

HIGH RESOLUTION SUB-DOPPLER EXPERIMENTS ON BENZENE

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ABSTRACT

It is shown that sub-Doppler spectroscopy enables one to resolve individual rotational states in the S_1 manifold of polyatomic molecules. This is an essential to the understanding of the primary photophysics within the molecule. Spectra of benzene are found to undergo substantial changes as the vibrational energy is raised within S_1 . Due to the increased density of vibrational states, Coriolis coupling, which is already seen at low energies, can lead to effective IVR above 3000 cm^{-1} excess energy. This onset of IVR may be responsible for the onset of "Channel Three" in benzene and probably produces gross changes in the photophysical behavior of any polyatomic molecule.

INTRODUCTION

Contrary to small molecules, which can only decay by radiative processes or at most dissociation, excited large polyatomic molecules can also undergo intramolecular nonradiative decay. One of the prime examples that showed the existence of such processes is the benzene molecule. This was concluded from the distinct deviation of the fluorescence quantum yield from unity after excitation of the molecule into the S_1 electronic state /1/. The reason for this deviation is the relaxation of the molecule into the triplet manifold, i.e. Inter-System-Crossing (ISC). Due to the high density of triplet states at the energy of the S_1 state, ISC is believed to be in the statistical limit and leads to the irreversible decay observed. A fairly smooth increase in the decay rate with the vibrational excess energy in S_1 would be expected from this model. However, a sudden nearly complete disappearance of fluorescence was observed starting at about 3000 cm^{-1} excess energy /2/. This drop in quantum yield could not be explained with an ISC process alone. In addition, from experiments aimed at estimating linewidths of states above 3000 cm^{-1} in S_1 an even more drastic increase of the nonradiative rate at around this energy was concluded /3/. Recent decay time measurements confirmed the strong increase of the decay rate, but the increase was not found to be as large /4/. Since none of the known relaxation processes of large molecules could explain these observations, a mystic "Channel Three" was invoked /3/. The nature of this "Channel Three" could not be determined from low resolution experiments with vibronic state resolution, and especially the discrepancy between decay rate measurements and "linewidth" measurements of /3/ remains a puzzle. To clarify the situation, decay time measurements and measurements of the homogeneous linewidth of single defined quantum states at rotational resolution are needed. Due to the Doppler broadening of about 1.7 GHz such experiments have to be performed with sub-Doppler resolution. To gain insight into the exact nature of the nonradiative process, states at the onset of "Channel Three" have to be observed.

EXPERIMENTAL TECHNIQUES

The experimental set up used for the recording of Doppler-free two-photon spectra and the investigation of the decay of individual levels has been described in detail previously /5,6,7/. Doppler-free excitation takes place if a molecule simultaneously absorbs two photons of equal energy and opposite direction of propagation from a standing wave light field. The light source in our experiments is a cw frequency stabilized single mode ring dye laser. For extremely high spectral resolution and very high sensitivity a cw Doppler-free experiment is performed within a concentric external cavity whose length is variable and locked to the laser frequency /5/. The UV-fluorescence following the two-photon-excitation of the molecules is monitored. The use of the external cavity increases the sensitivity by two orders of magnitude as compared to the simpler arrangement of a backreflected laser beam. A resolution of better than 10 MHz can be obtained with this set up /5/.

For the investigation of the decay of individual levels pulsed excitation of the molecules has to be used. Light pulses of 500 KW peak power and nearly Fourier transform-limited bandwidth are produced by pulsed amplification of the cw light /6/. With an additional parasitic cavity around the second amplifier the pulse length can be varied between 2.5 ns and 10 ns /7/. The decay time measurements are not performed within an external resonator like in the cw set up. Rather after passing through the sample cell the laser beam is reflected back into itself to allow the Doppler-free absorption. The resulting UV-fluorescence signal is either integrated for the recording of spectra or its time behavior is recorded with a transient digitizer. In the Doppler-free two-photon absorption process 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 /6,7/.

RESULTS AT LOW EXCESS ENERGY

To understand the rotational structure of vibronic bands, that is observable at sub-Doppler resolution, vibronic bands with very low excess energy in S_1 have to be analyzed at first. The deviations observed in the "Channel Three" regime can then be attributed to the unknown nonradiative process.

The lowest S_1 state reached by a strong two-photon transition is the 14^1 state at 1570 cm^{-1} vibrational excess energy. Both with the cw set up and the pulsed one the observed sub-Doppler spectrum of the 14^1_0 band is a line spectrum, with most of the lines corresponding to single rovibronic transition /8,9/. Part of the cw recording of the blue part of the Q-branch of this band is shown in figure 1. Each rotational line shown has been assigned within the model of a semirigid symmetric top. For the whole band more than 5000 lines were identified and a fit to the observed line positions yields extremely accurate values for the rotational constants and the quartic centrifugal distortion constants /10/.

In contrast to the situation described so far, in some places of

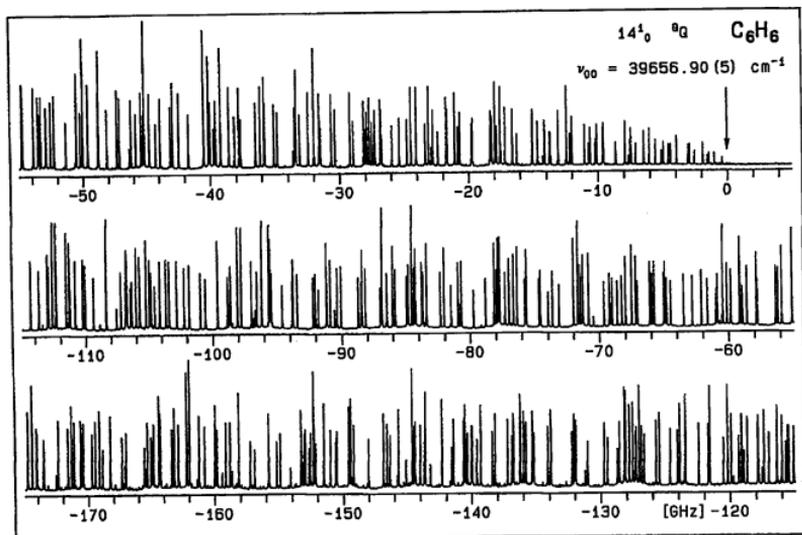


Figure 1. Part of the Doppler-free two-photon spectrum of the Q-branch of the 14^1_0 band of C_6H_6 /10/.

the spectrum, a line predicted by the symmetric top model is not found in the experimental spectrum. Instead two smaller lines are observed, one each to both sides of the expected position. These two lines can be explained as transitions to the two quasi-eigenstates, that originate from the coupling of the "light" zero-order rotational state of the 14^1 manifold to a "dark" zero-order state /11/. Due to the isolated nature of the coupling it can be concluded that the dark state belongs also to the S_1 manifold /11/. A detailed analysis shows that for fixed K values all lines within a range of J values show this kind of perturbation. The distance of the two quasi-eigenstates from the expected position of the light state shows the typical form of an avoided crossing /11/. Since both eigenstates belonging to one light state can be observed in our spectra, we are able to determine the size of the coupling matrix element for each pair. The coupling element on the order of 1 GHz is found to depend strongly on both J and K. Its exact dependence on the rotational quantum numbers agrees very well with that expected for perpendicular Coriolis coupling. We therefore conclude that some of the rotational states of the 14^1 vibronic state are coupled to rotational states of another vibrational state within S_1 by this mechanism. Since the two vibronic states have slightly differing rotational constants, only some of the rotational states will be in resonance and this explains the isolated nature of the perturbation.

With the pulsed set up the decay time of selected single quasi-eigenstates in 14^1 can be measured. We observed, that all states found to be unperturbed possess the same decay time /6/. This shows that the nonradiative decay of S_1 benzene does indeed happen in the statistical

limit and does not depend on the rotation of the molecule. However, for all perturbed states a significantly shorter decay time was found /6/. This can be explained by the fact that the dark vibronic state coupled to the 14^1 state decays much faster. The observed decay is then dependent on the degree of admixture of the dark state. Combining our knowledge from the spectroscopic analysis and from the decay time measurements we can even determine the decay time of the pure dark state. In this way the perturbations observed in the spectrum allow us to investigate the decay behavior of vibronic states that cannot be directly excited by either one- or two-photon absorption. The fact that the dark states have a faster nonradiative decay is important for the understanding of the observations within the "Channel Three" regime.

RESULTS AT HIGH EXCESS ENERGY

The 14^1 state of benzene discussed so far has a vibrational excess energy well below the onset of "Channel Three" at around 3000 cm^{-1} . On the contrary, the energy of the $14^1_0 1^2_0$ state is 3412 cm^{-1} and just slightly above this threshold. The rotational structure of the $14^1_0 1^2_0$ two-photon transition leading to this state should be nearly identical with that of the 14^1_0 band. However, a strong deviation is observed in the experiment /12/. This is demonstrated in figure 2, where the blue edge of the Q-branch of the $14^1_0 1^2_0$ is compared with the same part of

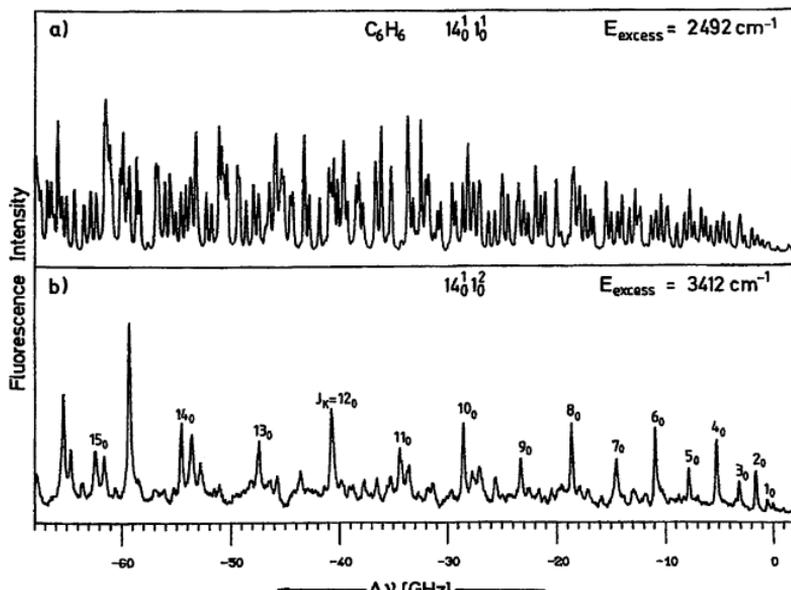


Figure 2. Comparison of identical parts of the Doppler-free two-photon spectrum of the $14^1_0 1^1_0$ band and $14^1_0 1^2_0$ band of C_6H_6 /12/.

the $14^1_0 1^1_0$ band /12/. The structure of the latter band was found to agree quite well with a symmetric top model /9/. In the $14^1_0 1^2_0$ band a strongly decreased number of lines is seen. In an absorption spectrum all rotational lines would be present, but due to a strongly rotational dependent nonradiative decay most rotational states do not fluoresce and are therefore not observed in our fluorescence-excitation spectrum. From the positions of the remaining lines and their alternating intensities it was found, that in the part up to about -60 GHz only lines with $K = 0$ are seen /5,12/. This can be understood by a strong parallel Coriolis coupling to a fast decaying dark state, since parallel Coriolis coupling does affect all rotational states but the $K = 0$ states. The existence of such a state with a very fast nonradiative decay is consistent with the observation made at low excess energy.

With our pulsed set up the decay times of the $K = 0$ states (seen as sharp lines in the spectrum of figure 2) were measured. Typical results are shown in figure 3 /7/. For all states single exponential decays were found within the experimental resolution and the decay rate increases monotonically with J . The values of the decay rate agree very well with the values found from the measurement of the homogeneous line-width of the same lines /7/. The J -dependence of the decay fits nicely the dependence expected for an additional perpendicular Coriolis coupling to a broadened dark state. The magnitude of the coupling matrix element is identical with the one found from the analysis of the perturbations in the 14^1_0 band. However, since the dark state is strongly broadened, no splitting of the lines results, but rather the light state is broadened and superimposed on the dark state. The decay behavior of the sharp one of the two lines, i.e. the observed increase in the non-radiative decay rate, is determined by the degree of mixture and the decay behavior of the dark state. The broad dark state is believed to be a combinational state containing quanta of low frequency out-of-plane modes, which are known to enhance the nonradiative decay /13/.

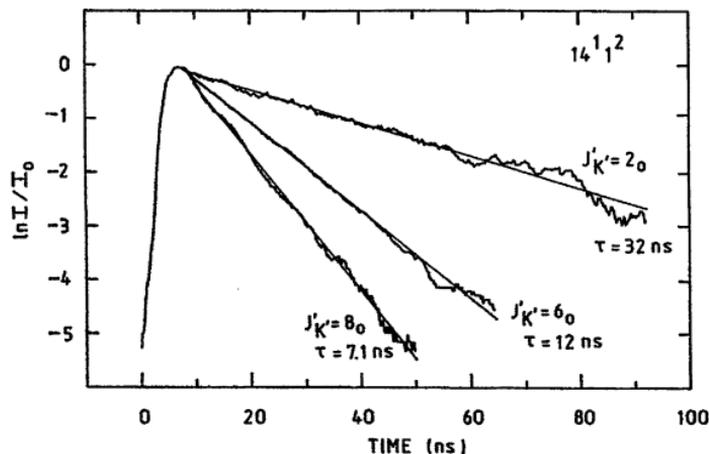


Figure 3. Decay curves for $K = 0$ states of the 14^1 state of C_6H_6 /7/.

SUMMARY AND CONCLUSIONS

The Doppler-free spectra of S_1 benzene discussed above clearly show the strong dependence of the nonradiative decay on the rotation of the molecule. Especially the strong influence of Coriolis coupling is seen. Since the rotational structure of vibronic bands can not be resolved with Doppler-limited spectroscopy, all previous measurements could only show the averaged decay behavior of bunches of eigenstates. This could even result in the observation of biexponential decays, as have been observed for states in the "Channel Three" regime /4/.

In view of the results presented, the "Channel Three" phenomenon is now understood as a strong increase in internal vibrational redistribution (IVR) to fast decaying dark states within the same electronic state. The density of vibrational states in S_1 needed for effective IVR is just reached at 3000 cm^{-1} excess energy. IVR is at least in part caused by Coriolis coupling. For all quasi-eigenstates investigated the nonradiative decay rate determined from decay time measurements is identical to that determined from linewidth measurements. The deviation found in previous low resolution experiments is believed to be mainly due to the limited experimental resolution and the different selection of the bunches of eigenstates in the different experiments.

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