Interpretation of a low-lying excited state of the reaction center of Rb.sphaeroides as a double triplet

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Abstract:
The recently observed transient absorption of the lowest excited state of the special pair $P^*$ at 2710 cm$^{-1}$ [1] is assigned as a singlet which arises from the coupling of the two lowest triplets from the two dimer halves. INDO calculations are used to predict its intensity. The analogy of the coupling mechanism to the trip-doublet spectrum from $P^+$ is shown and the influence of the double triplet on the Stark effect of $P^*$ is investigated.

Introduction
In recent femtosecond infrared spectroscopy of the reaction center excited states of Rb.sphaeroides up to 10000 cm$^{-1}$ an interesting spectrum has been observed. A relatively sharp band at 2710 cm$^{-1}$ is followed by a very broad around 5300 cm$^{-1}$ [1]. These bands have been interpreted as internal charge transfer states, where the extra broadening of the upper is seen as a result of mixing to higher excited states of the dimer. This interpretation can not explain that the higher state has more intensity, also the absence of the lower in the ground state spectrum and in the Stark effect spectrum would be in conflict with this model, since the CT state should mix appreciably with $P^*$. From our INDO calculations which are based on the X-ray structure of rps.viridis we have predicted earlier [2] the presence of a low lying excited state denoted $P^{**}$ which is a singlet component of a double excited state with a triplet on each of the two dimer halves. We obtained this state too low in energy as we know from the predicted energy positions of the lowest triplet. However, if we correct for this shortcoming of the INDO calculation, we predict this state to be at the position of the newly observed band. For the symmetric dimer it is an even state and therefore does not couple with $P^*$. There exists, however, an interesting one-electron coupling mechanism to the internal charge transfer states. This coupling is of the same nature as the one which provides intensity to the trip-doublet observed in the $P^+$ spectrum. In this paper we want to show that the $P^* \rightarrow P^{**}$ transition obtains its intensity from the CT states. Moreover the presence of the $P^{**}$ state helps to understand the unusual Stark effect spectrum of $P^*$ and provides insight into the internal asymmetry of the dimer. We start with the analysis of the spectrum of $P^+$, then we present an extended exciton model for the dimer which includes the CT and the double-triplet state. Analytical expressions are derived for the infrared transitions and the Stark effect. The relevant couplings are discussed in the framework of INDO calculations.

Simulation of the $P^+$ spectrum
The spectrum of $P^+$ [1,3] shows a very low energy transition at $\approx 2500 cm^{-1}$ with $80 Debye^2$ intensity and another transition of similar strength at $\approx 7500 cm^{-1}$ with an additional shoulder at higher transition energy. INDO calculations by us [2] as well as model studies by Breton et al [3] and by
Parson et al. [4] related the lowest transition to the hole transfer. The higher transition shows more complex configuration interaction [2]. Recent investigations by Reimers et al. [5] attributed also the low energy transition to the hole transfer between the two dimer halves and the higher band to a trip-doublet state. A quantitative understanding is still missing since the internal asymmetries of the dimer which are difficult to assess, influence the relative intensities in a sensitive way.

Here we want to discuss the experimental spectrum in the framework of a simplified four state model which incorporates the two cationic states $L^+$ and $M^+$ and the two lowest excitations for each of them which are the triplet-coupled doublets $L^+M^3$ and $M^+L^3$. A more detailed analysis including higher excited configurations explicitly will be given in a separate paper.

\[ H = \begin{pmatrix} E_1 - d_1 & U_1 & 0 & U_{12} \\ U_1 & E_1 + d_1 & U_{21} & 0 \\ 0 & U_{21} & E_2 - d_2 & U_2 \\ U_{12} & 0 & U_2 & E_2 + d_2 \end{pmatrix} \]  

(1)

Within this basis the positive charge is fully localized on $P_L$ for the first and third state and on $P_M$ for the other two. The delocalization of the charge is the result of the intermolecular resonance interaction $U_1, U_2$ competing with the small energy differences $2d_{1,2}$ of the symmetry related states. Such asymmetries arise from asymmetric interaction with the surrounding, e.g. hydrogen bonding to protein residues or from asymmetries of the two chromophores. We investigated especially the influence of the orientation of the two acetyl groups. A structure model where the oxygen and the methyl group of $P_M$ are exchanged is also consistent with the X-ray structure and leads to a large splitting of the intradimer charge transfer states which is needed to explain the strong dipole change of $P^*$ seen in the Stark spectrum. The two couples of states denoted by the indices 1 and 2 respectively interact via the matrixelements $U_{12}$ and $U_{21}$. A detailed analysis of the INDO results shows that the coupling $U_1$ is mainly given by the negative resonance interaction $-\beta_{LM}$ involving the molecular orbitals of two different charged states $P_L^+$ and $P_M^+$. For our analysis we want to interpret couplings for $P^+$ and $P^*$ within one set of molecular orbitals. We use localized SCF orbitals of the neutral dimer which are obtained switching off all resonance interactions between the two dimer halves during the SCF step. Electron correlation effects are important and the expression for $U_1$ becomes more complicated as configuration mixing takes place. We find that $U_1$ is underestimated by about a factor of 2 if the resonance integral $\beta_{LM}$ of the SCF orbitals of $P$ is used. For the coupling of the two trip-doublet states the reorganization effect is of little importance. The couplings of the lowest cationic states to the trip-doublets involve the transfer of an electron from the HOMO on one side to the LUMO on the other side. Here the reorganization effect leads to a significant increase of $U_{12}$ and $U_{21}$. These rather strong couplings induce the intensity of the trip-doublets. The results are summarized in table 1.

For a simplified analytical treatment we first diagonalize the two pairs of states with their asymmetries which we want to determine empirically. The couplings $U_{12}$ and $U_{21}$ are treated as a perturbation. We use the linear combinations of states

\[ \tilde{H} = S^{-1}HS = \begin{pmatrix} \cos(\phi_1) & \sin(\phi_1) \\ -\sin(\phi_1) & \cos(\phi_1) \end{pmatrix} \begin{pmatrix} \cos(\phi_2) & \sin(\phi_2) \\ -\sin(\phi_2) & \cos(\phi_2) \end{pmatrix} \]  

(2)

where the angles $\phi_{1,2}$ measure the degree of localization or delocalization and are given by
\[
\sin(\phi_j) = -\text{sign}(U_j)\frac{\sqrt{2}}{2} \sqrt{\frac{1}{d_j^2 + U_j^2} - \frac{1}{d_j^2}} \quad \cos(\phi_j) = \sqrt{1 - \sin^2(\phi_j)}
\]

Specifically one obtains $\phi_j = 0(\pm \frac{\pi}{2})$ if the lower state of a pair is localized on $P_L(M)$ and $\phi_j = \pm \frac{\pi}{4}$ if both states of the pair are fully delocalized. Within this model we can determine the main parameters empirically and compare them with our calculated ones. From the experimentally observed charge distribution of $\approx 65\%$ on $P_L$ we get $\sin^2(\phi_1) \approx 0.35$.

The intensity of the lowest transition is estimated as $(\frac{\pi}{2} \sin(2\phi_1))^2 \approx 0.23p^2$. If we take a value of $p=38$ Debye corresponding to the full center to center distance the calculated intensity of $330\text{Debye}^2$ is too large by a factor of about 3 to 4. The quantum calculations, however, reduce $p$ for the cationic states by the rearrangement of the electron system to a value of about 20 Debye and the calculated intensity ($90\text{Debye}^2$) is close to the experimental data of $80\text{Debye}^2$ for viridis. From the experimental transition energies we find approximately $2\sqrt{d_1^2 + U_1^2} \approx 2700\text{cm}^{-1}$. Together with $\frac{1}{2} \left(1 - \frac{d_1}{\sqrt{d_1^2 + U_1^2}}\right) = \sin^2(\phi_1) \approx 0.35$ we estimate the coupling and energy difference as $U_1 = 1300\text{cm}^{-1}$ and $2d_1 = 800\text{cm}^{-1}$. The value of $U_1$ is larger than the calculated $800\text{cm}^{-1}$. This discrepancy could be partly due to a geometry relaxation in the cationic state but also to the parameterization of the resonance integrals which was optimized with respect to transition energies. In our simulation (fig.1a) we accounted for this shortcoming and used the larger value of $1300\text{cm}^{-1}$. If we assume that the intensity of the trip-doublets is mainly borrowed from the hole transfer transition the total intensity of the two trip-doublets is given by $pU_1^2/(E_2 - E_1)^2 \approx 25D^2$ for the calculated coupling of $1600\text{cm}^{-1}$ and an energy difference of $7000\text{cm}^{-1}$. It depends sensitively on the value of the resonance coupling $U_12$. An increase of the coupling by a factor of 2 already gives more intensity for the trip-doublets than for the hole transfer band. The distribution of intensity over the two trip-doublet transitions depends on their degree of localization. In case of full localization of the lower trip-doublet on $P_M$ the intensity ratio of 2:1 is essentially given by the localization of the lowest doublets. If on the other hand the two trip-doublets form a pair of completely delocalized states which might be a reasonable assumption as the resonance coupling $U_2$ is larger in magnitude than $U_1$, the lower of the trip-doublet transitions gains about $\sin^2(\phi_1 + \frac{\pi}{4}) = 97\%$ of the intensity and the higher transition becomes rather weak. The calculated splitting of the two trip-doublets is for the symmetric dimer $2U_2 \approx 2000\text{cm}^{-1}$ but may be enlarged due to energy differences of the triplet states on the L and M halves. In our INDO calculations we found a rather small asymmetry only if we used the structure with the rotated acetyl on the M-half. Experimentally it is not possible to assign this state clearly which supports the conjecture of strong delocalization and the resulting low intensity. This conclusion differs from the assumptions made by Reimers and Hush [5]. If the trip-doublets borrow their intensity predominantly from the hole transfer band they will be essentially both polarized parallel to the vector $p$. This polarization is consistent with the experimental anisotropy of $0.298 \pm 0.028$ [1]. From the quantum calculations we find a value of 0.27. We like to point to the fact that the magnitude and direction of $p$ are largely influenced by the reorganisation of the electron system. For a transition parallel to the direction connecting the two magnesium atoms the calculated anisotropy has a much smaller value of 0.21. On the basis of this assumption Wynne et al [1] concluded that the intensity of the trip-doublet is not provided by the hole transfer. Instead they assume that the trip-doublet has the polarization of the Qy transition of $P_M$. The transition to the trip-doublet gains its intensity from the one-particle interaction between the two dimer halves as discussed by Reimers et al. A detailed analysis will be given in a forthcoming paper which shows that the transition dipole contains a contribution from the hole transfer transition and a smaller one from the Qy transitions of the two halves, the latter depending on the degree of
localisation of the $P^+$ states.

**Interpretation of the $P^*$ spectrum**

The electronic structure of the dimer in the Qy region is expected to show at least four states which are mixtures of two local excitations $P^*_L$ and $P^*_M$ and of two charge transfer states $L^+M^-$ and $M^+L^-$. The lowest excitation is mainly ascribed to the antisymmetric combination $P^*_L - P^*_M$ with some admixture of the charge transfer states. This excitation carries most of the Qy oscillator strength as the transition dipoles of the two dimer halves are nearly antiparallel. The second excitonic component, the so called upper dimer band carries much less intensity and overlaps with the absorption bands of the accessory monomers. From the absence of a strong Stark effect in this region it was concluded [8] that the upper dimer band couples only weakly to the CT states. The CT states are predicted to be in the region between the upper dimer band and the Qx transitions of the dimer. They cannot be observed in the absorption spectrum as they have only little intensity and are inhomogeneously broadened by electrostatic interaction with the environment. In addition to these four basic Qy excitations we now incorporate an additional excitation in this frequency region which can be visualized as two triplet excitations on the two halves which are coupled to a singlet double excitation of the dimer. It might be identified with the weak band at $15800\text{cm}^{-1}$ denoted by a star in fig.4 of [1]. According to our INDO results this double-triplet state $P^{**}$ couples strongly to the charge transfer states and may be important for the interpretation of the Stark effect of the dimer absorption. The coupling involves the transfer of an electron from an occupied orbital to an unoccupied orbital on the other dimer half and is therefore closely related to the coupling of the trip-doublets to the lowest cationic states. The energy of this state is underestimated by the INDO method for the applied parameters. As the lowest calculated triplet of the Bchl molecules comes out too low by about $1500\text{cm}^{-1}$ and the calculated energy of $P^{**}$ is close to $P^*$ or even slightly below [2,9,10] we expect the correct position of $P^{**}$ somewhat less than $3000\text{cm}^{-1}$ above $P^*$ which places it at the position of the lower and sharper $P^*$ absorption band of Wynne et al [1]. In the following we want to show that further support for such an assignment comes from the prediction of its intensity, its width and its Stark effect. We consider coupling of the following basic excitations: $P^*_L, P^*_M, L^+M^-, M^+L^-, P^{**}$ described by the interaction matrix [2]

$$H = \begin{pmatrix}
E(P^*_L) & W & \beta_{L\times M^*} & -\beta_{LM} & 0 \\
W & E(P^*_M) & -\beta_{ML} & \beta_{M\times L^*} & 0 \\
\beta_{L\times M^*} & -\beta_{ML} & E(L^+M^-) & 0 & -\sqrt{\frac{3}{2}}\beta_{L\times M} \\
-\beta_{LM} & \beta_{M\times L^*} & 0 & E(M^+L^-) & -\sqrt{\frac{3}{2}}\beta_{M\times L} \\
0 & 0 & -\sqrt{\frac{3}{2}}\beta_{L\times M} & -\sqrt{\frac{3}{2}}\beta_{M\times L} & E(P^{**})
\end{pmatrix}$$  \hspace{1cm} (4)

The factor $\sqrt{\frac{3}{2}}$ in front of the HOMO-LUMO cross coupling matrix elements results from the proper spin multiplicities. Contrary to $P^+$ the excited state $P^*$ is highly delocalized. So we start our analysis with a symmetric dimer with $E(P^*_L) = E(P^*_M) = E(\ast)$ and $E(L^+M^-) = E(M^+L^-) = E(CT)$. The excitations can be classified as symmetric or antisymmetric with respect to the $C_2$ symmetry operation. The interaction matrix reduces then to two blocks
\[
H(-) = \begin{pmatrix}
E(P^*(-)) & U_-\\
U_- & E(CT)
\end{pmatrix}
\]
and
\[
H(+) = \begin{pmatrix}
E(P^*(+)) & U_+ & 0 \\
U_+ & E(CT) & U_d \\
0 & U_d & E(P^{**})
\end{pmatrix}
\]
with the new coupling matrix elements \( U_- = \beta L^* M^* + \beta LM \quad U_+ = \beta L^* M^* - \beta LM \quad U_d = -\sqrt{6} \beta L^* M \), and the zero order excitonic energies \( E(P^*(\pm)) = E(*) \pm W \). (5)

As the integrals \( \beta LM \) and \( \beta L^* M^* \) involve similar atomic overlaps in the ring-I region they have the same sign. Therefore the coupling between excitonic and CT excitation is enhanced for the negative states whereas it is reduced for the positive ones, i.e., the upper dimer band will be largely decoupled from the two other positive excitations. In addition our INDO calculations gave a strong dynamic correlation effect for the upper dimer band largely reducing the coupling to the CT states. The coupling matrix elements of the other states \( U_- \) and \( U_d \) show only minor changes as can be seen from table 2.

Since the coupling \( U_+ \) is so small we treat it as a perturbation. Diagonalizing the strongly coupled states we get as approximate eigenstates of the symmetric dimer:

\[
|P^*(-)> = \frac{c_-}{\sqrt{2}} (P^*_L - P^*_M) + \frac{s_-}{\sqrt{2}} (L^+ M^- - M^+ L^-)
\]
\[
|CT(-)> = \frac{c_-}{\sqrt{2}} (L^+ M^- - M^+ L^-) - \frac{s_-}{\sqrt{2}} (P^*_L - P^*_M)
\]
\[
|P^*(+)> = \frac{1}{\sqrt{2}} (P^*_L + P^*_M)
\]
\[
+ \left( \frac{c_+ U^2}{E(P^*(+)) - E(CT(+))} + \frac{s_+ U^2}{E(P^*(+)) - E(P^{**})} \right) \frac{1}{\sqrt{2}} (L^+ M^- + M^+ L^-)
\]
\[
+ c_+ s_+ U_+ \left( \frac{1}{E(P^*(+)) - E(CT(+) - E(P^{**}))} \right) P^{**}
\]
\[
|P^{**}> = c_+ P^{**} + \frac{s_+}{\sqrt{2}} (L^+ M^- + M^+ L^-) + \frac{c_+ U^2}{E(P^*(+)) - E(P^{**})} \frac{1}{\sqrt{2}} (P^*_L + P^*_M)
\]
\[
|CT(+) > = \frac{c_+}{\sqrt{2}} (L^+ M^- + M^+ L^-) - s_+ P^{**} - \frac{c_+ U^2}{E(P^*(+)) - E(CT(+) - E(P^{**})} \frac{1}{\sqrt{2}} (P^*_L + P^*_M)
\]
where the mixing coefficients are given by ...

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By their interaction with the environment. This interpretation is also consistent with the different 

\[ E(CT) - E(P^*(-)) \approx E^\pm(+) \approx \text{intensity of the first three transitions in eq. 8.} \]

symmetry does not effect in lowest order the intensities of the first three transitions in eq. 8. Only the 

Substituting the experimentally identified energies and the calculated couplings gives the ordering 

\[ s_2^- < s_1^- < c_2^+ < c_1^+ \]. The intensities for transitions from the lowest excited state \( P^*(-) \) in this 

approximation

\[
\begin{align*}
\mu(P^*(-) \rightarrow P^*(+)) &= \frac{c_+}{2} (\Delta p_L - \Delta p_M) \\
&\quad + \left( \frac{c_+^2 U^2}{E(P^*(+)) - E(CT(+))} + \frac{s_+^2 U^2}{E(P^*(+)) - E(P^*)} \right) s_- p_{ct}^\pm \\
\mu(P^*(-) \rightarrow P**) &= s_+ s_- p_{ct} + \frac{c_+ s_+ U^2}{E(P^*(+)) - E(P^*)} \frac{1}{2} (\Delta p_L - \Delta p_M) \\
\mu(P^*(-) \rightarrow CT(+)) &= c_+ s_- p_{ct} - \frac{c_+ c_- U^2}{E(CT(+)) - E(P^*)} \frac{1}{2} (\Delta p_L - \Delta p_M) \\
\mu(P^*(-) \rightarrow CT(-)) &= \frac{1}{2} c_- s_- (\Delta p_L + \Delta p_M)
\end{align*}
\]

As the dipole changes \( \Delta p \) of the isolated chromophores are small, the main contribution of the first 

three transitions comes from the large dipole moment of the charge transfer states \( p_{CT} \) which from 

the INDO results has a magnitude of 32 Debye. So we predict for a nearly symmetric dimer that only 

the transitions to \( CT(+) \) and \( P^{**} \) should carry significant intensities.

**Symmetry breaking interactions and Stark effect**

Breakage of the \( C_2 \) symmetry causes a splitting of the two charge transfer states \( L^+ M^- \) and \( M^+ L^- \). Such perturbations easily arise from different orientation of the acetyl groups or from asymmetric 

interactions with the surrounding, including the local electric field. We model the splitting of the two 

local CT states by a perturbation operator of the form

\[
H' = \frac{\delta}{2} (|L^+ M^- \rangle \langle L^+ M^-| - |M^+ L^- \rangle \langle M^+ L^-|)
\]

\[
= \frac{\delta}{2} (c_+ s_- |P^*(-) \rangle \langle CT(+) + c_- c_- |CT(-) \rangle \langle CT(+) |
\]

\[ + s_+ s_+ |P^*(-) \rangle \langle CT(+) + c_- s_+ |CT(-) \rangle \langle P^{**}| + h.c. + \ldots \]

Here \( \delta \) is the perturbation parameter which admixes the states of different symmetry. The asymmetry 
does not effect in lowest order the intensities of the first three transitions in eq. 8. Only the transition 
to the fourth state \( CT(-) \) will borrow intensity from \( CT(+) \) as the two charge transfer states 
decouple into the localized states \( L^+ M^- \) and \( M^+ L^- \). On the basis of these results we interpret the 

\( P^* \) spectrum in the following way: The transition to the upper band at \( \approx 1500 \text{cm}^{-1} \) is difficult to 
assign since it is weak and overlaps with infrared active vibrations. The observed band at \( 2700 \text{cm}^{-1} \) 
represents the transition to the double-triplet state which is coupled strongly to the CT states. 
The broader band at \( 5000 \text{cm}^{-1} \) contains transitions to the two CT states which are split and broadened 
by their interaction with the environment. This interpretation is also consistent with the different
widths of the two bands. Only a small part of the width of the CT states is transferred. Figure 1b shows a simulation of the \( P^* \) spectrum using the calculated couplings from table 2. The energies of the transitions had to be adjusted slightly to fit the maxima of the experimental spectrum. Using the calculated couplings we have \( s_- = 0.37 \) and \( s_+ = 0.45 \). This gives a charge transfer contribution of 14% to the \( P^*(-) \) state and a total intensity of the \( P^* \) spectrum of \( s_-^2 p_{ct}^2 \approx 140 \text{Debye}^2 \) which is already close to the experimental value of \( 200 \text{Debye}^2 \). The simulation with the parameters from table 3 agrees quite reasonably with the observed intensities (fig.1). Further support for this assignment comes from the Stark spectrum.

The energy of the lower dimer band depends on the asymmetry \( \delta \). Using perturbation theory of fourth order with respect to \( \delta \) and second order in \( s_- \) and neglecting the zero order energy difference of the CT states we find

\[
E(\delta) = E(P^*-(-)) - \left( \frac{\delta}{2} \right)^2 s_-^2 \left( \frac{1}{E(CT)-E(P^*-(-))} - \frac{1}{E(CT)-E(P^+(-))} \right) + s_+^2 \left( \frac{1}{E(P^{***})-E(P^*(-))} - \frac{1}{E(P^{**})-E(P^*(-))} \right) - \left( \frac{\delta}{2} \right)^4 s_-^2 \frac{s_+^2}{(E(CT)-E(P^*-(-)))(E(P^{**})-E(P^*(-)))^2} \left( 1 - c_+^2 \frac{E(CT)-E(P^{**})}{E(CT)-E(P^*(-))} \right)^2 + \ldots
\]  

Even at zero electrical field asymmetric nuclear motions and static structural asymmetries contribute to the splitting of the CT states. Therefore we write \( \delta \) as the sum of a field dependent and a constant term

\[
\delta = \delta_0 + 2p_{ct}F
\]  

Expanding the energy as a function of the electric field we then have

\[
E(F, \delta_0) = E(0, \delta_0) + p(\delta_0)F + \alpha(\delta_0)F^2 + \ldots
\]

\[
p(\delta_0) = -2p_{ct}\delta_0 s_-^2 \left( \frac{1}{E(CT)-E(P^*-(-))} - \frac{1}{E(CT)-E(P^+(-))} \right) - \frac{1}{2}p_{ct}\delta_0^3 s_-^2 \left( \frac{1}{E(CT)-E(P^*-(-))}(E(P^{**})-E(P^*(-)))^2 \right) \left( 1 - c_+^2 \frac{E(CT)-E(P^{**})}{E(CT)-E(P^*(-))} \right)^2 + \ldots
\]

\[
\alpha(\delta_0) = -2s_-^2 \left( \frac{1}{E(CT)-E(P^*-(-))} - \frac{1}{E(CT)-E(P^+(-))} \right) + \frac{3}{2}p_{ct}^2 \delta_0^2 s_-^2 \left( \frac{1}{E(CT)-E(P^*-(-))}(E(P^{**})-E(P^*(-)))^2 \right) \left( 1 - c_+^2 \frac{E(CT)-E(P^{**})}{E(CT)-E(P^*(-))} \right)^2 + \ldots
\]

which shows the effective permanent dipole moment and polarizability of the lower dimer band.

For a symmetric dimer the dipole moment is zero and the polarizability is approximately given by

\[
\alpha_0 = -s_-^2 \frac{p_{ct}^2}{E(CT)-E(P^*(-))}
\]  

The dipole moment as well as the polarizability grow with increasing asymmetry. The higher order terms are small as long as the asymmetry \( \delta \) is small compared to the energy difference \( E(P^{**}) - E(P^*(-)) \). For the special pair we estimate \( E(P^{**}) - E(P^*(-)) = 3000 \text{cm}^{-1} \). The asymmetry which is necessary to explain the experimental Stark effect [9] is of the same order. Hence the higher order terms are in fact important. The Stark effect is strongly enhanced via the interaction with the state \( P^{**} \). For maximum mixture of the \( P^{**} \) and CT(+) states we have \( s_+^2 = 1/2 \). For \( E(CT) - E(P^*) = 6000 \text{cm}^{-1} \).
and $E(P^{**}) - E(P^*) = 3000 \text{cm}^{-1}$ this leads to an increase of 50% both for the dipole change and the polarizability. For $s^2 = 0.14$ the calculated dipole change is without this enhancement effect $(0.73(\delta/1000\text{cm}^{-1}) + 0.04(\delta/1000\text{cm}^{-1})^3)\text{Debye}$ which yields a value of $5.5\text{Debye}$ for $\delta = 4000\text{cm}^{-1}$.

In our INDO calculations such a large splitting resulted only for the acetyl rotated structure. Interaction with the $P^{**}$ state increases the permanent dipole moment by 17% to $6.4\text{Debye}$. This is roughly the correct magnitude consistent with our earlier assignment. The analysis of the experimental spectra, however, is complicated by its shape which contains contributions from the first and second derivative. Figure 1c shows a simulation using the calculated couplings from table 2 and the same adjusted energies as in figure 1b. The calculated Stark effect contains a significant contribution from the large polarizability of the dimer which shows up as a first derivative. We like to mention that our model also allows to calculate the higher order polarizabilities which have been investigated in recent experiments [11]. For the absorption changes proportional to the fourth power of the field our calculations predict a mixture of up to the fourth derivative of the absorption spectrum with the major contribution from the third derivative. These seems to be in qualitative agreement with the experiment.

**Conclusion**

Our model calculations strongly suggest that a double-triplet excitation $P^{**}$ of the dimer is in the energy region of the internal charge transfer states and is strongly coupled to them. We identify this state with the narrow band of the experimental $P^*$ spectrum at $2700\text{cm}^{-1}$. This interpretation explains the intensity and the relative small band width as compared to the broad band at higher energies which is typical for CT excitations. Furthermore mixture of $P^{**}$ and the CT states enhances the Stark effect which helps to explain the experimental data. The relatively strong coupling involves the transition of an electron from an occupied orbital located on one half to an unoccupied orbital on the other half. This coupling is largely analogous to the coupling of the lowest cationic state of $P^+$ to a trip-doublet state which has been invoked to explain the experimental $P^+$ spectrum. Our INDO calculations are based on a structure model where the acetyl of $P_M$ is rotated by $180^\circ$. This way the proper splitting of the CT states could be obtained.

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Figure caption

figure 1: simulated spectra from the exciton model using the parameters from table 3

(a) the experimental $P^+$ spectrum from [3] is compared with the calculated transitions shown as bars. As compared to the INDO results the HOMO-HOMO coupling has been enlarged by a factor of 1.8 to reproduce the position of the hole transfer band and the doub-triplets are shifted by 2800 cm$^{-1}$.

(b) the calculated $P^*$ spectrum (full curve) is compared with a fit of the experimental data by two Gaussians (broken curve) as described in [1]. The scale is the same for both curves. The higher intensity seen experimentally for the lower band could be explained if the coupling of the CT states to $P^{**}$ and $P^*(-)$ were enlarged as compared to the calculated values.

(c) the calculated Stark effect spectrum (curve) is shown together with the calculated absorption (reduced by a factor 0.05). The dimer band shows a mixture of first and second derivative with the minimum close to the position of the absorption maximum. The other excited states contribute only little to the Stark effect. The width of the dimer bands are as in earlier simulations of the room temperature spectra. The splitting of the CT states of 4000 cm$^{-1}$ is from INDO results on the M-acetyl rotated structure. The coupling of $P^{**}$ and the CT states is essentially the same as the coupling between the trip-doublets and the lowest cationic states of the dimer. The differences in table 3 are due to different reorganization effects.
Table 1: calculated coupling matrix elements of the lowest $P^+$ excitations. The left column shows the CI matrix elements of the main configurations as a function of one electron resonance integrals $\beta$ between localized orbitals of the neutral dimer groundstate. $L(M)$ and $L^*(M^*)$ denote the highest occupied and the lowest unoccupied orbitals of $P_{L(M)}$. The right column shows the effect of the reorganisation of the electron system in the cationic state.


table:
| zero order | with CI |
|------------|--------|
| $U_1 = -\beta_{LM} = 320 \text{ cm}^{-1}$ | $U_1 = 800 \text{ cm}^{-1}$ |
| $U_2 = \frac{1}{2} \beta_{L^*M^*} = -970 \text{ cm}^{-1}$ | $U_2 = -970 \text{ cm}^{-1}$ |
| $U_{12} = -\sqrt{\frac{3}{2}} \beta_{LM} = 565 \text{ cm}^{-1}$ | $U_{12} = 1370 \text{ cm}^{-1}$ |
| $U_{21} = -\sqrt{\frac{3}{2}} \beta_{L^*M^*} = 1050 \text{ cm}^{-1}$ | $U_{21} = 1770 \text{ cm}^{-1}$ |

Table 2: calculated coupling matrix elements for the lowest excited singlet states of the dimer. The left column shows the one electron resonance integrals of the main configurations. The right column shows the dynamic correlation effect.

| zero order | with CI |
|------------|--------|
| $U_- = \beta_{LM} + \beta_{L^*M^*} = -2180 \text{ cm}^{-1}$ | $U_- = -2100 \text{ cm}^{-1}$ |
| $U_+ = \beta_{L^*M^*} - \beta_{LM} = -1530 \text{ cm}^{-1}$ | $U_+ = -202 \text{ cm}^{-1}$ |
| $U_d = -\sqrt{\frac{3}{2}} (\beta_{LM} + \beta_{L^*M^*} = 1690 \text{ cm}^{-1}$ | $U_d = 1370 \text{ cm}^{-1}$ |

Table 3: parameters of the simulation fig. 1

| $L^+$ | $M^+$ | $L^+M^3$ | $M^+L^3$ | $P^*(-)$ | $P^*(+)$ | $L^+M^-$ | $M^+L^-$ | $P^{**}$ | $P^*(-)$ |
|-------|-------|--------|--------|---------|---------|--------|--------|--------|---------|
| 0     | -1290 | 0      | -1370  | 0       | 0       | 1370   | -1610  | 0      | 370     |
| 1610  | -1770 | 0      | 480    | 320     | -80     | 0      | 800    | 3000   |
| 6690  | 970   | 2500   | 0      | 800     | 370     | 180    | 0      | linewidth FWHM in cm$^{-1}$ |
| 7500  | 6530  | 1130   |        |         |         |        |        |        |

coupling matrix for $P^+$ in cm$^{-1}$

coupling matrix for $P^*$ in cm$^{-1}$
