Topical Review

Transient IR spectroscopy as a tool for studying photocatalytic materials

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Abstract

Over the years, a considerable amount of attention has been given to the thermodynamics of photocatalysts, i.e. to the location of their valence and conduction bands on the energy scale. The kinetics of the photoinduced charge carriers at short times (i.e. prior to their surface redox reactions) is no less important. While significant work on the transient electronic spectra of photocatalysts has been performed, the transient vibrational spectra of this class of materials was hardly studied. This manuscript aims to increase the scientific awareness to the potential of transient IR spectroscopy (TRIR) as a complementary tool for understanding the first, crucial, steps of photocatalytic processes in solid photocatalysts.

This was done herein first by describing the various techniques currently in use for measuring transient IR signals of photo-excited systems and discussing their pros and cons. Then, a variety of examples is given, representing different types of photocatalysts such as oxides (TiO₂, NaTaO₃, BiOCl, BiVO₄), photosensitized oxides (dye-sensitized TiO₂), organic polymers (graphitic carbon nitride) and organo-metalic photocatalysts (rhenium bipyridyl complexes). These examples span from materials with no IR fingerprint signals (TiO₂) to materials having a distinct spectrum showing well-defined, localized, relatively narrow, vibrational bands (carbon nitride). In choosing the given-above examples, care was made to represent the several pump & probe techniques that are applied when studying transient IR spectroscopy, namely dispersive, transient 2D-IR spectroscopy and step-scan IR spectroscopy. It is hoped that this short review will contribute to expanding the use of TRIR as a viable and important technique among the arsenal of tools struggling to solve the mysteries behind photocatalysis.

Keywords: IR spectroscopy, photocatalysis, transient spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

The 1972 Honda–Fujishima manuscript on the photoelectrochemical splitting of water [1] paved the way for thousands of scientific manuscripts aimed at utilizing the energy of photons for the degradation of contaminants in water, in air and on surfaces, as well as for the production of hydrogen from water. Generally speaking, these thousands of works reflect several research phases, from focusing at understanding the chemical mechanisms behind the degradation of specific molecules, towards active design of materials and methods that may increase the efficiency of photocatalytic processes.

The general scheme of a photocatalytic scenario, as deduced upon employing a variety of transient measurements techniques, is portrayed in figure 1. The first step (1) is light absorption, having a typical time of a few femtoseconds.
Phonons, acting as momentum suppliers, may be involved in this step, whenever the transition is indirect. It is often taken for granted that all absorption events by direct band gap semiconductors do not involve phonons, whereas all absorption events by indirect band gap semiconductors involve phonons. The actual situation may be more complex, since, in general, the energy of most absorbed photons is larger than that of the bandgap, hence intraband relaxation of the excess energy of conduction band electrons (2a) and valence band holes (2b) comes next. The duration of this step varies between several picoseconds to nanoseconds. The coupling between photo-excited charges and phonons may have a large impact on the efficiency of photoactive materials, as such interactions set a fundamental intrinsic limit to charge-carrier mobilities [2] and govern the charge-carrier cooling dynamics [3]. Then, the electrons diffuse within the conduction band (3a) while the holes diffuse within the valence band (3b). Part of the electrons and holes may be trapped in shallow traps ((3c and 3d)) located near the conduction band or near the valence band, respectively. These shallow traps are associated with the presence of defects or dopants within the bulk. While their presence may alter the diffusion constant (hence mobility) of the charge carriers, the shallow traps consume only a small part of the charge carriers’ energy. In certain cases, for example if the geometrical density of the traps is sufficiently high, the shallow traps’ states are split thus forming mini-bands within the forbidden gap (3c(b)) and 3(d(b)). Emission of light (or energy release to the photocatalyst) may occur upon recombination of electrons at the bottom of Ec with holes at Ev (3e), or by recombination of electrons trapped at shallow traps bands (3f). Another source for light emission may include a two-step process involving deep traps (3g). Carriers arriving at the surface may be trapped on surface shallow traps (4(a) and 4(b)) and eventually participate in redox on/near the surface (5(a) and 5(b)), or alternatively end-up in deep traps leading to recombination (4(c)) [4].

The charge carriers may interact to form weakly bound pseudo-particles (excitons). As such, they may diffuse together for some time, until they recombine. If the excitonic binding energy is less than or close to the thermal energy of the system the electrons and the holes will be separated within the bulk. Since at the long run the number of holes and the number of electrons arriving at the surface has to be equal (otherwise the material becomes more and more charged over time, which is impossible), the rate of surface redox reactions depends on their kinetic competition against surface recombination. To obtain high rate for a given ‘working’ half-cell reaction (for example, the oxidation of a specific contaminant), it is essential to minimize the accumulation of opposite charges in the vicinity of the ‘working’ charge. One way to achieve it is by supplying the right conditions for fast stripping of the counter charge. A good example for this claim is the role of dioxygen in the oxidation of contaminants by TiO2 [5]. A complementary approach is to make sure that each charge carrier will end up at a different location on the surface. This approach is manifested by the use of electrical bias (namely by a photoelectrochemical arrangement) [6], the utilization of composite photocatalysts with pre-designed band alignment [7] and the formation of photocatalytic particles having different electron collecting facets and hole-collecting facets. Another way, adequate only for very low photon flux, could be to try to separate the charge carriers not via controlling their location, but rather by controlling the diffusion time [8], so that the time it takes for the slower charge carrier (usually the hole) to arrive at the surface will be considerably shorter than the arrival time of the electron, leaving sufficient time for the latter to perform its reduction reaction prior to the arrival of the hole.
A large number of techniques have been used in a quest to better understand the fundamental parameters governing photocatalytic processes at their early stages. At present, it is impossible to identify one ‘silver-bullet’-type of technique that can unveil solely the mysteries behind photocatalysis thus facilitating the preparation of new photocatalysts having pre-designed properties. Most of these techniques can be categorized as ‘pump and probe’ techniques, i.e. techniques that rely of short photoexcitation pulse, followed by a second, fast, measurement which takes place at times that are defined relative to the excitation pulse.

The most common of these techniques are transient UV–vis absorption/reflection/photonoluminescence spectroscopies. Here, transient changes in the UV–vis spectra are considered to be directly related both to thermodynamics, i.e. to the energy-scale location of trap states/bands and to dynamics, i.e. to the population of these states. A large variety of photocatalytic materials were studied by this method, among which are TiO$_2$ [9, 10], carbon nitride [11], metal organic frameworks (MOFs) [12], dye-sensitized SrTiO$_3$ [13] and many more. Another common technique is time resolved microwave conductivity (TRMC), which is based on measuring the temporal behavior of a microwave beam impinging on the photocatalyst following its photoexcitation [14, 15].

Electron paramagnetic resonance (EPR) is often used to trace reactive oxygen species (ROS) formed at the surface of photocatalysts [16], and, indirectly, to provide valuable information on the trapping of photogenerated electrons [17]. To these methods one may add also time resolved photocharge (TRPC) measurements which, similar to the described above techniques, provide important information on the lifetime of the charge carriers [18] and on the role of charge-carriers separation distance in photocatalytic phenomena [19].

2. Transient IR spectroscopy (TRIR)

In dye molecules, the large spectral width of electronic transitions and their lack of specific features might lead to ambiguous interpretation, in particular when more than one chromophore is involved [20]. In contrast, vibrational spectroscopy, (Raman or IR) may provide more detailed information simply because of the richness of details and the potential ability to pinpoint a phenomenon in terms of functional groups and the interactions between them. Accordingly, transient vibrational spectroscopy is intensively implemented in the study of excited molecular species. That way, high resolution TRIR was used to study intramolecular processes such vibrational relaxation (for example, NO that had been excited to a superposition of the UV-excited IR spectrum ($A_1$) and the non-UV excited IR absorbance spectrum ($A_0$):

\[ A^* = xA_1 + (1-x)A_0. \]  

(1)

The difference spectrum $\Delta_{\text{abs}}$, defined as $A^* - A_0$, is then equal to $x(A_1 - A_0)$. In the case that the peaks in $A_1$ are sufficiently shifted relative to $A_0$, the $\Delta_{\text{abs}}$ spectrum is expected to reveal negative peaks (dips). The relation between $A_1$, $A_0$, $x$, and $\Delta_{\text{abs}}$ is given by:

\[ xA_0 + \Delta_{\text{abs}} = xA_1. \]  

(2)

Assuming that the negative peaks in the difference spectrum represent wavenumbers at which $A_1$ equals to zero (i.e. no absorption by the excited molecules) provides a means to obtain $A_1$ and to estimate $x$. This is done by artificially constructing a plot of $f + A_0 + \Delta_{\text{abs}}$ and altering the factor $f$ until the dip disappears [32]. At this point $f = x$ and the obtained spectrum is the unknown spectrum $A_1$ multiplied by $x$. This procedure is demonstrated in figure 2.

2.1. The dispersive approach

Dispersive units are characterized by spectral separation of the probing polychromatic IR pulse so that in each measurement a pulse of a distinct wavenumber impinges on the sample. The spectral separation is often obtained by a grating monochromator, at a relatively low spectral resolution (32 cm$^{-1}$) [33]. Detection is usually performed by HgCdTe (MCT) detectors, operating either as a single detector or as part of an array enabling simultaneous detection [34–36]. The probing IR pulse

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may be generated by a variety of methods such as utilizing part of the energy of the pumping laser (for example by a difference frequency mixing between two ultra-short visible pulses mixed in a nonlinear crystal [26, 37]), coupling NIR pulse to an optical parametric amplifier (OPA) [32, 38] or by up-converting a continuous wave laser with a variably delayed optical pulse [39].

In general, the IR range that is obtained by OPA is quite narrow, compared with the whole mid IR range. Indeed, many of the transient IR measurements provide spectra between 1980 cm\(^{-1}\) to 2200 cm\(^{-1}\) [18, 32]. Extending the probing range to the entire vibrational spectrum was reported in 2012 [40]. Here, the continuum was generated from 800 nm pulses by inserting several components in series: beta barium borate (BBO) crystal for doubling, a delay plate, a dual wave plate made of quartz and a tripling crystal. The three co-propagating colors were then focused, leading to filamentation and continuum IR generation.

2.2. Transient 2-dimensional IR spectroscopy (2D-IR)

2D-IR can be viewed as an extension to pump-probe transient absorption. In regular pump-probe experiments, obtaining sub-picosecond temporal resolution comes together with spectral broadening of the pump beam. 2D-IR provides a way to overcome the broadening of the pump, albeit at a cost of increasing significantly the complexity of the experimental set up. 2D-IR measurements are based on splitting the output pulse of a femtosecond laser into two pulses. One of the pulses (the so-called IR pump pulse), goes through a Fabry–Perot filter thus turning into a narrow-band pulse having a controllable

Figure 2. Resolving the unknown IR spectrum of the excited state \(A_1\). (A) The measured spectrum under excitation \(A^*\) (B) the two components of \(A^*\): \(A_0\) measured in the absence of excitation (dashed line) and the unknown \(A_1\) (solid line). In this artificial example the components were added according to \(x = 0.75\) (C) the difference spectrum obtained by subtracting the measured \(A_0\) from the measured \(A^*\). (D) \(f + A_0 + \Delta \text{Abs}\) plots, en-route for obtaining \(A_1\) and \(x\). Here, \(f = 0\) (dotted line), 0.25 (dashed-dotted line), 0.5 (dashed line), 0.75 (solid line).

Figure 3. The timing schemes of 2D-IR and T2D-IR set-ups.
center-frequency, which impinges on the sample. The wide bandwidth second pulse (probe pulse), also impinges on the sample, nevertheless, at a specific delay made by a delay line (figure 3, upper trace). A detector array, allowing for broadband spectral detection, is located downstream and monitors the spectral signal. By repeating the measurement at various pump frequencies, a 2D array of data (intensity as a function of pump frequency axis and probe frequency axis) is formed. The off-diagonal elements provide information about the unharmonicity of a specific mode (for example, the difference between $V_0 \rightarrow V_1$ versus $V_1 \rightarrow V_2$). Performing these measurements while varying the pump-probe delay provides information on the lifetime of the vibrationally excited state. An example for 2D-IR is portrayed in figure 4. The example, after [41, 42], presents two coupled vibrational modes (figure 4(A)), subject to IR pump & probe experiment. The various possible transitions, are mapped onto the 2D map, showing absorption intensities as a function of pump and probe frequencies. For simplicity, the two potentials in figure 4(A) are depicted as if they were de-coupled. The contours in the map are relative to the absorption spectrum in the absence of an IR pump pulse. The red and violet contours represent negative and positive values, respectively. In that manner, the two red contours along the diagonal originate from the depletion of the population at the ground state ($V = 0$) by the pump beam as well as from luminescence from the first excited state ($V = 1$), whereas the two red off-diagonal contours arise only from ground state population depletion. The off-diagonal violet contours ‘d’ and ‘c’ can be observed following the excitation of their mode to $V = 1$ by the pump beam. The other two positive contours ($a+b$ and $b+a$) represent a transition to the 1,1 state and should appear only if the two modes of vibration are coupled.

This approach was extended to study transient phenomena [43], including in photocatalytic materials, denoted as T2D-IR, by introducing another pulse, in the UV–vis range, acting to excite the material prior to performing the 2D-IR measurements (figure 3, lower trace). If the delay between UV–vis pulse and the IR (pump-probe) facilitiates to study relaxation processes. The T2D-IR has several variations, including locating the UV–vis pulse between the IR-pump pulse and the IR-probe pulse (‘triggered

Figure 4. A 2D-IR schematics map of two vibrational modes and the corresponding transitions. For clarity, the potentials in part A do not take into consideration coupling between the two modes, whereas the effect of coupling appears in the 2D-IR map.

Figure 5. A typical step-scan set-up.

Figure 6. The array of data in a step-scan configuration. Here, $\delta$ represents the wavelength. Reproduced from [96]. CC BY 4.0.
2.3. The step—scan approach

Measuring transient IR spectra by a step-scan technique [46] is based on fixing the moving mirror of an FTIR interferometer at a specific position and firing an excitation pulse at the sample (figure 5). Apart from impinging on the surface, the excitation pulse also triggers the FTIR MCT detector, which measures the intensity of the broad-band IR signal arriving from the IR source of the FTIR machine and transmitted through the sample as a function of time. This pump-probe procedure may be repeated several times (usually 10–40) in order to improve, later on, the signal to noise ratio. Then, the moving mirror of the interferometer is relocated at a next position and the whole process of excitation and measuring transmission as a function of time is repeated. At the end of the process a 2D array of data, i.e. intensity as a function of time and mirror position, is obtained (figure 6). A transmission spectrum is then obtained by Fourier-transforming the data points, in an orthogonal manner to the way they had been measured, i.e. by Fourier-transforming the interferogram comprised from intensities measured at a specific time relative to the trigger pulse at all mirror positions. The obtained single channel spectrum may be presented as an absorption spectrum (i.e. relative to a measurement in the absence of a sample) or, by subtracting the absorption spectrum at \( t = 0 \) from the absorption spectrum at some time \( t \), as a difference absorption spectrum.

The FTIR step-scan technique retains all benefits of FT spectroscopy compared with dispersive spectroscopy: simultaneous collection of information (Fellgett’s advantage), higher throughput (Jacquinot’s advantage) both of which leading to higher signal to noise ratio, better wavelength accuracy (‘Connes’ advantage) and lower sensitivity to stray light [47]. The temporal resolution of the measurements is limited by the duration of the excitation pulse as well as by the temporal resolution of the probing detector. At present, the best temporal resolution spectrum reported with a commercial step-scan FTIR machine is 2.5 ns, compared with picoseconds range reported with dispersive set-ups or by T2D-IR, however this inferiority is not inherent. Besides, while a resolution of 2.5 ns might be inadequate for observing the ultrafast processes occurring at a molecular level, this temporal resolution may be sufficient to trace processes occurring within solid materials, where the diffusion time is longer due to longer diffusion lengths and to the presence of trapping-detrapping phenomena. Another benefit of step-scan FTIR in comparison to the other TRIR methods is its lower complexity as it uses commercially-available, dual-use, apparatus. The step scan technique is in particular advantageous when a broad IR range has to be covered, as, unlike dispersive TRIR, it uses a broadband CW IR source.

In terms of time-correlation between the detector, the excitation-laser shot and the repositioning of the mirror there are two possibilities: letting the laser to operate independently as a master, so that the laser shot triggers the slave detector, or to use the FTIR machine to trigger the laser. For many lasers the time elapsing from receiving an external triggering signal until the actual shot is not sufficiently precise, so that the first option seems to be preferable.

Step-scan operation has its inherent restrictions. It requires that all excitation pulses cause the same effect on the sample. To fulfill this condition, the intensity and duration of all pumping pulses have to be identical. Averaging over several shots per mirror location may assist to reduce the effect of random peak-to-peak laser fluctuations. However, this is at the expense of increasing the overall measuring time and might increase the effect of errors originating from slow drift in the electronics of the detector or the laser beam. Another issue of concern is the requirement for a complete recovery of the sample within the time elapsing between successive shots. Failing to take this requirement into consideration might lead to the purchasing of pumping systems that are either inadequate, or at least not optimal, for specific types of phenomena. Residual mirror fluctuations upon repositioning may contribute to inaccuracies [48], however, this effect can be reduced by assuring an adequate stabilizing time between the repositioning of the mirror and actual measurements. The typical stabilization time is less than several milliseconds, whereas many of the pulsed lasers used for step-scan measurements operate at a repetition rate of 10–20 Hz, so that this required condition is easily met. Another issue of concern is measuring the signal prior to excitation, an essential spectrum required for studying transient changes. To obtain a reliable pre-excitation spectra and to have an idea about the stability of the pre-excitation signal, one may use not the actual laser shot as the detector trigger, but instead, use as a trigger an electronic signal that can be drained from the laser system slightly before the actual shot.

The transient phenomena studied by the step–scan approach are quite similar to those measured by the dispersive TRIR approach. These include, for example, studies on photo-dissociation [25], intramolecular proton release pathway and structural changes in bacteriorhodopsin [49, 50] as well on other photoactive proteins [51–53], spectroscopy of excited states of transition metal complexes [54–56], identification of transient radicals formed on zeolites [57, 58] and even dynamic deformations and rheo-optical properties of polymers [59, 60].

It should be noted that studying transient phenomena by the step-scan FTIR approach is not limited to excitation by a pulsed light sources. For example, modulating the potential of an electrode in a sinusoidal manner enabled to probe the dynamics of surface and solution species in ferricyanide/ferrocyanide redox couple [61]. More details on the step-scan technique, including a discussion on photoreflectance spectroscopy and on the difference between working with a dc detector versus ac detector, can be found in several mini-reviews [24, 62].

2.4. Transient infrared absorption-excitation energy scanning spectroscopy (TRIRA-ESS)

The TRIRA-ESS technique is based on scanning the excitation energy within the bandgap of the photocatalyst and using IR absorption at some short delay to probe photo-excited
electrons within the conduction band or at localized excited states below it. These two types of charge carriers can be distinguished by their different influence on the absorption spectrum and the decay kinetics. For example, the third harmonic (355 nm) of a pulsed Nd:YAG laser was used to pump an optical parametric oscillator producing a tunable output from 410 nm to 709 nm together with an idler beam (710–2630 nm), both of which used for excitation. IR beam at 2090 cm$^{-1}$ impinging at a delay of 250 ns was used for probing [63].

3. TRIR in photocatalysis

At large, the photocatalysis-related TRIR phenomena may be classified, based on their location, into three classes: signals originating from excited photocatalysts, signals related to excitation of photosensitizers followed by charge transfer to semiconductors or metals, and signals arriving from short-lived species formed on the surface of photocatalysts during the course of a photocatalytic process.

In what follows, several samples are presented representing these three classes. Whenever possible, the transient IR changes are discussed in the context of other transient measurements, and in particular transient changes as measured by the UV–vis absorption/reflection technique.

Generally speaking, the variations in the IR spectra of photocatalysts can be manifested by a shift in the whole baseline of the absorption spectrum, by a change in the intensity of existing peaks or their lineshape, by formation of new peaks and by splitting of existing peaks. In principle, the catalysts are not supposed to go through irreversible processes, therefore signals arriving from the photocatalysts are expected to decay over time. The decay constants, and the effect of the experimental conditions (for example, temperature and the presence of charge scavengers) may provide complementary information on the properties of the photocatalysts.

A positive drift of the whole spectrum (i.e. $\Delta_{abs} > 0$ regardless of wavenumber) may indicate that absorption of the IR photons excites charge carriers into a continuous band rather than to discrete levels. This transition could be either within the conduction band or from shallow midgap trap-states (figure 7). Intraband transitions require tight coupling with lattice phonons in order to conserve momentum. This results in increased absorption upon decreasing the wavenumber ($\nu$), according to $\Delta_{abs} \sim A V^{-g}$. The exponent ‘$g$’ may vary according to the type of coupled phonons ($g = 1.5$ for acoustic phonons in indirect semiconductors, 2.5 for optical phonons, 3–3.5 for ionized impurities) [64].

While a change in the whole baseline reflects IR absorption by electrons, changes in the intensity and location of specific vibrational peaks are likely to reflect changes in the local environment at which the nuclei vibrate. Transient appearance of new peaks and transient disappearance of existing peaks may be caused due to the presence of trapped charge carriers, provided that they are trapped in a specific place for a time longer than the time required for vibration ($10^{-14}$–$10^{-13}$ s). In that case, the potential experienced by the nuclei is altered and consequently the absorption frequencies are shifted. A small shift in terms of peak location and intensity, may affect the lineshape, whereas a large shift will facilitate to distinguish between the two populations. The number of spectral peaks affected by trapped charges can be quite large for two reasons: (a) due to the nature of normal modes, each nucleus may participate in several modes of vibration (b) each photocatalyst is likely to have several types of traps. Further contribution to inhomogeneous broadening may arise from interactions between vicinal traps and between neighboring charges.

![Figure 7. IR absorption mechanisms for UV-excited photocatalyst, leading to structure-free up-shift of the whole IR spectrum (left) and the corresponding changes in the transient IR spectrum (right). The dashed trace (A) represents the pre-excitation spectrum, whereas traces B, C and D represent the spectra at increasing relaxation times.](image_url)
Assuming that samples have a constant concentration and thickness, the intensity of a specific vibrational peak reflects a change in its (wavelength-dependent) absorption coefficient (\(\varepsilon\)). It is well established \cite{65} that
\[
\varepsilon \propto |\mu_{01}|^2 \propto \left(\frac{d\mu}{dq}\right)_{q=0}^2
\]
where \(|\mu_{01}|\), the transition moment between levels 0 and 1 is defined as \(|\mu_{01}| \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi_0^* \mu \psi_1 \psi_0 \xi \psi_1 d\xi d\zeta\) and \(\frac{d\mu}{dq}\) is the derivative of the dipole moment with respect to the displacement coordinate, near the equilibrium position of the vibrational mode. The presence of trapped charge carriers is likely to affect this derivative, and, accordingly, to alter the intensity of the peaks. The effect is expected to vary between different modes. It is known that substantial dipole derivatives arise due to vibronic interactions with low lying electronic transitions \cite{66}. Exceptional dipole derivatives arise when charge, self-localized in a polaron, moves in response to a vibration with appropriate symmetry, generating a strong dependence of dipole moment on vibrational displacement \cite{67,68}, as indeed was evidenced in the case of tetracyanoquinodimethane \cite{69}. It should be noted that the strength of the transition moment may be influenced not only by the presence of polarons but also by the presence of excitons \cite{70}, by dipole-dipole interactions \cite{71} and by changing the angle between the electric field vector of the excitation beam relative to the vibrational displacement vector \cite{72}.

A change in intensity, coupled with a small shift in the location of a specific peak is expected to be manifested by a change in the lineshape of the peak. Another cause for an asymmetric lineshape is the Fano effect, resulting from coupling between the discrete modes of vibration and the broad continuum of the conduction band \cite{73}.

The surfaces of photocatalysts have larger density of defects than the bulk, giving rise to larger density of states within the bandgap, which may serve as shallow traps or as deep traps. The surface is characterized also by the presence of physisorbed and chemisorbed molecules. Trapped charges in the vicinity of the surface may affect the distance and orientation of molecules adsorbed on the surface. Accordingly, it can be expected that trapped charge may affect the IR spectrum of adsorbed molecules, and, in particular, in the case of chemisorption, any peaks that represent the interaction between the surface and the chemisorbed molecules. Monitoring the effect of charge scavengers (whether electron scavengers or hole scavengers) on the transient changes in IR spectrum provides a way to differentiate between bulk phenomena versus surface phenomena, as the scavengers operate directly on the surface \cite{36}. A comparison between the effect of hole scavengers to that of electron scavengers facilitates to trace the type of charge carriers responsible for the measured alterations in the spectra. Another way, used for differentiation between bulk and surface phenomena is by using attenuated total reflection (ATR) IR spectroscopy. Here, a very elegant way to maximize the ability of the ATR technique in probing the surface was presented by Herlihy \textit{et al} who measured the

\[\text{Figure 8. The logarithm of the difference spectrum in TiO}_2 \text{ versus the logarithm of the wavenumber at various post-excitation times: 50 ns (squares), 1 \mu s (diamonds), 2 \mu s (triangles), 5 \mu s (X), 10 \mu s (+), 20 \mu s (filled circles). The figure was prepared based on data presented in [33].}\]

TRIR ATR signals of n-SrTiO\textsubscript{3} submerged in water, at a variable interface distance from the ATR crystal \cite{36}. Similar to the way by which ATR and external reflection modes are used for studying orientation in self-assembled monolayers, differentiation between the effect of p-polarized beam versus that of s-polarized beam revealed that the surface Ti-O stretch mode was perpendicular to the surface of the lattice. Another interesting outcome of this work was the observation that subsurface vibrations may couple to both solvent and electron dynamics.

4. Photocatalysts studied by TRIR

4.1. Titanium dioxide

Transient changes in the IR spectrum of titanium dioxide was measured by a dispersive approach, following excitation by a pulse of 355 nm light. A fast increase (faster than 50 ns) in the absorption of the whole IR spectrum (1000–4000 cm\textsuperscript{-1}), followed by a gradual decay back to the pre-excitation spectrum within 100 ms, was observed by Yamakata \textit{et al} \cite{31,74}. Despite its structure-less, non-specific nature, the extent of absorption change was found to negatively correlate with the IR wavenumber according to \(\Delta_{\text{abs}} = A \nu^{-(1.7 \pm 0.3)}\) \cite{75} (figure 8), which fits, within experimental error, the theoretical expected correlation.

As said above, the observation that the increase in the IR absorption was non-specific indicates the transition of photogenerated electrons into the conduction band either in an intra-band manner or from shallow midgap trap-states \cite{71}. In the latter case, the states in TiO\textsubscript{2} are expected to reside less than the energy corresponding to 1000 cm\textsuperscript{-1}, i.e. less than 0.12 eV from the conduction band. According to this explanation, the decay in the signal reflects the kinetics of recombination. A
faster decay of the signal was observed in the presence of O₂. This effect was attributed to capturing of electrons within 10–100 μs. In the presence of water vapor, a slow-down in the recovering of the IR signal was observed already within 2 μs from excitation. This effect became more noticeable at longer times so that a considerable amount of signal was measured even after 0.9 s. The effect of water was attributed to stripping of holes (injection of electrons from OH⁻ to the valence band), thus reducing the rate of recombination.

Subtracting the electron spectrum from the transient absorption spectrum, enabled to obtain the spectrum of trapped holes [76]. By monitoring the effect of electrons and holes scavengers it was concluded that trapped holes and electrons were localized on the surface of the photocatalyst whereas the free electrons were distributed in the bulk. A considerable body of research was performed on Pt/TiO₂, both under vacuum and in the presence of water vapor [77]. At short times (less than 2 μs) the effect of water vapor on the transient Δabs profile was similar for both TiO₂ and Pt/TiO₂. Nevertheless, this effect was quite different at longer times. Here, the presence of water vapor increased the decay rate of the Δabs profile with Pt/TiO₂, relative to vacuum, but decreased the decay rate in pristine TiO₂. This accelerated decay with Pt/TiO₂ was ascribed to an electron-consuming reaction by water.

More studies have been performed with Pt/TiO₂ exposed to methanol/water vapor mixtures [78] and to 2-propanol [79]. The exposure to methanol/2-propanol preserved the initial Δabs for at least 5–10 μs, manifesting the prevention of recombination by virtue of exhausting the holes. It should be pointed out that in these studies, the Δabs trace was used not only to follow the amount of excited electrons as a function of time, but also, by observing transient changes in specific bands at 1700 cm⁻¹ and 1640 cm⁻¹, to track the formation kinetics of acetone and to identify the presence of an intermediate (negatively charged acetone). Another specific change in the transient spectrum of TiO₂ had to do with the signal of OH adsorbed on the surface of the photocatalyst. Here, a transient increase in the absorption at 3654 cm⁻¹ was observed, together with a decrease at 3696 cm⁻¹ [71]. These changes were found to be relatively slow so that complete recovery of the spectrum was observed only after 100 ms.

Developing of means for measuring transient changes in the IR spectrum at the sub-nanosecond time domain enabled to differentiate between trapping at shallow traps (typical time = 15 ps) and trapping at unreactive deeper traps (typical time = 150 ps) [80]. Quite counter-intuitively, no correlation was found between the number of electron trapping sites and the decay rate to the deeper traps. Moreover, the quantitative relationship between the activity (as probed by the photocatalytic degradation rate of dichloroacetate) and the transient behavior at the sub nanosecond timescale was reported to be unclear.

A review, summarizing the work performed by non-TRIR techniques, in particular transient UV absorption, on the trapping dynamics of photogenerated electrons and holes in titanium dioxide, presented a large diversity in the measured decaying timescales, as t₁/₂ ranged from 50 fs to 50 ps for trapping, 1 ps to more than 20 ns for recombination and 300 ps to 100 μs for interfacial charge transfer [81]. In general, a correlation was found between longer decay times of Δabs in transient UV absorption/reflection measurements and higher activities. For example, time resolved emission quenching studies comparing different forms of titanium dioxide found an average decay constant of 1.99 ns for anatase and 1.65 ns for the less active rutile phase [82]. Likewise, it was found that decorating titanium dioxide with Pt islands, acting as electron sinks, extended the life time of trapped holes from the picosecond to the millisecond time scale [8, 83], in correlation with the observation of higher activity.

An interesting finding is the observed dependence of the relaxation time of the transient IR signal at 2100 cm⁻¹ on the sub-bandgap excitation energy, in particular the difference between excitation with 400–800 nm photons, versus excitation with 1000–1300 nm photons [84]. This difference provided a way to distinguish between transitions to the conduction band versus transitions between localized states within the bandgap. In a later work it was found by TRIRA-ESS that doping with Mg may act to eliminate intrinsic deep defect states and to weaken shallow defect states [63]. The decay curve at 2000 cm⁻¹ of UV–vis excited B-doped TiO₂ was compared with that of same material that did not contain B atoms on its surface. A larger signal and a slower decay of the latter gave rise to the claim that the amount of trapped electrons above the VB in B-free surface of TiO₂ was much larger than that of B-containing surface. In parallel, charge recombination was much faster in B-containing surface TiO₂ than in B-free surface of a B-doped TiO₂ [85]. Another surface effect in TiO₂ studied by TRIR is the effect of water on hole trapping. Here, it was shown that the first layer of adsorbed water enhances hole trapping on nanospheres but less on well-faceted nanoparticles [86, 87]. A comparison between the mid IR decay kinetics of anatase, rutile and P25 TiO₂ (comprising of 70%–80% anatase and 30%–20% rutile) in the presence of electron scavengers and hole scavengers gave rise to the claim that electrons migrate from rutile to anatase [88].

4.2. Graphitic carbon nitride

Graphitic carbon nitride (g-C₃N₄, denoted herein as gCN) is a metal-free conjugated semiconductor. This material attracts an increasing interest in its use as a photoactive material, in particular for water splitting, due to its low cost, the abundance of the elements it is made of, its adequate band gap for utilizing solar light (2.7–2.8 eV), and a conduction band position that facilitates the reduction of hydrogen as well as that of O₂. The material was modified by various ways in order to improve its efficacy, for example by nano-structuring [89], doping [90], copolymerization [91] and coupling with other semiconductors [92]. The effect of preparation procedure and temperature on the structural, physical and eventually on the photocatalytic activity was, and still is, a matter of debate [93].

Transient photoluminescence (PL) measurements of graphitic carbon nitride have revealed a three component relaxation curve, whose time constants (1, 5, 30 ns) depended on
the direction of exciton migration [94]. The electron transfer between graphitic carbon nitride and its exfoliated form was studied by femtosecond transient absorption spectroscopy performed in the NIR region of the spectrum [95]. The large number of observable vibrational transitions in gCN makes this material ideal for studying its transient behavior following excitation by means of TR-FTIR in the mid-IR region.

The transient IR signal of gCN was studied at a 2.5 ns resolution following pulsed excitation at 355 nm [96]. Two types of samples were compared. Both types, termed hereby as gCN510 and gCN650, were prepared by pyrolysis of melamine, nevertheless at different temperatures (510 °C and 650 °C, respectively). The main difference between these two types was the larger extent of heptazine polymerization in gCN650, as could be inferred from the positive correlation between the C:N and the C:H ratios versus the preparation temperature [97]. Figure 9(A) presents the evolution of the spectrum of gCN510 following excitation. The evolution involves specific changes in the intensity and location of the various peaks of gCN510. The temporal profile of the changes varied among peaks, suggesting the existence of a complex scenario, mapped onto the IR spectrum. Some peaks revealed a fast increase in the intensity (1038 cm\(^{-1}\), 1612 cm\(^{-1}\)) followed by fast decay (within 40 ns) to the pre-excitation shape. New peaks emerged a few ns after excitation (1981, 2198, 2415, 2619, 2695 cm\(^{-1}\)). These peaks were gradually red-shifted to 1879, 2109, 2287, 2517 cm\(^{-1}\) before disappearing app. 80 ns from excitation. A weak peak at 3613 cm\(^{-1}\) became considerably stronger right after excitation and was split at 40 ns into a doublet at 3562 cm\(^{-1}\) and 3715 cm\(^{-1}\). The intensity of the doublet was gradually reduced and the two peaks eventually merged some 180 ns from excitation. More details on the assignment of the peaks can be found elsewhere [89]. Despite the very high similarity between the pre-excitation spectrum of gCN510 and that of gCN650, the temporal behavior of the latter was found to be very different from that of the former (figure 9(B)). The most significance difference was the observation of very strong non-specific absorption along the whole measured range, beginning some 30 ns after excitation and lasting approximately 25 ns. This so-called ‘IR-blackening’ effect, was observed also when the gCN650 samples were exposed to electron scavenger (methyl viologen) during excitation but disappeared whenever the samples were exposed to hole scavengers such as ethanol or benzyl alcohol.

The difference between the transient behavior of gCN650 and that of gCN510 was explained by the presence of defects in the latter (NH/NH\(_2\) groups due to imperfect polymerization of the heptazine units), located all-over the gCN particle, not necessarily on its edges (figure 10). These irregular defects act to trap holes away from the surface. The irregularity of the positioning of the defects prevented defect-defect coupling, i.e. splitting of the energy levels of the defect sites. This is not the case in gCN650, where the high extent of polymerization by fast decay (within 40 ns) to the pre-excitation shape. New peaks emerged a few ns after excitation (1981, 2198, 2415, 2619, 2695 cm\(^{-1}\)). These peaks were gradually red-shifted to 1879, 2109, 2287, 2517 cm\(^{-1}\) before disappearing app. 80 ns from excitation. A weak peak at 3613 cm\(^{-1}\) became considerably stronger right after excitation and was split at 40 ns into a doublet at 3562 cm\(^{-1}\) and 3715 cm\(^{-1}\). The intensity of the doublet was gradually reduced and the two peaks eventually merged some 180 ns from excitation. More details on the assignment of the peaks can be found elsewhere [89]. Despite the very high similarity between the pre-excitation spectrum of gCN510 and that of gCN650, the temporal behavior of the latter was found to be very different from that of the former (figure 9(B)). The most significance difference was the observation of very strong non-specific absorption along the whole measured range, beginning some 30 ns after excitation and lasting approximately 25 ns. This so-called ‘IR-blackening’ effect, was observed also when the gCN650 samples were exposed to electron scavenger (methyl viologen) during excitation but disappeared whenever the samples were exposed to hole scavengers such as ethanol or benzyl alcohol.

The disappearance of the ‘IR-blackening’ effect in the presence of hole scavengers, but not in the presence of electron scavengers, proposed that the phenomenon was caused by holes arriving at the surface. This explanation seemed to be in-line with the observed lag-time of 30–35 ns. Such lag-time was not observed by transient photoluminescence measurements [87], suggesting that occupying the intra bandgap miniband from which photoluminescence occurs was not strongly coupled to the surface-trapping of holes.

The difference between the transient behavior of gCN650 and that of gCN510 was explained by the presence of defects in the latter (NH/NH\(_2\) groups due to imperfect polymerization of the heptazine units), located all-over the gCN particle, not necessarily on its edges (figure 10). These irregular defects act to trap holes away from the surface. The irregularity of the positioning of the defects prevented defect-defect coupling, i.e. splitting of the energy levels of the defect sites. This is not the case in gCN650, where the high extent of polymerization
prevented trapping in the bulk and promoted hole trapping on the surface. The trapped holes either populated discrete surface states located less than 0.07 eV below the conduction band or formed a miniband within the bandgap as a consequence of splitting of large number of vicinal trap-states at the surface. Since the active species are the electrons, gCN510 was expected to have a higher activity than gCN650, as indeed was found.

Of large interest was also the ensemble of peaks at 1900–2800 cm$^{-1}$. These peaks, which are hardly noticeable in non-excited gCN, became quite noticeable immediately after excitation in both types of samples. Their appearance was accompanied by a gradual red-shifting, peaked 60 ns after excitation, after which the peaks shifted back to their original position. This red shift was explained by IR transition not from the ground vibrational levels but from some populated vibrationally excited modes, reflecting the anharmonicity of the potential, or, alternatively, by an effect of the trapped charge on the internuclear potential.

The large diversity of transient spectral changes observed with graphitic carbon nitride demonstrate how photoinduced charge carriers may interact locally with the photocatalyst thus affecting localized vibrational modes. The temporal behavior of gCN serves as a very good example for the potential of TRIR, and, in particular, step-scan TRIR, as a tool for understanding photocatalytic phenomena.

4.3. BiOCl

The bismuth oxyhalide family of photocatalytic materials (BiOX, where X = F, Cl, Br, I or a mixture of them) attracts an increasing interest due to its inherent internal polarization caused by the layered structure of its members, comprised of Bi$_2$O$_2$ layers located between two layers of halogen atoms [98], which assists charge separation. The activity is known to be affected upon faceting the particles of the members of this group of materials. For example, the degradation of rhodamine B [99] was found to be promoted significantly in BiOCI particles that exposed large {001} facets. This effect was explained by the presence of high density of oxygen atoms at the surface, which contribute to the formation of oxygen vacancies in the bulk, forming shallow traps below the conduction band [100] or, in the case of photosensitization, to the accommodation of electrons injected from the photosensitized dye [101].

Transient changes in the FTIR signature of BiOCI were measured by the step-scan approach, revealing an interplay between transient IR changes, particles’ faceting and photocatalytic activity. Six types of BiOCI particles were prepared by applying a surface modifier (SDBS) during preparation [102]. The six types differed by the orientation of their facets and by the particles’ size, as manifested by SEM imaging and by monitoring the ratios between XRD peaks. By photodeposition of platinum islands on these particles, it was established that photoinduced electrons tend to accumulate primarily at the {001} facets.

Figure 11 presents the Step-Scan FTIR transient spectra of four types of pristine BiOCI. The main spectral transient change was an increase in the intensity of the Bi–O stretching mode peak around 523 cm$^{-1}$. The increase began, for all types of particles, approximately 10–15 ns after excitation, reached a maximum 25–50 ns from excitation and returned to its original intensity 70–130 ns from excitation. The increase in intensity correlated positively with the time required for returning to the original pattern. Except for one type of sample, increasing the ratio between SDBS and Bi during preparation led to sample that revealed less intensity growth in their 523 cm$^{-1}$ peak during the transient measurements. A blue shift to 550–580 cm$^{-1}$ was also observed. Returning to the pre-excitation position of the peak coincided with the decrease in the intensity to the pre-excitation values. Samples having large extent of (001) facets revealed a growing peak at 620–640 cm$^{-1}$.

A dramatic change in the transient behavior was observed upon exposure to propanol, manifested by a decrease in the transient intensity of the Bi–O peak (figure 12(B)). In contrast, exposure of the BiOCI particles to the electron scavenger methyl viologen led to a substantial increase in the transient Bi–O peak, relative to the behavior of this peak in the absence of any scavenger (figure 12(A)).
The activity of the various types of BiOCl was found to negatively correlate with the duration of the transient signals (figure 13), and with the maximal intensity of the transient Bi–O peak. In general, transient signals arising from photocatalysts (for example, signals measured by TRMC and absorption spectroscopy) correspond to the presence of free charge carriers. Therefore, the rate of decay in the transient signals is inferred as indicating a reduction in the concentration of free charge carriers, due to recombination, or on the other hand, trapping in shallow traps leading to photocatalytic activity. Accordingly, in some cases slow decay of transient signals is regarded as predicting high efficiency [103], whereas in other cases the opposite is inferred [104, 105]. The situation with the transient IR signal of BiOCl was somehow different. The negative correlation between duration (and intensity) of the transient signal versus the photocatalytic activity was explained based on the notion that the measured signal corresponded to the presence of species that were doomed to disappear without causing any surface reaction, for example species that had been trapped in deep traps. These trapped carriers could not participate in the surface reactions, hence the negative correlation between photoactivity and duration of transient signal.

For BiOCl, there were several indications that the transient IR signal originated at the surface of the photocatalyst, among which were the fact that the duration of the transient signal was found to be longer in small particles than in large particles and the effect of scavengers, operating at the surface. It was claimed that since the \{001\} planes were quite similar in all types of particles, the culprit for long signal duration and low photoactivity originated from lack of faceting in the side-walls. The fact that propanol, a hole scavenger, diminished the
transient FTIR signal, whereas methyl viologen, an electron scavenger, increased the intensity and duration of the transient signal suggested that only one type of carriers is responsible for the transient signal. Therefore, the Scan Step TRIR measurements seemed to contradict the notion that trapped excitons are responsible for the activity, as proposed based on photoluminescence measurements [106].

4.4. BiVO₄

Bismuth vanadate (BiVO₄) attracts an increasing scientific interest as a photoactive material, due to its narrow bandgap (2.3–2.9 eV, depending on phase), electronic structure, which is appropriate for water redox processes under visible light, low toxicity, stability in water and relatively low cost. This photocatalyst forms three main phases: monoclinic scheelite (ms), tetragonal zircon (tz) and tetragonal scheelite (ts) [107]. In the tetragonal phase, the Bi³⁺ cations are located at the centrosymmetric sites of BiO₆ polyhedrons, whereas in the monoclinic phase the Bi³⁺ cations are located off-center. Monoclinic bismuth vanadate is known to reveal excellent photocatalytic properties in comparison with the less-studied tetragonal phase. For this reason, almost all studies on the photoinduced properties of bismuth vanadate were performed on its monoclinic phase. Despite the excellent position of the energy bands in bismuth vanadate, its implementation as a photocatalyst is problematic due to its poor carrier transport properties (carrier mobility of 4 * 10⁻² cm² V⁻¹ s⁻¹). This is partially balanced by the relatively long life (40 ns) [108] of its photoinduced carriers, yielding a diffusion length as long as 70 nm [109]. Excitation of bismuth vanadate takes place within less than 0.5 ps [100]. For UV–vis photons, absorption involves coherent generation of the Ag mode phonon associated with motion between Bi³⁺ and VO₄⁻. This mode has a frequency of 62 cm⁻¹, corresponding to an oscillation period

Figure 14. SEM images of BiVO₄. (A) octahedron-shaped particles (scale bar = 400 nm) (B) prismatic-shaped particles (scale bar = 1000 nm). Reproduced with permission from [111].

Figure 15. Transient changes in the IR spectrum of monoclinic BiVO₄ (A) octahedron-shaped particles (B) prismatic-shaped particles.
of 0.5 ps. Following absorption, structural distortion in the lattice occurs at a time constant of 7–14 ps [100, 110].

The transient IR spectrum of two types of monoclinic bismuth vanadate was measured by step-scan TRIR [111], using a 5 ns excitation pulse at 355 nm. The two types differed in their shapes (figure 14). Type A had an octahedron shape, made of [120] family of facets, whereas type B was characterized by a prismatic shape. For both types, the only phase that could be recognized by XRD was the monoclinic phase. Both had similar particles’ size (800–1000 nm) as well as similar crystallites’ size, calculated to be 32 nm by the Scherrer equation. Their Raman spectra was almost identical and corroborated known studies [112]. Here, a strong V–O (s) peak appeared at 813 cm−1, a weak shoulder at 740 cm−1 was assigned to V–O (as) and a split V–O bending mode was noticed at 360 cm−1/323 cm−1 for the octahedron samples and 358 cm−1/325 cm−1 for the prismatic samples. A peak at 200 cm−1 for both types was assigned as Bi–O.

Figure 15(A) presents the transient changes in the FTIR spectrum of the octahedron-shaped monoclinic BiVO₄ particles. Prior to excitation, the spectrum was dominated by a wide band (520 cm−1–930 cm−1), peaked at 740 cm−1 with shoulders around 650 cm−1 and 810 cm−1 assigned to VO₄ [113, 114]. The Bi–O peak at 470 cm−1 was hardly noticed. Upon excitation, a growth at 600 cm−1 and at 800 cm−1 was observed within a few ns. Then, a noticeable increase in the shoulders of the wide band was observed, forming two peaks, around 660 cm−1 (assigned to Bi–O bending vibration [115]) and 800 cm−1, which surpass the V–O (asymmetric stretch) at 740 cm−1. In parallel, a growth in the intensity at 470 cm−1 (Bi–O) was noticed, beginning some 25 ns from excitation. These transient effect diminished within more than 175 ns. The transient behavior of the prismatic particles (figure 15(B)) was quite different, despite the common phase (monoclinic) both types of particles shared. Here, no splitting of the VO₄ band was observed and the transient changes were hardly noticeable.

The fact that the two types of samples differed by their shape, but not by their phase, suggests that the different spectral behavior reflected surface properties, rather than bulk properties. Indeed, Pt islands could not be deposited by photoreduction of H₂PtCl₆ on facets of the octahedron-shape particles, thus suggesting that the concentration of photoinduced electrons on these {120} facets was negligible. This was not the case with the prismatic particles, where photodeposited Pt islands were observed on part of the facets.

The photocatalytic activity of the octahedron-shaped monoclinic particles towards the reduction of Cr⁶⁺ to Cr³⁺ was found to be worse than that of the prismatic monoclinic particles by a factor of 2. This ratio was increased considerably when the photocatalytic measurements were performed in the presence of hexanol, a hole scavenger. These results can be rationalized based on examining the rate limiting half-cell reaction. Since all facets of the octahedron-shaped particles tend to accumulate holes, it is sensible that the reduction half-reaction was the rate limiting reaction. Accordingly, it is unlikely that increasing the rate of the oxidation half-reaction would contribute to the overall rate, since, eventually, the rates in both half-reactions have to be equal to prevent long term charging. In contrast, the prismatic particles may accumulate both electrons and holes on their surfaces. Consequently, in the absence of a sacrificial specie the rate limiting half-reaction is not the reduction of the chromium ion, but rather the oxidation of water. Therefore, any addition of a hole scavenger is expected to affect considerably the overall rate, as indeed was found.

Having this explanation in mind, the transient changes in the IR spectrum of the octahedron-shaped particles may be explained as originating from deep-trapped charge carriers, most likely at the surface or in close proximity to it. For BiVO₄, the nature of the trapped carriers could not be elucidated based on the FTIR signal solely. Other works, using a variety of techniques, suggested that the atomic distance between bismuth and oxygen atoms is contracted following excitation [100]. Alternatively, DFT calculations suggested that the symmetry of the four V–O bonds is broken into two pairs of equi-distance bonds due to the formation of localized small polarons following electron trapping on V⁵⁺ sites [116] or to three equi-length bonds and a fourth longer one. In parallel, holes are trapped on oxygen sites, however, in a less localized manner [117].

4.5. Other oxides

The dynamics of photoexcited electrons in NaTaO₃ was traced by dispersive TRIR spectroscopy [118]. Similar to the observations in titanium dioxide, the excited electrons presented a featureless increase in the absorption spectrum, which decayed within 0.5 ms from excitation. A comparison between various La-doped photocatalysts revealed a correlation between the amount of electrons and the measured water-splitting activity. Based on measuring the decay signal at 2000 cm−1, obtained from La-doped NaTaO₃, it was concluded that the time required for electron transfer from the photocatalyst to the co-catalyst was typically 1 μs. The effect of CoOₓ co-catalyst on the (μs to ms range) dynamics of photogenerated charge carriers in tantalum nitride revealed that most of the electrons were deeply trapped at defects originating from oxygen vacancies and reduced Ta atoms [119].

Hematite (α-Fe₂O₃) is currently regarded as one of the most promising photoanode materials due to its 2.1 eV bandgap, which is suitable for utilizing solar energy, and to its low cost, low toxicity and high stability. Despite its promising prospective for photoelectrochemical water splitting and the intensive work performed on its transient UV–vis absorption/reflection properties, there is hardly any work on its TRIR behavior. In one of the few works, TRIR measurements of free carrier intra-subband transitions at 2000 cm⁻¹ showed an ultra-fast decay component (0.2 ps). Wavelength-dependent kinetics were observed (in comparison with 15000 cm⁻¹), suggesting that the ultrafast decay component was not due to direct electron–hole recombination but rather due to trapping and cooling of free electrons [120].

Tungsten trioxide (WO₃) is another promising photocatalyst (E₉ = 2.6 eV). Transient IR absorption spectra was used in the context of studying the effect of particle size on its water
oxidation activity. It was found that the recombination of photoexcited electrons in the large particles was slower than that in fine particles [121]. The fast recombination in the small particles was attributed therefore to surface recombination. In a different work [122], a comparison was made between the temporal decay of $\Delta_{\text{abs}}$ at 2050 cm$^{-1}$ of WO$_3$, BiVO$_4$ and a heterojunction system. The differences in the temporal behavior confirmed the notion of charge carrier separation under visible-light excitation, persisting up to microseconds.

4.6. TRIR spectroscopy of dye-sensitized oxide photocatalysts

Interfacial electron transfer (ET) between adsorbed dyes and semiconductors are of large importance for designing highly efficient photovoltaic devices, in particular, dye-sensitized solar cells (DSSCs). The ultrafast electron injection in RuN$_3$-sensitized TiO$_2$ was studied mainly by transient absorption [123–125], that observed a fast ($<100$ fs) singlet metal-to-ligand charge transfer ($1\text{MLCT}$), and a slower (tens ps) triplet metal to ligand transfer ($3\text{MLCT}$). The same methods were used to study the effect of adsorbate energetics, excitation wavelength and electronic coupling of the process.

Direct monitoring of electron transfer rates from Ru bipyridine family of sensitizers to TiO$_2$, ZrO$_2$ and SnO$_2$ was accomplished by measuring changes in the mid-IR absorption spectra [29, 126] upon excitation by visible light. Similar to pristine TiO$_2$, an increase in the absorption along the whole spectral range was observed. This non-specific adsorption signal observed in the dye/TiO$_2$ system was attributed to IR spectral range was observed. This non-specific adsorption signal observed in the dye/TiO$_2$ system was attributed to IR absorption by electrons injected from the dye to the conduction level of the semiconductor. Based on the ultrafast injection of carriers from Ru–Bpyridine dyes into the TiO$_2$ it was claimed that the overall cell efficiency was not governed by injection but rather by trapped charge that reduce the quantum yield or, alternatively, by very slow recombination rates, having time constants of microseconds [29].

The use of transient IR spectroscopy facilitated to study the effect of different solvent environments, suggesting that the presence of adsorbed water lowered the band edge of TiO$_2$ thus diminishing the differences between a variety of nonaqueous solvents such as MeOH, EtOH and DMF [32]. Likewise, the kinetics of electron injection from a rhenium-bipyridine complexes adsorbed via different spacers to TiO$_2$ was studied by following transient changes in the IR spectrum of the dye. The temporal decay of $\Delta_{\text{abs}}$ at 2050 cm$^{-1}$ was observed. The red-shifted peak was attributed to vibrational transition in the MLCT excited state, since the CN stretching mode of an oxidized dye was known to be shifted further to the red (2025 cm$^{-1}$). By comparing transient changes in the spectra of coumarin-343 (which hardly absorbs in this IR region) attached to ZnO, it was possible to differentiate between signal attributed to injected electrons and signal that represented the excited state in the dye.

Figure 16 was sketched based on the results and explanations of Anderson et al [114], describing post-excitation transient IR changes in an ReCOA dye attached to ZnO. The Figure illustrates the positive and negative changes in the CO stretch vibrational transitions of the dye at various times. In addition to that, an increase in the absorbance along the whole spectral range was observed. Similar to other cases, this upward shift in absorption was attributed to excited electrons due to absorption by the semiconductor. This allowed to portray a detailed scenario of the sensitization and charge transfer process (figure 16(B)). Overall, the figure demonstrates the way by which transient changes in the IR spectrum of a single vibrational mode may provide detailed information on the whole charge injection scenario. It should be noted that overall, the same two timescales observed for (multi)pyridine dyes attached to TiO$_2$, reflecting a fast injection from the singlet state and a slower component from a lower energy triplet state, were found also in ZnO and ZrO$_2$ systems.

The charge transfer between a Ru complexes and titanium dioxide was studied by exciting the dye at
532 nm and measuring the absorption signal at 3440 nm (2906 cm\(^{-1}\)), based on the assumption that the 2906 cm\(^{-1}\) photons are primarily absorbed by the electrons in TiO\(_2\) [72], hence the absorption difference in the IR spectrum should be proportional to the concentration of electrons in the oxide, and the decay curve of the absorption should reflect the decay in the number of electrons (figure 17).

It was found that the electron injection yield from N3 dye to small particles (typical length 20 nm) was three times higher than the yield in the injection to large (typical length 170 nm) TiO\(_2\) particles [128]. This method was used to compare between dyes (N719, GD2, P251) with respect to their efficacy in injecting electrons to the oxide, as well as to differentiate between several decay mechanisms. For example, the dye N719 revealed a fast injection term with a time constant of 250 fs together with a slow term of 50 ps [129].

The same method was used to study plasmon-induced charge transfer in gold-TiO\(_2\) particles. Here, the decay in the IR transient absorption signal served to estimate charge recombination kinetics as a function of the diameter of the TiO\(_2\) particles [130, 131]. It was found that the charge recombination kinetics depended strongly on the particle size; for diameters in the range of 9–50 nm, the larger the diameter was, the slower were the recombination kinetics. The recombination kinetics were found to be independent of excitation intensity and the amplitude of the transient absorption signal was almost proportional to the intensity of the exciting laser, indicating lack of both non-linear excitation and second order recombination processes.

4.7. Organo-metallic photocatalysts

Molecular photocatalysts (mostly organo-metallic), operating as dissolved molecules in solutions, attract an increasing attention. From the point of view of TRIR measurements, this class of photocatalysts differs from particulate photocatalysts by two major factors. The first is the smaller charge diffusion distance with its obvious effect on the timescales involved in these processes, which are orders of magnitude shorter than the typical timescales in photocatalytic particles or films. Consequently, transient techniques that cannot provide temporal resolution at a level of picoseconds might be inadequate. The second factor is the effect of the solvent, due to its specific interactions with the molecular photocatalyst. The importance of the solvent is derived directly from the basic formulation of Marcus theory on charge transfer, as the solvent plays a key role through its polarization [132], affecting both the energetics of stabilizing species and the molecular dynamics that guide the electronic motion.

Among the many organo-metallic molecular photocatalysts are rhenium bipyridyl complexes, known by their ability to reduce CO\(_2\) to CO [133]. Ultrafast transient UV–vis measurements have revealed that the chain of events leading to the photocatalytic process begins with absorption of 400 nm light that excites the complex to a singlet MLCT state, which intersystem-crosses into a vibrationally hot triplet MLCT state that cools within 20 ps and survives for 60 ns.

The effects of polar solvents on the transient IR absorption spectra of Re(R\(_2\)-bpy complexes, R being COOH or COOEt), were studied by Asbury et al. [134]. The researchers used a visible pump (400 nm) and an infrared probe (1820–2200 cm\(^{-1}\)). The vibrational relaxation times of the three carbonyl stretching modes were monitored. While the three modes showed mode-specific shift in their location, their dynamics was found to be quite similar.

Transient 2D-IR was used to study the vibrational modes in the electronically excited state of Re(4,4'-dimethyl-2,2'–bpy)(CO\(_2\))\(_2\)Cl in dimethyl sulfoxide (DMSO). Here the near UV pulse preceded the IR pump by a few ps. This allowed to observe the dynamics of the carbonyl stretching mode during the process of solvation and vibrational cooling [135] and to demonstrate that it was possible to enhance or suppress transient phenomena by using polarized light and altering the angle between the near-UV pulse and the IR [136]. A comprehensive discussion of the effect of solvents on the spectral diffusion of several rhenium catalysts, as measured by transient 2D-IR measurements, was presented by Kiefer et al. [137].

4.8. TRIR spectroscopy of short-lived species formed at the surface of photocatalysts

Tracing the appearance of intermediate products by IR spectroscopy was reported already at the early days of studies in photocatalysis [138]. However, these measurements, at a temporal resolution larger than seconds, are beyond the scope of this manuscript, as they describe the formation of species that are not inherently unstable. In what follows, the discussion herein is limited to phenomena occurring within less than 1 ms.

Within this context, transient IR measurements were used not only to follow changes in the concentration of charge carriers in photocatalysts, but also to track the presence of short lived intermediate species formed on the surface of the photocatalyst. As an example, dispersive TRIR was used to monitor the liquid (D\(_2\)O) phase oxidation of 2-propanol on Pt/TiO\(_2\) [139]. The main spectral changes were a growth of peak at 1700 cm\(^{-1}\), assigned to C\(\equiv\)O and a past increase (faster than
0.5 µs) of a triple peak around 1640 cm\(^{-1}\) that decayed within 4 µs. These changes were attributed to the appearance of the anion radical of acetone.

5. Pros and cons of using TRIR in studying photocatalytic processes

The given-above examples clearly demonstrate that transient infra-red measurements may provide important information on the pre-redox stages of the photocatalytic process. TRIR can be useful in particular in materials revealing specific, localized modes, whose spectral changes may assist to pinpoint the location of traps and to study the where-about of electrons and holes. It is hoped that finding some relations between transient behavior and photoefficiency will pave the way for better understanding of the generic fundamentals of photocatalysis.

Saying so, one has to admit that TRIR measurements have their cons. Probably, the most important is the cost, in terms of required skills, equipment, manpower and time. Generally speaking, the shorter the time scale is, the higher is the cost. Using step-scan TRIR may reduce these expenses, since one may use commercially available FTIR spectrophotometers. For this reason, a special attention was given in this manuscript to step-scan TRIR over dispersive or t-2D-IR, although the latter technique may provide a more detailed information and, currently, also at a better temporal resolution.

An inherent obstacle for using TRIR in studying photocatalysis originates from the fact that the IR spectra of many photocatalytic materials, in particular oxides, consist of very wide bands, made of overlapping modes. This limits considerably the ability to measure and to understand subtle spectral changes. Nevertheless, it should be noted that even in such cases, it is still possible to obtain valuable information as demonstrated with BiVO\(_4\) and BiOCl. Moreover, as time evolves, there is an increasing interest in studying (metal) organic photocatalysts. Almost all of these materials have distinct IR spectra, hence are appropriate for TRIR studies.

Correct interpretation of the transient spectral changes can be quite a difficult challenge. To overcome this challenge it might be necessary to integrate results obtained by other techniques. Another way would be to confront TRIR results with theoretical predictions. It is sometimes claimed that density functional theory (DFT) is quite limited in its ability to predict geometries and vibrational energy levels in electronically-excited species. Nevertheless, there are quite a number of cases where DFT was used successfully for this purpose. One of these cases is the identification of intermediate species, measured by pico-second time resolved IR spectroscopy during the photoinduced dinitrogen release from arylpentazole [140]. Another example is obtaining the structural parameters of the excited state of 3-hydroxylavone solvated in acetonitrile by comparing the vibrational bands of intermediate states with the expected spectra based on DFT calculations [141]. Such comparison enabled to compare between several models namely an isolated molecule model, aggregation with solvent molecules model and a polarizable continuum model. Hence, tight collaboration between theoreticians and TRIR experimentalists may considerably promote the scientific outcome of TRIR mesasurements.

6. Summary and outlook

Over the years, a lot of attention was given to the thermodynamics of photocatalysts, namely to the location of their valence and conduction bands on the energy scale. However, it should be noted that suitable bandgaps and band positions are no more than a pre-requisite, since having the right bandgap at the right redox potential cannot, by itself, assure any photocactivity [142]. For this reason, the kinetics of the photoinduced charge carriers at short times (i.e., prior to their surface redox reactions) has enormous importance. While significant work on the transient electronic spectra of photocatalysts has been performed, mostly by transient UV–vis absorption/reflection/pholuminescence techniques, the transient vibrational spectra of this class of materials did not receive the attention it deserves. Hence, the potential of TRIR as a tool for understanding the way by which inorganic photocatalysts operate is currently far from being exploited. This is in quite in contrast to the utilization of transient IR measurements for studying ultra-fast photo-induced processes that occur in molecules, in particular in biological systems, such as the photosynthetic systems.

This manuscript aims at increasing the scientific attention to the potential of transient vibrational spectroscopy as a complementary tool for understanding the first, crucial steps of photocatalytic processes, en-route for designing highly efficient photocatalysts. This was done herein first by describing the various techniques currently in use for measuring transient IR signals of photo-excited systems and discussing their pros and cons. Then, a variety of examples is given, representing different types of photocatalysts such as oxides (TiO\(_2\), NaTaO\(_3\), BiOCl, BiVO\(_4\)), photosensitized oxides (dye-sensitized TiO\(_2\)), organic polymers (graphitic carbon nitride) and organo-metalic photocatalysts (rhenium bipyridyl complexes). Tracing transient intermediate products by TRIR was also covered, nevertheless in brief, since this manuscript is focused on the photocatalysts rather than on the fate of specific adsorbed species. These examples span from materials with no IR fingerprint signal (TiO\(_2\)) to materials having a distinct spectrum showing well-defined, localized, relatively narrow, vibrational bands (gCN). In choosing the given-above examples, care was made to represent the several pump & probe techniques that are applied when studying transient IR spectroscopy, namely dispersive, transient 2D-IR spectroscopy and step-scan IR spectroscopy.

While this short review demonstrates how TRIR can be utilized to understand photocatalytic processes, it definitively does not claim that TRIR is the ‘silver bullet’ that, by itself, will provide the knowhow required for designing the most efficient photocatalysts. We do believe that comprehensive understanding will be achieved only by integrating a variety of methods, and under the auspice of theoretical tools. Nevertheless, in order to make such an integration fruitful, it is necessary to
exploit each of the techniques to its maximum. It is hoped that this manuscript will contribute to expand the use of TRIR as a viable and important technique among the arsenal of tools struggling to solve the mysteries behind photocatalysis.

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