Optical hole burning and -free induction decay of molecular mixed crystals

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SUMMARY

The main theme in the research of which this thesis forms a part, is the dephasing after electronic (vibronic) excitation of organic guest molecules in suitable host crystals ("molecular mixed crystals") at low temperature. Our primary interest in this respect are purely electronic $S_0 - S_1$ singlet-singlet transitions of the guest.

Chapter 1 is an introduction to the subject and also provides a quantum mechanical background. Our research belongs to the field often called quantum electronics. The guest molecules may exhibit phase relaxation, for example due to interactions with the crystalline environment (phonon scattering), that change only the phase of the excited molecules while population relaxation between the molecular levels does not occur. Of course, population relaxation also is a phase disturbing process. For the systems studied by us, phase relaxation can be described in terms of the optical analogue of Bloch's transverse relaxation time T_2. It can be measured by inducing a macroscopic phase in the ensemble of guest molecules by excitation with coherent (laser) light. In the time domain one measures T_2 more or less directly, while in the frequency domain the homogeneous width of the transition under study is measured. This width is simply related to T_2. Although at low temperature the transitions of interest to us are often predominantly inhomogeneously broadened, the homogeneous width (dephasing time) can still be measured, using a number of coherent optical techniques. When we started our research in 1975, these techniques had not yet been applied to molecular mixed crystals. Therefore, this possibility had first to be demonstrated. To this end we studied the crystals in the temperature region $\lesssim$ 2 K, where most interactions between the guest and its host environment were expected to be frozen, so the fluores-

cence decay would dominate the dephasing.

The laser apparatus used is discussed in Chapter 2. We used single mode cw dye lasers in the Rhodamine 6 G region ($\sim$ 5600 - 6200 Å). Measurements were performed in the frequency domain (Chapter 3) as well as in the time domain. The latter experiments were implemented using laser frequency switching (in Chapter 5), and by gating the laser beam with an acousto-optic modulator (in Chapter 7).

In Chapter 3 photochemical hole burning studies are described of dimethyl-s-tetrazine (DMST) in durene and of s-tetrazine (ST) in benzene. In the DMST experiments this technique was used for the first time to determine homogeneous widths of molecular mixed crystal transitions. The DMST results showed that at temperatures < 2 K the contribution of electron-phonon coupling to the homogeneous width of electronic $S_0 - S_1$ transitions in these systems is small or even negligible. After our DMST results became known, IBM patented the possible application of photochemical hole burning in optical information storage systems of high density. The ST experiments yielded the surprising result that in the $S_0 - S_1$ transition the homogeneous width at the sides of the inhomogeneous line appears to be larger than at the top.

In Chapter 4 theories are developed for saturation hole burning with a population bottle-neck as well as for photochemical hole burning. In the latter case simulations were performed of the experimental hole burning results obtained for porphin in n-octane (by Völker et al.), for DMST in durene and for ST in benzene. It follows that for DMST and ST hole widths can be obtained (in the limit of low burning power and short burning time) that still equal twice the homogeneous width, despite the fact that the photodissociation probably proceeds by the consecutive absorption of two photons.

Chapter 5 describes an optical free induction decay (OFID) experimental study of pentacene in p-terphenyl (energetically lower sites). The most striking result is that the 135 MHz switched OFID curves show a consecutive-two-component decay. The long component is completely determined by the fluorescence lifetime, in agreement with the photon echo results. This result was thus independent of the excita-

tion bandwidth relative to the inhomogeneous width, which was an important conclusion. Our OFID result is compared to a number of optical coherent studies of the same system by other authors. Some causes for the consecutive-two-component behaviour are considered. Our OFID measurements (in combination with the experiments of Chapter 7) yielded a value for the electric dipole moment of the electronic $S_0 - S_1$ pentacene transition. At the end of this chapter the determination of pentacene ground-state vibrational dephasing times from line shape analyses of measured emission lines is discussed (which was also done for DMST in Chapter 3).

Chapter 6 treats theoretically the influence upon $S_0 - S_1$ OFID of an intermediate triplet state acting as a population bottle-neck. From the application to a few practical examples, this effect appears to restrict considerably the applicability of OFID as a T_2-determination method. The time limits imposed upon the intracavity switched OFID method are discussed.

In Chapter 7 the observation is described of fluorescence transients during $S_0 - S_1$ excitation of pentacene in p-terphenyl at $\sim$ 2 K, and their quantitative theoretical simulation. These transients again appear to be caused by the intermediate triplet state acting as a population bottle-neck, thus showing an earlier interpretation by Zewail et al. to be incorrect. From the simulations follows (in combination with the experiments of Chapter 5) an accurate value for the (very small) quantum yield of $T \leftarrow S_1$ intersystem crossing for the lower sites. An OFID experiment performed on the higher pentacene sites shows a beautiful illustration of the theory developed in Chapter 6.

In conclusion we state that the influence of the intermediate triplet state upon a number of coherent optical experiments where the $S_0 - S_1$ transition is excited, is described theoretically. This is applied to a number of practical cases. Actually, it has been shown that photochemical hole burning and OFID are applicable to molecular mixed crystal systems at temperatures $\lesssim$ 2 K. Some experimental results emerged (variation of hole width within the ST inhomogeneous line, consecutive-two-component OFID of pentacene), of which further study might prove very interesting. Moreover, these latter results show

that single frequency laser techniques yield new information, in addition to pulsed laser photon echo measurements, where a large part of the inhomogeneous line is excited.