

Selective functional group transformation using sulfur tetrafluoride to increase the spectral selectivity of FTIR spectroscopy

Stefan Zumbühl, Nadim C. Scherrer

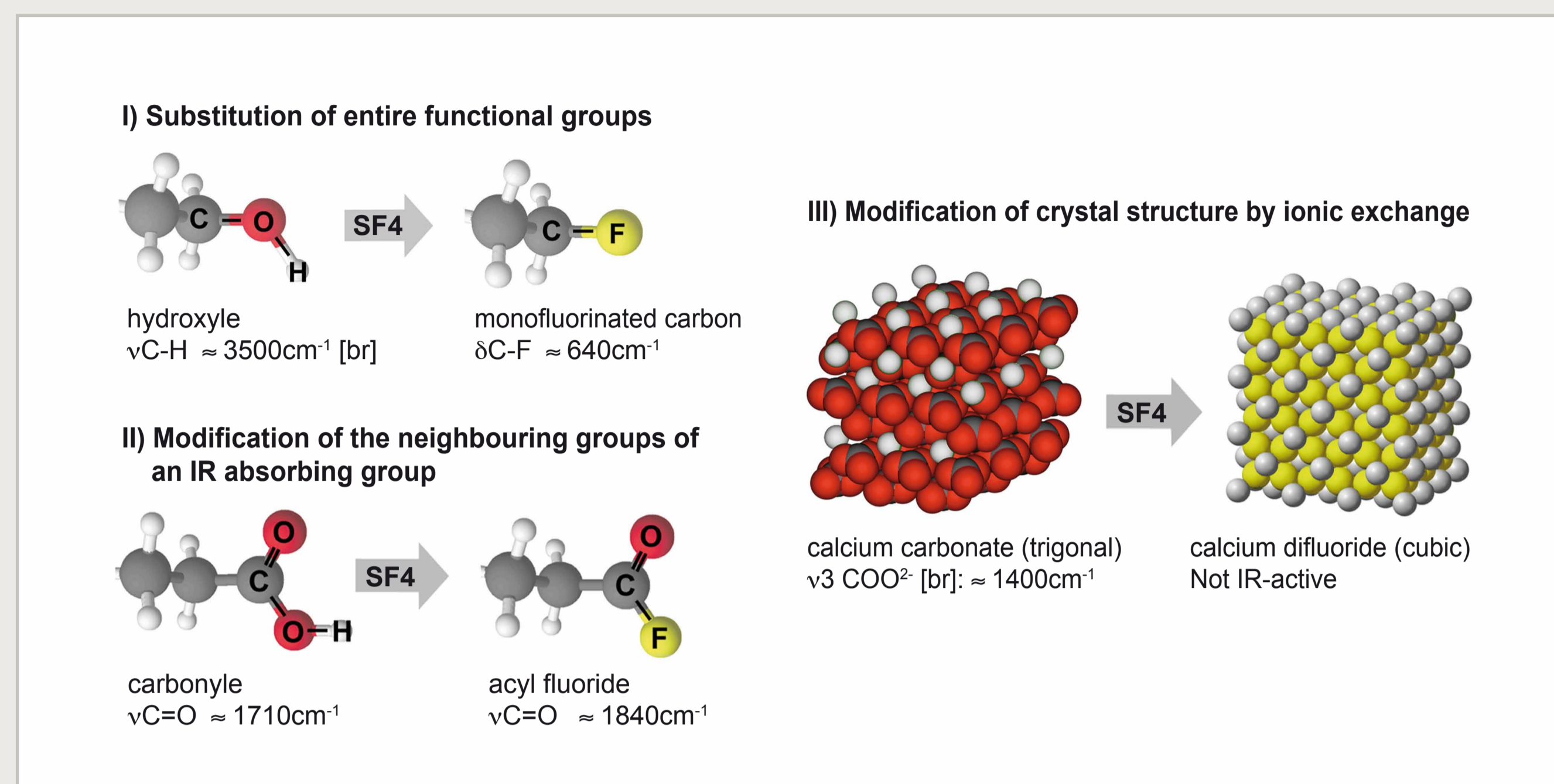
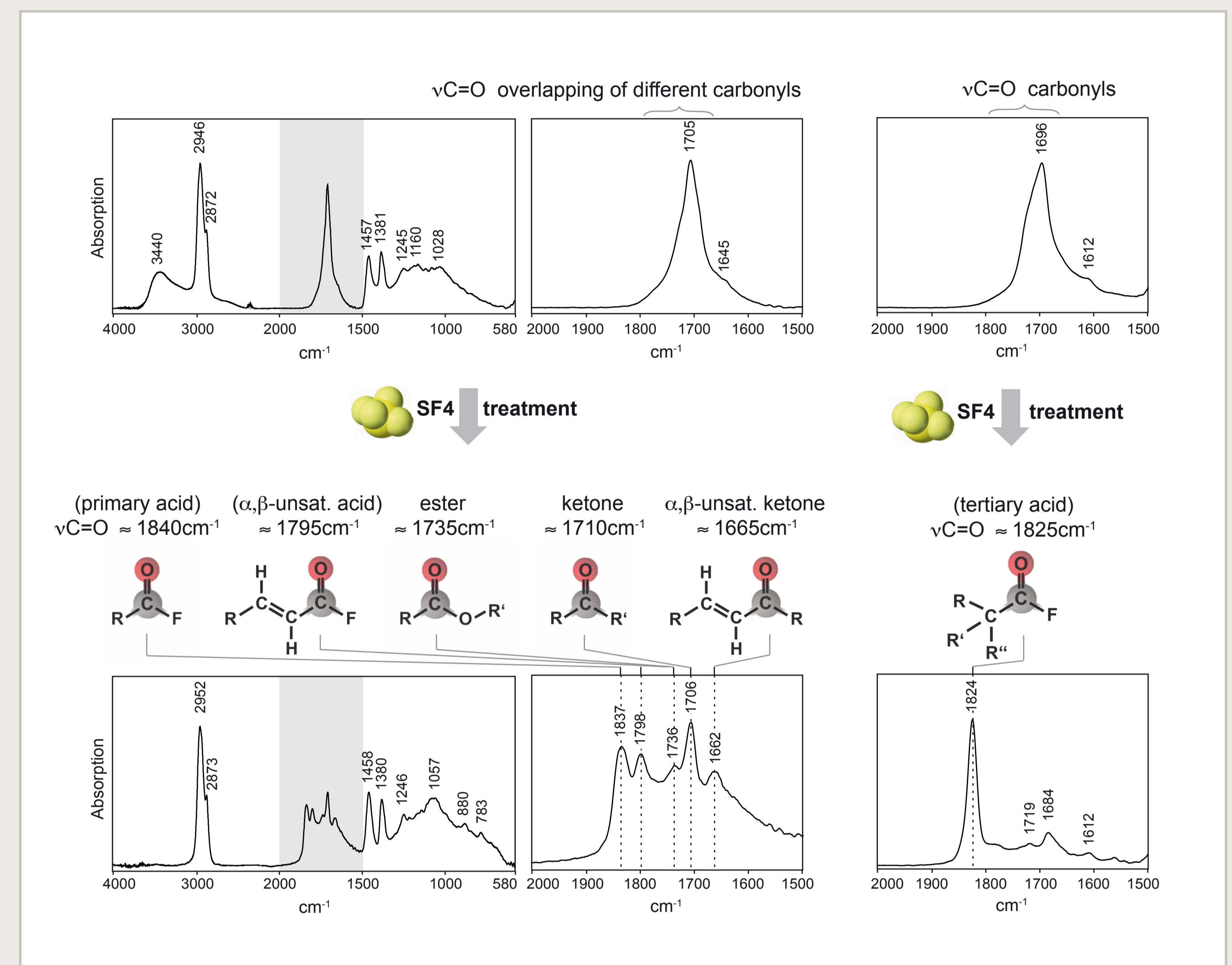


Figure 1 (above): Overview on the reactions of SF_4 with various functional groups and materials.

Figure 2 (right): Derivatisation of natural resins using sulphur tetrafluoride SF_4 . Triterpene resin mastix (on the left) exhibiting multiple functional groups within the raw material already, and the diterpene resin colophony (on the right), exhibiting mainly tertiary acids. Upper spectra show the FTIR response prior to derivatisation, whereas the lower spectra document the FTIR response upon treatment with SF_4 .



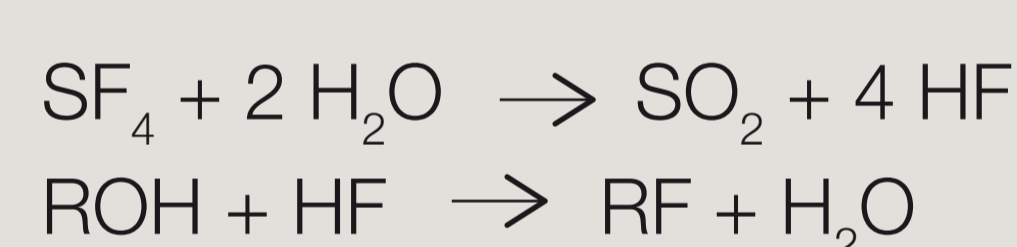
Introduction

Infrared spectroscopy (FTIR) is an established technique to characterise organic components in art conservation science and forensics. But there are limitations to the technique, particularly when analysing aged materials. IR signals often are strongly influenced by interfering functional groups. To characterise the different carbonyl groups using infrared spectroscopy, a selective functional group transformation technique using gaseous sulfur tetrafluoride was investigated to separate overlapping signals.

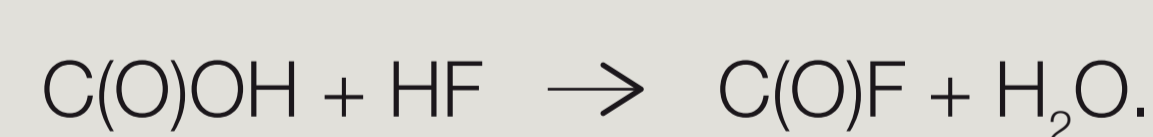
Derivatisation

The concept using the reactive gas SF_4 is based on the selective shifting of specific IR-bands by chemical pre-treatment of the sample to discriminate interfering signals. The principle is based on a controlled, characteristic and reproducible functional group modification. The concept of the fluorination technique aims at modifying the IR-absorption of a substance by characteristic alteration of the binding modes, since organofluorine compounds show characteristic and narrow IR bands. SF_4 converts hydroxyl, carbonyl, and carboxylic acid groups into mono-, di-, and trifluorinated functionalities, respectively. For each class of functional groups, different reactions take place under variable reaction conditions. Three principle strategies to eliminate spectral interferences from organic and inorganic materials are of interest for the practical application in chemistry using infrared spectroscopy (**Figure 1**).

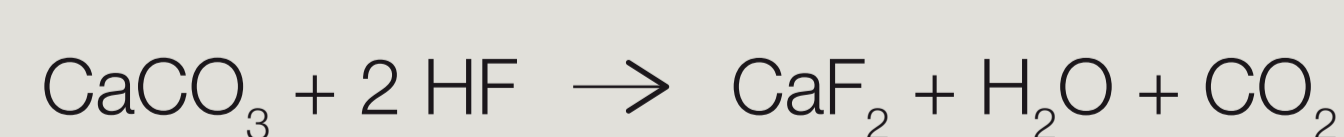
I) Substitution of entire functional groups with a fluorine atom. This exchange reaction leads to a new IR absorption position of the halogenated group. The reaction with a hydroxyle group leads to an organofluorine compound:



II) Modification of the neighbouring groups of an IR absorbing bond. It is well known that inductive effects have the greatest influence on the shift of the carbonyl stretching frequencies. In this context fluorination reactions are of interest, because fluorine exhibits high electronegativity and leads to strong signal shifts. Carboxylic acids, for example, can be transformed into acyl fluorides by this reaction:



III) Modification of the crystal structure by ionic exchange, leading to a change in the IR-activity of mineral compounds. This makes use of the fact that IR-absorption is strongly related to the crystal structure. The conversion of minerals into components that are not active in IR is of specific interest. This allows, for example, to eliminate broad absorption bands of various carbonates used as pigments and fillers and hiding the binder signals in paints or filled polymers.



Results and discussion:

To test the selectivity of this method, terpenes and terpeneous resins were fluorinated using sulfur tetrafluoride. Due to the ease of these raw materials to oxidise, resins commonly exhibit a broad and intensive carbonyl band, which arises from spectral overlaps of several functional groups. This research has demonstrated the selectivity of this derivatisation method, addressing the different acids selectively, with direct consequences to their carbonyl stretch vibrations, while ketones and ester groups remain unchanged. The various acyl fluorides generally show a characteristic band shift of around plus $\approx 130\text{cm}^{-1}$ against their original acids prior to fluorination. After fluorination, we observe a splitting of the broad $\nu(\text{C=O})$ -band into 6 separate $\nu(\text{C=O})$ -bands (**Figure 2**). Selective fluorination of the carboxylic acid groups unveils the primary acids at $\approx 1840\text{cm}^{-1}$, the tertiary acids at $\approx 1825\text{cm}^{-1}$ and the α,β -unsaturated primary acids at $\approx 1795\text{cm}^{-1}$. The shift of the different fluorinated carboxylic acid $\nu(\text{C=O})$ absorptions uncovers the signals from other carbonyls such as esters at $\approx 1730\text{cm}^{-1}$, ketones at $\approx 1710\text{cm}^{-1}$ and the α,β -unsaturated ketones at $\approx 1685\text{cm}^{-1}$.

This research has demonstrated the power of gaseous SF_4 derivatisation. The presented method substantially increases the selectivity of infrared spectroscopy for the characterisation of oxidative ageing products in organic materials, an achievement that is not possible applying standard FTIR without derivatisation.

Presentation:

Zumbühl S., Scherrer N.C. (2015): Selective Functional Group Transformation to Increase the Spectral Selectivity of FTIR Spectroscopy - Derivatisation of Bioorganic Compounds using Gaseous Sulfur Tetrafluoride, TECHNART 2015, Non-destructive and Microanalytical Techniques in Art and Cultural Heritage, Catania, 27-30 April 2015. <http://technart2015.lns.infn.it/images/BoA.pdf>

Publication:

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