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Charge transfer in thin films of donor–acceptor complexes studied by infrared spectroscopy

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ABSTRACT

The degree of charge transfer in thin films of organic charge transfer (CT)-complexes, which are deposited via thermal evaporation, is examined via infrared-spectroscopy. We demonstrate a linear relationship between the shift in the excitation energy of the CN-stretching mode of CT-complexes with the acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) and the charge transfer. The measured correlation corresponds very well with DFT calculations. For Na-TCNQ we observe a splitting in the peak of the CN-stretching mode, which can be explained by the coupling of two modes and was confirmed by the calculations. In CT-complexes with partial charge transfer the appearance of an electronic excitation is demonstrated.

1. Introduction

In the past years the interest in organic solar cells has grown due to their possible application in low-cost and large-area photovoltaic systems. Excitonic solar cells, like the well-known bulk heterojunction type [1], depend strongly on efficient charge separation at the donor–acceptor interface. In so-called charge transfer (CT)- complexes donor and acceptor molecules often form segregated stacks which are found to lie adjacent to each other [2]. The electronic, optical and structural properties of CT-compounds and hence their performance in devices depend on the degree of charge transfer (Z) between the donor and acceptor stack. Z can be understood as the probability of the transferred electron to be found on the acceptor molecule. The described structure of adjacent donor and acceptor planes leads to a multiplicity of interfaces between donor and acceptor domains, which makes these materials an ideal model system for BHJ cells [3,4]. Often, the lowest-energy optical transition occurs between the non-charge-transferred and the charge-transferred state. Depending on the choice of materials, the absorption band of the CT-transition can be shifted into the near-infrared (NIR) regime [5]. Additionally, electrons and holes are preferentially transported along the acceptor respectively donor plane axes in the CT-crystal [6]. Hence, CT-compounds are also very interesting materials for optical or optoelectronic applications in the NIR range, e.g. as IR photodetectors or solar cells. For device applications, thin-film architectures are preferred over single crystals due to easier handling [7,8]. Here, we report on the degree of charge transfer in thermally evaporated thin films of tetrathiafulvalene–7,7,8,8-tetracyanoquinadimethane (TTF–TCNQ) and derivatives based thereof. We used infrared spectroscopy to examine the degree of charge transfer from the frequency shift of

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the CN-stretching mode of TCNQ molecules as it has been shown for single-crystalline materials by Chappell et al. [9]. Additionally we compared our experimental results to density-functional theory (DFT) calculations, which give a solid explanation for our observations.

2. Experimental

Pentacene, TTF, TCNQ, 2,3,5,6-tetrafluoro-TCNQ (F_4TCNQ) and dibenzo-TTF (DBTTF) were purchased from Sigma–Aldrich® and were used as-received. For evaporating sodium we used an Alvasource® purchased from Alvatec. The compounds with a molar ratio of 1:1 between donor and acceptor were prepared by solving donor and acceptor molecules separately in tetrahydrofuran (THF) at elevated temperature (70 °C). Upon complete solvation the solutions were mixed. After a few days and slow solvent evaporation, dark crystals were collected by filtration of the remaining solvent. The shape and color appearance of the collected CT-crystals were completely different to that of the single crystal form of donor and acceptor molecules. Deposition of thin films of CT-complexes was carried out via thermal evaporation in a vacuum chamber ($p < 5 \times 10^{-6}$ mbar) from quartz crucibles at crucible temperatures of around 200 °C. The film thickness was measured with a quartz crystal microbalance (QCM). For the Na-TCNQ sample we co-evaporated Na and TCNQ from different crucibles with the corresponding rates for a 1:1 M ratio in the compound. All samples are approximately 100 nm thin and were grown at an approximate rate of 2.5 nm/min. For IR spectroscopy in transmission mode we used doubleside-polished Si and KBr single crystals. The Si substrates, cleaved from a 0.74 mm thick wafer to 10 mm × 10 mm pieces, were cleaned with a standard procedure in acetone and isopropanol in an ultrasonic bath. The KBr substrates were cleaved to 10 mm × 10 mm × 1 mm with no further treatment prior to deposition. Infrared spectroscopy in the range from 450 to 9000 cm^{-1} with a resolution of 4 cm^{-1} was accomplished using a Vertex 80V spectrometer (Bruker Optics). As detectors we used DLaTGS (mid IR) and InGaAs (NIR). The spectrometer was pumped to a pressure of 2 mbar. The shown spectra represent the average of 2000 individual scans.

3. Calculation of the vibrational spectra of TCNQ

The molecular geometry of TCNQ in the gasphase was optimized using the BP86 density functional [10,11] with a split valence basis set (SV (P)) including polarization functions on all atoms other than hydrogen [12]. The same level of theory was used for the analytic calculation of harmonic vibrational frequencies at zero temperature. All frequencies were scaled by 0.99 [13]. The resolution of identity approximation was used throughout [14]. All calculations were carried out with the TURBOMOLE software package [15]. For the charged TCNQ molecule, we add 0.1 ... 1.0 electrons into the lowest unoccupied orbital (LUMO) of the neutral molecule. The geometry of the partially charged molecule was calculated using the same level of theory as specified above. In order to allow spin polarization, unrestricted density functional theory was used. We are aware of the fact that a partially charged molecule has no physically observable counterpart. However, the partial charge, as specified by the charge number Z, can be understood as the probability of finding the transferred charge on the acceptor molecule. Due to the interaction at the donor–acceptor interface, the molecules at the interface cannot be treated individually. However, once the amount of charge transfer at the interface is known and can be specified for the individual molecules, the normal modes of the partially charged molecule can be easily obtained by calculating the properties of the TCNQ molecule with fractional occupation numbers corresponding to the charge number Z [10,11].

4. Results and discussion

4.1. Neutral TCNQ

In order to cross-check our simulation with experimental results, we compared DFT calculations of a neutral TCNQ-molecule with the measured relative infrared transmission of a TCNQ thin film. The spectra are shown in Fig. 1. Due to adhesion problems of TCNQ on the substrate, first we evaporated 20 nm of pentacene and then 80 nm of TCNQ on top. Since we are mainly interested in the CN-stretching mode, which appears due to the CN-triple bond at 2226 cm^{-1}, pentacene seems to be a suitable template layer, as no specific vibrational features appear in the spectral range of interest [16] (see Fig. 4). To distinguish the vibrational features of pentacene and TCNQ and to model the dielectric function of TCNQ, also a model of the pentacene film was needed. Therefore a second sample with a film of pure pentacene (≈150 nm) was prepared and used to model the dielectric function of pentacene. This model was used to derive the dielectric function of TCNQ from the measured IR-spectrum of the two-layer system. The fits were performed with the SCOUT software [17]. To model the dielectric function of both materials we used Brendel oscillators that account for homogeneous and inhomogeneous broadening, as reported by Glaser et al. [18]. For the dielectric background we used $\epsilon_{\infty,\text{pentacene}} = 2.4$ [19] and $\epsilon_{\infty,\text{TCNQ}} = 3.388$ [20]. As result of the described fitting process a dielectric model for the dielectric function of pentacene, which corresponds very well with reported dielectric functions [16], and a model for TCNQ were obtained. The dielectric function is plotted in Fig. 1(top graph). The DFT calculation delivered only the resonance frequency and relative intensity of individual peaks, because of which each peak was treated as a Brendel-oscillator with Lorentzian damping (4 cm^{-1} as the experimental resolution) and Gaussian broadening (3 cm^{-1}) to obtain the calculated spectrum as depicted in Fig. 1 (bottom graph). The main stretching (ν) or deformation (δ) vibrations of measured and calculated IR-spectra were assigned by comparing position and strength in the two spectra. Now we compare the fitted and the calculated relative transmission spectrum as shown in Fig. 1. In the range between 750 and 2500 cm^{-1} the seven strongest peaks of TCNQ show good agreement between experiment and calculation. The difference between the measured and the calculated frequency of the vibronic modes is around 35 cm^{-1} for the CN-stretching mode and

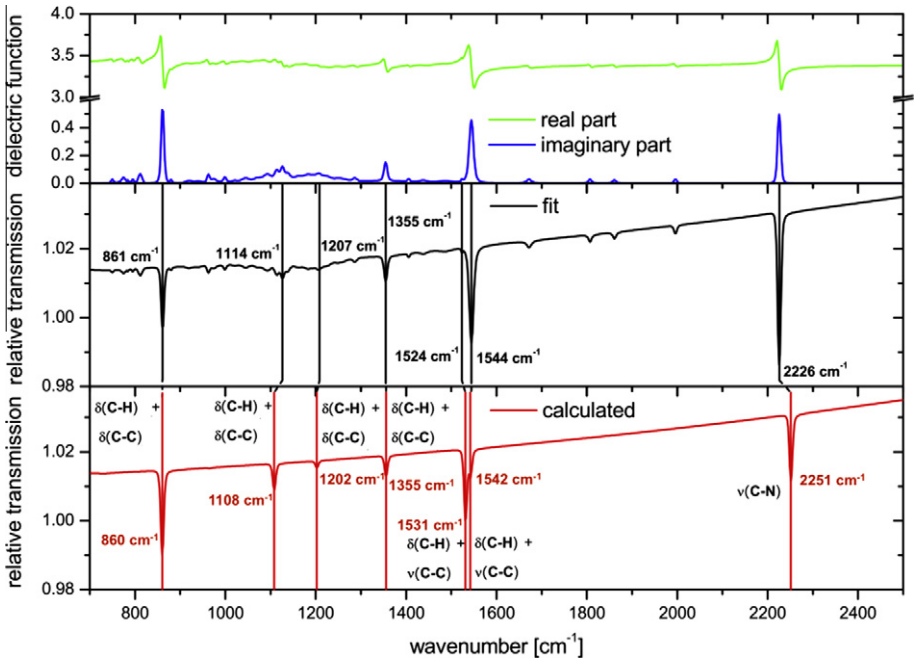

Fig. 1. (top) Dielectric function as derived by fitting the IR-spectra of the two-layer system. (middle) Measured infrared spectrum of neutral TCNQ from 700 to 2500 cm^{-1}. Reference: bare Si-substrate. (bottom) Calculated spectrum of neutral TCNQ. The stretching (ν) and deformation (δ) vibrations are indicated, as well as the frequency of the TCNQ-modes.

10 cm^{-1} for the remaining. The larger deviation for the CN-mode can be attributed to the harmonic approximation [21]. We observe additional peaks in the measured spectrum, which appear due to molecular interaction in the thin film. Since all DFT calculations were performed in the gasphase, these peaks cannot be observed in the simulated spectrum. The peak positions of the measured IR spectrum are in good agreement with the measurements on a single crystal TCNQ by Lunelli and Pecile [22].

4.2. TCNQ radical anion and CT-complexes with integer charge transfer

We now compare the measured spectrum of Na-TCNQ with the simulated spectrum of the TCNQ radical anion (see Fig. 2a). Due to the low electronegativity of sodium, full charge transfer from sodium to TCNQ can be assumed. Eight of the measured peaks are in good agreement with the simulated spectrum. The difference between the measured and calculated absorption frequencies is around 15 cm^{-1}. For Na-TCNQ we observe a splitting of the CN-stretching mode, which is as well consistent with the calculation. As a further reference, we took IR spectra of DBTTF-F_4TCNQ, since this system shows integer charge transfer [23]. This is due to the strong electron accepting properties of F_4TCNQ. In Fig. 2b and c, we compare spectra of Na-TCNQ, DBTTF-F_4TCNQ, TCNQ and F_4TCNQ on Si. For neutral TCNQ and F_4TCNQ the CN-stretching mode appears at 2226 cm^{-1}. As it has been proven for DBTTF-F_4TCNQ, compounds with integer charge transfer exhibit splitting of the CN-stretching mode as well as a shift of the CN-mode to lower energies. The same behavior is observed for Na-TCNQ from which we indicate that $Z_{\text{Na-TCNQ}} = 1e^-$. We conclude, that the second CN-stretching mode as predicted by calculations, can be observed in the experimental IR-spectra of CT-compounds with $Z = 1e^-$ like Na-TCNQ and DBTTF-F_4TCNQ.

4.3. CT-complexes with partial charge transfer

Now, CT-complexes with partial charge transfer shall be discussed. In Fig. 3 spectra of DBTTF–TCNQ, DBTTF and TCNQ on Si in the range from 600 to 1000 cm^{-1} and from 700 to 2400 cm^{-1} are shown. Comparing DBTTF–TCNQ to pure DBTTF and TCNQ, we observe shifting of the resonance frequencies of all vibronic modes, including the CN-stretching mode. This is due to the charge transfer between the donor and acceptor molecules. Since there are no spectral features of DBTTF close to the CN-stretching mode of TCNQ, the latter can be assigned unambiguously and therefore be used as an indicator for the degree of charge transfer. The peak position shifts from 2226 cm^{-1} for the pure sample to 2209 cm^{-1} for DBTTF–TCNQ. No information can be retrieved from other peak positions, as the remaining peaks have a closer overlap and cannot be assigned unambiguously to either of the two species. Furthermore, in DBTTF–TCNQ we observe a wide absorption band arising at 4500 cm^{-1} and peaking at 6200 cm^{-1}, which corresponds to an excitation energy of 0.8 eV. This corresponds well to previous measurements of the optical band gap of single-crystalline DBTTF–TCNQ [24]. It has to be noted, that this absorption band cannot be assigned to any of the intrinsic species, but is an effect which arises from the interaction of donor and acceptor as a complex.

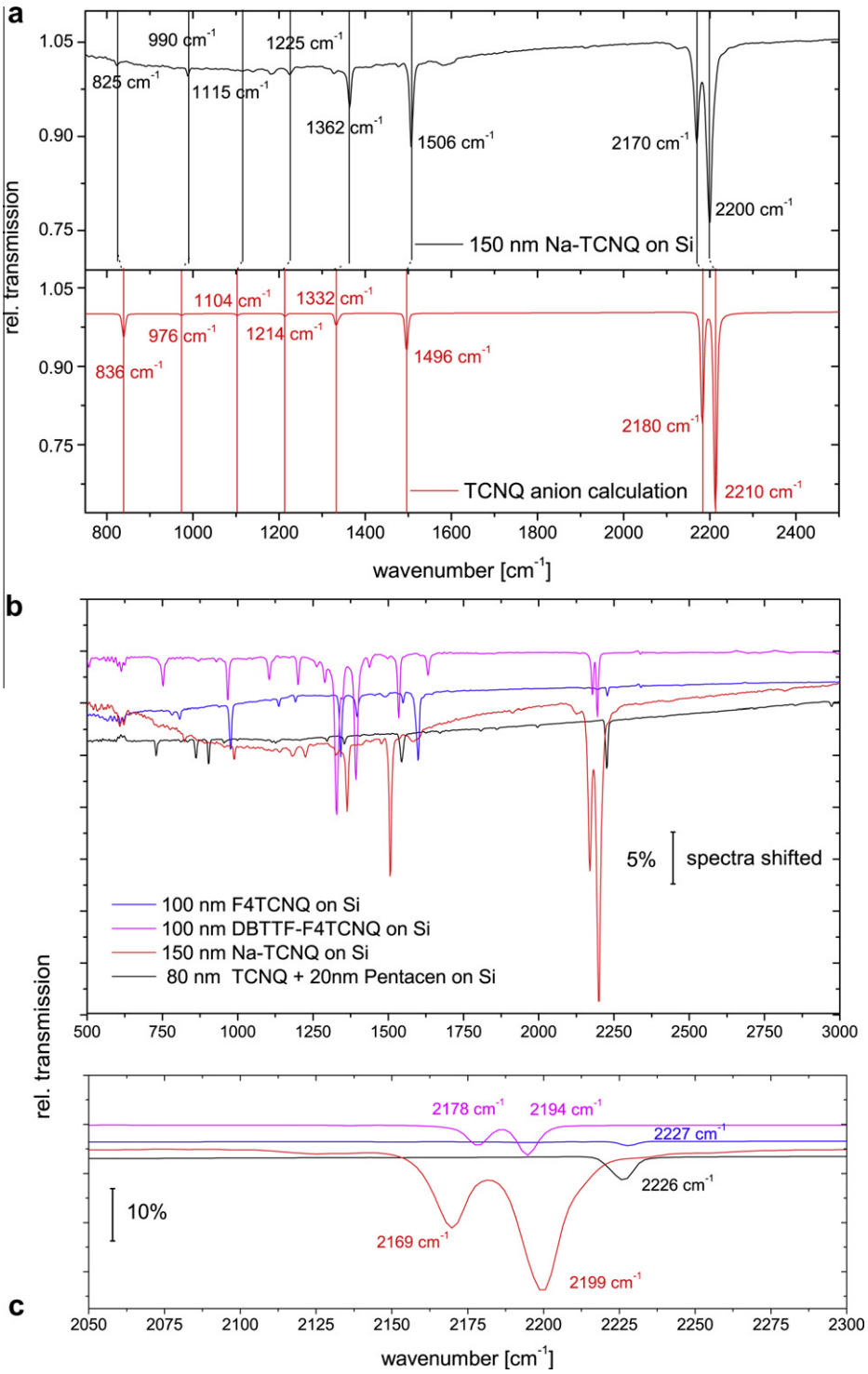

Fig. 2. (a) Measured and calculated infrared spectrum of ionized TCNQ from 700 to 2500 cm^{-1}. (b, c) Infrared spectra of F_4TCNQ, DBTTF-F_4TCNQ, TCNQ and Na-TCNQ on Si from 500 to 3000 cm^{-1} and 2050 cm^{-1} to 2300 cm^{-1} . The CN-stretching mode of F_4TCNQ and TCNQ splits in the CT-compounds due to the integer charge transfer. The spectra are shifted so the exact position of the peaks can be illustrated.

To complete our investigation on the effect of charge transfer in TCNQ based CT-complexes we studied the TTF–TCNQ system, which can be seen as the archetypal molecular conductor since reports of Heeger and co-workers [25]. Adhesion problems made any comparison of TTF–TCNQ with the spectra of pure TTF and TCNQ

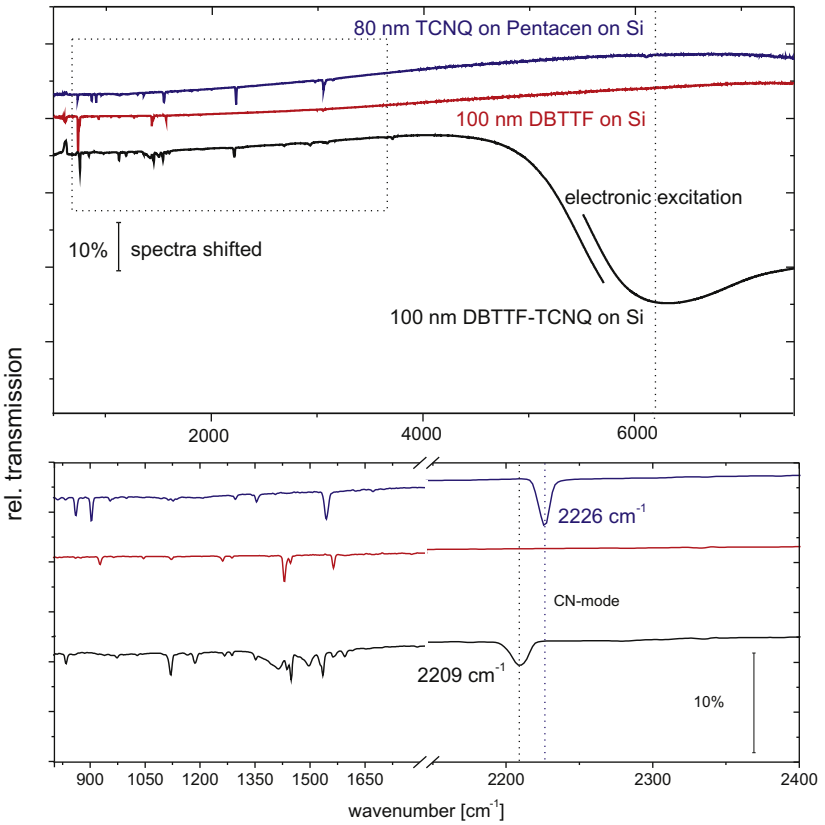

Fig. 3. (top) Infrared spectra of TCNQ, DBTTF and DBTTF–TCNQ on Si from 600 to 7500 cm^{-1}. For DBTTF–TCNQ also the spectrum in the NIR range is shown. We see around 6000 cm^{-1} a wide absorption based on electronic excitation. The discontinuity around 5500 cm^{-1} arises due to the change from a DLaTGS to an InGaAs detector for the NIR-measurement. (bottom) IR-spectra of TCNQ, DBTTF and DBTTF–TCNQ from 800 to 2400 cm^{-1}. The CN-stretching mode shifts in the CT-complex to smaller frequencies.

impossible. Due to a high vapor pressure at room temperature and no substrate cooling capability of the deposition system, TTF did not adhere on the substrate nor on the oscillating crystal. Preparation of intrinsic TTF thin films was – even using organic template layers – not possible. Accordingly, we compare data of TTF–TCNQ to pure TCNQ. For both samples we used the same pentacene templating layer on KBr and Si substrates for reasons of better film quality. Test experiments (data not shown here), indicate that there are no apparent shifts in the peak positions when comparing films grown on KBr and Si as used for the previous samples. Fig. 4 shows the IR results for TTF–TCNQ and TCNQ thin films. The CN-stretching mode can be clearly identified, since TTF does not show any vibration bands in this spectral range [26]. We observe that the respective peak shifts about 20 cm^{-1} to smaller energies at 2206 cm^{-1}. Additionally, a broad absorption band arises at around 700 cm^{-1} peaking at 2200 cm^{-1}, which can be assigned to the charge transfer excitation, corresponding to an energy of 0.3 eV.

It can be argued that the crystal structure of the thin film can affect the interaction between donor and acceptor and therefore has a strong influence on the infrared spectrum. As part of an investigation on phase separation in mixed CT-compounds (to be published elsewhere), we studied extensively the crystalline structure of the presented samples in this paper using X-ray diffraction (XRD), atomic force microscopy, transmission electron microscopy and electron diffraction. The thin films show a polycrystalline structure with domain sizes below 1 μm. It was indicated by XRD measurements, that the crystalline order of single grains complies with lattice parameters seen in single crystals. Furthermore, we performed angle dependent IR transmission measurements and did not observe any additional absorption bands or energetic shifts. The results allow us to conclude, that there is no influence of the crystal orientation on the vibronic modes.

4.4. Correlation between Z and the frequency of the CN-mode

To investigate the influence of the charge transfer on the CN-stretching mode, the CN-vibrations of TCNQ, TTF–TCNQ, DBTTF–TCNQ and Na-TCNQ are shown in Fig. 5. When comparing to pure TCNQ, a shift to lower energies is observed. The observed shifts are determined with an accuracy of 4 cm^{-1} resulting from the reading error and the instrument resolution. In studies of Kagoshima et al. and Kistenmacher et al. the charge transfer in TTF–TCNQ ($Z_{TTF-TCNQ} = 0.55e^-$) and DBTTF–TCNQ ($Z_{DBTTF-TCNQ} = 0.32$ e^-) was determined from calculations based on exact atom positions and bonding lengths, which were measured via

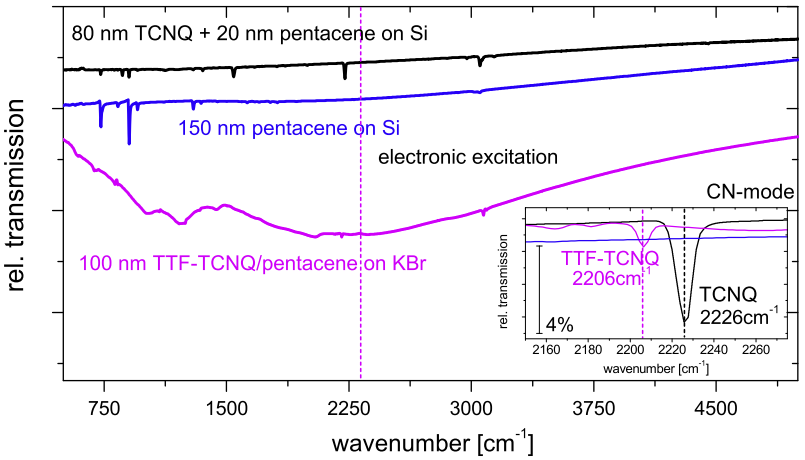

Fig. 4. Infrared spectra of TTF–TCNQ/pentacene on KBr, pentacene and TCNQ/pentacene on Si from 600 to 7500 cm^{-1}. Due to electronic excitation, a wide absorption starting at around 1000 cm^{-1} is visible. The CN-stretching mode shifts in TTF–TCNQ to smaller frequencies.

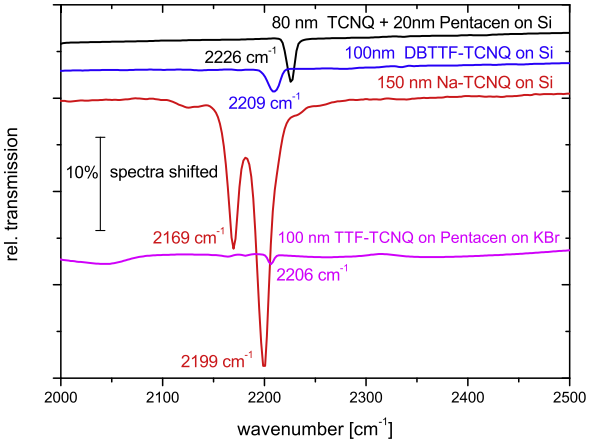

Fig. 5. Exact peak position of the CN-stretching mode in TCNQ, TTF–TCNQ, DBTTF–TCNQ and Na-TCNQ.

X-ray diffraction [27,28]. The results of our and the referenced work are summarized in Table 1. According to the discussion of Fig. 2 we assign zero and integer charge transfer to TCNQ and Na-TCNQ, respectively. Plotting the energy of the CN-mode against Z, we obtain Fig. 6. The datapoints from Table 1 are depicted with full triangles. A linear fit was applied to the data points. Due to the uncertainty of $Z_{DBTTF\text{-}TCNQ}$, which is discussed by Kistenmacher et al. [28], a fitting weight factor of $\frac{1}{2}$ is assigned to this data point, whereas all other data points are fully weighted in the linear fit. Under the given conditions, the best fit results in a slope of -26 cm^{-1}/e^- and a y-axis intercept at 2226 cm^{-1}.

Furthermore, the vibrational spectrum of TCNQ as a function of the charge number Z was calculated. In Fig. 6, the energy of the two CN-stretching modes b_{2u} full circles and b_{3u} open circles symmetry is plotted against the charge number Z. The corresponding movement of the atoms is shown in the inset in Fig. 6. The slope resulting from the calculation for the b_{2u}-mode is -39 cm^{-1}/e^- and the y-axis

Table 1
Correlation between charge transfer [26,27] and the frequency shift of the CN-mode in CT-complexes with TCNQ.

CT-complexes	Z [e^-]	CN-mode [cm^{-1}]
TCNQ	0	2226
DBTTF–TCNQ	0.32	2209
TTF–TCNQ	0.55	2206
Na-TCNQ	1	2199

intercept is at 2230 cm^{-1}, which corresponds well to the experiment. The frequency of both modes decreases with increasing negative charge on the TCNQ molecule. Since the LUMO of the TCNQ molecule is antibonding with respect to the CN-bond, its occupation weakens the CN-bond resulting in lower frequencies. This is also confirmed by the increased length of the CN-bond (see Fig. 6) with increasing charge transfer Z. While the vibration of b_{2u} symmetry is infrared active for all partial charges, the calculated intensity of the vibration of b_{3u} symmetry suddenly increases for $Z > 0.5e^-$ so that this vibration becomes observable in the vibrational spectrum (see Fig. 2). The increase of the intensity can be attributed to the increased negative partial charge being located on the dicyanomethine group of the TCNQ molecule. With increasing charge number Z, the negative partial charge increases from 0.25 to $0.58e^-$ as indicated by the Mulliken charges. Thus, the local dipole moment of the vibration of b_{3u} symmetry is significantly higher which results in higher infrared activity. It is interesting to note that both vibrations show a discontinuity between $Z = 0.4e^-$ and $0.5e^-$. However, the discontinuity is more pronounced for the asymmetrical stretching b_{3u}. The energetically closest vibration belonging to the same irreducible representation b_{3u} is the bending vibration of the hydrogen atoms in the molecular plane which shows the same change from infrared *active* to infrared *inactive* for $Z < 0.5e^-$. The change of activity can be attributed to the decreasing partial charge of the hydrogen atoms so that the change of the dipole during the vibration becomes smaller which results in a lower

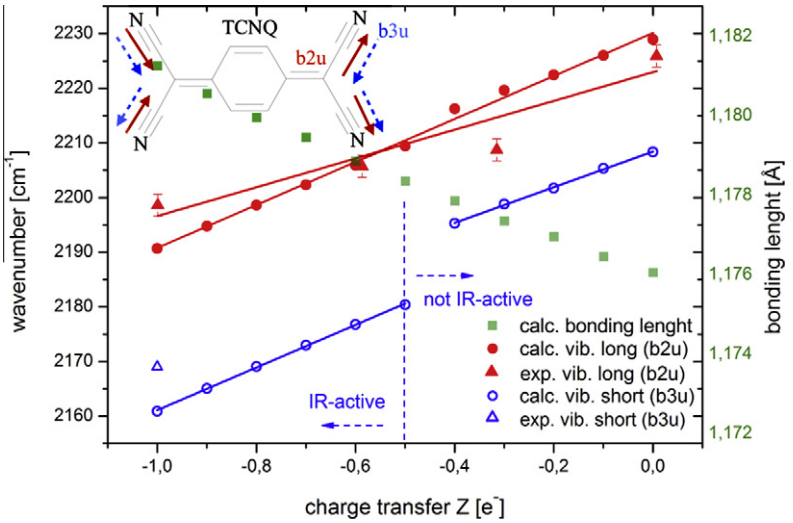

Fig. 6. Calculated and measured linear correlation between charge transfer and frequency shift of the CN-stretching modes b_{2u} and b_{3u} in CT-complexes with TCNQ. The vibration through the long (b_{2u}) and the short (b_{3u}) axis of the TCNQ molecule is marked with continuous and dotted arrows.

infrared activity. Since the hydrogen bending and the asymmetrical CN-stretching vibrations belong to the same irreducible representation, coupling of the two modes is allowed by symmetry and introduces a discontinuity for $0.4e^- < Z < 0.5e^-$. The calculated linear correlation between the charge transfer and the frequency shift of the b_{3u}-mode is shown in Fig. 6, indicated by open circles. We observe a major discontinuity in the b_{3u} characteristics at a partial charge transfer of about $0.5e^-$. The measured excitation energy of the b_{3u}-mode for Na-TCNQ is depicted with a open triangle. The deviation of 9 cm^{-1} between theory and experiment is small and can be attributed to the harmonical approximation used in the calculations. Further measurements on CT-complexes with $Z > 0.5e^-$ need to be done to confirm the influence of the mode coupling as predicted by DFT calculations.

5. Summary

We studied the charge transfer in vacuum evaporated thin-films of CT-compounds with TCNQ via IR-spectroscopy. The peak position of the CN-stretching mode was used as an indicator for the charge transfer between donor and acceptor. It was demonstrated, that the influence of the molecular charge Z on the vibrational spectrum can be calculated using a very simple theoretical model. This permits the determination of the molecular charge transfer Z by comparison of the measured and calculated vibrational spectrum. We compared pure TCNQ and the fully charge transferred Na-TCNQ. A significant shift of the frequency of the CN-mode and the appearance of a second peak was observed and was also demonstrated in spectra of F_4TCNQ and DBTTF-F_4TCNQ. We suggested, that the second peak appears due to the coupling of two modes in CT-compounds with $Z > 0.5e^-$. In complexes with a partial charge transfer like TTF–TCNQ and DBTTF–TCNQ a smaller shift of the CN-stretching mode peak was determined and the appearance of an electronic excitation was observed. All CN-peak positions can be correlated with the amount of charge transfer and a linear relationship was suggested. DFT calculations confirmed this experimental result and give a good explanation, that the measured second peak in CT-complexes with $Z > 0.5e^-$ results from the coupling of two modes.

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