CHAPTER 1

Introduction

1.1 Background

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References
1.1 Background

In this thesis optical experiments are described in which the effect of quantum electrodynamical interactions between dye-molecules and the radiation field on the linear and first-order nonlinear optical properties is studied. A separation is made between (A) the interaction of dye-molecules with their own radiation field, and (B) the interaction of dye-molecules with the emitted field of neighbouring dye-molecules. In case (A) spectral properties are studied of fluorescing molecules placed in front of metallic mirrors. Interference effects are observed, due to reflections from the mirror-surface. In the second type of experiments (B), intermolecular interactions in dye-doped monolayers are studied by means of second-harmonic generation. The efficiency of second-harmonic generation is studied as a function of the distance between, and as a function of the mutual orientation of the dye-molecules. The effect of a nearby metallic surface on the first-order nonlinear optical properties is considered.

The interest in the fluorescence properties of dye molecules in front of a mirror originated from the work of DeMartini et al. [1,2]. In their work the angular dependence of the spontaneous emission of a thin Ruby crystal in front of a mirror was interpreted in terms of changes in the zero-point electromagnetic field density, caused by the presence of a nearby mirror. The observed emission pattern is explained as a clear evidence for the physical reality of the zero-point electromagnetic field. In chapter 2 of this thesis, however, it is shown that the angular and spectral localization effects observed can be explained also classically as resulting from self-interference in spontaneous emission from a Wiener-fringe pattern [3]. These interference effects were found to be useful also in a study of the optical dynamics of excited dye-molecules in polymer films (chapter 3), and in a study of the coherence properties of light emitted by molecules placed in front of a mirror (chapter 4).

In connection to the work on luminescence in front of highly reflecting surfaces ideas developed to study also second-harmonic generation in front of
these surfaces. Especially, we were interested in the influence of a mirror on the macroscopic and microscopic local-fields, for which second-harmonic generation can act as a very sensitive probe. Knowledge of the local-field is important for the interpretation of experimental results in terms of molecular properties. In order to observe strong second-harmonic signals asymmetric dye-molecules were arranged in a non-centrosymmetric way by means of the Langmuir-Blodgett monolayer technique [4]. As a reference point we first started to analyse the (microscopic) local-field inside monolayers by using glass substrates (chapter 6). The microscopic local-field is altered by varying the distance between, and by changing the mutual orientation of the dye-molecules. The effect of a metal substrate could then be compared to results obtained on glass substrates (chapter 7).

1.2 Outline

In this section a short description of the contents of each chapter is given. The relation between successive chapters is discussed.

In chapter 2 the effect of a mirror on the fluorescence spectra of molecules contained in a 1-2 \( \mu \text{m} \) thick polymer layer is discussed. Two kinds of interference effects need to be considered for a correct description of the fluorescence spectrum. In the first place interference occurs between the directly emitted wave and the wave reflected by the mirror (see Fig.1.1), also called wide-angle interference [5]. Secondly, fringes are formed upon interference between the direct and reflected wave of the exciting laser beam. A spatially modulated pattern of excited molecules is formed (Wiener grating) [6]. In case of micron thick layers this grating is essential in the detection of the wide-angle interference. In the absence of this grating wide-angle interference cannot be resolved spectrally.

The other way around, using a pulsed excitation source, wide-angle interference can be used to study the effect of phase relaxation (dephasing) [7] during the formation of the Wiener grating, the subject of chapter 3. Dephasing causes a loss in coherence in the ensemble of excited molecules, and
consequently reduces the visibility of the Wiener grating. By measuring the visibility of the observed interference fringes in the fluorescence spectrum as a function of the time delay between the direct and the reflected laser pulse, a dephasing time of 100 fs at room temperature could be measured for the dye molecule nile blue dissolved in poly(4-vinylpyridine). The time delay between the two pulses was varied by changing the distance between the emitting layer and the mirror. The distance could be determined from the observed interference period. A major advantage of this new technique is that only low-excitation powers are needed; it suffices to detect the spontaneous emission of the sample.

In chapter 4 we discuss coherence properties of light emitted by a thin fluorescing film (1-2 μm) placed in front of a mirror. The field correlation between different points in space and time is calculated, and is found to
deviate from a general scaling law, as first formulated by E. Wolf [8]. The consequence of this deviation from the scaling law is that the detected emission spectrum is not invariant on propagation, in contradiction to normal light sources (i.e. blackbody radiation) [9]. Emission spectra of a fluorescent film in front of a mirror have been measured at different points in space, and were found to depend on the distance from the light source, and the angle of observation. The observations agree well with theory.

In the above described experiments the distance between the fluorescing molecules and the metallic mirror surface was larger than the wavelength of emission (≈0.6 μm). Energy transfer to the metal substrate could therefore be neglected. The effect of energy transfer on fluorescence properties of molecules separated less than 10 nm from the mirror is the subject of chapter 5. Energy transfer is caused by the coupling of the oscillating dipole with its fictitious image dipole in the metal substrate [10]. The coupling is brought about by the near-field of the radiating dipole. This situation is comparable to the case of two coupled pendulums [11]; the amplitude oscillates back and forth between these two pendulums. However, the difference is that the image dipole is strongly damped compared to the inducing dipole. The image dipole dissipates energy into the metal substrate by various scattering processes [10], leading to a decrease of the excited state lifetime by several orders of magnitude. In case the excited state lifetime becomes as short as the pure dephasing time, a broadening of the fluorescence spectrum is observed. This broadening has not been noticed before. The distance dependence of the above mentioned phenomena is described in chapter 5. A comparison with theory is made.

In the second part of this thesis intermolecular interactions in monolayers of dye molecules are studied by means of second-harmonic generation. In a second-harmonic generation experiment the effective surface nonlinear polarization $P_i(2\omega)$ at frequency $2\omega$ is measured, where $P_i(2\omega)$ is given by [12]:

$$P_i(2\omega) = \sum_{j,k} \chi_{ijk}^{(2)}(2\omega,\omega,\omega) E_j(\omega) E_k(\omega),$$  \hspace{1cm} (1.1)$$

here $E_{j,k}(\omega)$ is the field strength at frequency $\omega$ along the $j,k$ axis. The quantity of interest is the second-order surface susceptibility $\chi_{ijk}^{(2)}(2\omega,\omega,\omega)$, a
proportionality constant relating the nonlinear polarization $P_i(2\omega)$ to the applied fields. Molecular parameters are contained in this term according to [13]:

$$\chi_{ijk}(2\omega,\omega,\omega) = N_s < T_{ijk}^{\lambda\mu\nu} > \beta_{\lambda\mu\nu}, \quad (1.2)$$

where $N_s$ is the surface density of nonlinear active molecules, $T_{ijk}^{\lambda\mu\nu}$ the coordinate transformation matrix connecting the molecular axis system to the laboratory frame, the angular brackets $<>$ denote an average over the molecular orientations, and $\beta_{\lambda\mu\nu}$ is a tensor component of the molecular nonlinear polarizability. Eq.(1.2) is only valid in case interactions between molecules can be neglected, i.e. the microscopic local-field can be neglected. In case of interactions significant deviations from linearity of $\chi_{ijk}(2\omega,\omega,\omega)$ in surface density $N_s$ can be expected.

In chapter 6 the macroscopic surface susceptibility of dye-doped Langmuir-Blodgett monolayers is studied as a function of surface density. Deviations from a linear behaviour of $\chi_{ijk}(2\omega,\omega,\omega)$ with surface density are found. The experimental results are confirmed by theoretical calculations assuming a certain ordering of the molecules at the surface. The ordering of the molecules is revealed by second-harmonic generation and by linear absorption spectroscopy.

In chapter 7 second-harmonic generation in front of a metallic mirror is studied. The frequency doubling efficiency is again measured as a function of surface density. In front of a mirror the applied field components differ in magnitude from the applied fields in front of a glass substrate. Therefore induced dipole moments have different directions, leading to different interactions within the monolayer. Less pronounced deviations from linearity are found. Also described are experiments in which the distance between the mirror and the optical nonlinear monolayer is varied over a range from 1 to 6 nm. The efficiency of second-harmonic generation is found to decrease for small distances from the mirror. The results are explained in terms of energy transfer. Here energy transfer again leads to an enhanced damping rate of the
optical transition, which is expected to reduce the molecular nonlinearity.

References