

Rotationally resolved spectra of the 6_0^1 and $6_0^1 1_0^1$ band of benzene in a moderately cold molecular beam: Spectral and dynamical analysis

E. Riedle, Th. Knittel, Th. Weber, and H. J. Neusser

Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstr. 4, D-8046 Garching, West Germany

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Rotationally resolved spectra of the 6_0^1 and $6_0^1 1_0^1$ band of benzene, C_6H_6 , in a supersonic molecular beam at rotational temperatures between 8 and 50 K are reported. The spectra consist of lines of 85 MHz linewidth. An unexpectedly low saturation intensity of $\approx 10^4$ W/cm² is found for the observed one-photon transitions, and it is shown that the saturation intensity differs for different rotational lines within one vibronic band. The rovibronic line spectra are analyzed within the framework of a rigid symmetric top model and highly precise values of the rotational constants are determined. In addition, the rotationless transition frequencies ν_{00} are obtained with high precision. The spectrum of the 6_0^1 band shows no signs of rotational perturbations, while the $6_0^1 1_0^1$ band at higher vibrational excess energy shows indications of perturbations for lines with K' above 10. The decay times of single rotational states within the $6^1 1^1$ vibronic state are reported and no rotational dependence of the decay time is found in agreement with the statistical limit character of the interstate nonradiative process.

I. INTRODUCTION

The resolution of the rotational structure of the UV spectrum of large molecules is not possible with the resolution of about 1×10^6 of conventional Doppler-limited spectroscopy. However, recently we were able to show that the complete resolution of the rotational structure of the vibronic bands of benzene is possible after elimination of the Doppler broadening.^{1,2} The method used was Doppler-free two-photon spectroscopy of benzene at room temperature. The extremely high resolution of 2×10^8 achieved in these investigations allowed the identification of isolated rotational perturbations³ and the observation of the homogeneous line width of single rovibronic states.⁴ In a pulsed experiment at a somewhat reduced resolution of 1×10^7 the measurement of the decay time of single rovibronic quantum states was possible.^{5,6} One of the striking results of these investigations was a strong rotational dependence of the nonradiative decay rate in the "channel three" regime.⁵

While most of the spectroscopic investigations of benzene with Doppler-limited resolution and consequently unresolved rotational structure were performed on one-photon allowed transitions, the rotationally resolved spectra so far were all recorded for two-photon allowed transitions. Due to the high symmetry of benzene (D_{6h}) different final states are accessible by one- and two-photon spectroscopy. Therefore, the high degree of rotational selectivity found in the two-photon sub-Doppler work³⁻⁶ cannot directly be compared with the previous investigations and the question may arise whether the results (e.g., line broadening, varying decay times) are special results of the two-photon states investigated in our previous work or are rather a common characteristic of all states at a distinct vibrational excess energy independent of the symmetry and character of these states.

The best resolved *one-photon* UV spectra of benzene in the literature still remain the Doppler-limited spectra of Callomon, Dunn, and Mills (CDM) of more than 20 years ago.⁷

Since that time experimental methods have been greatly improved, but these new methods were not yet used to record electronic one-photon spectra of the prototype organic molecule benzene at increased resolution. In this work we want to show that the combination of an extremely narrow bandwidth pulsed tunable laser system with a well collimated pulsed molecular beam permits the observation of rotationally resolved one-photon spectra of benzene under conditions of moderate rotational cooling. The combined use of narrow band width lasers and collimated molecular beams has rendered spectra of a number of molecules at a resolution well below the room temperature Doppler-width before, but in these investigations the needed laser frequency was either in the visible region⁸ or could be reached fairly conveniently by direct frequency doubling of a cw laser.⁸⁻¹⁰ This is not valid for the $S_1 \leftarrow S_0$ system of benzene, but pulsed amplification of the cw laser and consequent frequency doubling is shown to be a very efficient way to produce the desired narrow bandwidth UV light. The pulsed nature of the laser system allows the use of a pulsed molecular beam, which requires a much smaller vacuum system than the continuous molecular beams used in conjunction with cw lasers.

II. EXPERIMENTAL

The scheme of our experimental setup is shown in Fig. 1. It basically consists of an extremely narrow bandwidth pulsed tunable UV laser system, a pulsed molecular beam apparatus, and the detection electronics.

To produce the narrow bandwidth tunable UV laser light, the output of a commercial single mode cw dye laser (CR 699/21; Coumarin 102 dye; $\Delta\nu \approx 1$ MHz) is amplified in three stages (Coumarin 307 dye) pumped by 10%, 20%, and 70%, respectively of the output of a XeCl excimer laser (EMG 1003 MSC).^{6,11} At the wavelength of about 510 nm, typically 200 mW of cw light are sufficient to obtain light pulses with 5 to 10 mJ energy from 100 mJ pump pulses. The

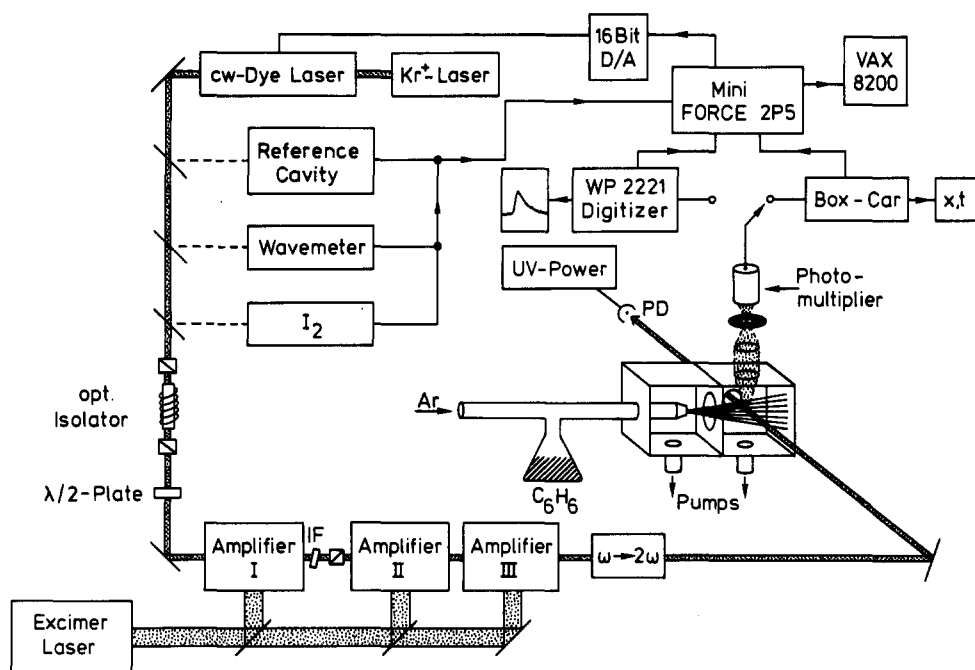


FIG. 1. Experimental setup for the recording of one-photon sub-Doppler fluorescence excitation spectra of benzene at moderate rotational cooling. The cw dye laser is pulsed amplified and frequency doubled. The laser beam is crossed perpendicularly with the pulsed collimated molecular beam.

frequency width of the resulting visible pulses is about 50 MHz (see Sec. III A), i.e., they are nearly Fourier transform limited in frequency space. The pulse length of 15 ns, which is slightly shorter than the length of the pump pulses, would correspond to a frequency width of 30 MHz. To decouple the amplifiers from the cw laser, an optical isolator consisting of two polarizers and a home built Faraday rotator is used. Amplified spontaneous emission resulting from the first amplifier stage is effectively suppressed by spatial filtering, a narrow bandwidth interference filter and an additional polarizer between the first two amplifier stages.^{6,11} The narrow bandwidth pulsed light is frequency doubled in a BBO crystal. No attempt has been made to maximize the efficiency of doubling, since the resulting pulse energy of typically $400 \mu\text{J}$ is by far sufficient to saturate all investigated transitions (for details see Sec. III B 2). Indeed, the UV light is typically attenuated by a factor of 100 for the recording of spectra. No change of the phase matching angle was needed during a single scan of the cw dye laser of up to 30 GHz.

The spectral purity of the cw light is monitored with a scanning Fabry-Perot interferometer (FPI) and its frequency is routinely measured to an absolute accuracy of better than 0.02 cm^{-1} with a commercial wavemeter (Burleigh, WA 20). For a highly precise absolute calibration of the spectra, the I_2 absorption spectrum is recorded simultaneously and compared with the spectrum of Ref. 12. A precise relative frequency scaling is obtained from the transmission spectrum of a 150 MHz free spectral range (FSR) confocal FPI (Burleigh, CFT 500) which was evacuated and temperature stabilized. Its FSR was determined to better than 1 part in 10^5 by comparison with the I_2 spectrum.¹² To avoid problems with variations in phase shift with changing wavelength,¹³ Al-coated mirrors were used in the FPI leading to a finesse of 7.

The unfocused narrow bandwidth UV light with a beam diameter of about 2 mm is crossed perpendicularly with a supersonic beam of benzene, which is formed by expanding

pure benzene or a mixture of 60 Torr benzene and varying amounts of Ar (up to 2.5 bar partial pressure) through a $200 \mu\text{m}$ nozzle. The nozzle is mounted in a modified fuel injection valve, which is capable to produce gas pulses of typically $500 \mu\text{s}$ duration. The distance between the nozzle and the interaction region could be varied between 0 and 200 mm. The vacuum chamber consists of two parts, pumped by turbo molecular pumps with 330 and 170 ℓ/s pumping speed, respectively. Typically a background pressure of 4×10^{-5} Torr was maintained in the second chamber to ensure collisionless excitation conditions. To record sub-Doppler one-photon excitation spectra, the interaction region is imaged onto a 2 mm aperture by two planoconvex fused silica lenses of 80 mm focal length and 37 mm effective aperture. The light transmitted through the aperture is detected by a photomultiplier (56 DUVP; Valvo). The small solid angle of collection proved to be sufficient for the recording of the spectra with superior signal to noise ratio. It is worth mentioning, that in a recent experiment to record the rotationally resolved electronic spectrum of the cyclopentadienyl radical,¹⁴ a similar setup to the one reported here was used, but a somewhat lower effective collimation of the molecular beam and a larger laser linewidth resulted in a three-fold larger experimental linewidth than reported here. For optimum spectral resolution and lower background pressure a home built skimmer with a circular opening of 1.5 mm diameter was placed between the nozzle and the interaction region. The total UV power transmitted through the apparatus was recorded with a photodiode to allow normalization of the spectra. To hinder stray light of the laser from reaching the photomultiplier, a light baffle consisting of apertures of 8, 7, and 6 mm diameter is installed at the entrance side of the beam chamber and a Brewster-angled window on the exit side.

The signal from the photomultiplier was either integrated in a SR 250 gated integrator to record spectra or its waveform was digitized in a Tektronix WP2221 system for decay

time measurements. Data were stored in a Mini FORCE 2P5 and finally transferred to a VAX 8200 computer for evaluation. For the recording of decay curves, the laser was not scanned with the commercial control unit, but instead by the output of a computer controlled 16 bit DA converter. By this procedure the laser frequency can be positioned on top of any desired spectral feature for sufficient time.

III. RESULTS AND DISCUSSION

A. Spectral resolution of the collimated beam experiment

In a collimated molecular beam the distribution of transversal velocities (i.e., the transversal translational temperature) is strongly reduced and, as a consequence, the Doppler width decreases drastically. The experimentally observed linewidth of single transitions is determined by the homogeneous width of the molecular lines, the heterogeneous width due to the reduced Doppler width and the linewidth of the laser. In the investigated case of benzene transitions leading to excited states with relatively low vibrational excess energy in S_1 , the homogenous linewidth is expected to be on the order of a few MHz at most, since the decay time of these states is known to be just slightly less than 100 ns¹⁵ and collisional broadening can certainly be neglected in the molecular beam. As the laser bandwidth is about 70 MHz, the homogeneous width does not significantly enter into the measured linewidth.

The effective collimation of the molecular beam is given by the distance between the nozzle and the laser beam-molecular beam interaction region and the observed size of the interaction region, as determined by the quality of the imaging optics and the size of the aperture in front of the photomultiplier. If we used a skimmer to collimate the beam mechanically, the distance between nozzle and skimmer becomes determining. However, too high a collimation will lead to a low number of observed excited molecules and consequently a low signal. A reasonable value for the effective collimation is found, if it is good enough to reduce the distribution of transversal velocities (i.e., in the direction of propagation of the laser beam) and consequently the residual Doppler width to a value comparable to the laser linewidth. Any better collimation will only reduce the signal, but not lead to a significantly better resolution. It is also worth mentioning at this point, that the Doppler width does not only depend on the collimation of the beam but also on the absolute velocity of the molecules. In a supersonic expansion the velocity of the seeded gas (benzene) is approximately equal to the thermal velocity of the carrier gas. To reduce this value argon ($M = 40$ amu) was preferred to helium ($M = 4$ amu) as a carrier gas in our experiments.

To measure the linewidth of our laser, we chose to record a spectrum with a known homogeneous width of the molecular lines of significantly less than the laser width. From cw Doppler-free two-photon spectroscopy¹⁶ and decay time measurements⁶ we know that this condition is fulfilled for the rotational lines in the $14_0^1 1_0^1$ two-photon band. Therefore, the pulsed amplified visible laser light was not frequency doubled but directly focused onto the molecular beam in order to induce two-photon transitions to the elec-

tronically excited state. To obtain a reasonable signal, the molecular density had to be kept high by choosing a small distance of about 5 mm between the nozzle and the laser. The resulting two-photon spectrum in the vicinity of the known rotationless origin of the $14_0^1 1_0^1$ band is shown in Fig. 2 (c). In comparison with room temperature conditions^{2,11,16} a narrow Q-branch spectrum is observed, as is typical for the rotational cooling at the backing pressure of 1.5 bar. Since two-photon absorption with one laser beam is not Doppler-free and the collimation of the molecular beam is low in this experiment, the residual Doppler width is quite large and the rotational structure is not resolved. To resolve the rotational structure a Doppler-free two-photon experiment was performed, which is expected to lead to Doppler-free transitions independent of the collimation of the molecular beam. The visible laser beam was reflected back by a spherical mirror and the Doppler-free spectrum shown in Fig. 2(b) was obtained. The rotational structure is now resolved as expected for a Doppler-free experiment. The rotational cooling in the molecular beam ($T_{\text{rot}} = 7.6$ K) can nicely be seen from the comparison with the room temperature spectrum of our previous work¹¹ shown in Fig. 2 (a). This spectrum was mea-

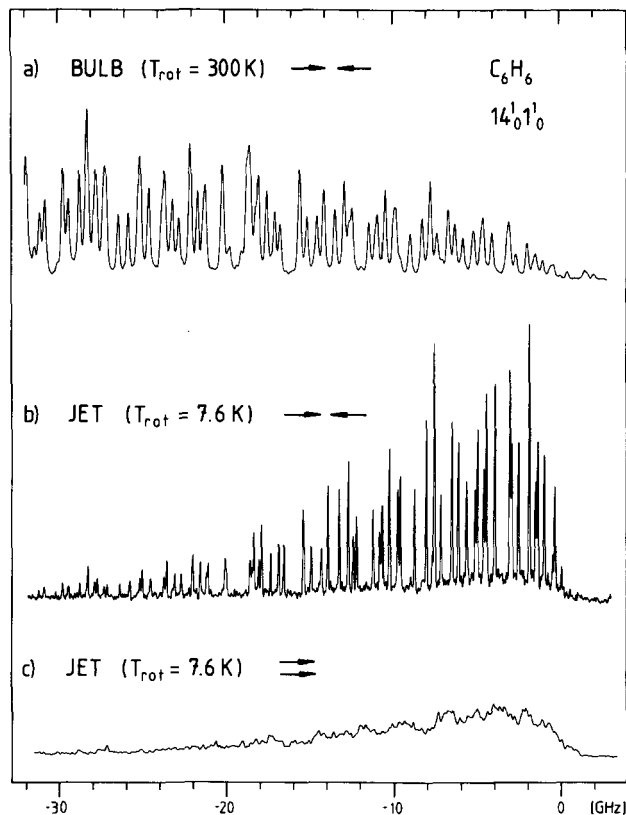


FIG. 2. Two-photon excitation spectra of the $14_0^1 1_0^1$ band of benzene, C_6H_6 , recorded under different experimental conditions after excitation with the visible light of the pulsed amplified cw laser. (a) Part of the Doppler-free spectrum obtained in a fluorescence cell at room temperature (Ref. 11). (b) Doppler-free spectrum after absorption of two photons from counterpropagating light beams in a noncollimated supersonic molecular beam. Both rotational cooling and rotational resolution is observed under these conditions. (c) Doppler-limited two-photon spectrum after excitation with one laser beam in a noncollimated supersonic molecular beam. No rotational resolution is obtained due to the limited collimation of the molecular beam.

sured with a pulsed amplified laser with a somewhat larger frequency width. To our knowledge the spectrum shown in Fig. 2 (b) is the first Doppler-free two-photon spectrum at jet conditions reported for a molecular system. To ensure that no power or saturation broadening is observed, the laser focus was placed 4 cm in front of the interaction region and thus the diameter of the laser beam in the interaction region increased to about 0.5 mm. This resulted in a considerably higher fluorescence signal. The measured linewidth in the Doppler-free jet spectrum [Fig. 2 (b)] is 70 MHz. This allows us to estimate that the frequency width of the visible laser is 50 MHz and upon frequency doubling increases to the value of 70 MHz observed in the Doppler-free two-photon spectrum.

A last point to be considered in this discussion of the achievable resolution is possible saturation or power broadening in the one-photon spectra. It will be shown later (Sec. III B 2), that for correct intensities of the rotational lines in the sub-Doppler one-photon spectrum, very low laser intensities have to be used in the experiment. If this condition is met, no broadening due to the laser power is observed.

B. The 6_0^1 band of C_6H_6

1. Experimental conditions

The 6_0^1 band of C_6H_6 at an Ar backing pressure of 1.5 bar was measured with the high resolution setup described in Sec. II. These expansion conditions lead to a rotational temperature of about 8 K. The distance between the nozzle and the interaction region was chosen to be 6 cm and no skimmer was used. Five overlapping individual scans of the cw dye laser were needed to cover the whole band under these conditions. The frequency scale was linearized by comparison with the transmission signal of the 150 MHz FSR confocal FPI. The resulting total spectrum is shown in Fig. 3. Clearly the rotational structure of the vibronic band is resolved for the observed linewidth of 130 MHz. The sharp spectral features in most cases correspond to individual rovibronic tran-

sitions. The moderate rotational cooling allows the observation of many transitions and therefore a precise analysis of the rotational structure of the band. In a previous experiment Beck *et al.*¹⁷ were also able to resolve single rotational lines in the 6_0^1 band of benzene with a laser of tenfold larger linewidth, but only under conditions of extreme rotational cooling and the consequent drastic reduction of the spectrum to 13 observed lines. The excellent signal to noise ratio in the spectrum of Fig. 3 is a consequence of the high spectral quality of the laser system used in this work. In the pulsed amplification the linewidth of the cw laser is homogeneously broadened and no structure in the frequency distribution is present, as it is typical for light pulses of narrow bandwidth pulsed oscillators with a few oscillator modes of fluctuating intensity. In our experiment the pulse to pulse fluctuations of the signal are less than 10% and it suffices to use a scan speed, which is equivalent to 15 pulses per observed linewidth in the molecular spectrum. In addition a digital polynomial filter¹⁸ is used for smoothing of the raw data.

2. Power dependence of line intensities

Before we analyze the rotational structure of the spectrum, we would like to comment on the dependence of the relative line intensities on the laser intensity. For experimental reasons the investigation of this question was documented best for the $6_0^1 1_0^1$ band, but identical results were found for the 6_0^1 band and the discussion of both results is presented in this section. In Fig. 4 part of the (normalized) R-branch spectrum is shown on an extended frequency scale as recorded with three largely varied laser intensities. The assignment of the transitions is indicated on top of every line. It is obvious that the relative intensities of the rovibronic lines depend strongly on the laser intensity. Note for example the $2_0 \leftarrow 1_1$ transition as compared to the $2_2 \leftarrow 1_1$ transition. This observation can be explained in the following way.

The strength I_{KJ} of a rovibronic transition in the absence of saturation is given by

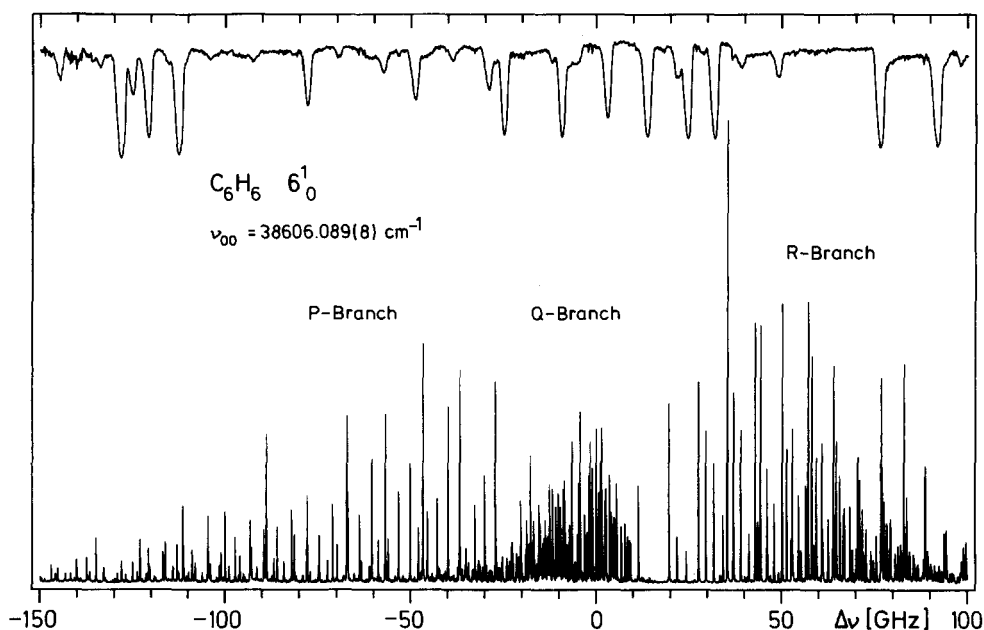


FIG. 3. Rotationally resolved one-photon excitation spectrum of the 6_0^1 band of benzene, C_6H_6 . The iodine absorption spectrum shown in the upper trace is used for the precise absolute calibration of transition frequencies.

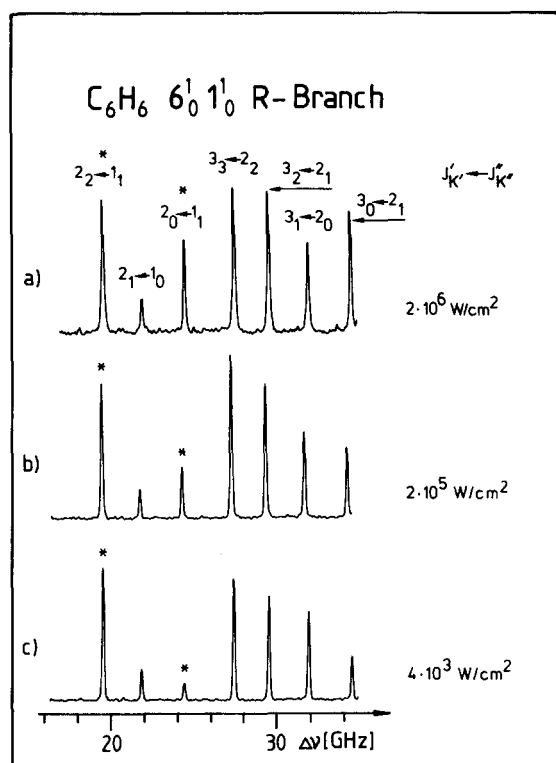


FIG. 4. Part of the rotationally resolved one-photon spectrum of the $6_0^1 1_0^1$ band of C_6H_6 , at different intensities of the exciting laser light. Note the changing relative intensities of the different rovibronic transitions. Intensities of lines marked by an asterisk are discussed in the text.

$$I_{KJ} = \tilde{C} \cdot A_{K \leftarrow J} \cdot (2J'' + 1) \cdot g_{K \leftarrow J} \cdot e^{-E''_{rot}/kT_{rot}} \quad (1)$$

The constant \tilde{C} is the strength of the vibronic transition, which is not dependent on the rotational quantum numbers and thus the same for all rovibronic transitions investigated in Fig. 4. $A_{K \leftarrow J}$ is the Hönl–London factor¹⁹ for the particular rovibronic transition. The factor $(2J'' + 1)$ describes the spatial M degeneracy of the rotational ground state and the factor $g_{K \leftarrow J}$ the nuclear spin degeneracy. Finally, $\exp(-E''_{rot}/kT)$ is the Boltzmann factor for the relative population of the ground state. If we compare the two lines $2_2 \leftarrow 1_1$ and $2_0 \leftarrow 1_1$, we find that the M degeneracy and the relative population of the ground state are equal for both transitions and the differing intensity of the lines under low intensity of the laser is exclusively caused by the differing Hönl–London factors (2.0 for the $2_2 \leftarrow 1_1$ transition as compared to 0.33 for the $2_0 \leftarrow 1_1$ transition). For low laser intensity the ratio of line intensities observed in the spectrum of Fig. 4(c) reflects the differing Hönl–London factors. At increasing laser intensity all rotational transitions are going to be saturated and finally there would be equal population of the ground and the respective excited state. In this limiting case the fluorescence signal would no longer be given by the Hönl–London factors, but rather by half the number of molecules originally in the appropriate ground state. For the two lines ($2_2 \leftarrow 1_1$ and $2_0 \leftarrow 1_1$) under consideration, this number of molecules is equal as both originate from the same state and an equal intensity of the lines would be observed. This limiting case is not yet quite reached in the spectrum shown

in Fig. 4 (a), but the two lines already possess similar intensity. The transition $2_2 \leftarrow 1_1$ is already completely saturated, while the transition $2_0 \leftarrow 1_1$ is not yet. This rotational selectivity of the saturation leads to the observed dependence of the relative line intensities on the laser power.

Besides the limited laser intensity available, there are a number of reasons which can prevent the described ideal saturation behavior for particular transitions: (i) The absorption of an additional photon can lead to ionization of the molecule and thereby decrease the fluorescence signal. (ii) Due to the nonuniform intensity distribution of the laser in the interaction region, both medium and high intensity behavior is observed at the same time.

From the results presented in Fig. 4, a preliminary value of 1×10^4 W/cm² can be determined for the saturation intensity of the strongest rotational lines in the 6_0^1 and $6_0^1 1_0^1$ bands of benzene. This value differs by a factor of 1000 from the value of 1×10^7 W/cm² determined previously,²⁰ but it seems very reasonable in view of the fact that the laser linewidth is smaller by this very factor of 1000 in the present study and the spectral brightness is increased accordingly. To measure spectra with interpretable line intensities, we used laser intensities below 10^4 W/cm². These low intensities also ensured that no power broadening is observed.

3. Assignment of the spectrum and determination of rotational constants

The assignment of the individual lines in the rotationally resolved spectrum of the 6_0^1 band to the values of the quantum number J of the rotational angular momentum \mathbf{J} and K , the quantum number of the projection of \mathbf{J} on the figure axis, is straightforward following the analysis of Callomon, Dunn, and Mills (CDM).⁷ There are three main branches in the spectrum corresponding to lines with $\Delta J = -1, 0, +1$, i.e., the P , Q , and R branch. These are nicely separated under our experimental conditions. For the observed perpendicular transition⁷ it holds that $\Delta K = \pm 1$. CDM pointed out that each rotational state in the degenerate 6^1 final state is split into the $-l$ and $+l$ vibrational angular momentum substates due to Coriolis coupling. Transitions with $\Delta K = +1$ lead to $+l$ states and transitions with $\Delta K = -1$ lead to $-l$ states. The rotational part of the transition energy is given by

$$\begin{aligned} \Delta E_{rot} = & B' \cdot J' \cdot (J' + 1) + (C' - B') \cdot K'^2 \\ & - 2 \cdot C' \cdot \zeta'_{eff} \cdot l' \cdot K' \\ & - [B'' \cdot J'' \cdot (J'' + 1) + (C'' - B'') \cdot K''^2]. \end{aligned} \quad (2)$$

The quantities denoted with '' refer to the ground state as usual, while those denoted by ' refer to the excited state. $\zeta'_{eff} = -\zeta'_0$ refers to the Coriolis coupling constant of the degenerate excited state. The value of the vibrational angular momentum quantum number l is 1 for the 6^1 vibronic state.

All observed lines down to about 1% of the highest observed intensity could be unambiguously assigned within this model. A total of 353 lines with J', K' up to 22 were used to fit the rotational constants of the excited state by a standard least-squares method. For the electronic ground state

the values of Pliva and Pines²¹ for B''_0 and C''_0 (see also Table I) were used. The resulting constants for the 6^1 state are reported in Table I together with the previous best set of values determined by CDM. The standard deviation of the fit, i.e., the rms deviation between observed and expected line positions, is 13.9 MHz and thereby about one order of magnitude below the observed linewidth. This shows that the 6^1 band can be completely reproduced by the energy formula of Eq. (2). There are no perturbations in the rotational line structure observed. The new values of the rotational constants shown in Table I are significantly larger than the previous ones of CDM. In addition, a slightly positive rotational defect $\Delta' = I'_{C,v} - 2 \cdot I'_{B,v}$ of $+0.049 \text{ amu } \text{Å}^2$ is calculated from the values of B'_v and C'_v . A rotational defect of similar magnitude has already been reported for the two-photon allowed 14^1 state.^{1,16} The values of the rotational constants of this state are included in Table I for comparison. In view of the observed negative sign of the rotational defect of the 14^1 state, it was interpreted as a possible indication of a slight nonplanarity of the S_1 benzene.¹ However, for the 6^1 band the rotational defect has changed sign and therefore it is more likely that the rotational defect observed for all investigated vibronic states of benzene is not due to an inertial defect of the equilibrium moments of inertia but rather produced by harmonic averaging, rovibrational coupling, and/or anharmonic terms.

In our determination of the rotational constants of the 6^1 state a value for C''_0 of $0.094\,880\,9 \text{ cm}^{-1}$ was used. This value of C''_0 has not been determined experimentally, but rather it was calculated according to $C''_0 = B''_0/2$ (Ref. 21) in analogy to the planarity condition $C''_{\text{eq}} = B''_{\text{eq}}/2$. Pliva and Pine estimate the uncertainty of this assumption to be $\pm 2 \times 10^{-4} \text{ cm}^{-1}$. A change in C''_0 by $2 \times 10^{-4} \text{ cm}^{-1}$ due to this uncertainty does not alter the value of B'_v determined from the rotationally resolved spectrum of the 6^1 band at all, but it changes the value of C'_v by an equal amount. The value of ζ' would be altered by ± 0.0035 . The error limits given in Table I do not include this uncertainty, but only the uncertainty of our frequency calibration and the statistical error. The uncertainty in C''_0 would lead to a value of Δ'' of $\pm 0.374 \text{ amu } \text{Å}^2$ and to values of Δ' of $+0.458$ and $-0.359 \text{ amu } \text{Å}^2$. Such a large rotational defect in the S_1

state does not seem reasonable and might be taken as an indication that the rotational defect in the S_0 state is indeed very small.

4. Determination of ν_{00}

The analysis of the rotational structure of a vibronic band does allow the precise determination of the rotationless origin ν_{00} of the band. Certainly, our detailed analysis of the rotationally resolved spectrum should yield a value of ν_{00} only limited by the accuracy in the measurement of absolute laser frequencies. To obtain a high accuracy in the calibration of the spectrum, the iodine absorption spectrum at the fundamental laser frequency was measured simultaneously with the benzene spectrum. The result is shown in the upper trace of Fig. 3. In addition, in a separate experiment we checked that the molecular beam is crossed exactly at right angle by the laser beam and no Doppler shift is present. For that purpose the laser beam was reflected into itself after leaving the vacuum chamber. If the crossing were not perpendicular, all lines in the spectrum would be doubled due to the different angle of the incoming and the reflected light, and therefore the correct adjustment of the crossing angle is seen as a disappearance of this doubling.

The exact definition of ν_{00} is given by

$$\nu_{00} = \Delta E(J''_{K'} \leftarrow J''_{K''}) - \Delta E_{\text{rot}} \quad (3)$$

with $\Delta E(J''_{K'} \leftarrow J''_{K''})$ the total transition energy for the transition from the $J''_{K''}$ electronic ground state level to the $J''_{K'}$ level of the 6^1 vibronic level and ΔE_{rot} as given in Eq. (2). It should be noted that the additional term $C'\zeta'^2$ given by Herzberg,²² which would amount to 0.030 cm^{-1} for the 6^1 band, is not included in the definition of Eq. (3).

The value determined for ν_{00} is given in Table II. For comparison earlier determinations from other laboratories are included. The value of Ref. 23 was actually calculated from their reported position of the band maximum and the reported separation of the band maximum and the origin. The value of Ref. 30 is calculated from the reported frequencies of two maxima in the Doppler-limited spectrum. It is interesting to note that both determinations of ν_{00} from Doppler-limited room temperature spectra^{7,23} deviate significantly from our value. We compared the maximum-to-

TABLE I. Rotational constants and Coriolis coupling constant ζ_{eff} of several vibrational states of C_6H_6 . The derived rotational defect $\Delta = I_C - 2 \cdot I_B$ is also given for each state. For the nondegenerate S_0 and 14^1 state the value of ζ_{eff} is 0.

State	$B \text{ (cm}^{-1}\text{)}$	$C \text{ (cm}^{-1}\text{)}$	ζ_{eff}	$\Delta \text{ (amu } \text{Å}^2\text{)}$	Reference
S_0	0.189 761 8 (14)	$C''_0 = B''_0/2^a$...	0	21
6^1	0.181 0 (5)	$C'_v = B'_v/2$	-0.60 (5)^b	0	7
6^1	0.181 778 (2)	0.090 865 (3) ^c	-0.5785 (5)^c	$+0.049$	this work
$6^1 1^1$	0.181 648 (2)	0.090 855 (3) ^c	-0.5519 (5)^c	-0.063	this work
14^1	0.181 283 6 (16)	0.090 711 0 (8) ^c	...	-0.142	16 ^d

^a Constrained according to the planarity condition. A possible error of $\pm 2 \times 10^{-4} \text{ cm}^{-1}$ is assumed.

^b An improved value of -0.575 is quoted according to a private communication by J. H. Callomon in Ref. 25.

^c Values were determined with $C''_0 = B''_0/2$. The uncertainties given do not contain the uncertainty of this assumption. For details see the text.

^d Values were calculated from the values of ΔB and ΔC given in Ref. 16.

TABLE II. Rotationless origin ν_{00} (cm⁻¹) of the 6_0^1 and $6_0^1 1_0^1$ band of C₆H₆.

6_0^1	$6_0^1 1_0^1$	Reference
38 608.5	...	7
38 607.6	39 530.9	23 ^a
38 606	39 530	27
38 606.18	...	30 ^b
38 606.089 (8)	39 529.630 (8)	this work

^a Values derived from the position of the band peak and the peak origin separation of 3.7 cm⁻¹.

^b Reference 17 in the work of Chewter *et al.* (Ref. 30) is identical to preliminary work of the present investigation.

origin separation for spectra calculated with our set of rotational constants and the one given by CDM, but could not explain the large deviation in this way. The deviation actually seems to reflect a fairly large error in the frequency calibration of the previous Doppler-limited spectra. Indeed, recent Doppler-limited Fourier transform UV spectra of the 6_0^1 band confirm this idea. The results of these new spectra recorded at room temperature will be reported in a separate communication.²⁴

The high accuracy in the determination of ν_{00} of the 6_0^1 band should prove quite useful in the precise determination of the frequencies of the normal modes of S_1 benzene. Indeed, the large deviation found for ν_{00} might be paralleled by a similar inaccuracy in T_{00} , the pure electronic transition frequency. As the value determined by CDM,⁷ which is currently used in the normal coordinate analysis,^{25,26} is closely linked to their determination of ν_{00} of the 6_0^1 band, some significant changes in the values of the fundamental frequencies might be the consequence of the detected deviations of ν_{00} .

C. The $6_0^1 1_0^1$ band of C₆H₆

1. Rotational analysis

The rotationally resolved spectrum of the $6_0^1 1_0^1$ band was measured at Ar pressures of 0.1, 0.5, and 1.5 bar. A preliminary assignment of the spectra and the evaluation of the relative intensities of the $J' = K'$ lines of the *R* branch show that these pressures lead to rotational temperatures of 50, 15, and 8 K, respectively. In Fig. 5 the main part of the $6_0^1 1_0^1$ band at $T_{\text{rot}} = 15$ K is shown. The resolution of 85 MHz was obtained by insertion of a skimmer between the nozzle and the excitation region for improved collimation of the molecular beam. The analysis of the spectrum was performed similarly to the 6_0^1 band.

In the spectrum recorded at 8 K rotational temperature, 252 lines were assigned with J', K' up to 17. The rotational constants were fitted according to Eq. (2) and included in Table I. The value for the rotationless transition frequency ν_{00} is included in Table II. The standard deviation of the fit is 19.0 MHz. This is significantly larger than the value obtained for the 6_0^1 band. If only the 227 lines with $K' \leq 10$ are used for the fit, a standard deviation of 12.3 MHz results. From this it may be concluded, that the low K' states are unperturbed in agreement with the unperturbed character of the $6^1 1^1$ state reported by Stephenson *et al.*²⁷ for extreme rotational cooling. For K' values larger than 10, significant deviations of experimental and calculated line positions are found. Since lines with K' up to 22 could be fitted without inclusion of higher order terms in the energy formula [Eq. (2)] for the 6_0^1 band, it seems very unlikely that the deviations observed can be interpreted in terms of centrifugal distortion or other higher order effects. Instead, we believe that there are slight rotational perturbations, like they have been previously identified in the two-photon bands 14_0^1 and $14_0^1 1_0^1$.^{3,28} To clarify this situation, an attempt was made to

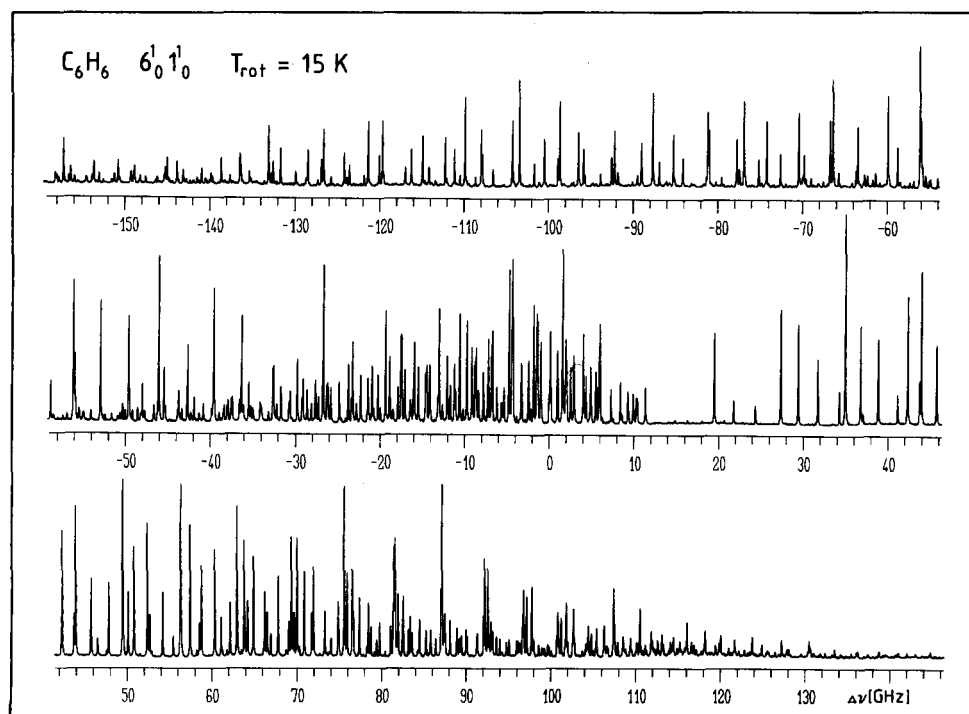


FIG. 5. Rotationally resolved excitation spectrum of the $6_0^1 1_0^1$ band of benzene, C₆H₆. The relatively high rotational temperature of 15 K was obtained by a low pressure (0.5 bar) of the Ar carrier gas in the expansion. To obtain the observed linewidth of 85 MHz, a skimmer was used for improved collimation of the molecular beam.

assign lines with higher J' and K' values in the recording at $T_{\text{rot}} = 15$ K. This was not uniquely possible in the crowded Q and R branch, but seemed possible at first sight in the P branch. Unfortunately, however, the relevant portion of the spectrum around -7 cm^{-1} rotational energy contains a large number of rotational lines, which clearly do not belong to the $6_0^1 1_0^1$ band. Stephenson *et al.*²⁷ did indeed find additional bands at -6 and -9 cm^{-1} from the $6_0^1 1_0^1$ band in their low resolution spectra at extreme rotational cooling, which they assigned as $6_0^1 1_0^1$, $6_0^1 18_0^1$ of $^{13}\text{C}^{12}\text{C}_5\text{H}_6$ and $17_0^2 1_0^{\pm 2}$, $16_0^3 17_0^1$ of C_6H_6 , respectively. At the rotational temperature of 15 K the intensity of the P -branch lines in the vicinity of these considerably weaker bands seems to be just the same as the one of the rotational lines from these weak bands and therefore the unique assignment of presumably perturbed lines is not possible. Only at the rotational temperature of 50 K the P branch of the $6_0^1 1_0^1$ band has gained so much intensity in this part of the spectrum that a unique assignment seems possible and the clear identification of the observed deviations should be possible. The assignment of the large number of lines in the 50 K spectrum is now in progress.

2. Decay times of individual rovibronic states

Since nearly all rovibronic lines were resolved in the spectrum of the $6_0^1 1_0^1$ band at 8 K and for the resolution achieved with the pulsed amplified laser light, we were able to measure the decay curves for various individual rovibronic states. Typical results are shown in Fig. 6. For all cases a clean single exponential decay over more than 5 times the decay time was found. The values for the decay time of all investigated rovibronic states are tabulated in Table III.

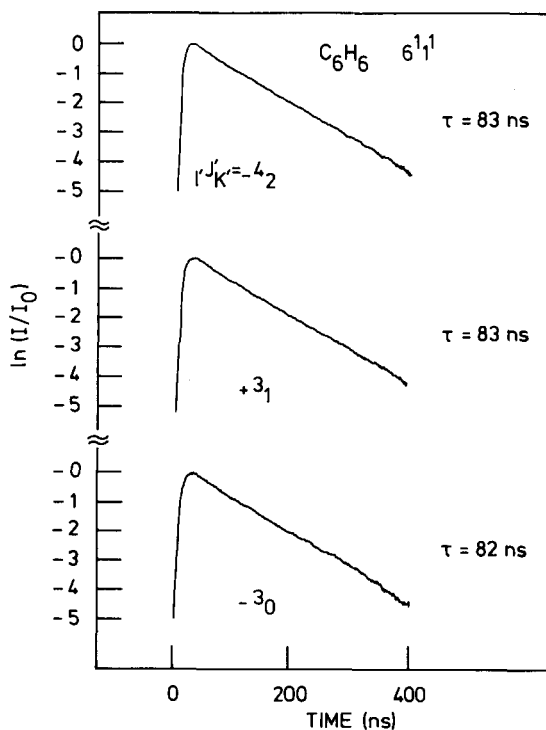


FIG. 6. Fluorescence decay curves after pulsed selective excitation of three individual rotational states of the $6^1 1^1$ vibronic state of C_6H_6 .

TABLE III. Measured decay times for several selectively excited rotational levels within the $6^1 1^1$ vibronic state of C_6H_6 . The values are accurate to ± 3 ns. For each state the rotational branch (ΔJ) for excitation is indicated.

State l', J', K'	Excitation branch	Decay time τ (ns)
$+1_1$	R	78
$+2_2$	R	77
$+2_1$	R	78
$-2_0(41\%) + -5_2(59\%)$	Q	83
$+3_1$	R	83
-3_0	R	82
$+4_3$	R	83
-4_3	Q	78
$+4_2$	Q	83
-4_2	Q	83
-6_4	Q	81
-6_0	Q	78
$+7_6$	Q	79
$+7_1$	Q	78
$-10_0(43\%) + -9_2(57\%)$	Q	83

Within the experimental uncertainty, no dependence on the quantum numbers J' , K' , and l' is observed. This is in accord with the unperturbed nature of the low K' rotational states of the $6^1 1^1$ vibronic state and our recent results for unperturbed rotational states in the 14^1 vibronic state.⁶ The average value of all decay times in Table III of 80 ± 3 ns is in good agreement with the value of 82 ± 2 ns reported recently for not rotationally resolved investigation of the $6^1 1^1$ state.¹⁵ This corroborates our previous conclusion,⁶ that the responsible nonradiative relaxation process, which is most likely ISC, is in the statistical limit.

IV. SUMMARY AND CONCLUSION

Rotationally resolved fluorescence excitation spectra of the 6_0^1 and $6_0^1 1_0^1$ bands of benzene, C_6H_6 , at moderate rotational cooling (8 to 50 K rotational temperature) are reported. The spectra were recorded by crossing a well collimated pulsed molecular beam with the beam of an extremely narrow bandwidth tunable pulsed UV laser. Single rovibronic lines with an experimental linewidth as low as 85 MHz were resolved. The rotational structure of both bands was analyzed and a fit to the observed line positions rendered highly precise values for the rotational constants. The 6_0^1 rotational band structure was found to be totally unperturbed, while in the $6_0^1 1_0^1$ band indications of rotational perturbations were found for rotational states with $K' > 10$. In addition, the frequencies of the rotationless origin of the bands were determined with high accuracy.

Decay time measurements were performed for individual rotational states in the $6^1 1^1$ vibronic state and no rotational dependence of the decay time was found, in accord with the unperturbed character of the states and the statistical limit character of the responsible electronic nonradiative process. This behavior is comparable with the behavior of the 14^1 two-photon state at similar excess energy. Hence, we may conclude that in the region below the onset of "channel three" the spectroscopic behavior of all states independent of their symmetry is governed by sparse coupling to other vibrational states in S_1 , whereas the dynamic behavior is due

to a nonradiative electronic coupling process in the statistical limit.

The employed experimental method should now allow us to investigate the "channel three" region in benzene at rotational resolution even for the one-photon allowed bands originally investigated²⁹ and compare the results with previous high resolution studies of two-photon allowed bands.^{4,5} Such investigations are presently in progress in our laboratory. In addition, the selective excitation of single quantum states is now possible with great efficiency. This should open the way to rotationally resolved double resonance spectroscopy of large molecules. These investigations should provide valuable information for the understanding of vibration rotation couplings and their influence on the nonradiative decay of large molecules.

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