Ultrafast Vibrational Spectroscopy Reveals the Primary Photochemical Processes of a Ferracyclobutadiene

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Introduction

Alkyne metathesis [1] is an important transformation in polymer chemistry. The reaction is transition-metal (TM) catalyzed and involves the intermediacy of metallacyclobutadienes (MCBD), i.e. four-membered heterocycles containing a TM as the heteroatom. MCBDs of groups 6, 7, and 9 TMs have been isolated and characterized in great detail [2]. However, MCBDs containing a group-8 TM have been entirely unknown until very recently, when the synthesis of a ferracyclobutadiene (FeCBD, species [A]) was reported (cf. Fig. 1a and Ref. below). Compound [A] is dressed with three carbonyl (CO) ligands in addition to the bidentate didehydroallyl moiety that is common to all MCBDs. We have recently initiated an extensive research program aimed at exploring the photochemistry of such FeCBDs in an effort to access yet unknown ferracycles with light and to explore their catalytic activities for alkyne metathesis and similar chemical transformations [3].
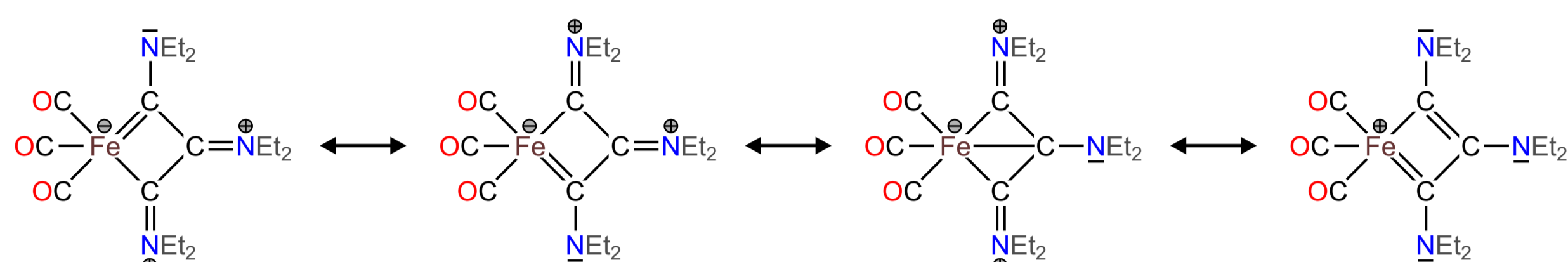
Mesomeric Lewis structures of the cationic FeCBD [A]. The couterion is BF_4^-.

## Molecular Structure and Linear Spectroscopy

[A] features a four-membered heterocycle that is characteristically puckered. The metal center is embedded in a square pyramidal coordination environment with one of the three CO ligands adopting the apical position and the two C_α atoms assuming basal positions. The two remaining equatorial sites are occupied by a pair of carbonyls. Thus, the three COs ehibit a local C_{3v}-symmetry around the metal center:
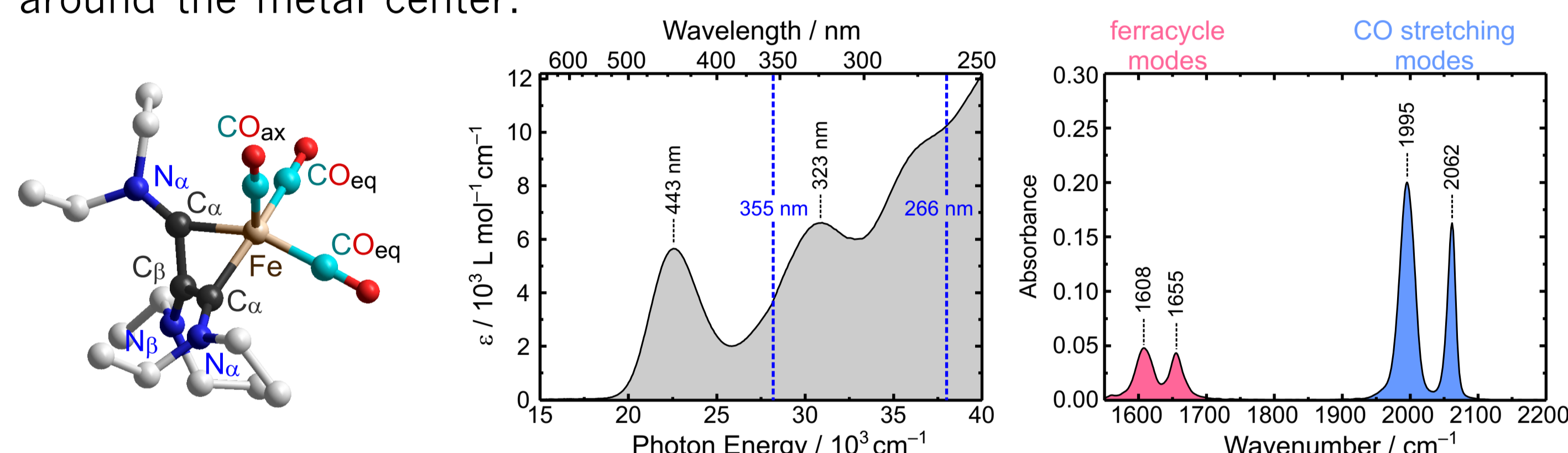
Molecular structure of [A], UV/Vis- and FTIR-spectrum of [A] in liquid acetonitrile solution at room temperature. The photochemical studies were carried out with pulses centered at 355 nm and 266 nm, thereby exciting metal-to-CO charge transfer transitions. The vibrational spectrum highlights the regions of the CO stretching and ferracycle ring modes. Symmetry splits the three CO stretches into a totally symmetric mode and a pair of antisymmetric modes with relative IR band intensities of 1:2 (symmetric:antisymmetric).

Photochemistry from time-resolved FTIR-spectroscopy

To identify the nature of the photochemical products, nanosecond laser flash photolysis was conducted with step-scan-FTIR detection. A product spectrum was obtained, which was stationary on a time scale of several seconds indicating that the photolysis results in the formation of a thermodynamically stable product, i.e. compound [B]:


[A] from stationary FTIR
[B] from preparative photochemistry
[B] from step-scan-FTIR:
What is its structure?
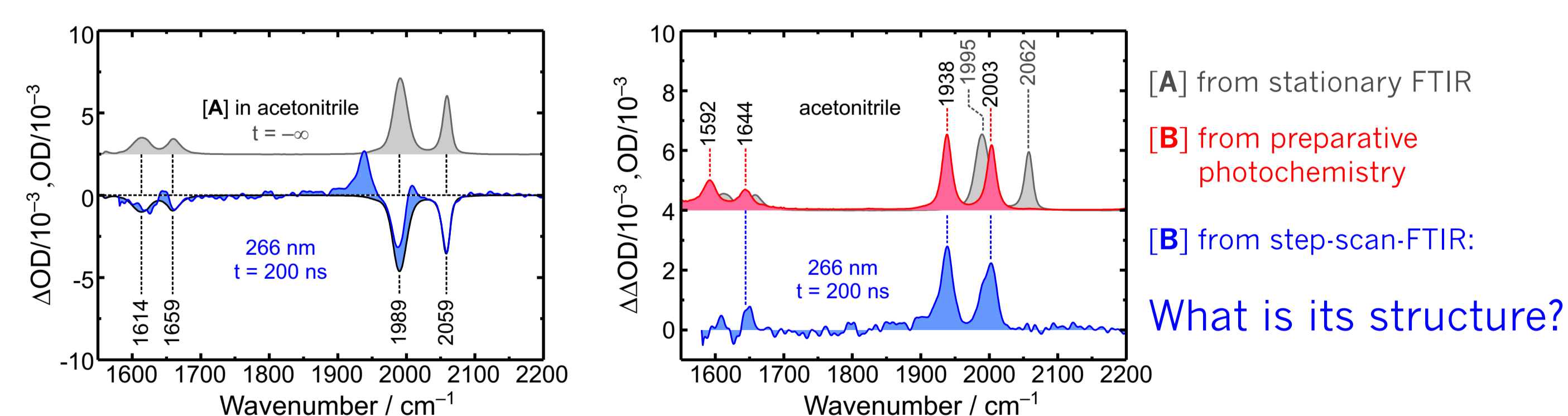
The ratio of the frequency-integrated band areas of the two CO-bands of [B] is 1:1 suggesting that photolysis of [A] results in decarbonylation (i.e. loss of a CO-ligand).
The carbonyl bands of [B] are downshifted with respect to those of [A] indicating that CO is replaced by a better electron donor. This would increase the electron density at the metal, which in turn would enhance the metal-to-CO backbonding, soften the CO-bonds and thus, downshift their stretching frequencies with respect to [A].
Acetonitrile is a better electron-donor than CO. [B] can be a dicarbonyl with an acetonitrile attached to the iron. Which CO-ligand is cleaved - A basal or the apical one?
Synthesis can clarify this issue!
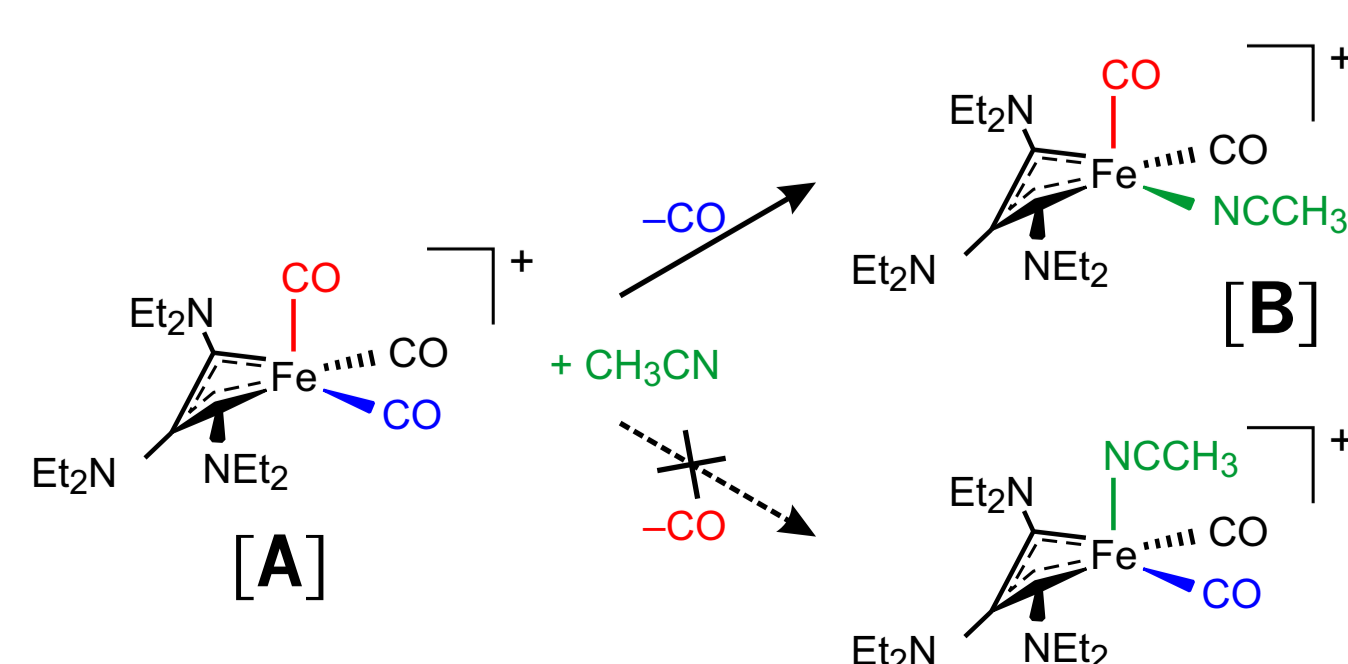
Femtosecond spectroscopy

To characterize the time-scales and molecular-level mechanisms of the primary processes following electronic excitation of [A], UV-pump mid-IR probe spectroscopy was conducted in the region of the CO-stretches.
A comparison between FTIR and pump-probe data demonstrates that the system is photostationary after ~600 ps, i.e. the acetonitrile product [B] is fully formed.

The femtosecond mid-IR spectra reveal three distinct signal components:

Product absorption ([B], spectrum known)
Excited state absorption ([A*], unknown)
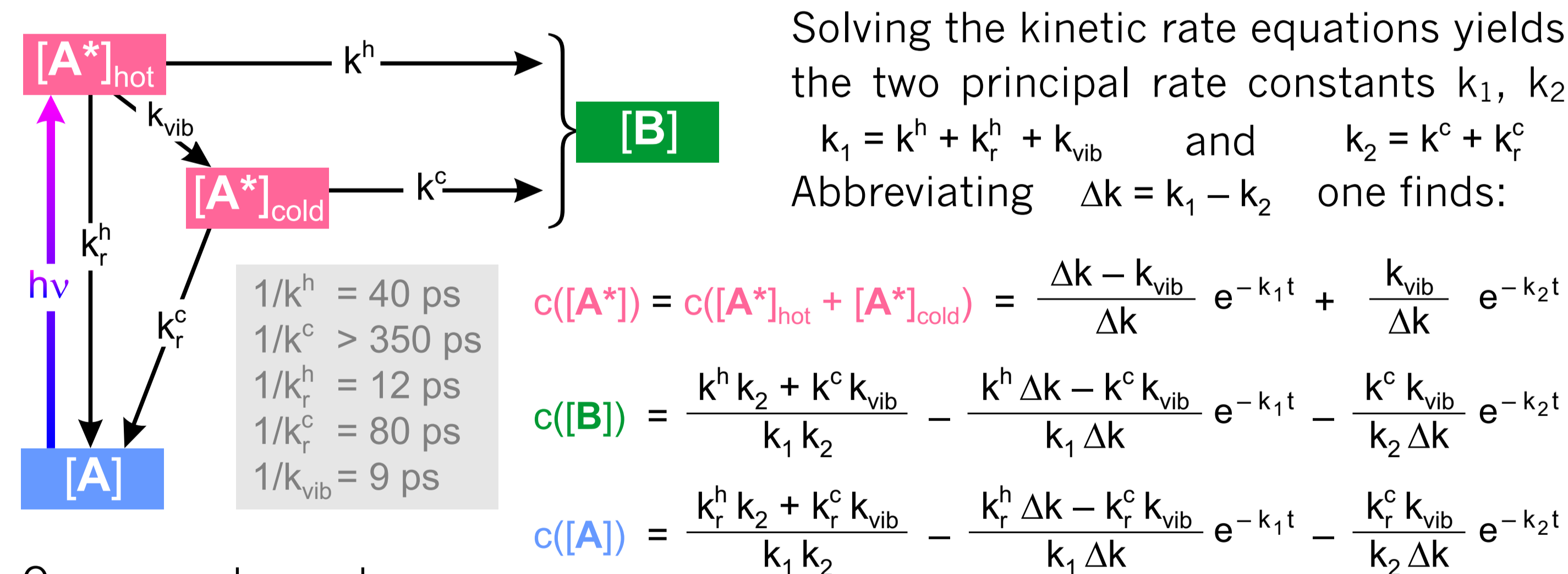Ground state bleach ([A], spectrum, known)
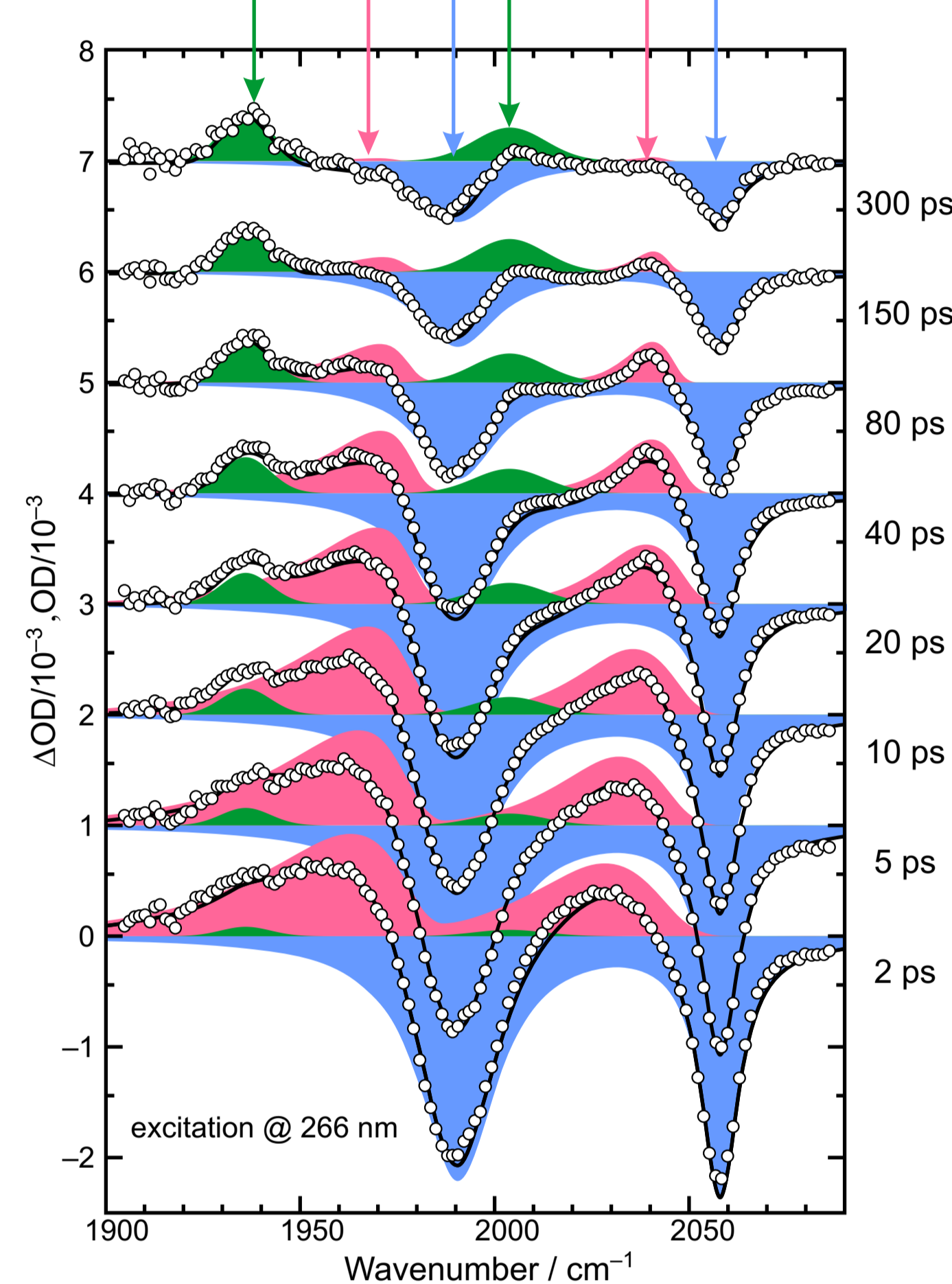
Qualitative observations:

➤ The ground state bleach partially recovers on a time scale of ~200 ps.
➤ The excited state absorptions decay on a time scale of ~200 ps.
➤ The excited state absorptions dynamically shift to higher frequencies.
➤ The excited state absorptions spectrally narrow with time.
➤ The product absorption grows in on a time scale of ~200 ps.

Shifting and narrowing indicative of vibrational cooling in excited state.
Product formation directly from the excited state.

Kinetic modeling

Time-traces recorded at characteristic probe wavenumbers can be fitted phenomenologically with biexponential kinetics. Thus, a satisfactory model needs to return at least two principal rate constants. A most primitive model that is able to capture the spectro-temporal mid-IR response is shown below:

$1/k^h$ = 40 ps
$1/k^c$ > 350 ps
$1/k_r^h$ = 12 ps
$1/k_r^c$ = 80 ps
$1/k_{vib}$ = 9 ps

Solving the kinetic rate equations yields the two principal rate constants k_1, k_2
$k_1 = k^h + k_r^h + k_{vib}$ and $k_2 = k^c + k_r^c$
Abbreviating $\Delta k = k_1 - k_2$ one finds:

$$c([A^*]) = c([A^*]_{hot} + [A^*]_{cold}) = \frac{\Delta k - k_{vib}}{\Delta k} e^{-k_1 t} + \frac{k_{vib}}{\Delta k} e^{-k_2 t}$$

$$c([B]) = \frac{k^h k_2 + k^c k_{vib}}{k_1 k_2} - \frac{k^h \Delta k - k^c k_{vib}}{k_1 \Delta k} e^{-k_1 t} - \frac{k^c k_{vib}}{k_2 \Delta k} e^{-k_2 t}$$

$$c([A]) = \frac{k_r^h k_2 + k_r^c k_{vib}}{k_1 k_2} - \frac{k_r^h \Delta k - k_r^c k_{vib}}{k_1 \Delta k} e^{-k_1 t} - \frac{k_r^c k_{vib}}{k_2 \Delta k} e^{-k_2 t}$$

Component spectra
[A*]: two entangled Log-normal distributions with area ratio 2:1 (tricarbonyl) center frequencies and widths scale as
$[\tilde{v}_{1,2}(t) - \tilde{v}_{1,2}(0)] / [\tilde{v}_{1,2}(\infty) - \tilde{v}_{1,2}(0)] = e^{-k_{vib} t}$ and $\Delta_{1,2}(t) = \delta_{1,2} e^{-k_1 t} + \gamma_{1,2} e^{-k_2 t}$
[B]: two entangled Gaussians with area ratio 1:1 (dicarbonyl, exp. available)
[A]: two entangled Lorentzians with area ratio 2:1 (tricarbonyl, exp. available)

Singlet vs Triplet vs Vacancy

The experimental data contain no unambiguous evidence for an intermediate, coordinatively unsaturated dicarbonyl species [V], which may arise prior to solvent attachment. To obtain insight into its IR-signatures, DFT calculations (BP86/TZVP, PCM) have been conducted.
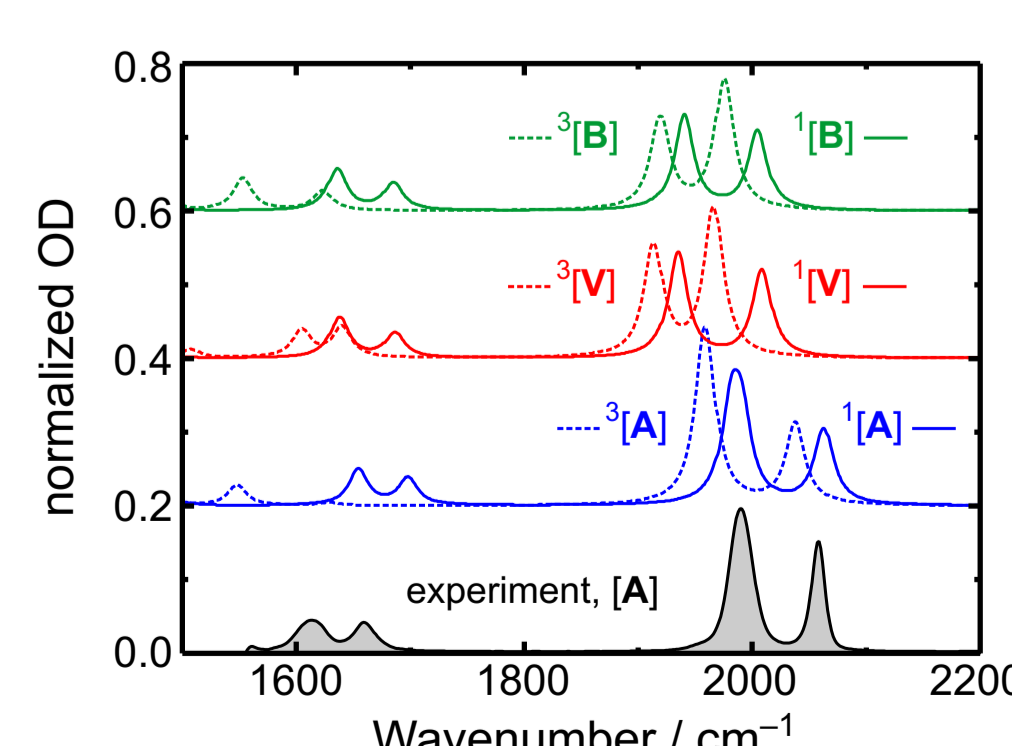
It turns out that [B] and [V] are virtually indistinguishable with IR-spectroscopy in the CO-region. Additional experiments in the ring mode are required. Moreover, no fluorescence is detected indicating that [A*] is actually a triplet rather than the optically accessed singlet state

References
from the authors:
Chem. Eur. J. (2015) **21**, 17184-17190