INTRODUCTION AND SUMMARY

This thesis deals with the spectroscopic properties of p-benzoquinone (PBQ). The most interesting feature of PBQ for our purposes, is the fact that PBQ contains two filled non bonding n-orbitals that are localized at the oxygens (fig. 1). As in formaldehyde, the precursor of all ketones, the lowest optical excitations in PBQ are, in a simple one electron model, due to excitations of an electron from an oxygen n-orbital into the ring system (1). Since PBQ contains two inversion related n-orbitals two types of nπ* excitations of opposite parity are formed. In a zero order picture there are two ways one can visualize these excitations.

In the first, the interaction among the \( n_1 \) and \( n_2 \) orbitals (fig. 1) is assumed to be so strong that delocalized \( n_\pm = z^{-\frac{1}{2}} (n_1 \pm n_2) \) orbitals are formed and optical excitations can be considered to arise from excitations from these \( n_\pm \) orbitals into the \( \pi \)-electron system. This description would be in line with the ideas put forward by Heilbronner et al. (2) who considered 'through space' and 'through bond' interactions to be responsible for and capable of producing large splittings (\( \sim 1 \) eV) among the \( n_+ \pi^* \) and \( n_- \pi^* \) excitations in diazines and diketones.

Fig. 1. p-Benzoquinone-\( h^+_d \) (PBQ-\( h^+_d \) and the choice of the axes system. The \( n \)-orbitals on the oxygen atoms are schematically depicted by lobes.
Fig. 2.

A. Single crystal absorption spectrum of PBQ-H₄ at 1.8⁰K. The incoming light is perpendicular to the 20₁ plane, almost identical to the molecular plane. The light is polarised along the 102 (p) axis which makes an angle of 55⁰ with the molecular z axis. The crystal thickness is 0.245 mm. Indicated are the assignments of the lines as derived from our Stark experiments.

B. The splitting of the singlet B₁g origin. The lowest energetic absorption is the magnetic dipole allowed g-inversion level; the other line corresponds to the u-inversion level.
The second way starts by assuming that the $n_1 m^*$ and $n_2 m^*$ excitations are very localized. In fact one could formally consider the PBQ molecule to be built up from two 'connected' C=O chromophores, somewhat like a formaldehyde dimer. In this case the $n_1 m^*$ and $n_2 m^*$ excitations interact through exchange (3) forces in the $m^*$ triplet states and through both Coulomb and exchange forces (3) in the $m^*$ singlet states. The latter description of course is intimately related to the treatment of Frenkel excitons in molecular crystals and was originally proposed for the description of molecules containing two aza groups by El-Sayed et al (4). This intramolecular exciton model is physically very appealing but, as always, experiments should decide what the best zero-order description is. It is also of interest to note here that the difference between an intramolecular and Frenkel exciton lies in the fact that in the former case the excitations are coupled by the molecular force field and in the latter case by the phonon force field.

In this thesis we will present experiments that show that the intramolecular exciton model proposed previously by El-Sayed (4) gives an excellent zero order description for the lowest $m^*$ excitations in PBQ. It will also be shown that the dynamic coupling induced by the molecular force field completely dominates the observed spectra. Fig. 2A shows the visible light single crystal absorption spectrum of PBQ at 1.8° K. This spectrum was first reported by Sidman (5) who tentatively assigned the most intense line at 18946 cm$^{-1}$ to the spin forbidden orbitally allowed $^3A_u (m^*)$ state. Later Chowdhury and McClure (6) confirmed the triplet character of this state with a Zeeman experiment. The very weak and sharp absorption at 18620 cm$^{-1}$ appeared to be the most puzzling feature of the spectrum.
From a polarized Zeeman study Trommsdorff (7) concluded this line to be the origin of the $^{3}A_u\,(n\pi^*)$ state. Klump (8) correlated the absorption and phosphorescence spectra of PBQ in different host crystals and assigned the lowest absorption to the $^{3}B_{1g}\,(n\pi^*)$ state, made allowed by static crystal field mixing with the $^{2}A_u\,(n\pi^*)$ state. Another interpretation of the spectrum was suggested by Francis (9) and Koyanagi (10). They analyzed the spectrum in terms of the spin and orbitally forbidden $^{3}B_{1g}\,(n\pi^*)$ state and the origin thereof was positioned at 18620 cm$^{-1}$ in the pure crystal. At this stage we started our spectroscopic investigation of PBQ and decided to perform Stark effect measurements on the absorption spectrum to discriminate among the different suggestions made. In case of two close lying $n\pi^*$ states of different parity one expects the electric field to mix these states thereby relaxing the Laporte selection rules. In the course of our experiments Trommsdorff (11) by means of an extensive study on the singlet and triplet absorption spectra of PBQ and derivatives obtained convincing spectroscopic evidence that the $^{3}B_{1g}\,(n\pi^*)$ state indeed is the lowest triplet state in PBQ. In this thesis we will show that our experiments completely confirm this assignment.

The results of our Stark effect study are presented in chapter II for the singlet states and in chapter III for the triplet states. It is shown in chapter II that the Stark effect study has also resolved one of the most puzzling features in the singlet spectrum, the splitting of the $^{1}B_{1g}\,(n\pi^*)$ origin (see fig. 2B). As a result of these measurements our understanding of the visible light PBQ absorption spectrum at present is as follows:
1. The splitting of the $^1B_{1g}$ ($\Pi^*$) origin is due to an inversion splitting induced by strong vibronic coupling among the two lowest $g$ and $u \Pi^*$ singlet states.

2. A similar situation occurs in the triplet states but here the $g$-inversion level (origin of the $^3B_{1g}$ triplet state) can only be observed in an electric field.

3. The lowest observed absorption at 18620 cm$^{-1}$ is assigned as the $u$-inversion level of the $^3B_{1g}$ ($\Pi^*$) state induced by vibronic coupling with the allowed $^3A_u$ ($\Pi^*$) state at 18946 cm$^{-1}$.

We have continued our investigation with a study of these most interesting vibronic coupling effects. Chapter IV is devoted to an extensive study of the lowest $^3B_{1g}$ ($\Pi^*$) triplet state as this state is accessible to detailed spectroscopic experiments. Phosphorescence was detected at low temperature in different host crystals (8-10). As always the vibrational envelope of emission spectra contains important information about the distortion of a phosphorescent state (12-16). Moreover, one can study the magnetic properties by optically detected magnetic resonance (ODMR) techniques (17). Anomalous sensitivity of the spectral and magnetic properties to isotopic substitution is also reported in chapter IV and these features are shown to be characteristic for a pseudo Jahn-Teller (18) distorted state. To illustrate this hypersensitivity here the absorption spectrum of the asymmetric 'isotope' substituted PBQ molecule toluquinone (PBQ-CH$_3$) is given in fig. 3. In comparing this spectrum with the PBQ absorption spectrum (fig. 2) we conclude that the spectroscopic properties of the $\Pi^*$ triplet states change dramatically on methyl substitution. Since this effect can not be explained by a direct mixing of the $g$ and $u \Pi^*$ states on methyl
The polarized absorption spectrum of toluquinone at 1.8° K. The polarization conditions are the same as in PBQ (see fig. 2). The crystal thickness is 0.2 mm. The assignments given are obtained from the spectroscopic study of Trommendorff (11). The absorptions between the singlet and triplet \( B_{1g} \) origin are all triplets with the same spin orbit characteristics as the \( B_{1g} \) origin. This was concluded from our polarized Zeeman experiments.
substitution, this further confirms the strong vibronic coupling between these states as these processes are very sensitive to the vibrational force field. In chapter V the nπ* triplet absorption and emission spectrum of a to PBQ related diketone anthraquinone (AQ) are presented. Although the AQ and PBQ absorption spectra look very dis-similar it will be shown that similar vibronic coupling effects dictate the spectral properties of the nπ* states in both molecules.

In the final chapter of this thesis a vibronic coupling model is developed that explains the most important spectroscopic results of PBQ and AQ. It is demonstrated that for the very close lying g and u nπ* states the coupling via the nuclear kinetic energy operator plays a very important role. The elegance of the model is that if one starts with Herzberg-Teller (HT) (19) coupled Crude-Born-Oppenheimer (CBO) (20) nπ* states one obtains simple analytical expressions for the nuclear kinetic energy coupling terms. Only two parameters, the HT matrix element V_{12} and the energy difference ΔE_o between the CBO states, are needed to define the problem. The most interesting conclusion derived from the model calculations is that for the g- and u-inversion levels of the lowest nπ* triplets the Born-Oppenheimer (21) approximation is no longer valid. Spectroscopically this means that one cannot assign the states observed to particular potential energy surfaces as is suggested in chapters III-V. Finally we suggest that for the description of all close lying electronic excited states in polyatomic molecules the neglect of the nuclear kinetic energy operator is not warranted.