Carbonyl Spectator Bonds as Sensitive Sensors for Charge Transfer Reactions on the Femtosecond Time Scale

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The feasibility of using the vibrational Stark effect for the observation of charge transfer reactions on a short time scale is demonstrated. The photoinduced oxidation of ferrocenophanone induces a fast shift of the carbonyl stretching frequency which is observable by femtosecond time-resolved IR spectroscopy. The observed shift is in good agreement with the IR spectrum of chemically oxidized ferrocenophanone and with theoretical predictions based on vibrational Stark effect calculations. The time dependence of the signal mirrors the charge transfer dynamics on the fs to ps time scale, as observed by optical spectroscopy. This shows that the vibrational Stark effect provides access to observing charge transfer reactions in the IR on the fs time scale. Since the Stark effect is sensitive to changes of the electric field alone, the sensor bond does not need to be part of the molecular system under investigation, but may be a noninvolved "spectator" bond located in its immediate surroundings.

Introduction

The dynamics of photoinduced charge transfer or dissociation reactions are difficult to observe by optical spectroscopy whenever the electronic transitions of short-lived molecular intermediates are not well known, overlap, or are located in the experimentally not easily accessible UV range, as is to be expected for small molecules and, in particular, for the products of dissociation processes.[1] We propose to monitor such charge transfer and dissociation reactions via their effect on the vibrational frequency of suitable sensor bonds. The recent developments in the field of ultrafast laser technology[2] extended the time scale of infrared measurements into the femtosecond time domain, so that even the fastest charge transfer reactions can be followed in real time using such sensor bonds.

The sensor bond may be (i) part of the donor/acceptor system itself and thus experience vibrational frequency shifts as a direct result of the altered electronic configuration, or (ii) it may be a "spectator bond" in its immediate environment.

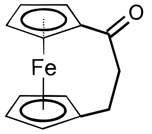
(i)Vibrational frequency shifts of redox-active sites accompanying a charge transfer reaction are well known. For example, in quinones, which have been used widely in electron donor/acceptor compounds,[3] shifts of the C═O and C═C stretching frequencies of more than 100 cm^{-1} occur upon reduction.[4] Similarly, upon coordination of CO to metal ions, a large shift of the carbonyl frequency is observed, arising from π^*-back-bonding and electrostatic effects.[5] This sensitivity of the CO-stretching frequency to the metal charge was used to probe charge transfer reactions in various redox systems involving metal carbonyls down to the picosecond time scale.[6]

(ii) In a more general approach, electrostatic effects on the vibrational frequency of a "spectator" bond can be utilized (vibrational Stark effect). In contrast to redox systems where the electron density at the sensor bond is directly altered by the charge transfer reaction, the vibrational Stark effect should allow one to monitor changes of the electron density from a distance. The sensor group in this case may be either within the molecule under investigation or located in its immediate environment.

Here we show the feasibility of the latter approach by monitoring on the femtosecond time scale the oxidation dynamics of the divalent iron cation in a ferrocenophanone via the stretch frequency of a spectator carbonyl group, which is located on the bridge connecting the two cyclopentadienyl moieties.

Materials and Methods

[3]-Ferrocenophan-1-one (**1**) and [3]-ferrocenophan-2-one (**2**) were prepared following published methods.[7,8] Details on the X-ray structure determination of **2** are given in the Supporting Information. Oxazine 1 (Lambda Physik) and CH_2Cl_2 (Merck, UVASOL) were used as supplied.



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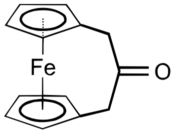

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Infrared spectra were recorded on an FTIR spectrometer (Perkin-Elmer, Series 1600) in a 0.5 mm CaF_2 cuvette. Chemical oxidation of the ferrocene derivatives was achieved by treating a deaerated 5 mM solution of 1 or 2 in CH_2Cl_2 with a stoichiometric amount of $AgBF_4$. Formation of the ferrocenium cation was confirmed by its characteristic absorption around 620 nm[9] and by the characteristic paramagnetic shifts in the ^1H NMR spectrum.

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Femtosecond pump−probe measurements were performed with a regeneratively amplified titanium sapphire laser system. The setup for optical parametric generation of excitation pulses at 650 nm (pulse length 150 fs, pulse energy up to 5 μJ, repetition rate 1 kHz) and for probing absorbance changes in the visible and near-IR spectral region has been described previously.[10] Probe pulses were generated by selecting a 15 nm wide portion out of a white-light continuum generated by focusing 1 μJ pulses at 780 nm into a 2 mm sapphire window. The probe pulses were delayed with respect to the pump pulses via a variable delay line and focused on the excited sample volume under a small angle to the excitation beam. Probe pulse energies before and behind the sample were detected with Si diodes and digitized with integrating A/D converters. Transient absorbance changes were measured by chopping the pump light at 500 Hz and referenced to the separately measured excitation pulse energies. For all measurements, the probe polarization was adjusted to be at magic angle with respect to the pump polarization.

IR probe pulses around 6 μm were generated by difference frequency mixing the signal and idler output of a white-light seeded BBO optical parametric amplifier (pumped at 780 nm) in a 2 mm $AgGaS_2$ crystal.[11] The IR light thus generated had a spectral width of 130 cm^{-1}. A spectral resolution of 3 cm^{-1} was obtained by using a 30 cm focal length monochromator with a 130 lines/mm grating (blazed for 6 μm) behind the sample. The IR pulses were detected with liquid nitrogen cooled HgCdTe detectors; pump−probe geometry and detection scheme for measuring transient absorbance changes in the IR were the same as those employed for measurements in the visible. The pump−probe cross-correlation width was estimated to be approximately 200 fs from pump−probe experiments on a thin Si wafer.

For all time-resolved measurements, the concentration of **2** in CH_2Cl_2 was kept at 1 M to ensure rapid quenching of photoexcited oxazine 1.[10] The concentration of oxazine 1 and the optical path length were 10^{-4} M/1 mm and 2×10^{-3} M/57 μm for measurements in the visible/near-IR and IR, respectively.

Results and Discussion

Vibrational Stark Effect. An external electric field affects the vibrational Hamiltonian via its projection on the dipole vector of the vibrational mode, thus altering the frequency and the absorption cross section of the vibrational transition. Of particular interest here are carbonyl groups with their large IR cross sections around 1700 cm^{-1}. Ab initio and semiempirical calculations on formaldehyde[12] predict a tuning rate of the carbonyl vibrational frequency on the order of 5×10^{-7} cm^{-1}/(V/cm) and a fractional decrease of the absorption cross section by approximately 2×10^{-9}/(V/cm), corresponding to a shift of 45 cm^{-1} and a change of the absorption cross section by 18% for a carbonyl at a distance of 4 Å from a unit charge and oriented parallel to the electric field. In light of the typical width of carbonyl vibrational bands of 10−20 cm^{-1}, these shifts are significant and should be easily detectable. Similar effects were predicted[13] and observed[14] for free CO and the CO ligand in cytochromes.[15] Also, changes observed in the amide I′ band of photosynthetic reaction centers[16] and small de novo peptides[17] after charge shifts were in agreement with these predictions.

The carbonyl stretching mode of the ferrocenophanones **1** and **2** is expected to be affected by changing the charge on the ferrocene unit mainly via the vibrational Stark effect and thus should provide a good model for the proposed class of electrostatic sensors. This is true in particular for **2**, whose X-ray structural data[18] show the carbonyl π-bonding orbital to be approximately orthogonal to the cyclopentadienyl π-orbitals, thus ruling out any significant coupling between these orbitals. We calculated the electric field changes at the carbonyl group upon oxidation of the ferrocene unit with the help of X-ray structural data.[18] The additional charge was assumed to be evenly distributed over the iron and the cyclopentadienyl rings,[19] as indicated by INDO calculations[20] and Mössbauer spectroscopy.[21] From the calculated electric field change, a shift of the carbonyl stretching frequency after oxidation of ferrocene derivative **1** by approximately 45 cm^{-1} and a decrease of the cross section on the order of 20% are predicted.[22] For **2**, the carbonyl group is at a slightly larger distance to the ferrocene unit and is oriented at a larger angle to the electric field. Thus, a smaller shift of the carbonyl stretch frequency of 32 cm^{-1} and a decrease of the cross section by 13% are expected upon oxidation of **2**.

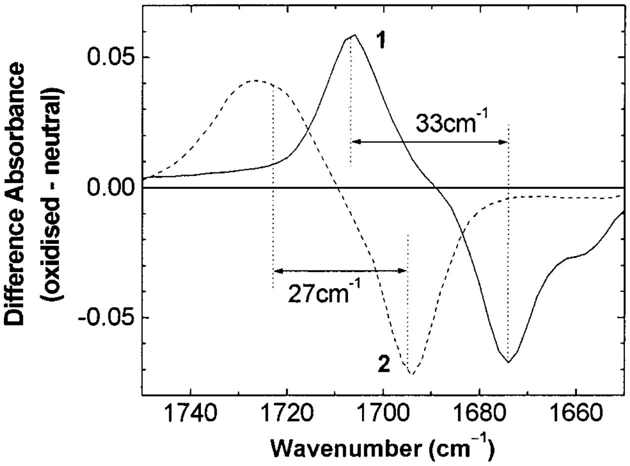

Figure 1. Static (FTIR) difference absorbance spectra (chemically oxidized − neutral) of ferrocene derivatives **1** (solid line) and **2** (dashed line) in CH_2Cl_2. Also shown are the positions of the maxima in the FTIR spectra of each species.[23]

Experimentally, chemical oxidation of **1** and **2** was found to shift the carbonyl stretching frequency by 33 cm^{-1} and 27 cm^{-1}, respectively, Figure 1.[23] These values are in reasonable agreement with the expected shifts. Especially the slightly smaller shift of the carbonyl stretching frequency after oxidation of **2**, as compared to **1**, supports the notion that the shift is dominated by the Stark effect. The integrated IR cross section of the carbonyl band is found to be reduced upon oxidation by approximately 20% for **1** and 15% for **2**, again in good agreement with the predictions. Deviations of the observed shifts and cross section changes from the predicted values may arise from the inadequacy of applying Stark effect calculations on the C═O stretching in formaldehyde to more complicated molecules. Furthermore, solvent screening was neglected in the calculations. We can conclude that the observed changes in the carbonyl stretch vibration upon chemical oxidation of **1** and **2** are dominated by the vibrational Stark effect and that the carbonyl stretching frequency is a sensitive sensor for the redox state of **1** and **2**.

Femtosecond Time-Resolved Measurements. Recently, photoinduced electron transfer from ferrocene derivatives to various acceptor molecules has been observed in fs time-resolved measurements by following transient absorbance changes of the acceptor in the visible spectral region.[10,24] Because of its small extinction coefficient in the visible region, no spectral response of ferrocene could be detected in these experiments. Thus, the interpretation of the observed signals

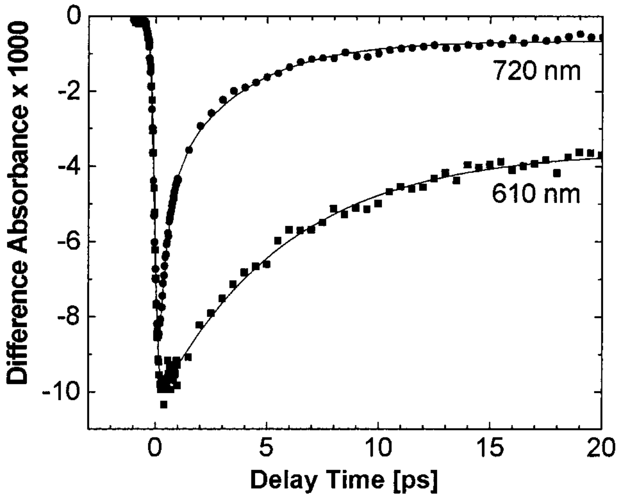

Figure 2. Time dependence of the difference absorbance of oxazine 1 (10^{-4} M in CH_2Cl_2) at 720 nm (stimulated emission, circles) and 610 nm (ground state absorbance bleach, squares) after excitation at 650 nm in the presence of ferrocene derivative **2** (1 M). The solid lines are the results of least-squares fits to a multiexponential decay function with constant background, convoluted with a Gaussian instrument response function with a fwhm width of approximately 210 fs.[10] Fit results at 720 nm: 370 fs (62%), 3.4 ps (34%), constant background 4%. Fit results at 610 nm: 5.8 ps (56%), 38 ps (25%), 280 ps (9%), constant background 10% (data at delay times longer than 20 ps are not shown here, but were included for fitting).

as arising from electron transfer could be confirmed only indirectly by the observation of an ultrafast magnetic field effect on the recombination dynamics of the photoinduced radical pair due to spin chemical effects.[24] We show here that the carbonyl group of ferrocene derivative **2**, acting as "spectator" bond in the above sense, makes it possible also to observe directly the time dependence of the redox state of the electron donating ferrocene derivative. Femtosecond time-resolved IR measurements on the electron donor complement measurements in the visible spectral region on the electron acceptor, thus yielding a more comprehensive picture and unambiguously assigning the observed signals to an electron transfer reaction.

Measurements in the Visible Spectral Region. The time dependence of the stimulated emission from the oxazine 1 singlet excited state at 720 nm and the ground state recovery at 610 nm were measured after excitation at 650 nm in the presence of ferrocene derivative **2** at a large concentration (1 M), Figure 2. The stimulated emission of oxazine 1 was found to decay with a major fast component with a time constant of 370 fs and a smaller component with 3.4 ps, Figure 2. In a previous study the dependence of the nonexponential quenching dynamics of a photoexcited dye on the concentration of the ferrocene quencher was investigated in detail.[10] In accordance with these results, we conclude the fast component observed here to arise from static quenching in oxazine 1-ferrocenophanone contact pairs, whereas the slower component reflects quenching of those excited oxazine 1 molecules with no quencher molecule in immediate proximity. The slightly different values for the time constants observed here and in the previous investigation[10] arise from the different ferrocene substituents and solvents used in the two studies.

The ground state recovery of oxazine 1 in the presence of 1 M ferrocene derivative **2** is dominated by a component with a time constant of 5.8 ps, followed by smaller components with 38 and 280 ps, Figure 2. Moreover, the ground state does not recover completely on the accessible time scale of a few nanoseconds. The delayed ground state recovery shows that the quenching process leads to the formation of an intermediate state involving oxazine 1 (thus directly ruling out energy transfer as quenching mechanism), which decays in a highly nonexponential way. Previously, charge transfer from a photoexcited dye to ferrocene has been suggested as the relevant quenching mechanism.[10] Compelling evidence for this mechanism was found when a magnetic field effect on the ground state recovery of oxazine 1 was observed on the ps-time scale in the presence of high concentrations of ferrocene.[24] The charge transfer yields a singlet-phased radical pair which undergoes (magnetic field dependent) singlet−triplet mixing. The relevant reaction scheme is shown in Figure 3. Triplet-phased radical pairs are prevented from recombination to the singlet ground state, and the nonexponentiality of the oxazine 2 ground state recovery is an immediate consequence of the radical spin dynamics. The recovery is not complete on the picosecond time scale, since some radical pairs escape geminate recombination and diffusively recombine on a much slower time scale.

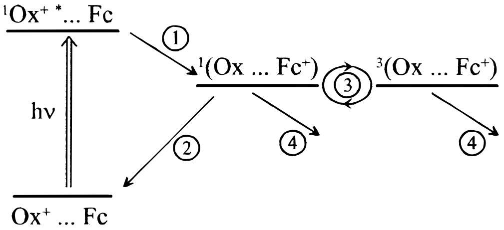

Figure 3. Simplified reaction scheme describing the relevant processes occurring after photoexcitation of oxazine 1 (Ox^+) in the presence of ferrocenes or ferrocenophanones (Fc): 1, forward charge transfer; 2, back charge transfer; 3, singlet−triplet mixing; 4, cage escape. For details see text.

The only experimental evidence for charge transfer as the quenching mechanism is the observed magnetic field effect on the ground state recovery of oxazine 1. No direct spectroscopic evidence for charge transfer or for the participation of ferrocene in the intermediate state is available from measurements in the visible/near-IR due to the small extinction coefficient of ferrocene. In contrast, transient IR spectroscopy now makes it possible to directly follow also the temporal evolution of the putative electron donor, the carbonyl-containing ferrocene derivative **2**.

Measurements in the IR. The transient difference absorbance spectrum of ferrocene derivative **2** in the carbonyl region measured at a delay time of 1 ps after excitation of oxazine 1 is shown in Figure 4. As shown, the transient absorbance spectrum at 1 ps agrees well with the static difference spectrum between the chemically oxidized and neutral ferrocene derivative **2**. Thus, the intermediate state, which is formed upon quenching of excited oxazine 1 with a dominant time constant of 370 fs and decays with a dominant time constant of 5.8 ps, is shown to involve an oxidized ferrocene moiety. This constitutes the first direct spectral evidence of fast electron transfer from a ferrocene derivative to an excited electron acceptor.

Because of the strong absorbance of the sample around 1695 cm^{-1}, it was not possible to accurately measure the absorbance bleach near the maximum of the vibrational band. However, the minor deviations of the time-resolved and static difference spectra for wavenumbers below 1690 cm^{-1} are significant and reproducible. They may arise from carbonyl groups on neighboring ferrocenophanone molecules which are not directly involved in the charge transfer but are close enough to the reacting molecules to feel the ensuing electric field changes. Due to the high concentration of ferrocenophanone, which is needed to ensure ultrafast static quenching of oxazine 1 on the

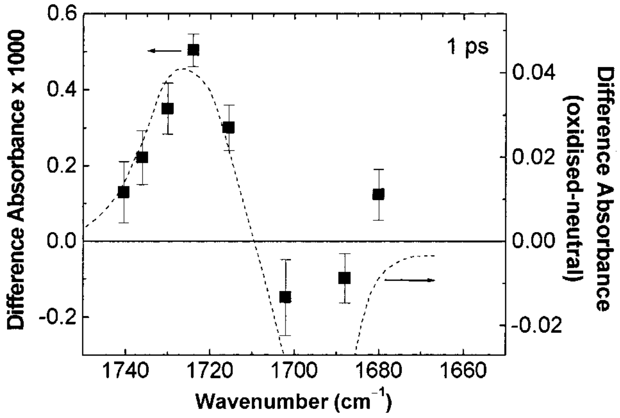

Figure 4. Time-resolved difference absorbance spectrum (squares, left ordinate) of ferrocene derivative **2** (1 M in CH_2Cl_2) at a delay time of 1 ps after excitation of oxazine 1 (2×10^{-3} M) at 650 nm. Also shown is the static difference absorbance spectrum of Figure 1 (chemically oxidized − neutral, dashed line, right ordinate).

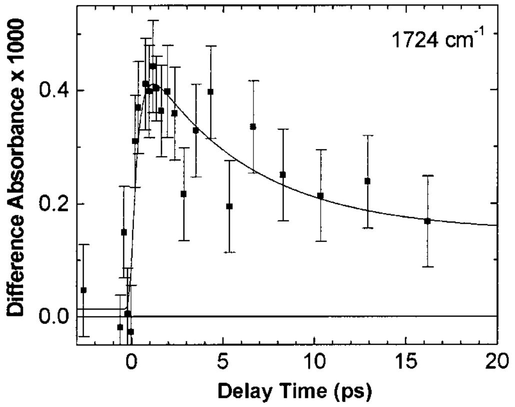

Figure 5. Time dependence of the difference absorbance of ferrocene derivative **2** (1 M in CH_2Cl_2) at 1724 cm^{-1} after excitation of oxazine 1 (2×10^{-3} M) at 650 nm. The solid line is the result of a least-squares fit with fixed time constants $\tau_1 = 0.37$ ps (rise) and $\tau_2 = 5.8$ ps (decay), as determined from measurements in the visible spectral region, and a constant, representing slower decay components, convoluted with the experimental response function, represented by a Gaussian with a width of 200 fs.

femtosecond time scale, there is a significant probability of several ferrocenophanone molecules being near each oxazine 1 molecule. The random orientation of their carbonyl groups with respect to the reacting molecules should lead to an overall broadening of the carbonyl band upon charge transfer, which could well explain the observed deviations. Alternatively, the deviations may be due to coupling of the electron transfer to the carbonyl stretch, resulting in the excitation of higher vibrationally excited states, whose absorbance is anharmonically shifted to lower frequencies. More detailed measurements are needed to identify the origin of these deviations.

The time dependence of the transient absorbance at 1724 cm^{-1}, Figure 5, mirrors the concentration of oxidized ferrocene derivative **2**. The observed IR signal is fully compatible with the dynamics observed in the visible region. This is shown by the solid line in Figure 5, which represents the results of a nonlinear least-squares fit of the IR data based on the time constants of the fastest components for forward and reverse charge transfer, as determined from the data in the visible region. Here, we refrained from including in the fit the minor kinetic components observed in the visible because of the significant noise of the IR data obtained with the current experimental setup. Furthermore, a thorough analysis will have to take into account coherent contributions to the observed signal,[25,26] since the carbonyl vibrational transition has a dephasing time on the order of 1 ps. Again, the significant noise in the present data made such an analysis unfeasible. Further technical improvements, which will allow measurements with significantly improved signal-to-noise, are currently in preparation in our lab.

Measurements in the visible allow the determination of forward and backward charge transfer dynamics only from measurements at several wavelengths: Forward charge transfer dynamics are observable in the stimulated emission of photoexcited oxazine 1, whereas backward charge transfer dynamics can be determined only from measurements of the ground state recovery. The IR signal, on the other hand, is a direct measure of the concentration of ferrocenophanone in the oxidized state and thus has the advantage of allowing the direct observation of both processes in one measurement.

Thus, charge transfer dynamics can be well monitored in the infrared. As shown here, this may allow one to obtain a more comprehensive picture of a redox process by observing both partners separately. However, infrared spectroscopy will be even more useful for the investigation of redox systems where both partners have no suitable absorbance bands in the visible spectral region, in particular, redox systems involving small molecules.

The vibrational Stark effect is sensitive to changes of the electric field alone and allows one to monitor changes of the electron density *from a distance*. Therefore, the sensor group does not need to be part of the molecules involved in the reaction, but may be located in the immediate surroundings. Measurable Stark shifts can be expected as long as the spectator group is within a maximum distance from the reacting system, which can be estimated from the Stark tuning rate. Typical Stark tuning rates for carbonyls are on the order of 5×10^{-7} cm^{-1}/(V/cm),[12] implying a maximum distance of 6−7 Å, at which the shift becomes comparable to the width of the carbonyl band.

Conclusions

The results presented here clearly demonstrate the potential of time-resolved IR spectroscopy on "spectator" bonds for sensing remote changes of a distribution of charges which are not accessible by optical spectroscopy. For the redox system investigated here, it was shown unambiguously that electron transfer is the dominating quenching process of photoexcited oxazine 1 in the presence of ferrocenes. The carbonyl frequency shift upon changing the ferrocene charge is dominated by the vibrational Stark effect. Since the carbonyl sensor is sensitive to electric field changes alone, the method can be extended to systems where the spectator bond is not part of one of the participating molecules, but is integrated in the environment of the redox system under investigation. This might be of particular interest in organized environments and supramolecular structures; for example, one may use the carbonyls already present in proteins or DNA/PNA for following electron or proton transfer reactions in biomolecules.

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Supporting Information Available: Cartesian coordinates and crystal data for [3]-ferrocenophan-2-one (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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