

LARGE FINITE SYSTEMS

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TABLE OF CONTENTS

PREFACE	ix
P. J. DE LANGE and J. KOMMANDEUR / The Quantum Yield of Non-Resonant Light Scattering	1
E. C. LIM / Excited States of Molecular Dimers	11
A. AMIRAV / Rotational Effects on Intramolecular Radiationless Transitions - "The Story of Pyrazine"	19
R. MARQUARDT and M. QUACK / The Dynamics of Polyatomic Molecules During and After Coherent Excitation	31
R. D. LEVINE / Spectral Fluctuations in Finite Systems	45
R. KOSLOFF, A. HAMMERICH and M. A. RATNER / Time Dependent Quantum Mechanical Calculations of the Dissociation Dynamics of the Cluster $\text{He}_n\text{-I}_2$	53
W. W. DULEY / Properties of Large Finite Systems : Constraints from Astrophysical Observations	67
H. LEVANON / Porphyrin Dimers : The Photoexcited Triplet State as a Probe for Structure and Dynamics	75
M. CASTELLA, P. CLAVERIE, J. LANGLET, Ph. MILLIE, F. PIUZZI and A. TRAMER / Coupling Between Locally Excited and Charge Transfer States of Jet Cooled Molecular Complexes	83
R. VAN ZEE, W. B. BOSMA, T. ZWIER, M. C. DUVAL and B. SOEP / Intermolecular Potential and Dissociation of Excited State Mercury Ammonia Complexes	101
J. FARGES, M. F. DE FERAUDY, B. RAOULT and G. TORCHET / From Five-Fold to Crystalline Symmetry in Large Clusters	113
T. P. MARTIN, T. BERGMANN and B. WASSERMANN / Cluster Energy Surfaces	121

R. S. BERRY / Phase Changes : The Interplay of Dynamics and Equilibrium in Finite Systems	135
U. LANDMAN, R. N. BARNETT, C. L. CLEVELAND and J. JORTNER / Electron Localization in Water Clusters	145
S. LEUTWYLER and JURG BOSIGER / Rare-Gas Solvent Clusters : Order-Disorder Transitions and Solvent Shell Effects	153
R. J. LE ROY, J. C. SHELLEY and D. EICHENAUER / Spectra, Structure and Dynamics of SF₆-(Ar)_n Clusters	165
G. KURISKI and A. NITZAN / Lasing and Stimulated Raman Processes in Spherical and Spheroidal Droplets	173
O. ECHT, M. KNAPP, C. SCHWARZ and E. RECKNAGEL / Electron Attachment to Clusters	179
H. HABERLAND, C. LUDEWIGT, H-G. SCHINDLER and D. R. WORSNOP / Beams of Electrons Solvated in Clusters	195
N. R. KESTNER and S. DHAR / Theoretical Studies of Sodium Water Clusters : Their Ionization and Excitation Energies	209
D. SCHARF, U. LANDMAN and J. JORTNER / Isomerization in Alkali-Halide Clusters Induced by Electron Attachment	217
D. THIRUMALAI / Electron Localization by Atomic and Molecular Clusters	231
E. BLAISTEN-BAROJAS, I. L. GARZON and M. AVALOS / Structural and Dynamical Properties of Clusters on a Substrate	241
D. J. DONALDSON, S. SAPERS, V. VAIDA and R. NAAMAN / Photodissociation of Methyl Iodide Clusters	253
U. EVEN, P. J. DE LANGE, P. J. RENKEMA and J. KOMMANDEUR / The Yield of Exo-Electrons from Cluster Bombardment of Metallic Surfaces	265
J. M. ANDRE / The Role of Large Oligomers in Designing Materials of Interest for their Electrical and Optoelectronic Properties	277
E. SCHUMACHER and M. KAPPES / Isolated, Bare Metal Clusters : Abundances and Ionization	289
J. KOUTECKY, V. BONACIC-KOUTECKY, I. BOUSTANI, P. FANTUCCI and W. PEWESTORF / Electronic Structure and Basic Properties of Small Alkali Metal Clusters	303

K. D. BIER, T. L. HASLETT, A. D. KIRKWOOD and M. MOSKOVITS / Laser Spectroscopy of Matrix-Isolated Clusters : Diatomic and Triatomic Manganese	319
A. NITZAN / Small Dielectric Clusters : Size and Shape Dependence of Photophysical and Photochemical Properties	333
F. HENSEL / Fluids That Exhibit Changes in Electronic Structure	345
M. SHAPIRO and T. SEIDEMAN / Coherent Control and Laser Catalysis of Chemical Reactions	361
J. M. DRAKE, J. KLAFTER and P. LEVITZ / Studies on the Structure of Porous Silicas : The Fractal Dilemma	379
E. RIEDLE / Doppler-Free Spectroscopy, an Opportunity for State Specific Investigations in Large Molecules	387
INDEX OF SUBJECT	399

DOPPLER-FREE SPECTROSCOPY, AN OPPORTUNITY FOR STATE SPECIFIC INVESTIGATIONS IN LARGE MOLECULES

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ABSTRACT. Conventional high resolution spectroscopy in the gas phase allows the selection of single vibronic states of large molecules. The extreme rotational cooling in a supersonic jet can be of great help for this selection. However, many investigations point to the important role of rotation-vibration coupling for the dynamic behaviour of large molecules. Sub-Doppler experiments like Doppler-free two-photon spectroscopy permit the necessary resolution of single rovibronic transitions. It is demonstrated for the example of benzene, that experiments can now be performed, which completely resolve the rotational structure of the vibronic bands and permit the measurement of the line width and the decay behaviour of single rovibronic states. These investigations lead to a detailed understanding of the influence of rotation on the spectroscopy and the dynamics of the benzene molecule.

1. INTRODUCTION

Spectroscopy is the prime source of information on the energy levels, the structure and the dynamic behaviour of molecules. Especially high resolution optical spectroscopy has contributed a large deal to the present understanding of molecular systems. For large molecules the obtainable resolution in conventional studies is principally limited by the Doppler-broadening in the gas phase. This prevails in most cases the observation of single rovibronic transitions. The additional problem of hot band congestion and extensive rotational inhomogeneous broadening was partially overcome by the use of supersonic jets and their low rotational and vibrational temperatures. However, still the vast majority of all dynamic investigations of large molecules is only able to study single vibronic levels (SVL) instead of single rovibronic levels (SRVL).

In recent years different Doppler-free techniques were developed to increase the resolution beyond the limit set by the Doppler-broadening and successfully tested for atomic systems and small molecules /1/. The application of these techniques to the study of large molecules is nontrivial due to the large number of thermally populated levels and the complexity of their spectra. However, recently a number of investigations have shown, that techniques like Doppler-free two-photon spectroscopy /2/, spectroscopy in highly collimated molecular beams /3/, intermodulated fluorescence /4/ and saturation spectroscopy /5/ render rotationally resolved spectra even for these molecules. In addition to the rotationally resolved spectra also line width measurements /6/ and decay time measurements /7,8/ of single rovibronic states were obtained and even the measurement of emission spectra of these states seems now possible. The experimental arrangements needed for these investigations and typical results, that show the importance of such ultra high resolution experiments, will be discussed for the example of Doppler-free two-photon spectroscopy of benzene.

2. CW DOPPLER-FREE TWO-PHOTON SPECTROSCOPY

2.1. The experimental set up

The recording of Doppler-free two-photon spectra is based on the simultaneous absorption of two photons from counter-propagating light beams of an extremely narrow band tunable laser /9/. Contrary to the Doppler-broadened absorption of two photons from one laser beam, the Doppler-shift of the two photons balances itself exactly for this situation and a Doppler-free spectrum can be observed. Since the absorption probability in the two-photon process is very weak and depends quadratically on the laser intensity, a dramatic increase in signal is observed if the experiment is not performed by simple backreflection of the laser beam but rather within the standing wave field of an external resonator /6,10,11/. The experimental set up derived from this consideration and used in our experiments is shown in fig. 1 and has been described in detail /6,12/.

The high spectral resolution (1 MHz) is provided by a cw ring laser system (Coherent CR 699/21) pumped by the violet lines of a Kr⁺ laser (CR 3000K UV) and providing typically 300 mW laser power around 5000 Å with Coumarin 102 dye. The benzene cell is placed within the concentric external resonator (mirrors of 70 % and 99 % reflectivity), whose length is locked to the laser frequency. Experiments are

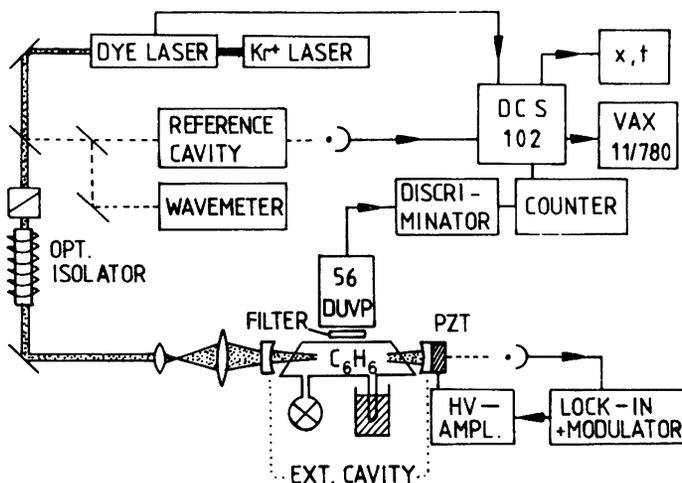


Figure 1. Experimental set up used for the recording of Doppler-free two-photon spectra of benzene /6,12/.

typically performed with benzene pressures below 1 torr to achieve nearly collisionless conditions. The fluorescence emitted by the excited molecules is monitored with a single-photon-counting system, i.e. fluorescence excitation spectra are recorded. For the calibration of the spectra the transmission of a highly stable 150 MHz Fabry-Perot-Etalon is recorded simultaneously with the molecular spectrum. The free spectral range of this etalon has been measured to 1 part in 10^6 .

2.2. The rotationally resolved spectrum

As a typical result the first 6 cm^{-1} of the Doppler-free spectrum of the Q-branch of the 14^1_0 -band of C_6H_6 at 39656.90 cm^{-1} is shown in fig. 2 /13,14/. The spectrum consists of 6 individual laser scans and the frequency scale has been linearized according to the transmission pattern of the 150 MHz FPI /15/. The observed lines correspond to well resolved single rotational lines. The Doppler-width of 1.7 GHz would not allow the resolution of the individual rovibronic transitions since typically 10 lines are located within the Doppler-width. All the lines can be assigned within the model of a semirigid symmetric top. A fit to the observed line positions renders the rotational constants of the excited state with an accuracy of 10^{-7} cm^{-1} and the quartic centrifugal distortion constants with an accuracy of 10^{-10} cm^{-1} /15/. A similar accuracy has even been reached for the asymmetric top molecule benzene- d_1 /16/.

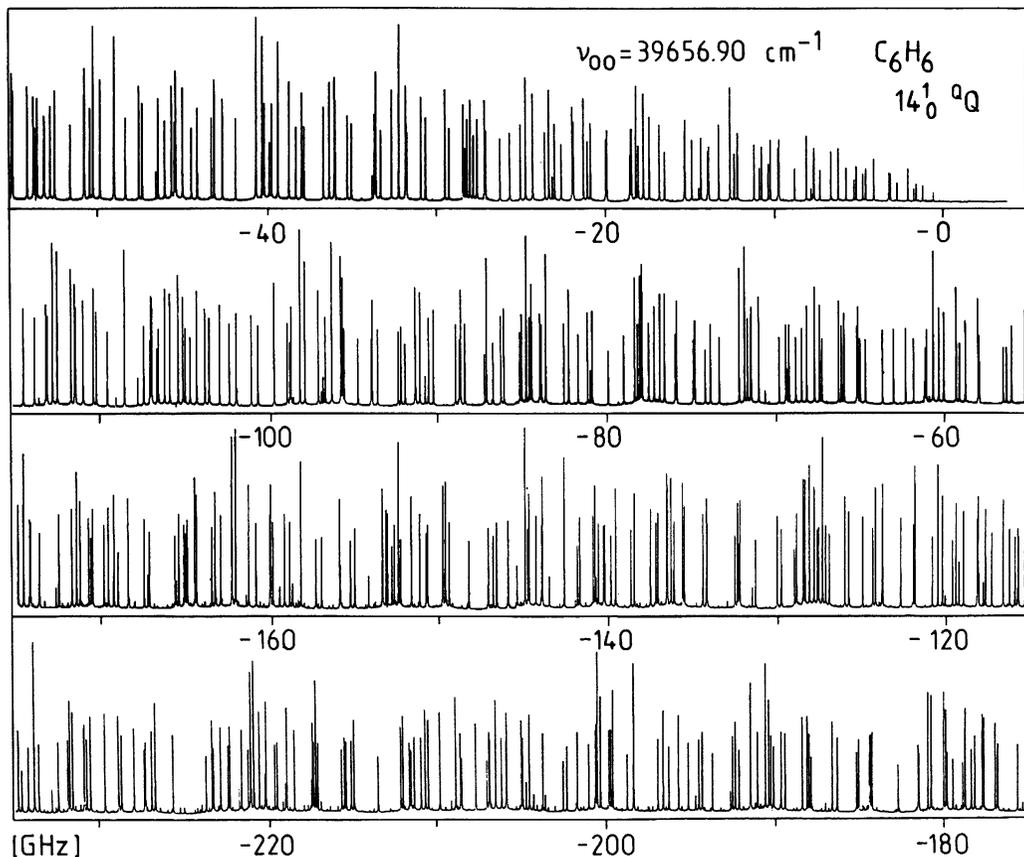


Figure 2. Part of the Doppler-free room temperature spectrum of the Q-branch of the 14^1_0 -band of C_6H_6 /13,14/. Every line corresponds to an individual rovibronic transition. All the lines have been assigned.

The remaining deviations (residuals) between the calculated line positions and the observed ones are about 10 MHz. This extreme agreement is demonstrated in fig. 3 for the 14^1_0 -band of 1,3,5- $\text{C}_6\text{H}_3\text{D}_3$ /15/. It is again seen, that Doppler-free two-photon spectroscopy allows the complete resolution of the electronic spectrum and the spectrum is extremely well reproduced with the simple model of a semi-rigid symmetric top.

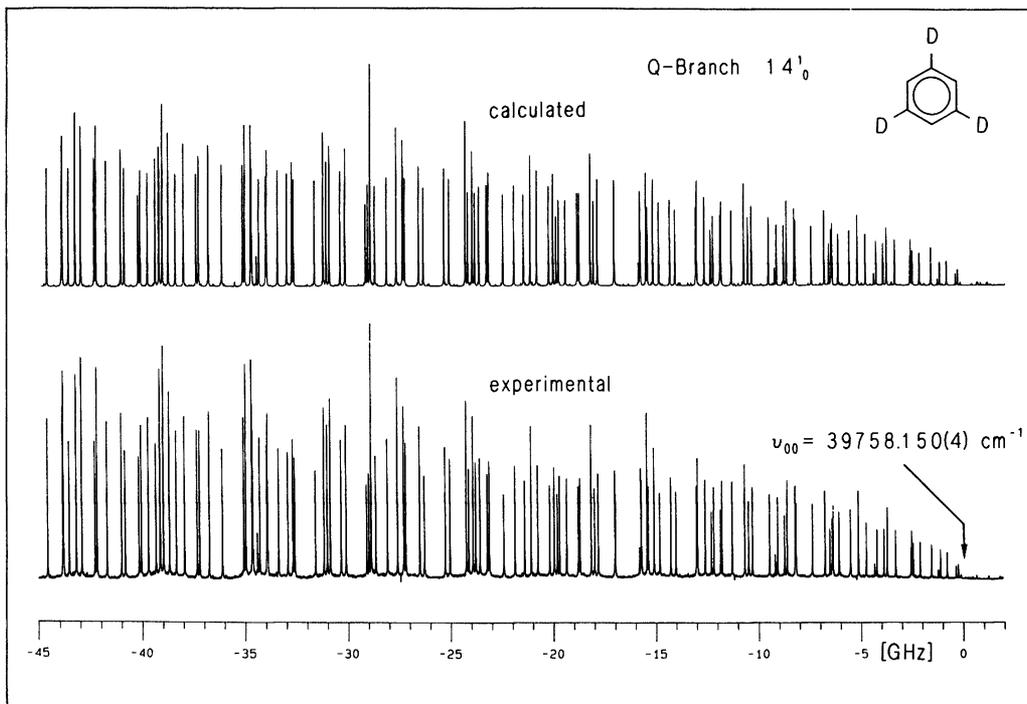


Figure 3. Part of the Doppler-free spectrum of the Q-branch of the 14^1_0 -band of 1,3,5- $\text{C}_6\text{H}_3\text{D}_3$. The experimental spectrum (lower trace) is compared to the calculated spectrum (upper trace) of a semirigid symmetric top /15/.

2.3. Perturbations in the spectrum

In some parts of the spectrum, at higher rotational energy, differences between the experimental spectrum and the calculated one are observed. Single lines of the calculated spectrum are not observed in the experimental one, instead two weaker lines are observed at slightly shifted positions /17/. If these pairs of lines are labeled with the rotational quantum numbers of the missing line, the dependence of the deviations on the quantum number J of total angular momentum can be plotted for each value of K , the quantum number of the projection of \vec{J} on the figure axis of the molecule. The result is shown in fig. 4 for the Q-branch of the 14^1_0 -Band of C_6H_6 /13,14/.

The typical J -dependence of the deviations found is that of an avoided crossing. A careful analysis shows /17/, that the observed perturbations are caused by the coupling of light rotational states of the 14^1 vibronic state to

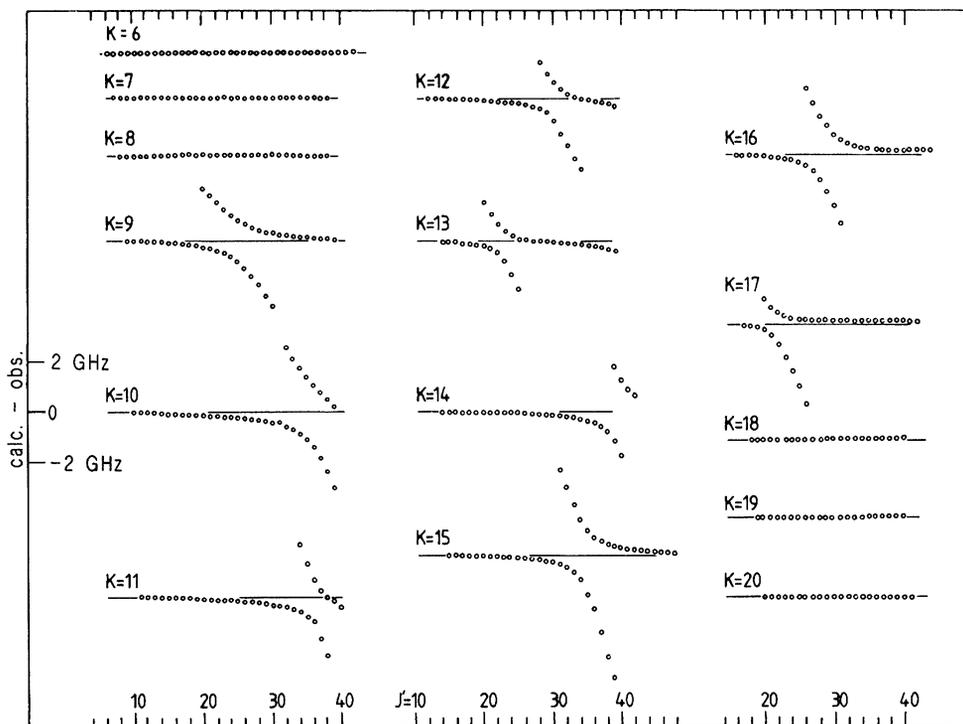


Figure 4. Residuals (calculated - observed) of the frequencies of rotational lines in the spectrum of the 14^1_0 -band of C_6H_6 as a function of the final state quantum number J' for several values of K' /13,14/.

dark rovibronic states in the electronic S_1 state. As a result two eigenstates with mixed vibronic character result and both can be seen in the spectrum. These are the two lines observed in the experimental spectrum. From the positions of the two lines the coupling matrix element can be calculated for each pair /18/. The coupling shows a strong dependence on J and K . This leads to the conclusion that the observed coupling must be caused by perpendicular Coriolis coupling rather than by anharmonic or parallel Coriolis coupling /18/. This rotational dependence of the vibronic nature of the eigenstates can only be determined from rotationally resolved spectra.

2.4. Homogeneous line width measurements

The broadening of the transitions of large molecules due to fast nonradiative decay can normally only be inferred from the diffuseness of the vibronic bands /19/. Only for extremely strong broadening beyond the residual rotational

contour in a supersonic jet and the favourable condition of widely spaced vibronic bands is a measurement of line broadening even for the GHz resolution of Doppler-limited spectroscopy possible /20/. However, such an experiment will not reveal the rotational dependence of the broadening. On the other hand, the extremely high resolution ($\Delta\nu$ below 10 MHz) of our cw set up allows the measurement of homogeneous line widths of single rovibronic transitions. This has been shown for the $14^1_01^2_0$ -band of C_6H_6 at 3412 cm^{-1} vibrational excess energy /6/. In this band only the $K = 0$ lines are observed in our rotationally resolved fluorescence excitation spectra /21/, since all $K \neq 0$ states decay very rapidly and no fluorescence is observed from these states. The remaining $K = 0$ lines are also broadened and the broadening is found to increase from 1.3 MHz for the $J = 0$ state to 46.1 MHz for the $J = 14$ state /6/. This strong rotational dependence of the homogeneous line width shows the importance of rotationally resolved observations for the determination of the decay behaviour of excited states of large molecules.

2.5. Emission spectra

The vibronic character of excited molecular states can be determined from SVL emission spectra. However, the analysis of line positions shows, that the vibronic character depends strongly on the rotational state of the molecule (see above). Therefore the SRVL emission spectrum is needed for the identification of the coupled background states. To obtain such an emission spectrum, a single rovibronic state has to be pumped in a Doppler-free experiment and the emission has to be spectrally resolved. This requires, that the dye laser frequency remains in resonance with the molecular transition frequency for a long time, typically to a precision of 1 MHz/h. In addition enough fluorescence intensity has to be produced to allow spectral resolution. These problems have recently been solved in our laboratory. First emission spectra of single rovibronic states will be presented in a forthcoming publication /22/.

3. PULSED DOPPLER-FREE TWO-PHOTON SPECTROSCOPY

3.1. The experimental set up

For the investigation of the decay of individual levels pulsed excitation of the molecules has to be used. The experimental set up is shown in Fig. 5 /7,13/. Extremely narrow band pulsed laser light is produced by pulsed amplification of the cw light. With three stages of excimer laser pumped amplifiers we can generate light pulses of 500 KW peak power and nearly Fourier transform limited bandwidth. With an additional parasitic cavity around the second amplifier the pulse length can be varied between 2.5 ns and 10 ns and the frequency width accordingly between 50 MHz and 180 MHz. After passing through the sample cell the laser beam is reflected back into itself to allow the Doppler-free absorption. The two beams are counterclockwise circularly polarized to suppress the Doppler-broadened background /23/. The resulting UV-fluorescence signal is either integrated for the recording of spectra or its time behaviour is recorded with a transient digitizer. It is worth mentioning that in Doppler-free two-photon absorption all molecules regardless of their velocity contribute to the observed signal. Molecules are only excited to one single level if the laser frequency is set to a resolved rotational line in the spectrum regardless of the number of lines within the Doppler-width. This allows the observation of the decay of an individual level /7,8/.

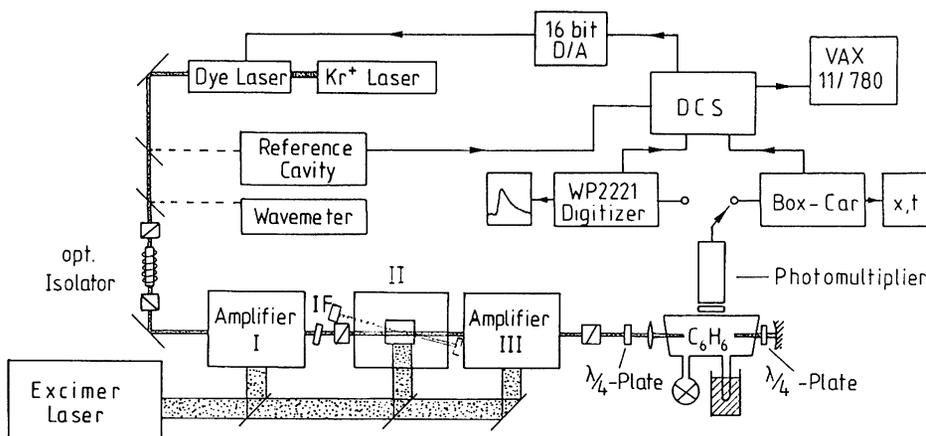


Figure 5. Experimental set up for decay time measurements of individual rotational levels of S_1 benzene. Fluorescence decay is observed after pulsed Doppler-free two-photon excitation with the amplified light of the cw laser (taken from ref. 7,13).

3.2. The resolution achieved with pulsed excitation

The resolution achieved with the pulsed set up is limited by the length of the light pulse to about 100 MHz. This is by one order of magnitude lower than the resolution achieved with the cw set up. However, still most of the rotational lines in the two-photon spectra of the Q-branch can be resolved [23], as can be seen from the upper part of fig. 6 [7]. The top spectrum shows part of the Doppler-free spectrum of the 14^1_0 -band of C_6H_6 as recorded with the cw set up and the lower spectrum the same spectral range as recorded with the pulsed set up. Clearly the resolution of single rovibronic lines can be seen.

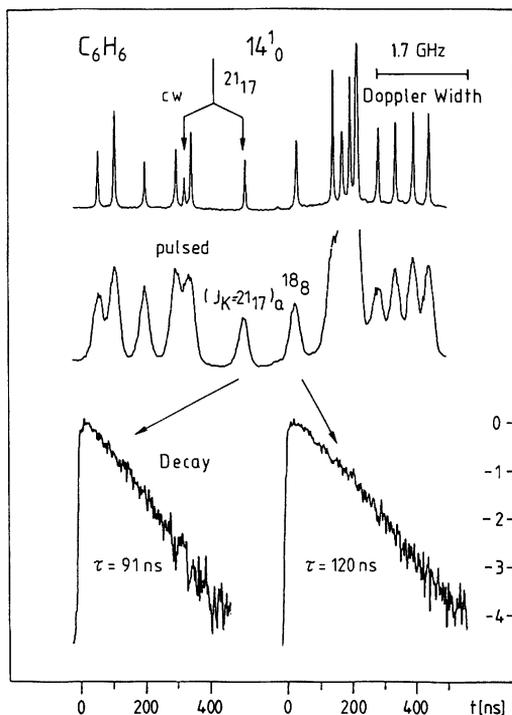


Figure 6. Part of the Q-branch of the 14^1_0 -band of C_6H_6 under the high resolution of the cw set up (top) and the lower resolution of the pulsed set up (middle trace). At the bottom the fluorescence decay curves measured for the two neighbouring lines ($J'K'=2117$)_a and $J'K'=188$ are shown on a half-logarithmic scale. Both lines are well resolved, even with the pulsed set up. $J'K'=(2117)$ _a is one component of the perturbed zero order state $J'K'=2117$, whereas $J'K'=188$ is an unperturbed state (taken from ref. 7).

3.3. Decay time measurements

The resolution of single rovibronic lines with the pulsed set up allows the measurement of the decay behaviour of single rovibronic states. These measurements have been performed for a number of states in the 14^1 manifold /7/. Two examples are shown in the lower part of fig. 6. All decay curves measured were found single exponential. For states found unperturbed in the spectral analysis a constant decay time was found independent of the rotation of the molecule. This is in agreement with theoretical predictions for a inter-system-crossing (ISC) decay in the statistical limit /24/.

The two decay curves shown in fig. 6, however, show a differing decay behaviour of the unperturbed $J'_{K'}=188$ and the perturbed ($J'_{K'}=2117$)_a state. The faster decay results from the coupling of the light 14^1 rotational state to a dark state, that decays much faster. Through the above mentioned mixing of the states, the resulting eigenstate has a decay time intermediate between the dark and the light state. Since the spectral analysis allows us to determine the degree of mixing of the states, we can determine the decay time of the unperturbed dark state from the measured decay time of the eigenstate. It is found to be much shorter than the decay time of the 14^1 state. In this way does the measurement of the decay of perturbed states allow the determination of the decay behaviour of states normally not observable (i.e. dark states).

4. SUMMARY AND CONCLUSION

Sub-Doppler techniques can be used successfully for the complete rotational resolution of the electronic spectrum of large molecules. In this article this has been demonstrated for the example of Doppler-free two-photon spectroscopy of benzene. The rotational resolution is important for the investigation of dynamic processes, as rotation-vibration coupling (seen as perturbations in the spectrum) influences the decay behaviour of large molecules significantly. The extremely high resolution of the cw set up allows the measurement of the homogeneous line width of single rovibronic lines. Doppler-free excitation with extremely narrow band pulsed laser light permits the measurement of the decay time of single rovibronic states.

The increased selectivity in sub-Doppler spectroscopy will lead to a more detailed understanding of the dynamical processes in large molecules. In view of the presented examples of strong rotational effects on the decay behaviour

of benzene, one should be very careful in the interpretation of experimental results with limited spectral resolution. The experimental set up needed for sub-Doppler investigations is nontrivial, but the existing problems can be overcome by careful design of the experiment. The wealth of additional information available from experiments with completely defined molecular states will certainly justify the invested effort.

5. ACKNOWLEDGEMENT

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