers¹⁹ in the emission from the $6^1 1^3$ state was recently shown by Suzuki and Ito to decrease considerably upon rotational cooling in a supersonic jet.²¹

The brief survey presented above demonstrates that there exists a variety of results from different experimental techniques which point to a fast, nonradiative decay channel opening around 3000 cm^{-1} vibrational excess energy. These results can be divided into two categories: first, investigations *without* rotational state selection (the majority of all investigations) which yielded strongly differing values for the decay time and the "linewidth" of the same vibronic state. Second, investigations *with* selection of eigenstates which showed excellent agreement between the decay time¹⁴ and the homogeneous linewidth¹⁵ of every eigenstate probed. However, the selection of single eigenstates was achieved by Doppler-free, two-photon spectroscopy and therefore only states could be investigated which differ in symmetry from the ones investigated in most of the experiments without rotational resolution, since these employed one-photon excitation. To be able to interpret all results with a common model it is therefore desirable to measure rotationally resolved spectra of one-photon bands below and in the "channel three" regime.

We were previously able to show that rotationally resolved one-photon spectra of benzene at low vibrational excess energy can be obtained by the combination of an extremely narrow band UV source with a well collimated

molecular beam.²² Both fluorescence detection²² and ionization detection²³ were successfully applied. In this work we use these techniques to record rotationally resolved spectra of the $6_0^1 1_0^3$ band, which was the lowest excess energy band to be found broadened in the original work of Callomon *et al.*² On the basis of these results we will be able to decide whether the previously observed diffuseness of the contour can really be interpreted as an increase of the homogeneous linewidth to the extent that was concluded in Ref. 2 and ultimately led to the postulation of "channel three."

II. EXPERIMENTAL

The experimental setup for the recording of rotationally resolved one-photon spectra of benzene was described in detail previously.^{22,23} Only a brief review will be given here with particular emphasis on modifications for the present investigation.

The light of a cw single-mode dye laser is pulsed amplified and frequency doubled in a BBO crystal to obtain tunable UV pulses with a frequency width (FWHM) of about 100 MHz. Coumarin 102 dye was used in both the cw laser and the three amplifier stages to obtain the necessary wavelength of 2417 \AA . For relative calibration of the spectra, the transmission spectrum of a highly stable Fabry-Perot interferometer was recorded simultaneously and the well known absorption spectrum of Te₂²⁴ was used for absolute calibration. The laser light beam is crossed perpendicularly with a well collimated pulsed supersonic molecular beam of C₆H₆ seeded in Ar. To monitor the excitation of the molecules, we can either detect the emitted fluorescence or we can ionize the excited molecules with the UV photons ($\lambda = 273.85\text{ nm}$) from a second frequency-doubled dye laser (FL 2002 E; Lambda Physik) and detect the mass selected molecular ions in a time-of-flight mass spectrometer. The amplifier chain for the cw laser and the second dye laser are pumped by the output of the two discharge tubes of an EMG 150 excimer laser. Due to a small difference in the discharge time of the two tubes and different optical paths the ionization pulse of 10 ns length is delayed by 11 ns with respect to the narrow bandwidth excitation pulse of 5 ns length.

For the recording of fluorescence excitation spectra the pulse length of the excitation laser was stretched to 8.5 ns by careful alignment of the amplifier chain to ensure the highest possible spectral resolution. To record decay curves of individual rotational states in the $6^1 1^3$ vibronic state it was found necessary to shorten these pulses. This was done by the addition of a parasitic cavity around the second amplifier stage.¹⁴ UV pulses of 1.5 ns length and an increased spectral width were obtained in this way. In addition, in decay time measurements the normally used 56 DUVF (Valvo) photomultiplier was replaced by a R 2024U-06 (Hamamatsu) Micro-Channel-Plate photomultiplier with a time resolution (FWHM) of 700 ps. The output signal was delivered with a short RG 213 line to a Tektronix WP2221 wave form digitizing system with a resolution of 600 MHz.

III. RESULTS

The $6_0^1 1_0^3$ band is the lowest band which was found to display an anomalous diffuse structure in the original work

by Callomon *et al.*² These authors interpreted the diffuseness in the rotational contour as due to a broadening of the homogeneous linewidth of the numerous rovibronic transitions contributing to the contour. They were conscious of the limitations of their experiment due to the Doppler broadening present under room temperature conditions and the limited resolving power of the spectrograph. For this reason the spectra at high excess energy were compared to recordings with limited experimental resolution of bands known to possess sharp structure under high experimental resolution and approximate values of the "linewidth" were obtained in this way.

With the experimental setup described in Sec. II, we are now able to measure the rotationally resolved spectrum of the band under discussion. Even though the present experimental conditions are not identical to the original work by Callomon *et al.*,² i.e., the rotational temperature in the jet is far below room temperature, this spectrum should allow us to judge whether the observed diffuseness is indeed caused by a broadening of the individual rovibronic lines.

A. Fluorescence excitation spectrum of the 6₀¹1₀³ band of C₆H₆

The fluorescence excitation spectrum of the 6₀¹1₀³ band of C₆H₆ (3287 cm⁻¹ vibrational excess energy) at an Ar backing pressure of 0.5 bar and a partial pressure of 60 Torr benzene (corresponding to a rotational temperature of 15 K) was measured with the experimental setup described in Sec. II. The UV intensity was attenuated sufficiently to avoid saturation of individual rovibronic transitions.²² The main part of the resulting spectrum is shown in the upper part of Fig. 1. From our previous investigation of the 6₀¹ and 6₀¹1₀¹ bands²² we know that the rotational structure of the various 6₀¹1₀ⁿ bands should be very similar, since additional quanta of the totally symmetric ν₁ ring stretch mode do not signifi-

cantly change the value of the Coriolis coupling constant ζ'_{eff} which determines the general appearance of the vibronic bands of benzene.^{1,22} Therefore, the well understood regular spectrum of the 6₀¹1₀¹ band²² (1444 cm⁻¹ excess energy) is included in Fig. 1 (lower part) for comparison. The experimental conditions for this recording were identical to the present ones, but much less fluorescence signal was detected for the 6₀¹1₀³ band in agreement with previous quantum yield measurements.¹¹ At our spectral resolution the spectrum of the 6₀¹1₀¹ band consists of lines corresponding to individual rovibronic transitions.²² The overall structure of both bands is indeed similar, i.e., a well separated R branch is observed at higher energies, a dense Q branch in the center, and a P branch at lower energies. However, the detailed appearance of the two bands shows a number of significant differences:

(i) The number of sharp lines (rovibronic transitions) found in the 6₀¹1₀³ band is smaller than in the 6₀¹1₀¹ band. For example, in the region of the Q branch (−45 to 13 GHz) the number of lines with more than 10% intensity of the strongest feature decreases from 89 in the 6₀¹1₀¹ band to 54 in the 6₀¹1₀³ band. This is similar to the Doppler-free, two-photon spectrum of the 14₀¹1₀² band at similar excess energy.^{13–15} The reduction of the number of sharp lines in the 14₀¹1₀² band was interpreted as a highly rotationally selective nonradiative decay of the individual rovibronic states.^{13–15} Since the electronic nonradiative decay of S₁ benzene is known to be in the statistical limit and not to depend on the rotation,^{16,17} the rotational selectivity was attributed to a primary IVR process in S₁.

(ii) A close inspection of various lines in the spectrum of the 6₀¹1₀³ band shows that the linewidth of individual transitions is broadened from 85 MHz in the 6₀¹1₀¹ band to 150 MHz (0.005 cm⁻¹) for the strongest lines and a few hundred MHz for weaker features. The value of 150 MHz does still contain a contribution from the experimental reso-

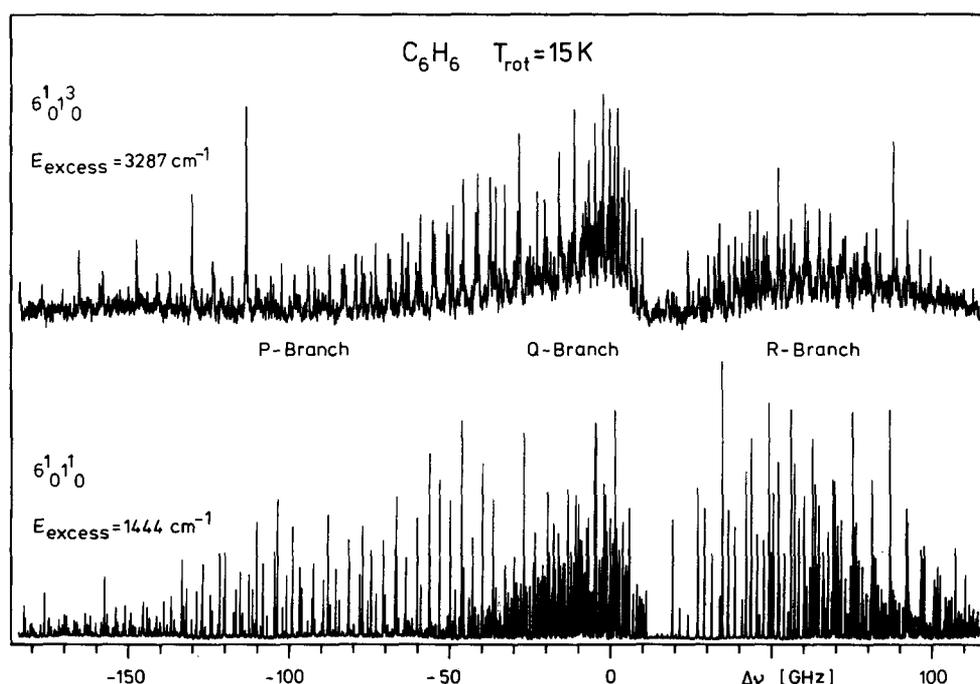


FIG. 1. Rotationally resolved fluorescence excitation spectra of the 6₀¹1₀¹ (lower trace) and the 6₀¹1₀³ (upper trace) band of C₆H₆. The vibrational excess energy of the 6¹1 state is 1444 and 3287 cm⁻¹ for the 6¹1¹ state. Both spectra were recorded under conditions of moderate rotational cooling which lead to a rotational temperature of 15 K.

lution and presents, therefore, only an upper limit for the homogeneous width of the lines. However, it is drastically lower than the width of 0.3 cm^{-1} determined by Callomon *et al.* for this band.² Instead, the observed linewidth is in reasonable agreement with the width expected from decay time measurements.¹¹ The observed variation of the linewidth with the rotational state does again parallel the situation in the $14^1_0 1^2$ state.¹⁵

(iii) The intensity of the strongest lines in the *Q* branch of a regular vibronic one-photon spectrum of benzene is smaller by about a factor of 2 than in the *P* or *R* branch. This is due to the different Hönl–London factors for the various transitions. The maximum value of the Hönl–London factor for *Q*-branch transitions is 1.0 for $K'' = 0$ and decreases for higher K'' , while for the *P*- and *R*-branch lines a maximum Hönl–London factor of 2.0 is found for $K'' = J''$, and it decreases for decreasing values of K'' . This situation is indeed observed in the spectrum of the $6^1_0 1^1_0$ band. If we interpret the decrease of intensity of a particular transition in the fluorescence excitation spectrum as an increased nonradiative decay,¹³ we can rationalize the strong appearance of the *Q*-branch lines in the spectrum of the $6^1_0 1^3_0$ band as relatively slow decay of states with low K' . This qualitative observation will be discussed further.

(iv) The intensity of lines in the *P* branch decreases much faster with distance from the rotational origin (close to the *Q* branch) and therefore with the value of J' as expected for the rotational temperature of 15 K. This is, again, similar to the situation in the $14^1_0 1^2$ band.^{14,15} There is, however, a regular structure of strong lines observed both in the far part of the *P* branch and the *R* branch (less pronounced) which will be discussed in detail in Secs. IV and V.

(v) In the usually very dense *Q* and *R* branches a significant broad background is observed. If the reduced number of

sharp lines is indeed due to the fast decay of some of the rotational states in the $6^1_0 1^3$ vibronic state, this background can be interpreted as the overlapping (heavily broadened) transitions to these states.

To summarize, there are a number of sharp lines observed in the $6^1_0 1^3_0$ band, which are tentatively interpreted as transitions with low K' . The width of these transitions is dramatically lower than the previously reported value of the "linewidth" for this band.² There is, however, also evidence for a strong rotational dependence of the decay of individual rovibronic states and hence of the width of the corresponding transitions. Due to the heavily perturbed nature of the spectrum, a definitive assignment of the rotational structure could not be performed for this fluorescence excitation spectrum. The general features of the $6^1_0 1^3_0$ band (accessed by one-photon transitions) parallel the ones found previously in the $14^1_0 1^2_0$ band (accessed by two-photon transitions).

B. Decay behavior of individual rotational states of the $6^1_0 1^3$ vibronic state

The fluorescence decay of the $6^1_0 1^3$ vibronic state was recorded after excitation via a number of randomly selected, sharp spectral features in the vicinity of the *Q* branch of the $6^1_0 1^3_0$ band (marked in the upper trace of Fig. 2). Due to the lack of an assignment of the spectrum, we do not know how many individual rovibronic transitions are contained in each feature, but a comparison with the well understood spectrum of the $6^1_0 1^1_0$ band suggests that most peaks should be due to single transitions. In a preliminary experiment we found that the pulse length of close to 10 ns of the exciting laser was longer or comparable to the decay time. We therefore shortened the laser pulse with the technique described in Sec. II. In addition, the Ar backing pressure was raised to 1.5

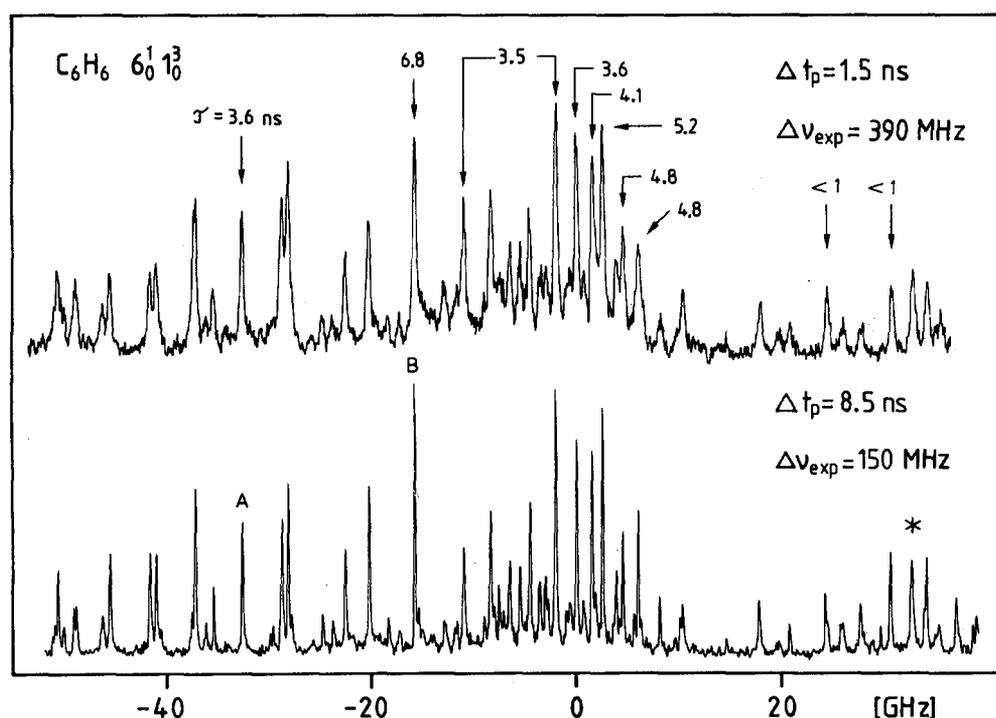


FIG. 2. Central part of the rotationally resolved fluorescence excitation spectrum of the $6^1_0 1^3_0$ band of C₆H₆ recorded under experimental conditions which lead to a rotational temperature of 8 K. The duration of the exciting laser pulse was 8.5 ns for the recording of the spectrum shown in the lower part while it was 1.5 ns for the spectrum shown in the upper part. This shortening of the laser pulse increases the experimental frequency width of a single line from 150 to 390 MHz but it allows the measurement of the decay times of the individual rovibronic states populated through the various transitions. Measured decay times are shown in the upper spectrum for selected transitions marked by arrows. The decay curves after excitation at frequency positions A and B are shown in Fig. 3. For explanation of the spectral feature marked by an asterisk in the lower spectrum, see the text.

bar for increased rotational cooling. In Fig. 2 the central part of the spectrum of the $6_0^1 1_0^3$ band is shown for a laser pulse length of 8.5 ns (lower trace) and 1.5 ns (upper trace). The increased rotational cooling is seen to result in a reduction of the broad background (in agreement with the interpretation as heavily broadened lines with high K' and therefore high J' , which are now suppressed) and the shortening of the laser pulse is seen to lead to a decrease in the spectral resolution. However, it is still sufficient to resolve individual features in the spectrum.

Typical fluorescence decay curves are shown in Fig. 3 for the two lines marked A and B in the lower trace of Fig. 2. A single exponential decay is observed within experimental accuracy for these two excitation frequencies as for all cases investigated. This is in disagreement with the observation of a biexponential decay observed by Sumitani *et al.* at much lower spectral resolution.¹¹ The various measured decay times are indicated in the upper trace of Fig. 2 and summarized in Table I. They are seen to vary from line to line. For the two investigated *R*-branch lines (at 24 and 31 GHz) the decay time was too short to be resolved, but this might be an experimental artifact due to the underlying background in this part of the spectrum. The longest observed decay time is more than twice as long as the slow component ($\tau = 3.2$ ns) of the biexponential decay observed previously,¹¹ while the inability to resolve the decay of the *R*-branch lines, as well as the broadened nature of some of the lines in the spectrum (compare, for example, the line at 33 GHz, marked by an asterisk), is in qualitative agreement with the previously observed short component of < 0.5 ns.¹¹ If we keep in mind that in this previous investigation the rotational structure was not resolved and that we see a strong rotational dependence of the decay, we can interpret the apparent biexponential decay as a superposition of various single exponential decays and not an inherent property of the $6^1 1^3$ vibronic state.

C. Delayed two-color MPI spectrum of the $6_0^1 1_0^3$ band of C_6H_6

The fluorescence excitation spectrum of the $6_0^1 1_0^3$ band could not be assigned due to its heavily perturbed nature. If all contributions in the spectrum from fast decaying states could be suppressed, a greatly simplified spectrum might be observed and there would be better hope for a detailed assignment. For the decay times of at most a few ns this was not possible by gating of the photomultiplier. Instead, a delayed two-color, two-photon ionization technique was used. The extremely narrow band UV laser was used to excite the benzene molecules to the S_1 state and the second dye laser with a delay of about 11 ns ionized those molecules which were still in the electronically excited S_1 state after this delay. To understand the effect of this technique, we have to keep in mind, that in fluorescence detection the quantum yield is *inversely proportional* to the nonradiative decay rate. On the other hand, the probability that a particular excited rovibronic state is detected decreases *exponentially* after excitation. The detailed analysis of the pulse shapes of the excitation laser and the ionizing laser showed that there is little

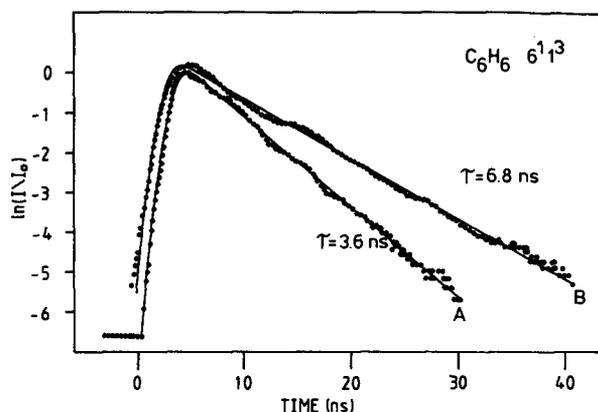


FIG. 3. Decay of fluorescence after population of two different rotational states of the $6^1 1^3$ vibronic state of C_6H_6 via the transitions marked A and B in Fig. 2. The dots represent the experimental values, the line is the result of the convolution of the measured system response (including the finite laser pulse width) and the single exponential decay fitted to the experimental points.

temporal overlap of the two pulses and there is only a negligible chance that molecules are ionized within 2 ns after excitation. Therefore, all states with a decay time of about 1 ns or less will not be seen in the delayed multiphoton ionization (MPI) spectrum while long lived states with a decay time of up to 7 ns will give rise to a strong signal.

The result of this experiment is shown in the upper trace of Fig. 4. The spectrum of the $6_0^1 1_0^3$ band has now changed considerably as compared to the fluorescence excitation spectrum shown again in the lower trace. The molecular beam conditions for the two recordings were identical. In the delayed MPI spectrum the broad background in the *Q* and *R* branch has disappeared completely, the number of lines was reduced even further (in particular the broadened lines have disappeared) and the regular structures in the far *P* and *R* branch have become very pronounced. It should be noted that for the regular $6_0^1 1_0^3$ band the delayed MPI spectrum (11 ns delay) is absolutely identical to the fluorescence excitation spectrum. This is in line with the long decay time of 82 ns of the $6^1 1^1$ state.^{20,22}

These qualitative observations show that the interpretation of the fluorescence excitation spectrum in terms of rotationally selective decay is correct and the delayed MPI technique can, indeed, be used for fast gating. Due to the finite length of the laser pulses, which is necessary for the high spectral resolution, the selective attenuation of lines in the delayed MPI spectrum can not be easily used to evaluate the relative decay rates. The spectrum is, however, so much simplified and the high sensitivity of the ionization detection has rendered such a good signal to noise ratio in the spectrum, that a detailed rotational analysis of the band can now be performed. Due to the heavily perturbed character of the band, this assignment has to be discussed in some detail.

IV. ASSIGNMENT OF THE ROTATIONAL STRUCTURE OF THE MPI SPECTRUM

The MPI spectrum of the $6_0^1 1_0^3$ band obtained by the delayed laser technique consists of a largely reduced number

TABLE I. Measured fluorescence decay times after selective excitation of sharp rotational features in the $6_0^1 1_0^3$ band of C₆H₆. The assignments were derived from the detailed analysis of the delayed MPI spectrum (see the text).

State $i_0^J K'$	Excitation branch	ΔE_{rot} [GHz] of excitation line	Decay time τ (ns)
2_0	<i>P</i>	-32.788	3.6
$+1_1$	<i>P</i>	-15.920	6.8
7_0 (40%) + -6_1 (60%)	<i>Q</i>	-11.104	3.5
-2_1 (30%) + 4_0 (70%)	<i>Q</i>	-2.145	3.5
3_0	<i>Q</i>	-0.149	3.6
2_0	<i>Q</i>	1.379	4.1
1_0	<i>Q</i>	2.384	5.2
$+3_1$	<i>Q</i>	4.374	4.8
$+2_1$	<i>Q</i>	5.850	4.8
2_0	<i>R</i>	24.135	<1
-3_1	<i>R</i>	30.511	<1

of rotational lines as compared to a regular perpendicular band like the previously analyzed 6_0^1 and $6_0^1 1_0^1$ bands.²² The rotational analysis cannot, therefore, be performed in the same way as for the regular bands. We can, however, hope that the remaining lines are not shifted in a random fashion and assignments can be performed by observation of regularities in the spectrum. Such a lack of frequency shifts and the rotationally selective, nonradiative decay thought responsible for the reduced number of lines could be explained by intrastate coupling in the weak coupling limit to fast decaying (broadened) background states in S_1 like in the previously analyzed $14^1 1^2$ state.¹³⁻¹⁵

A close inspection of the spectrum does, indeed, reveal that not only the prominent strong structures in the far *P* and *R* branch mentioned above are arranged in a regular way, but *all* 143 lines in the spectrum can be grouped in a small number of regular systems. These systems are marked in Fig.

5 below and above the delayed MPI spectrum of the $6_0^1 1_0^3$ band. The distance between neighboring lines in these systems is decreasing or increasing by a constant value. Such behavior indicates that the lines belong to transitions with constant ΔJ and ΔK and either constant J' or K' . A similar example was previously found for the blue part of the *Q* branch of the $14_0^1 1_0^2$ band, where only transitions with $K' = K'' = 0$ were observed.¹³⁻¹⁵ In a rigid rotor approximation the position of rotational lines is given by^{1,22}

$$\begin{aligned} \Delta E_{\text{rot}}(J', K' \leftarrow J'', K'') &= B' \cdot J' \cdot (J' + 1) + (C' - B') \cdot K'^2 \\ &\mp 2 \cdot C' \cdot \xi'_{\text{eff}} \cdot K' - [B'' \cdot J'' \cdot (J'' + 1) \\ &+ (C'' - B'') \cdot K''^2] \end{aligned} \quad (1)$$

with the Coriolis coupling constant ξ'_{eff} which describes the splitting between the vibrational angular momentum sub-

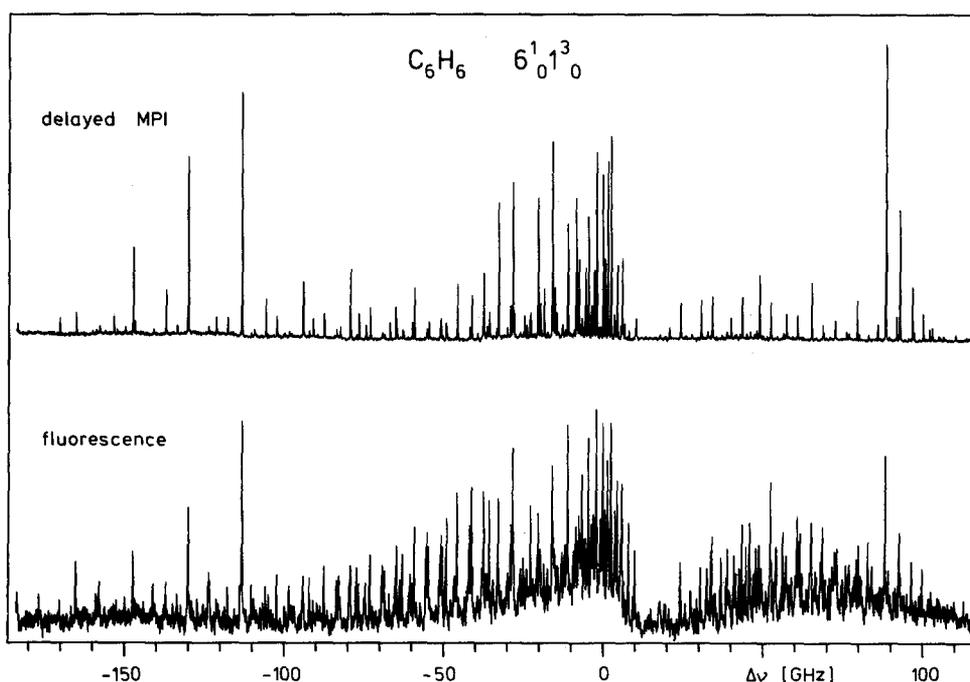


FIG. 4. Comparison of the rotationally resolved spectrum of the $6_0^1 1_0^3$ band of C₆H₆ under identical expansion conditions in the jet as recorded by fluorescence detection (lower trace) and by delayed MPI detection (upper trace). For a discussion of the differences, see the text.

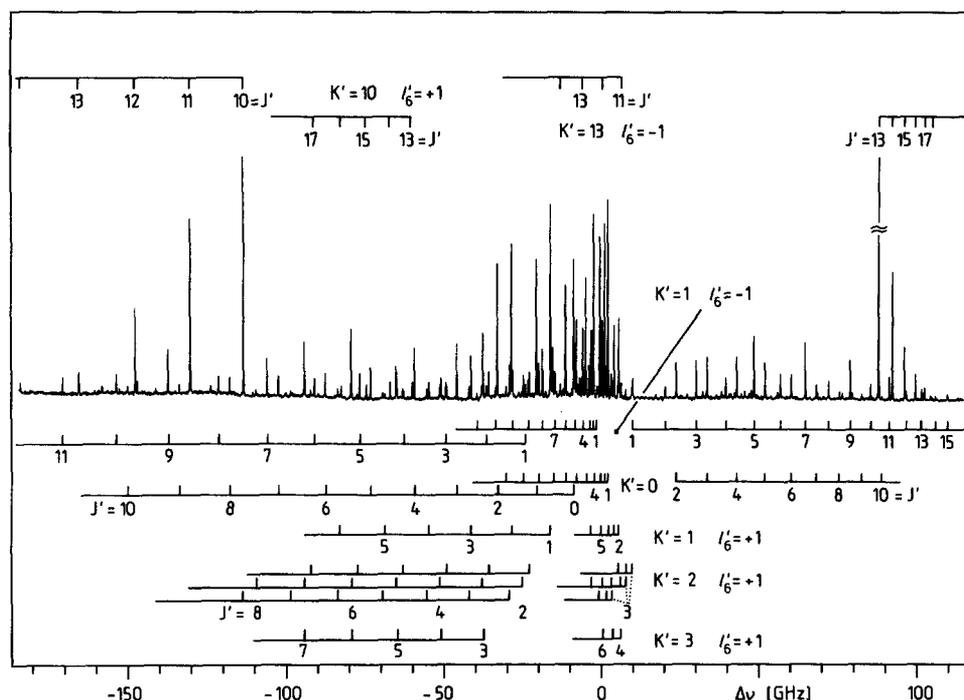


FIG. 5. Assignment of the rotational structure of the $6_0^1 1_0^3$ band of C₆H₆ (detected by delayed MPI). The regular systems of lines marked by the horizontal scales belong to transitions with constant K' and ΔK . The particular value of J' and K' of each line was determined from the distance from the neighboring lines as described in the text. The transitions to $K'=2, l'_6 = +1$ states are split into three components as indicated by the dotted lines.

states $l'_6 = -1$ and $l'_6 = +1$ of the degenerate ν_6 state of e_{2g} symmetry for $K' > 0$. The “-” sign in Eq. (1) is to be used for the $l'_6 = -1$ substate and the “+” sign for the $l'_6 = +1$ substate. $\Delta J = J' - J''$ can be $-1, 0$ or $+1$ ($P, Q,$ or R branch) and $\Delta K = K' - K''$ can be -1 or $+1$ for the perpendicular band under investigation.¹ For lines with constant ΔJ and ΔK the distance

$$\begin{aligned} \delta E(J', J' + 1) \\ = \Delta E_{\text{rot}}(J' + 1, K' \leftarrow J' + 1 - \Delta J, K' - \Delta K) \\ - \Delta E_{\text{rot}}(J', K' \leftarrow J' - \Delta J, K' - \Delta K) \end{aligned}$$

between neighboring lines with constant K' is given by

$$\Delta J = -1: \delta E(J', J' + 1) = 2 \cdot \Delta B \cdot (J' + 1) - 2 \cdot B'', \quad (2)$$

$$\Delta J = 0: \delta E(J', J' + 1) = 2 \cdot \Delta B \cdot (J' + 1), \quad (3)$$

$$\Delta J = +1: \delta E(J', J' + 1) = 2 \cdot \Delta B \cdot (J' + 1) + 2 \cdot B''. \quad (4)$$

The distance $\delta E(K', K' + 1)$ between neighboring lines with constant J' is given by

$$\begin{aligned} \Delta K = -1: \delta E(K', K' + 1) = 2 \cdot \Delta(C - B) \cdot K' \\ + (C' - B' - 3 \cdot C'' + 3 \cdot B'' + 2 \cdot C' \cdot \zeta'_{\text{eff}}) \end{aligned} \quad (5)$$

$$\begin{aligned} \Delta K = +1: \delta E(K', K' + 1) = 2 \cdot \Delta(C - B) \cdot K' \\ + (C' - B' + C'' - B'' - 2 \cdot C' \cdot \zeta'_{\text{eff}}). \end{aligned} \quad (6)$$

Both cases would explain the observed increase or decrease of the distance between neighboring lines in each system by a constant value. Since for the planar benzene molecule $\Delta(C - B) \approx -\Delta B/2^{22}$ and the value of ΔB for the $S_1 \leftarrow S_0$ transition is well known, the magnitude of the observed changes allows us to decide that we observe systems of constant K' . From the position of each system of lines within the rotational contour the value of ΔJ can easily be decided. B'' is well known²⁵ and ΔB obtained experimentally for each system and therefore Eqs. (2) to (4) even render the absolute value of J' for each line. The resulting values for *all* observed transitions are indicated in Fig. 5.

For transitions with common J', K' , and ΔK but varying ΔJ the relative distance depends only on the well known value of B''^{25} and we can therefore decide which systems in the $P, Q,$ and R branch lead to the same excited states. These groups of up to three systems are marked at the same vertical position in Fig. 5. The whole band thus reduces to only seven groups of line systems with common K' and ΔK . Transitions to all other values of K' do not appear in the $6_0^1 1_0^3$ band. Even for the remaining K' values, the range of observed J' values differs considerably. This indicates that the nonradiative decay responsible for the disappearance of lines is not only K dependent but also J dependent. However, the J dependence of line intensities is found to be very smooth.

After the J assignment has been determined from purely systematic considerations and no *a priori* assumptions, we have to try to find the values of K' and ΔK of each of the seven groups of line systems. For this purpose we have to remember that the $6^1 1^3$ state is degenerate and each rovibronic level splits into a $l'_6 = -1$ and a $l'_6 = +1$ sublevel.¹ $l'_6 = -1$ sublevels can only be accessed in the electronic transition via $\Delta K = +1$ transitions and $l'_6 = +1$ sublevels via $\Delta K = -1$ transitions.^{1,22} The Hönl-London factors, which govern the relative intensity of lines, are largest for transitions with $\Delta K = -1$ and K' close to J' in the P branch, $\Delta K = \pm 1$ and $K' \approx 0$ in the Q branch and $\Delta K = +1$ and K' close to J' in the R branch. Therefore, the strength of a particular system in the various branches of the spectrum gives an initial guess on the value of K' and ΔK . In addition, an upper limit for K' is given by the lowest value of J' observed for the system. Furthermore, transitions with $\Delta K = -1$ (to $l'_6 = +1$ states) can be observed for the P branch down to $J' = K'$, in the Q branch to $J' = K' + 1$ and in the R branch to $J' = K' + 2$. This situation is observed for the four systems marked lowest in Fig. 5. Last, but not least, a fortuitous detail of benzene spectroscopy gives us one unambiguous assignment without need for other reasoning. States with

$K' = 1$ and $l'_6 = -1$ can only be accessed via $\Delta K = +1$ transitions from $K' = 0$ ground states. The statistical weight of these states is 7 for J'' even and 3 for J'' odd. The resulting alternation of line intensities is clearly observed for the group of systems marked just below the experimental spectrum in Fig. 5. They can, therefore, directly be assigned as transitions with $\Delta K = +1$, $K' = 1$, and $l'_6 = -1$. The other K' and l'_6 assignments shown in the lower part of Fig. 5 follow from this assignment easily, if only fairly regular behavior of the K' dependence of the line positions is assumed and the abovementioned consequence of $J' > K'$ is remembered. For the two systems observed mainly in the far parts of the P and R branches, the assignment of $K' = 10$, $l'_6 = +1$ and $K' = 13$, $l'_6 = -1$ shown at the top of Fig. 5 is not quite so secure, but we believe it to be correct to ± 1 for K' and absolutely for l'_6 .

With the assignment of *all* observed lines now performed, we can try to fit rotational constants to the whole band and determine the frequency ν_{00} of the rotationless origin. For this purpose we first calculate values for B'_v for each group of line systems (i.e., for each value of K' and l'_6) separately. The resulting values are summarized in Table II. For comparison the values of B'_v for the 6^1 ,²² $6^1 1^1$,²² and the $6^1 1^2$ state²⁶ are included in Table II. It is seen that the somewhat smaller values of B'_v for the $6^1 1^3$ state are in line with the trend in these states at lower excess energy. However,

there is a significant variation of B'_v on K' and l'_6 . This indicates that the various rovibronic states are slightly shifted in a J' and K' dependent way. This can also be concluded from the fact that no good fit of C'_v and ζ'_{eff} on the K' dependence of line positions is possible. There is a strongly K' dependent irregular deviation of the positions of about ± 500 MHz to any reasonable set of rotational constants and, in addition, the weaker J' dependence evidenced by the varying values of B'_v . This variation of the line positions can be understood as rotationally dependent coupling to other (dark) S_1 states in the strong coupling limit in addition to the coupling in the weak limit to heavily broadened states which is responsible for the disappearance of most lines of the band. Such a coupling in the strong limit is known to lead to isolated perturbations (i.e., shifts and splittings of lines) at low vibrational excess energy in S_1 .^{27,28}

Due to the lack of a good fit of the rotational constants to all lines in the spectrum also the determination of the frequency ν_{00} of the rotationless origin is not straightforward. Since any rotationally selective shift of lines is, in general, expected to be least likely for $K' = 0$ states and also the value of B' determined from these states agrees quite well with the average from all lines, we used the $K' = 0$ lines for the determination of ν_{00} . The resulting value is included in Table II together with the previously determined values for the 6_0^1 , $6_0^1 1_0^1$, and $6_0^1 1_0^2$ band.

TABLE II. Values of the rotational constant B'_v and the rotationless origin ν_{00} for the bands $6_0^1 1_0^q$ of C₆H₆. For the $6^1 1^3$ state analyzed in this work separate values of B'_v are given for all the K' , l'_6 states observed in the delayed MPI spectrum. The average value of B'_v for the vibronic state was calculated from all values shown except the $K' = 2$, $l'_6 = +1$ states, which were found to be split in three components.

Vibronic state	ν_{00} (cm ⁻¹)			B'_v (cm ⁻¹)
6^1 ^a	38 606.089 (8)			0.181 778 (2)
$6^1 1^1$ ^a	39 529.630 (8)			0.181 648 (2)
$6^1 1^2$ ^b	40 452.091 (8)			0.181 537 (3)
		K'	l'_6	
		10	+1	0.181 466 (9)
		3	+1	0.181 349 (52)
		2	+1 ^c	0.181 486 (3)
				0.181 645 (14)
				0.181 464 (13)
		1	+1	0.181 496 (18)
$6^1 1^3$	41 373.461 (12)	0		0.181 447 (5)
		1	-1 ^d	0.181 417 (1)
			P,R Q	0.181 501 (3)
		2	-1	0.181 491 (26)
		13	-1	0.181 424 (3)
		average		0.181 449

^a Taken from Ref. 22

^b Reference 26.

^c Separate values are given for the three components observed.

^d Different effective values are found for P and R transitions and Q transitions due to rotational l resonance with $q = -0.84 \times 10^{-4}$ cm⁻¹ (see the text).

Two final points found in this detailed analysis should be mentioned. First, the position of the *P*- and *R*-branch transitions to $K' = 1, l'_6 = -1$ states do agree very well, but there is a deviation from the *Q*-branch positions which depends linearly on $J' \cdot (J' + 1)$. This is due to rotational *l*-type doubling of the $K' = 1, l'_6 = -1$ states²⁹ with a value of $q = -0.84 \times 10^{-4} \text{ cm}^{-1}$. The observation of this doubling is a further confirmation of the assignment given. Second, it can be seen from Fig. 5 that the $K' = 2, l'_6 = +1$ states are all split into three components with a maximum distance of about 5.5 GHz. The sum of the intensities of the three lines is in good agreement with the intensity of the unsplit lines with neighboring K' . The splitting can be understood as coupling in the strong coupling limit to two background states with reasonable coupling matrix elements on the order of 2 GHz.

To summarize, the rotational structure of the delayed MPI spectrum of the $6_0^1 1_0^3$ band was completely assigned. There are only transitions to a few low values of K' and to two higher values of K' observed, i.e., all other states decay very rapidly on the time scale of our experiment. In addition, there are rotationally dependent shifts of the observed lines and a splitting of the $K' = 2, l'_6 = +1$ lines. With the assignment of the delayed MPI spectrum, a partial assignment of the fluorescence excitation spectrum is also possible. This leads to the assignment of the states, whose decay behavior was measured (compare Table I) and the observation that the broadened lines seen in the fluorescence excitation spectrum are most likely transitions to states with K' values close to the values of the lines observed in the delayed MPI spectrum.

V. DISCUSSION

A. Comparison of one- ($6^1 1^3$) and two-photon ($14^1 1^2$) states

From the detailed assignment of the MPI spectrum presented in Sec. IV, it is seen that only rotational states of the $6^1 1^3$ vibronic state of C₆H₆ with $l'_6 = +1$ and $K' = 1, 2, 3, 10$, states with $K' = 0$ and states with $l'_6 = -1$ and $K' = 1, 13$ give rise to detectable lines. The decay time of these states is on the order of a few ns. Most likely, states with other values of K' and l'_6 decay fast on the time scale of our experiment. This highly selective disappearance and appearance of lines is similar to the one observed previously¹³⁻¹⁵ for the $14^1 1^2$ state. For this state it was found that at low rotational energy only $K' = 0$ states decay slowly while at the much higher rotational energies accessible in the room temperature experiment mainly $K' \approx J'$ states survive for a long time. From this similarity it can be concluded that the rotational selectivity of the nonradiative decay of "channel three" benzene is not a sole property of the b_{2u} vibrational state excited in two-photon spectroscopy, but rather a more general feature at the onset of "channel three." Since it is not known whether this rotational selectivity vanishes again at even higher vibrational energies any data from experiments in the "channel three" region without rotational selection have to be considered with extreme caution since they present averaged values and any possible rotational selectivity is obscured.

Aside from this similarity there is, however, also a significant difference between the $14^1 1^2$ state and the $6^1 1^3$ state. The decay time of the $K' = J' = 0$ state of the $14^1 1^2$ state at 3412 cm^{-1} vibrational excess energy was found to be $>55 \text{ ns}$ ¹⁴ (quite comparable to the decay time of low excess energy states) while all the low rotational states of the $6^1 1^3$ state at the somewhat lower excess energy of 3287 cm^{-1} have a considerably smaller decay time of less than 10 ns. An explanation for this situation and the pattern of long lived rotational states in the $6^1 1^3$ state will be presented next.

The exclusive appearance of the $K' = 0$ lines in the blue part of the spectrum of the $14_0^1 1_0^3$ band was interpreted as parallel Coriolis coupling in the weak coupling limit to one rapidly decaying (broadened) background state.^{14,15} The coupling matrix element scales linearly with K' ($V_z \sim \zeta CK$); it is, therefore, not existent for $K' = 0$, and the $K' = 0$ states are nearly unperturbed. The observation of mainly states with low K' in the $6^1 1^3$ state might be explained at first sight with a similar model, i.e., one single decay channel (coupled state). However, the decay of these states with low K' is by about 1 order of magnitude faster than the decay of the $6^1 1^2$ state ($\tau = 72 \text{ ns}$ ²⁰) in contrast to theoretical predictions that the decay rate should only increase by less than a factor of 2 between the $6^1 1^2$ and the $6^1 1^3$ state.³⁰ This indicates that there is at least one additional decay channel (coupling) present, which is also active for the very lowest rotational states. In addition, there is a strong asymmetry in the decay behavior of the $l'_6 = +1$ and $l'_6 = -1$ components, i.e., for $l'_6 = +1$ states are observed up to $K' = 3$ while $l'_6 = -1$ components are only seen for $K' = 1$. This, again, cannot be explained by Coriolis coupling alone, since there is no dependence of the coupling matrix element on the vibrational angular momentum quantum number l . Even more seriously, the $K' = 10, l'_6 = +1$ states and the $K' = 13, l'_6 = -1$ states are found to decay slowly, but not states with neighboring values of K' . Such a nonmonotonic appearance of lines cannot be understood in terms of the smooth J and K dependence of any known coupling matrix element but only in terms of very intricate resonance and interference conditions.

B. Coupling model

Polik *et al.*³¹ recently presented model calculations for coupling in the weak coupling limit of one optically accessible state $|\psi_0\rangle$ to a manifold of states $\{|\phi_k\rangle\}$, $k = 1, 2, 3, \dots$, 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

$$\langle \psi_0 | H | \tilde{\psi}_k \rangle = \tilde{v}_{0k} = |\tilde{v}_{0k}| e^{i\theta_k} \quad (7)$$

between the state $|\psi_0\rangle$ and each state $|\tilde{\psi}_k\rangle$. θ_k is the phase of the eigenfunction $|\tilde{\psi}_k\rangle$. It was shown by Polik *et al.* that 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

$$\Gamma = \Gamma_0 + \sum_k \left[\frac{|\tilde{v}_{0k}|^2(\tilde{\Gamma}_k - \Gamma_0)}{(\tilde{E}_k - E_0)^2 + (1/4)(\tilde{\Gamma}_k - \Gamma_0)^2} \cos 2\theta_k + \frac{2|\tilde{v}_{0k}|^2(\tilde{E}_k - E_0)}{(\tilde{E}_k - E_0)^2 + (1/4)(\tilde{\Gamma}_k - \Gamma_0)^2} \sin 2\theta_k \right]. \quad (8)$$

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 rotational states of the $6^{11}3$ or $14^{11}2$ vibronic states, if we associate the state $|\psi_0\rangle$ with this light zero order state, the states $|\phi_k\rangle$ with one or more broadened background states in S_1 , and the continuum with the dense manifold of highly excited T_1 and/or S_0 states. As we will show, new interference effects are therewith introduced which give an explanation for the observed nonmonotonic appearance of lines in the $6_0^1 1_0^3$ band.

Equation (8) reduces to the well known formula for coupling in the weak limit to *one* broad state^{32,33} which was used for the analysis of linebroadening in the $14^{11}2$ state in our previous work,¹⁴ 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 nonvanishing 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 sin and cos terms in Eq. (8) together with the dispersive dependence on \tilde{E}_k [third term in Eq. (8)] will lead to significant cancellation of the contributions from the $|\phi_k\rangle$ states and Γ will not be much greater than Γ_0 .

For the $6^{11}3$ state under investigation, all these details could combine in the following way: Γ is greater than Γ_0 for all low values of K' due to one broad background state and increases monotonically for higher values of K' due to the rotational dependence of the coupling strength (e.g., parallel Coriolis coupling) to a second state. If Γ , and therefore the decay rate, is high enough, the appropriate lines are not seen in our spectrum. However, for $K' = 10$, $l'_0 = +1$ and $K' = 13$, $l'_0 = -1$ the two decay channels interfere destructively, i.e., their contributions to the decay width Γ cancel to a large degree as described, and the lines are seen in the spectrum. While the observed highly nonmonotonic behavior cannot be explained by coupling to one background state, we cannot exclude involvement of more than two states. Too large a number would, however, be incompatible with the concept of selective interferences and also be hard to explain in view of the relatively low total density of background states ($118/\text{cm}^{-1}$ for all symmetries^{19,34}).

Obviously, this model could also give an alternative explanation for the slow decay of the $K' = 0$ states of the $14^{11}2$ vibronic state. On the other hand, the appearance of low K' states in both investigated cases must still be considered strong evidence for the involvement of rotation-vibration

coupling (e.g., Coriolis coupling) in the primary process of the nonradiative decay of "channel three" benzene.

C. Comparison with previous low resolution results

Let us now turn to a comparison of our new data on the decay of the $6^{11}3$ state with previous results and even more generally to the a critical comparison of the various results on "channel three." In the original report of Callomon *et al.*,² the $6^{11}3$ state was the lowest excess energy state found to be broadened. They deduced a "linewidth" of 0.3 cm^{-1} for this state from a comparison of the diffuse spectrum of the $6_0^1 1_0^3$ band with spectra of inherent sharpness, which were recorded with limited resolution. The comparison of the resulting nonradiative decay with earlier decay time measurements of states of low excess energy³ showed the dramatic increase in the decay rate which led to the postulation of "channel three." The experimental linewidth of the sharpest lines observed in our experiments and the single exponential decays of a few ns lead to an estimate of the homogeneous linewidth of the longest lived rotational states of about 0.001 cm^{-1} . This is by more than 2 orders of magnitude less than the value deduced by Callomon *et al.*² The broadened lines, which were also observed in our experiment, have a width of about 0.01 cm^{-1} and an even larger linewidth has to be assumed for all the states not observed. This could mean that the discrepancy of about 2 orders of magnitude between decay rates deduced from the "lifetime" measurements^{3,6,11} and the "linewidth" measurements^{2,5,19} in experiments without rotational resolution is a consequence of the particular ensemble of rotational states that was excited in these experiments. Fluorescence lifetime experiments select the longest lived states with reasonable quantum yield, while "linewidth" measurements (particularly in absorption) will just as effectively see the fast decaying states (possibly the high J, K states predominantly observed at room temperature). In addition, it should be mentioned that the observation of splitting of lines (e.g., the $K' = 2, l'_0 = +1$ states) in several components dispersed over about 0.2 cm^{-1} might give an alternative explanation for the observed diffuseness of the contours² in the "channel three" regime. It is therefore not appropriate to deduce a value of the nonradiative decay rate from this diffuseness, but rather just an estimate of the range of frequencies, each rotational state contributes to. This modeling would be similar to the notion of IVR decay rates by Parmenter and co-workers.¹⁹ However, both in our experiment and the one of Callomon *et al.*² and later Aron *et al.*⁵ the coherence width of the excitation source was not large enough to prepare a coherent superposition of all eigenstates, which contain a contribution of the light state and therefore no dynamic IVR process could be observed. Finally, an IVR decay rate or vibrational dephasing rate should certainly be distinguished from the electronic nonradiative decay rate.

In view of our new results for the nonradiative decay of the various rotational states of the $6^{11}3$ vibronic state, it is interesting to ask what remains of the original observations leading to the postulation of "channel three." Definitively,

the sharp rise of the nonradiative decay rate of S_1 states accessible by optical transitions, as concluded by Callomon *et al.*,² is washed out if individual rotational states are observed. A rotational selectivity of the nonradiative decay is found for both the b_{2u} states (e.g., $14^1 1^2$) accessed by two-photon excitation and the e_g states (e.g., $6^1 1^3$) accessed by one-photon excitation and seems to be quite general for S_1 benzene around 3000 cm^{-1} excess energy regardless of the vibrational symmetry. What remains, is good evidence that starting at roughly an excess energy of 3000 cm^{-1} vibrational state mixing within the S_1 state of benzene by anharmonic and rotation–vibration coupling (observed already at low excess energy^{16,27,34}) becomes so frequent, that there is very efficient mixture of the vibrational states accessed by the optical transition with the many background states which are not accessible by optical transitions due to the high symmetry of benzene and selective Franck–Condon factors. This conclusion is in good agreement with the evidence from emission spectra^{19,21} and MPI photoelectron spectra.¹⁸ At least some of these background states are believed to be strongly coupled to the highly excited S_0 electronic state^{35–37} and their decay is much faster than that of the optically accessible states. This differing decay behavior could well be a consequence of their differing vibrational character in qualitative agreement with theoretical investigations.^{35–37} Since we do not know whether states with similar vibrational character but excess energy below 3000 cm^{-1} are sharp or broad, nothing can be said about the excess energy dependence of the decay rate for this type of vibronic states. The admixture of the background states then leads to the turn over from ISC to IC previously concluded for the “channel three” regime.^{8,10} From the rotational analysis of the $6_0^1 1_0^3$ band we can estimate the number of admixed states. The splitting of the $K' = 2, l'_g = +1$ states in three components leads to at least two other sharp states and the appearance of sharp interference patterns (for $K' = 10, l'_g = +1$ and $K' = 13, l'_g = -1$) shows us that there are at least two broad states involved. This places a lower limit of five to the number of coupled states, while the high selectivity observed in our spectra leads us to the conclusion that there are probably less than ten states involved. For a comparison it should be mentioned that Parmenter and co-workers¹⁹ concluded five to seven states to be coupled, in good agreement with this estimate.

VI. SUMMARY AND CONCLUSION

In this work we presented rotationally resolved spectra of the $6_0^1 1_0^3$ band of benzene at an excess energy of 3287 cm^{-1} . The fluorescence excitation spectrum with an experimental resolution of 150 MHz shows a reduced number of sharp lines as compared to regular vibronic bands of benzene and a broad background which is believed to be due to coupling to broadened background states in S_1 . The decay of the fluorescence signal following excitation of various sharp features in the spectrum is found to be single exponential and to vary strongly with the molecular rotation, i.e., the nonradiative decay is highly rotationally selective. If the excitation of the benzene molecules is monitored by ionization with a sec-

ond UV laser, which is delayed with respect to the excitation laser, an MPI spectrum is obtained, which lacks the broad background of the excitation spectrum and shows a greatly simplified rotational structure. This rotational structure was completely assigned and it was found that mainly lines with extremely low values of K' appear in the spectrum but also a few lines with considerably higher K' . A model is presented which explains these findings as coupling of the light zero order $6^1 1^3$ state to a small number of broadened background states. This coupling leads to the disappearance of most lines in the spectrum, but also the isolated appearance of lines with higher K' values which is understood as interference between the decay channels given by the broadened background states.

The relatively slow decay of the zero order $6^1 1^3$ state is in strong disagreement with the “linewidth” of 0.3 cm^{-1} found previously for this vibronic state.² This large “linewidth” of the $6^1 1^3$ state and other vibronic states of higher energy led Callomon *et al.* to the conclusion that the nonradiative decay of S_1 benzene increases drastically around 3000 cm^{-1} excess energy and they concluded a “channel three” decay process from the increase.² Since we cannot confirm this drastic increase of the nonradiative rate of the optically accessible states, we see no more need to invoke an extra “channel three” nor can we confirm the observation of a biexponential decay by Sumitani *et al.*, which was interpreted as a reversible isomerisation.¹¹ Instead, we believe that the mixing and decay behavior of the optically excited states of S_1 benzene can be well explained by the known decay channels of ISC and IC and IVR as a primary process.

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