Charge-transfer in some physical processes

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Abstract. The background of the intra- and inter-molecular electron transfer and some properties of charge transfer states (excitons) are mentioned. On the example of gas sensors the importance of the charge transfer in the dark is discussed. The utilization of the photoinduced charge transfer in electronic processes is demonstrated on the examples of photoconductivity, polymer photodegradation and molecular orientation.

1. Introduction
Dark and photoinduced electron transfer is an important process which influences many physical phenomena. The transfer of electron from a donor to acceptor is a quite obvious process observable even in dark. As a result is the formation of charge transfer complex with a characteristic optical absorption in (very often) visible spectral region. Acceptor-gas sensors work on this principle. In the optically excited state, there is a much stronger charge transfer, caused by the transfer of an electron from the highest occupied molecular orbital of donor to the lowest unoccupied molecular orbital of acceptor. As a result a charge-transfer exciton (ion-pair of the positive and negative species) is formed. It concerns an excited, neutral and polar state which influences many electronic processes, among others photoconductivity, polymer photodegradation and molecular orientation. The paper summarizes some facts included with the invited lecture at the 16\textsuperscript{th} International School on Condensed Matter Physics: Progress in Solid State and Molecular Electronics, Ionics and Photonics.

2. Intramolecular charge transfer (CT)
We will demonstrate the electron transfer on the H\textsubscript{2}CO model of the benzaldehyde molecule (1, scheme 1). Each bond corresponds to a pair of bonding/antibonding orbitals, single bond being filled $\sigma$ orbitals and the double bond consisting of a filled $\sigma$ orbital and a filled $\pi$ orbital of higher energy. The lone pairs of the oxygen atom are filled non-bonding orbitals. The set of energy states is shown in figure 1 [1]. The n-$\pi^*$ excitation removes on electron from the O atom, this electron is transfered into the $\pi^*$ orbital localized half on the C atom and half on the O atom. When orbitals are localized in...
different zones of the molecule, the transition implies a charge transfer (CT). It is usually accompanied by a change in dipole moment, so long as the molecule has no centre of symmetry. The molecule usually has two parts which can be distinguished as “electron donor” and “electron acceptor”.

![Chemical structures of materials mentioned in this paper](image)

**Scheme 1.** Chemical structures of materials mentioned in this paper:

1: Benzaldehyde, 2: 3’,3’-dimethyl-6-nitro-2,3-dihydrospiro[benzothiazole-2,2’-[2H]chromene, 3: 1,3,3-trimethyl-2-[2(5-nitro-2-oxidophenyl)vinyl]-3H-indol-1-iium, 4: CTT conformer of 3, 5: Poly[methyl(phenyl)silylene, 6: 3-diethylamino-1-propylsulphonamide substituted Zn-phthalocyanine, 7: Dibenzoyl peroxide.

![Electronic excitations in benzaldehyde molecule](image)

**Figure 1.** (a) Electronic excitations in benzaldehyde molecule. Transitions: (1) \( n \rightarrow \pi^* \), (2) \( \pi \rightarrow \pi^* \), (3) \( \sigma \rightarrow \sigma^* \). (b) Charge transfer during the \( n \rightarrow \pi^* \) excitation.

**2.1. Charge transfer in photochromic compounds**

The process mentioned above is often observable in photochromic molecules. The photochromic process can be schematically presented as a photoreversible reaction which, in its simplest form, can be written as:
In general, $h\nu_1$, the activating radiation (associated with electromagnetic energies from the ultraviolet and visible regions), causes a molecule, X, (with an absorption maximum at a wavelength $\lambda_1$) to convert to a product, Y (absorbing at $\lambda_2$). The reaction is not necessarily complete; the concentrations of X and Y depend on the thermodynamics of the system and kinetics of processes taking place under given conditions. As a typical example can be mentioned the molecule of 3',3'-dimethyl-6-nitro-2,3-dihydrospiro[benzothiazole-2,2':[2H]chromene (2, scheme 1) which undergoes a reversible photochemically driven reaction, resulting in production of highly polar merocyanine, 1,3,3-trimethyl-2-(5-nitro-2-oxidophenyl)vinyl]-3H-indol-1-i um (3, scheme 1) [2,3]. The overall mechanism responsible for the photochromism may be described as a heterolytic bond cleavage and ring opening, but there are also cis-trans bond conversions and triplet-triplet contributions to the mechanism. In the mentioned example several conformers with different dipole moments can be formed (e.g., structure 4). The dipole moments are: the basic compound $2 - 5.9$ D, the conformer $3-12.8$ D, $4-12.0$ D [4].

2.2. Charge transfer during polaron transport

This effect will be demonstrated on a semiconducting polymer, poly[methyl(phenyl)silylene] (PMPSi, 7, scheme 1). Polysilanes with their uninterrupted chains of silicon atoms and with significant electron delocalization along the polymer chain [5] are interesting photosensitive materials. They also possess promising photoconductive properties [6-8]. PMPSi chain, with methyl and phenyl groups on each silicon atom, behaves as molecular wire with weak intermolecular interactions. Slowly moving charge carrier induces a deformation of PMPSi soft molecule; atoms in charged molecule (or its part) are shifted to new positions to preserve minimal potential energy. The new conformation and charge redistribution result in the change of frequencies of vibration modes. All these variances move along with the charge carrier (together they form a so-called polaron quasiparticle) and create a potential well around it. This self-trapping process results in the decrease of charge carrier mobility. Thus, the charge carrier is localized on a monomer unit (or on several of them) and further transport needs a charge transfer to the neighbor monomer unit (or to the chain consisting of several of them). Similar situation arises if two chain sequences are separated by some irregularity, e.g., all-trans chain conformation or by chain cis-conformation by branching points. In this case CT plays also an important role.

On molecular level, three factors, the electronic coupling (electron transfer integral) $t$ between the individual parts of the molecule, the reorganization energy $\lambda$ during the charge transport, and the effective length of the electron transfer $L$, are important for the charge movement. It is assumed that charge carrier localized on a molecular segment and its transport – hopping can be described by Marcus theory [9,10]. The rate of the transfer can be then expressed as

$$k = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\beta kT}} r^2 \exp\left(-\frac{\beta}{4kT}\right)$$

where $h$ is the Planck constant, $t$ is the transfer integral that reflects the strength of electronic interactions between two adjacent species, $T$ is the temperature, $k$ is the Boltzmann constant, and $\beta$ is the total reorganization energy. The reorganization energy $\beta$ consists of two terms $\beta_1$ and $\beta_2$ (equations 2-4).

$$\beta = \beta_1 + \beta_2$$

$$\beta_1 = E_s(Q_N) - E_s(Q_s)$$
Here, $E_s(Q_s)$ is the total electronic energy of the charged state with the geometry of a neutral molecule (segment), $E_s(Q_s)$ is the total energy of the charged state with the geometry of a charged molecule, $E_N(Q_s)$ is the total energy of the neutral state with the geometry of a charged molecule (segment), $E_N(Q_N)$ is the total energy of the neutral state with the geometry of a neutral molecule (segment). $\beta$ is frequently called as reorganization energy. $\beta^2$ as polaron binding energy. Electron transfer integral of the charge $t$ can be calculated according to Ref. [11] as

$$t = \frac{E_{HOMO} - E_{HOMO-1}}{2}$$

i.e., as the energies splitting of HOMO and HOMO–1 levels which are assumed to be energy levels responsible for charge carrier (here positive charge, hole) transport. The meaning of the parameters $E_s(Q_N)$ and $E_s(Q_s)$ is the following:

At the beginning of the charge transfer process the charge carrier is localized on the molecule (molecular segment) – the localization energy is $\beta_2$. After the charge hop on another molecular segment its geometry starts to change and self-trapping process begins. The final localization energy is $\beta_2$. Simultaneously, the back conformation charge of the first molecular segment proceeds – the energy needed is $\beta_1$. Note, the both energies, $\beta_1$ and $\beta_2$, are comparable.

2.3. Photoinduced charge transfer in PMPSi and molecular electret network formation

It has been shown that the first long-wavelength absorption band in PMPSi with the maximum at $\lambda_{\text{max}} = 325$ nm is formed mainly by the delocalized $\sigma - \sigma^*$ transitions in the Si backbone. The dipole moment of this transition is directed along the polymer backbone. The $\pi - \pi^*$ aryl-like excitations are responsible for the short wavelength absorption with the maximum at 276 nm ($\alpha = 5.2 \times 10^4$ cm$^{-1}$).

During the ($\sigma - \sigma^*$) excitations, an electron is promoted from the bonding to an antibonding orbital. This process is followed by electron transfer along the polymer chain. Thus, an electron-hole pair is formed. However, the pairs generated in the same chain segment very often recombine geminately with a very fast decay rate, due to the electron delocalization on the Si backbone. An electron transfer to phenyl group stabilizes the pair. The intrachain electron transfer is possible as it follows from electrochemical experiments [12,13]. Thus, quite strong dipole of the type Si backbone-phenyl is formed (see figure 2). The exposure with the linearly polarized light results in the angularly dependent excitation of the main chain segments which are oriented parallel to the electric field vector of the exciting light. Figure 3 shows the polar diagram of the absorbance at 333 nm.

Figure 2. Schematic representation of the formation of an induced dipole in PMPSi chain.
This dipole is quite stable because of the formation of metastable electronic states. It was mentioned above that during the polaron formation [14] (and similarly during the energy transport [15] the deformation of the silicon chain occur. Positive polaron is characterized by Si–Si bond stretching; at the same time, the Si–Si–Si bond angles damp out. The stretching of the bonds and the shrinking of the chain conformation leads to the formation of metastable [16] electronic states in the HOMO-LUMO gap (band-edge states) with quite long lifetime.

Figure 3. Polar diagram of the absorbance at 333 nm after the irradiation with linearly polarized light of 333 nm (HBO 100 W, 7 min). Electric field vector visualizes the electric field vector of the incident light.

Due to the long lifetime of ion-pairs, the detection of dipoles by means of liquid crystal alignment experiments was possible. The details of the experiment can be found in Ref. [17]. The measurements of the photoinduced dichroism in the PMPSi films and the azimuthal anchoring energy of the liquid crystal deposited on these films revealed the absence of correlation in their exposure-dose kinetics. The azimuthal anchoring energy of the liquid crystal reached its maximum just at the beginning of the irradiation when the dichroism was still negligible (cf. figure 4). On further irradiation the dichroism increased but the azimuthal anchoring energy of liquid crystal dropped to zero. Because the liquid crystal – polymer surface interactions include dispersive (van der Waals), polar, and steric terms we ascribe the result shown in figure 5 to the polar species and steric effects [18].

Figure 4. Changes of azimuthal anchoring energy of liquid crystal (Merck, LC 2 LT-4801) (1) and dichroism calculated at 333 nm (2) on irradiation of PMPSi film with linearly polarized light of He-Cd laser (λ = 325 nm, P = 10 mVcm⁻²).

The “nano-electret” network mentioned above can be used for the fabrication of polarized light emitting diodes. If on the light-treated surface an electroluminescent material is deposited molecules trend to be oriented due to the interactions with the dipoles and polarized electroluminescence is observed [19].

3. Intermolecular charge transfer
In case of the crystal which consists from molecules of D type, under the excitation the following reaction can take place:

\[ D + D^* \rightarrow D^+ + D^- \]
Here, D is the molecule in the ground state, D* is the molecule in the excited state and \( \delta \) is the amount of charge transferred from one to another molecule. As the result an ionic-pair or charge-transfer exciton is formed. In organic materials the term charge-transfer exciton is to denote an excited, neutral and polar state, where the exciton radius is only one or two times the nearest-neighbor intermolecular distance [20].

The charge-transfer (CT) energy \( E_{CT} \), as dependent on distance \( r_{CT} \) molecules D and D*, may be described by a Coulomb-type law [21]

\[
E_{CT}(r_{CT}) = E_{g-opt} - \frac{e^2}{4\pi\varepsilon_0 r_{CT}}
\]

where \( E_{g-opt} \) is the optical energy gap (separation energy between nonrelaxed negative and positive polaron levels), \( e \) is the unit charge and \( \varepsilon_0 \) is the electric permittivity. Note, that conduction levels of relaxed states of positive and negative molecular polarons are separated by the adiabatic energy \( E_{g-ad} \). Expression (6) shows that \( E_{CT}(r_{CT}) \) dependence has a convergence limit \( r_{CT} \to \infty \), which is determined by the width of optical energy gap. The situation is demonstration in figure 5. Charge-transfer states are formed after the autoionization and thermalization of excited molecule. The dissociation of charge-transfer (ion-pair) state leads to the free charge carrier generation.

The presence of acceptor (A) molecules supports electron transfer. The transfer can be realized even in the dark and charge transfer complex can be formed. In this case the relation (6) is substituted by the relation (8)

\[
D + A \rightarrow D^{\delta} + A^{-\delta}.
\]

As a result of this reaction is the formation of charge-transfer complex (\( \delta < 1 \)) or paramagnetic radical salt (\( \delta = 1 \)). The transition energy is usually found in the visible spectral region.

In the optically excited state, there is a much stronger CT interaction, caused by the transfer of an electron from the highest occupied molecular orbital of donor D to the lowest unoccupied molecular orbital of acceptor A. The energy of this transition depends on the ionization energy of D, the electron affinity of A, and the Coulombic and polarization energy gained by creating two oppositely charged ions in a polarizable material. Since optical transitions take place in times of \( \leq 10^{-15} \) s, the contributions of molecular rearrangement are not great; the energy of the transition may be written as
where \( C \) is the Coulombic energy of the two charges, \( P \) is the polarization energy of the CT dipole, \( I_D \) is the ionization potential of the donor, and \( A_C \) is the electron affinity of the acceptor. Very often the transition energy is found in the visible spectral region.

The photoinduced electron transfer from a donor to an acceptor is a very important process in charge carrier photogeneration. Then, the photoconductivity is mainly influenced by an extrinsic process via a nonrelaxed exciplex formed between singlet excitons of the donor and acceptor-like dopands or photooxidation products \( A \). The following mechanism is proposed:

\[
\begin{align*}
D^* + A &\rightarrow (D^* \cdots A) \rightarrow (D^* \cdots A^\cdot)^* \rightarrow D^* \cdots A^\cdot \rightarrow D^+ + A^-.
\end{align*}
\]

Here, \((D^* \cdots A)\) represents an encounter complex, \((D^* \cdots A^\cdot)^*\) a nonrelaxed exciplex state, \((D^* \cdots A^\cdot)^*\) the CT state and \(D^+ + A^-\) free charge carriers. The process \(\rightarrow \) is a thermalization, the process \(\rightarrow\) represents free charge carrier generation via electric field induced dissociation CT state. The electric field dependence of the charge photogeneration efficiency is strong and can be described by the Onsager theory of geminate recombination of ion pairs [22]. Measurements performed with PMPSi and pyrromellitic dianhydride acceptor indicate that both the lifetime and concentration of the ion-pairs increase in the presence of acceptor.

Note, that in polymers pendant groups can act as acceptor centres. In this case the electron transfer from the backbone to the pendant side group leads to the formation of intramolecular CT state. From the point of energy structure, these CT states are localized below the conduction level.

### 3.1. Acceptor-gas sensors

The change of the absorption spectra of CT complexes can be utilized in the construction of sensors for acceptor-like gases. Here, also CT process between the sensing material (donor) and the detection medium (acceptor gas) plays an important role. As an example we will present NO\(_2\) sensor based on 3-diethylamino-1-propylsulphonamide substituted Zn-phthalocyanine (ZnPcSu, see scheme 1, 6).

Capobianchi et al. [23, 24] proposed a two-step mechanism of NO\(_2\) interaction with phthalocyanines (Pcs). First step consists of transferring one electron from Pc to NO\(_2\). During the second step, another electron is transferred from Pc to the gas molecule, thus forming bication of Pc complexed with two NO\(_2\) molecules:

\[
\begin{align*}
MePc + NO_2^- &\leftrightarrow (MePc)^+ \cdots NO_2^- \\
(MePc)^+ \cdots NO_2^- &\leftrightarrow (MePc)^2+ \cdots 2NO_2^-.
\end{align*}
\]

The equilibrium of the first step is shifted in the direction of reaction products. The second step reaction is equilibrated closer to the initial reagents. This explains the partial reversibility of NO\(_2\) sensors reported in literature.

Absorption spectra of Pc consist of two main bands: Q-band at 600 – 700 nm and Soret band with the maximum at about 350 nm. It was found, that the spectrum of ZnPcSu is slightly changed in the presence of NO\(_2\) – see figure 6. A new band at about 500 nm appears (decrease of the differential transmittance \(\Delta T\)). Intensity at the same time transmittance in the range of Q-band increases. From this result we suspect that CT complex is formed between ZnPcSu (donor) and NO\(_2\) (acceptor). It supports the mechanism proposed by Capobianchi et al. Note, that a typical optical absorption of phthalocyanine CT complexes appears near 500 nm [25].
Figure 6. Differential optical transmittance spectra of ZnPcSu film exposed to NO\textsubscript{2}. Optical absorption spectrum of ZnPcSu film (dashed line), is given for comparison [26].

The charge-transfer complex formation usually increases free charge carrier concentration. Nitrogen dioxide causes increase the conductivity of ZnPcSu thin film as it is shown in figure 7. It also confirms the hypothesis of CT complex [26].

According to quantum chemical calculations the interaction of NO\textsubscript{2} with central Zn atom is very probable. Interactions of NO\textsubscript{2} with Pc conjugated skeleton and/or sulphonamide substituents are very weak if any. Oxygen from NO\textsubscript{2} forms the coordination bond Zn···O=N=O. Electron density of HOMO is shifted to NO\textsubscript{2}, confirming the CT complex formation. Theoretical spectral are in agreemental observations.

3.2. Polymer photodegradation: The improve of UV degradation efficiency by means of CT process

UV exposure of poly(organylsilanes) results in photobleaching and Si-Si bond scission, producing low-molecular-weight fragments. Thus, the interesting use of polysilanes is in area of photolithography due to the fact that polysilanes can be easily changed to materials having completely disparate properties when exposed to radiation. The contribution of polysilanes to large scale integrated circuit manufacturing technology is that silicon atoms included in the polymer chain are not recognized as impurities in silicon devices. Other metal atoms can cause contamination problems. For efficient photolithography process materials with high speed of photostimulated reactions are needed. Even though the photodegradation of polysilanes is quite fast, an enhancement is eligible. We will present a possibility concerning the increase of the photodegradation efficiency in PMPSi by electron acceptor additive utilizing the charge transfer process. As mentioned above the formation of intramolecular charge-transfer exciton chain-phenyl result in an 36 \( \mu \)s which follows from flash photolysis measurements) the electron can move back to the chain and recombine with delocalized hole (cation radical) which results in charge equilibrium and chain stabilization. If strong electron acceptor additive is present, the electron can be transferred to the additive and in the case of anion radical unstability the back electron transfer to chain is limited, quantum efficiency of photodegradation increases. For experiments, dibenzoyl peroxide (BP, 9, scheme 1) was used.

The degradation of PMPSi chain under UV illumination is accompanied by two changes in absorption spectrum: Absorbance decreases and its maximum is shifted to higher energies. It means that bonds scission of polysilane chain takes place. Figure 8 shows the dependence of the maximum shifts on the UV illumination time for PMPSi (curve 1) and PMPSi+BP (curve 2).
Two possible reactions were tested to understand the interactions of PMPSi chain and the additive which is assumed to be in anion radical form.

(a) In the first case, the electron is localized on the additive molecule for a significant time. During the localization silicon bonds in the main chain is weakened and chain can undergo a bond scission. However, the electron relaxation back to polymer limits the photodegradation efficiency.

\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
+ 8.3 \text{ kcal/mol} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
- 46.4 \text{ kcal/mol} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O}
\end{align*}
\]

Scheme 2. Two ways of the splitting of dibenzoyl peroxide anion radical.

(b) The second case requires the presence of a non-stable bond in anion radical of the additive [27]. Thus, a radical and a anion (nucleophilic) group is expected to be formed (see scheme 2). The later can subsequently attack positive charged silicon chain. The additive molecule must satisfy the condition that its energy in a separate state (nucleophilic anion and radical) must be lower than the energy in a joint state (anion-radical).

**Conclusion**

In some physical and chemical processes an electron transfer is important both in the dark and excited state. Especially the charge transfer between an optically excited donor and an acceptor can improve quantum efficiency of charge carrier photogeneration, polymer degradation and liquid crystal alignment. The knowledge of the charge transfer mechanism is also important to understand polaron transport and functionality of some gas sensors.

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