Methods and methodology for FTIR spectral correction of channel spectra and uncertainty, applied to ferrocene

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ABSTRACT

We present methodology for the first FTIR measurements of ferrocene using dilute wax solutions for dispersion and to preserve non-crystallinity; a new method for removal of channel spectra interference for high quality data; and a consistent approach for the robust estimation of a defined uncertainty for advanced structural χ_r^2 analysis and mathematical hypothesis testing. While some of these issues have been investigated previously, the combination of novel approaches gives markedly improved results. Methods for addressing these in the presence of a modest signal and how to quantify the quality of the data irrespective of preprocessing for subsequent hypothesis testing are applied to the FTIR spectra of Ferrocene (Fc) and deuterated ferrocene (dFc, Fc-d$_{10}$) collected at the THz/Far-IR beam-line of the Australian Synchrotron at operating temperatures of 7 K through 353 K.

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1. Introduction

Weak signals in FTIR spectroscopy can often be discarded due to spectral interference caused by excessive noise, contamination from atmospheric gases, channel spectra, environmental contamination, crystallinity, general harmonics, noise contamination or related issues. We have recently shown that the IR spectra can provide details of the dynamics of fluxional molecules such as ferrocene (Fc) where a key observation is the temperature dependence of the IR spectra [1]. That work has highlighted the need for refinement of the approaches to improve and define the quality of IR spectra. In this contribution we outline methods developed to (i) allow removal of artefacts from interference and channel spectra, and (ii) atmospheric contamination, (iii) present a method for collection of solution-like spectra from samples at temperatures between RT and 6 K and (iv) outline an approach for defining and validating the uncertainty of spectral characteristics and the quality of the data.

Since the measurements of first IR spectra of Fc [2,3], it may be surprising that IR spectroscopy has not been used more to study structural dynamics of molecules. Part of the reason lies in major

challenges in both theory and experiment. The stereochemistry and dynamics of Fc have been the focus of much speculation [1]. Investigation of the temperature dependence of vibrational spectra of Fc is important for reliable modelling of the conformations, not previously studied. Data with high accuracy and precision is required to model subtle structural dynamics associated with the relative rotation of the two Cp rings of Fc [4]. However, collection of high quality IR spectra over a range of temperatures of the sample is often challenging due to effects such as contamination of channel spectra or fringing [5] and wedging errors [6]. Channel spectra arise as periodic interference patterns particularly due to reflections at the sample surfaces. Most commonly these effects are managed by manipulation of the interferogram. However, these approaches were found to give unsatisfactory results when applied to weak spectral features. We show that alternate strategies of filtering can yield more stable band profiles that can be used in quantitative analysis. The approach has been applied to obtain temperature-dependent IR spectra of Fc and its fully deuterated analogue dFc (Fc-d$_{10}$).

2. Experimental

Spectra were collected from protonated ferrocene (Fc) and deuterated ferrocene (dFc) samples at the THz/Far-IR beam-line, Australian Synchrotron. The THz/Far-IR beam-line at the advanced

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third generation Australian Synchrotron offers high spectral resolution(up to 0.00096 cm^{-1}), where the light source of ~200 μm and a projected width ~2000 μm which can be treated as a point source resulting in a highly-collimated beam which is required to obtain high resolution. The highly polarised radiation generated by the synchrotron offers high sensitivity with minimal background scattering. These features of the synchrotron beam together with a Bruker IFS 125/HR Fourier Transform (FT) spectrometer, and modern equipment make it a beam-line well-suited for accurate measurements with a variety of sample types in different sample environments.

Gas phase spectra were collected at 353 K using a 600 mm long variable-path glass cell (M22-V from Infrared Analysis) which offers a base path of 2.2 m (4 passes); for this experiment the number of passes was set to 16 yielding a total path length of 8.8 m. The cell was equipped with a pair of 5 mm thick, 25 mm diameter KBr windows with a 0.5° wedge to minimise fringing; the cell was wrapped with a heating tape connected to a temperature controller set to 350 K. The gas-cell was coupled to a Bruker IFS 125/HR FT spectrometer, and the spectra were measured at resolutions of 0.5 cm^{-1}, 0.05 cm^{-1} and 0.005 cm^{-1}; data were collected using a liquid nitrogen cooled midband MCT detector (600–12,000 cm^{-1}) and a liquid helium cooled Boron-doped Si photodetector (400–750 cm^{-1}).

At each resolution, 5–10 sets of measurements were made with a total of 10–20 repeated measurements for each set of data. Multiple measurements were able to confirm the reliability of the resulting spectra. Spectra were referenced against an empty sample path and the effects of wax support was removed separately.

Spectra from dilute [frozen] solutions have also been measured over a range of temperatures from 7 K to 300 K. Measurements were made using solid, concentrated solution and dilute solution for both Fc and dFc compounds over a range of temperatures. Crystalline Fc powder was dissolved in paraffin wax at ca. 80° C and quickly cooled to yield a solid solution. The sample was transferred to a standard pellet press with Teflon discs used to stop the wax from sticking to the stainless steel pellet faces. The self-supporting discs (ca. 70 mg) could then be transferred to the cryostat. Samples with < 1% Fc gave spectra consistent with the solution phase species. Spectra were measured at different temperatures using Cryogen-cooled cryostat, and temperature was maintained using a Displex refrigerator. A Si Bolometer detector available at the beam-line was used for the collection of the spectra in the 300–700 cm^{-1} region.

3. Results and discussion

3.1. Improved gas phase spectra preprocessing of low molecular weight contaminants using higher resolution data

The combination of a low vapour pressure (79.8 Pa at 350 K [7]) and a small transition-dipole moment of the bands sensitive to the Fc conformation results in spectra that are sensitive to contaminants from leakage of atmospheric gases into the cell. Sample gas phase FTIR spectra were contaminated by bands due to increasing concentrations of atmospheric gases (CO_2 + H_2O) with time.

Since it was not possible to resolve this issue within the beam time allocation, preprocessing was required to remove the sharp spectral features (CO_2, H_2O). In this case the rotation-vibration lines of CO_2 and H_2O are concentrated within 1–2 data points if high-resolution data is collected and are well-separated. A search function identified and removed the H_2O and CO_2 lines from the signals replacing the features by the average of the neighbouring data points. The resolution of the spectra was then digitally lowered to an appropriate value and the baseline correction and noise filtering applied. For Fc good quality spectra were obtained with a resolution of 0.05 cm^{-1}. While the net contamination of the sample increases with time, and so is more pronounced for measurements at higher
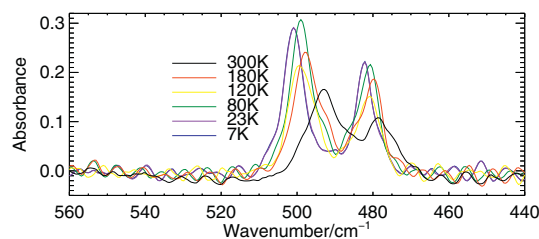
Fig. 1. Absorbance ($\ln(I_0/I)$) of dilute Fc in paraffin wax over a range of temperatures, corrected for solvent background, prior to application of the modified Butterworth approach. Partially processed spectra are clearly affected by periodic noise and residual offset, to be addressed with the Butterfield methodology. Notice also the spectra are strongly dependent upon temperature.

resolution, this is more than offset by the difficulty of removing the broader contaminant bands at lower resolution (0.5 cm^{-1}, 0.05 cm^{-1}). Counterintuitively, better quality spectra of dFc could be obtained from measurements with 0.005 cm^{-1} resolution. This methodology can relate to weak signals or gas-phase IR data sets, whenever contaminated by low molecular weight species.

One might expect that rapid low-resolution scans might minimise or eliminate the leaking of air into the cell. A surprising result is that the contamination is removed much more effectively with higher resolution spectra, very clearly seen for dFc, because the contaminants are low-weight materials with sharp spectral features. Hence, the process is much simpler and cleaner at high resolution even when the 'so-called' high-resolution data is unable to separate band components of the sample of interest.

3.2. Use of frozen solutions of paraffin wax for low-temperature dispersion and solution spectra

Paraffin wax may be an ideal solvent support for low-temperature IR measurements of lipophilic solutes. The use of paraffin mineral oil (Nujol) as a medium for the measurement of IR spectra of solids has a long history, including the use by Lippincott et al. in 1958 [3]. The use of longer chain, higher MP paraffin wax has a key advantage that a self-supporting disc can be prepared at room temperature, suitable for mounting samples.

Paraffin wax was chosen as the solvent to avoid Fc–Fc interactions from solution and frozen solution. It is believed that frozen paraffin solutions avoid crystallization or reaction with the solute and change of phase, and therefore that dilute solutions of Fc or dFc in paraffin could yield largely isolated molecules [8]. This thereby can in principle approach the ideal density functional theoretical computations for isolated molecules. As with Nujol, the molecular weight and composition of paraffin wax are ill-defined, so that a solvated modelling of the environment using e.g. Density Functional Theory (DFT) is not particularly feasible; nonetheless experimental advantages mean that effective modelling can be made with fewer assumptions and avoiding the experimental problems of molecular clustering.

IR spectra recorded from solid solutions of Fc in paraffin wax over the temperature range 7 K to 300 K in the region near 500 cm^{-1} are shown in Fig. 1. The focus on the bands in this region is based upon their predicted sensitivity to the relative conformations of ferrocene. The band profiles can be strongly affected by interference effects (channel spectra, Figs. 1, 2) and even qualitative analysis requires correction for these effects.

3.3. Preprocessing: multi-pass channel spectra interference

The spectra are (often) affected by channel spectral noise: sinusoidal modulations due to multiple reflections of IR beam between
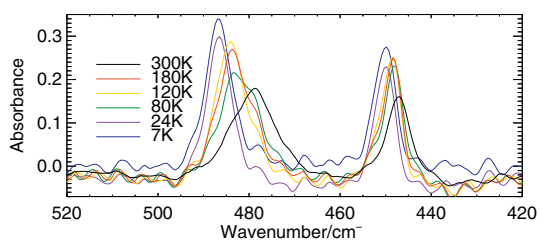
Fig. 2. Absorbance ($\ln(I_0/I)$) of dilute dFc in paraffin wax over a range of temperatures, corrected for solvent background, prior to application of the modified Butterworth approach. Similar to Fc, partially processed spectra of dFc are affected by periodic noise and residual offset.

Fig. 3. Fast Fourier Transform (FFT) of an input IR spectra of Fc (top). Fluctuations were removed with a low-pass filter function in transformed space as illustrated, using a Butterworth filter of order 1 (bottom). While the higher frequency cut-off yields a sharper filter and a smoother filtered spectrum, the lower cut-off of 30–40 achieves very good results in a smooth manner and is used in this analysis [9] .

parallel surfaces of samples, cell and detector windows in the optical path of the spectrometer [10] (Figs. 1, 2).
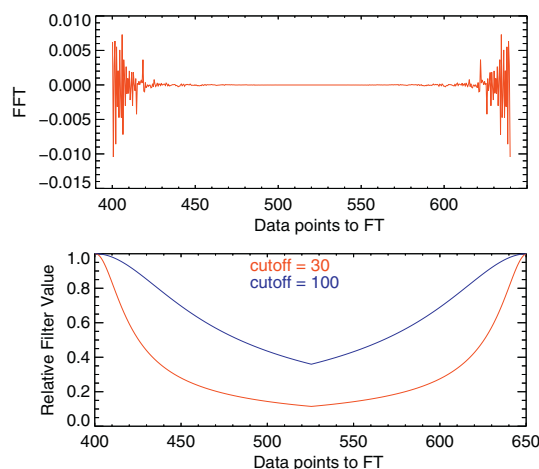
The final step of pre-analysis was therefore the correction of the periodic signal from the channel spectra absorbances. Numerous publications have discussed this from 1970 [11] with simple filters [5,12,13] to modern analyses of the interference pattern [10,14–17]. Different approaches to handle channel spectra contaminating IR spectra with collimated radiation have been reported recently [18,19]. Reported techniques improved signal-to-noise, yet either failed to remove completely the effects of channel spectra or significantly altered the band profile. The best correction to transmission spectra appeared to be obtained with synthetic background spectra simulating channel spectra. Although different approaches are in practice to obtain Fourier transform IR spectra, standardisation of the approaches, error analysis and accuracy determination can enhance the applicability of IR spectroscopy.

The Butterworth filter method [9] has been applied to remove periodic noise in many areas of electronics [20]. The Butterworth method uses the fast Fourier transform (FFT) with a low pass filter removing undesired high frequency noise prior to reconverting data from the frequency domain into the physical domain (Fig. 3). A key advantage of this novel approach is that the filter is not sharp and discontinuous but is smooth, and ergo minimises distortions of the original spectrum. In particular there should generally be no distortion in shift of the centre-of-mass (wavenumber) of the profile. The filter in standard application was in some cases sufficient for a range of data, though we do find significant distortion can occur if the signal frequencies aliase or overlap with the channel spectral frequencies.

Fig. 4 illustrates the robustness and stability of the method used against both shift (distortion) of the mean frequency, distortion of the profile shape, structure and amplitude, and a limit at which distortion becomes manifest. A popular approach in IR spectroscopic processing to smooth high-frequency noise is to use an implementation of the Savitzky-Golay spline smoothing which is a moving average fitting a low-order polynomial [21]. This smooths noise and structure equally, so the distortion is roughly the same scale and magnitude as the reduction of channel spectra. Other methods including zeroing of the peak region in the fourier transform or having a sharp cut-off filter introduce much more distortion.

The Butterworth approach can be optimised for particular frequencies and periodicities, but can also distort the peak profile shape as it suppresses the higher-frequency noise. The distortion, when significant, is addressed by interpolation from well-defined fluctuations in the nearby background to the region of the IR signal bands.

Fig. 4 illustrates a spectrum not able to be corrected satisfactorily by direct application of the Butterworth filter. The spectral bands are weak and are less than 5 times the amplitude of the lower frequency channel spectra (Fig. 4a). Fig. 4b) follows application of a standard low-pass Butterworth filter with a cut-off frequency of 40 Hz and

order 1 (the same qualitative effect and features are seen for any order from 1 through 15). This removes the channel spectra and most of the other high-frequency noise or structure; but also introduces significant distortion into the peak profile. The choice of cut-off frequency is a little arbitrary, in that too low a cut-off frequency (≤ 1) will destroy a large amount of structure; whereas too high a cut-off frequency (≥ 100) will not remove the channel spectra. The problem is commonly more challenging in FTIR because the structural signal and channel interference spectral frequencies nearly overlap one another. This is a good example because the spectral features have similar frequencies to those of the channel spectra; the bands of interest are well-separated from other bands and the performance of the filter at higher and lower wavenumber can be assessed.

In this case, we sought to define the background oscillatory structure over the spectral region by replacing a oscillatory background estimate in the region with an oscillatory structure approximately matched in phase and amplitude with the observed spectral oscillations, derived from the adjacent background region. The Butterworth filter hence removes the channel spectra in the background while not destroying the profile oscillations of the spectral profile. It is therefore in this sense minimally distorting. The oscillatory structure is then subtracted from the experimental spectrum. If the cutoff frequency is too low, then the underlying oscillatory structure will be distorted (Fig. 4c) and the channel spectra will not be well-treated in the background; if the cutoff frequency is too high then higher frequency noise can be added (Fig. 4e).

The channel spectra is almost eliminated, just like with the direct Butterworth method, yet now the resulting structure is almost independent of the cut-off frequency. Good results were obtained across a range of robustness of the cut-off for a minimally-distorted spectrum given by Fig. 4d) of 25–50. Any remaining distortion is almost unobservable, and yet the channel oscillations are largely eliminated. This is a key advantage of this approach to application of such a filter.
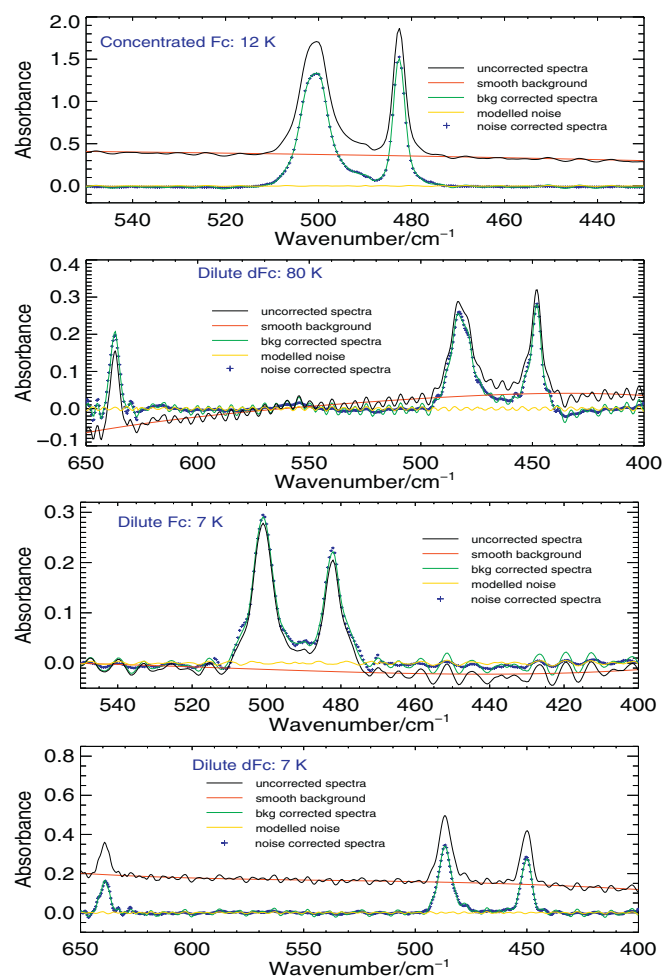
In Fig. 5, the solid black lines, with noise, are determined using the uncorrected intensities. A thickness variation between the reference (blank wax) and the actual samples contributes a background offset for the determined absorption spectra ($-\ln(I_{sample}/I_{blank})$). To correct for the background offset and periodic noise, a simple methodology is illustrated in Fig. 5. The background offset in normalised spectra due to thickness variation between the sample and the reference was modelled and corrected using a second order polynomial function
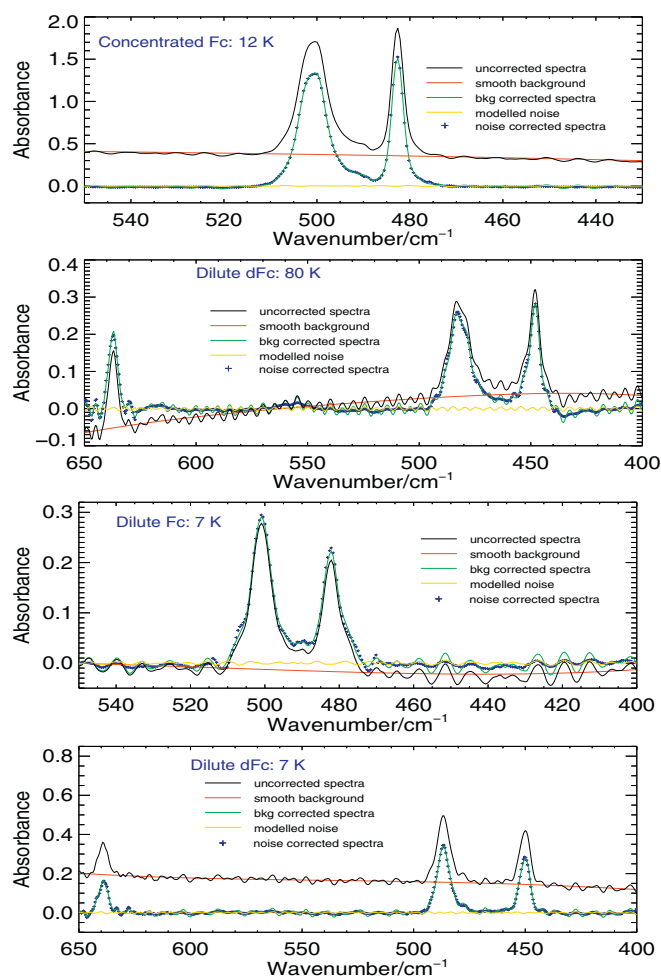
Fig. 4. Absorbance ($\ln(I_0/I)$): The original green spectrum (a) is converted to the purple spectrum (b) when the Butterworth filter is applied over the whole spectrum. The signal in the peak region is then affected by distortion caused by the filter. To correct this, the noise in the peak region is interpolated from the surrounding filter, matching the phase of the oscillations. The remaining three spectra illustrate the corrected results when cutoff frequencies of (c) 1 (black), (d) 40 (red) and (e) 100 (blue) are applied. The cutoff is fairly robust, but setting the cutoff too low or too high fails to remove the noise distortion. A cutoff frequency of 30–40 was found to be optimal for this application. The robust region of frequency cutoff of 30–40 has reduced distortion. This plot used a Butterworth of order 1, but results were similar and gave the same qualitative results from order 1 through order 15. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. A methodology for the correction of periodic noise from channel spectra in IR spectra of Fc, applied to four data sets. The broad linear trend of the background is due to large-scale frequency-dependent absorbance ($\ln(I_0/I)$). Butterworth filtering reproduced the noise over the background of the IR spectra, which was then interpolated over the peak regions. Modelled noise (yellow solid line oscillations) was then scaled and subtracted from the IR spectra represented by the black solid lines. Notice that the background channel spectra are very heavily suppressed, much more than is possible by other methods; but that the channel spectral artefacts in the peaks are also partially corrected, with minimal distortion of other spectroscopic features include peak rations and integrated areas. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

shown by the red solid line in Fig. 5. The periodic signal (channel spectra) was modelled using the Butterworth FFT (Fast Fourier Transform) [9] as shown by the orange coloured oscillations. Subtraction of the modelled systematic allowed the determination of noise-free IR absorption spectra as indicated by the blue solid lines. Corrected spectra show no observable distortion in the removal of oscillatory noise. A critical question, though, is the quantitative improvement of the spectra with this approach to removal of the channel spectral noise, especially by comparison with prior methods in the literature.

The improvement is by factors of 3–7 times relative to uncorrected spectra (Table 1). These estimates can be improved either by a better definition of background structure and removal or of course by optimising the functional further. The results may be compared with recent investigations using alternate methods [18] which obtained improvements of factors of 2–3 in typical structure-free regions. While one should be careful comparing methods with different noise levels, this augurs well for the method discussed here. We also compared these results on the same data set with treatment by a straight

Savitzky-Golay spline as discussed above, and compared with a straight Butterworth filter. In both cases the improvement factor was about 2–3, similar to some other prior approaches, but this involved significant distortion of the peaks and minima of the spectral region. In particular, there are good reasons why this current modified Butterworth approach should generally be superior to other methods discussed here, in that other methods often introduce large distortions and discontinuities either in original or transformed space. One can also compare this improvement to those of 1.6 or so given in earlier papers back to 1976 by e.g. removing central spikes of the interference fringe [5]; and to recent discussions directly removing a single fourier component from 2011 [19] yielding improvements by a factor of about 2–3 depending upon range. In those cases strong residual oscillations remain very clear and easily visible after correction. Conversely, the same residuals are largely unobservable in our processed spectra. Hence the improvement is impressive and appears to be significantly better than the table vales represent.

Table 1
Large signal-to-noise improvements on correction as illustrated in Fig. 5. The two regions selected of wavenumber k have the greatest and lowest noise levels in a fixed-size region before correcting for channel spectra interference, so prove the robustness of the approach. σ is the standard deviation across the range indicated in units of absorbance so is a direct measure of quality, relative to the magnitude of the absorbance. The spectrum of diluted dFc at 80 K yielded the greatest residual noise after correction for the channel spectra, so is the worst case observed in the data sets, yet still provides dramatic improvement. Note especially that while the final plots yield a σ, the channel oscillations are in all cases almost unobservable, and the residual noise is largely contributed by other sources.

Sample	Region, k, cm^{-1}	Improvement factor $[S/N]_{corrected}/[S/N]_{raw}$	σ (raw/corrected)
Concentrated Fc, 12 K	450–465	4.5	0.0152/0.00339
	520–535	4.8	0.0153/0.00317
Dilute dFc, 80 K	540–550	2.92	0.00898/0.00308
	595–610	3.38	0.00900/0.00266
Dilute Fc in wax, 7 K	410–425	6.7	0.0151/0.00225
	520–535	3.3	0.00482/0.00147
Dilute dFc in wax, 7 K	415–430	3.1	0.0114/0.00371
	570–585	4.5	0.00801/0.00179

3.4. Need for a quantitative definition of quality of data and uncertainty for IR spectra

It is often a very difficult problem to define the accuracy or data quality of a given IR data set. In general high resolution is defined to observe vibrational PQR branches and excitations, but these are generally only resolved for small molecules, and do not apply in our situation. Instead, the spectra become broad multiplets in general, with a temperature dependence of widths. One can instead define quality from very strong signals (or signal-to-background) but this usually is defined by the sample (e.g. solid, concentrated samples rather than weak gas samples at elevated temperatures or dilute samples), so that this is not clear in many data sets and may yield distortions by saturation and non-linearities. One can look at a pattern of the functionality of the spectrum with temperature and this is certainly a valuable indicator, but should only support the definition of quality rather than define it. Similarly, the agreement of a data set with a provisional hypothesis is often cited as a statement of quality but is a post facto confirmation of quality. Another common approach is to compare the spectrum with past literature, preferably collected under similar conditions, to verify or support the data at a certain level of confidence. Again this is not quantitative. It can be argued that a good qualitative indicator is absence of (visible) contamination, whether in sample preparation or experimental data.

Conventional key failings of quality are exactly what we have been describing — contamination lines from water vapour or carbon dioxide; interference oscillations before or after normalisation by the background, which especially arise from multi-path IR and again especially from weak signals; or missing peaks or peaks dominated by a solvent band, or results where the background and sample signals do not normalise and are inconsistent, possibly due to a drift with time. At high absorbances, non-linear responses distort the band profiles. We have demonstrated that corrections of contamination on gas-phase spectra, and sinusoidal noise of temperature series IR spectra in condensed phase allowed the determination of IR spectra with excellent data quality (Figs. 6 and 7). The correction of periodic oscillations (Fig. 3) allowed the determination of high quality data. The spectra (Fig. 6) are highly reproducible across a scan and also across repeated scans. The spectra presented here are determined from the average of corrected bands. The quality of spectra can also be noticed from the excellent consistency when the spectra are compared from two independent measurements. However, this is also an heuristic of quality, rather than a defined value which can be used in advanced analysis.

We must be able to define a noise signal and thereby a signal-to-noise; or define a standard deviation or rms noise, systematic or error field associated with the data. In many cases this is a strong function of the peak profile, for example with $\sqrt{N}$ noise. With FTIR signals, however, the background is relatively featureless over the region of active bands, and the signal is generally weak. Ergo, the background is locally a stable and uniform function and may be evaluated by the local noise or residual structure in the spectrum. Hence a key contribution to the consistency and quality of the spectrum is the smoothness and clarity of the data across the range of interest.

3.5. Two independent approaches to the assessment of IR quality

3.5.1. RMS deviation from a smooth background represents the stochastic noise of the final spectrum

Uncertainties of the spectra were determined as the *rms* deviations in structure-free background above and below spectral peaks after harmonic correction and filtering. Uncertainties across the whole spectral region, including the background, are then based on the assumption that local noise and variance is dominated by the large background and large background subtraction so that the peak spectra have effectively a constant variance per channel irrespective of derived scaled absorbance. The uncertainties are propagated to the spectra and used in the analysis to investigate the relative goodness of fits from χ_r^2 minimisation. The local robustness and variability of this include some classes of imperfection in the prior processing and filtering. Some estimates based upon different background noise regions can certainly vary uncertainty (variance) estimates by up to a factor of two; yet this implies that the estimates may be valid and accurate to this level.

3.5.2. Scan-repeat reproducibility (precision)

One can compare the local variation of near-background signal to the scan-repeat reproducibility (after processing, Fig. 7) and confirm that these two estimates agree and include both statistical uncertainty and contributions from systematic uncertainty. This generates a self-consistent standard deviation, and hence permits the definition of signal-to-noise or (better) signal-to-uncertainty in order to pursue chemical modelling and hypothesis testing. In principle this could be compared to the raw statistic of the count N arising from the background level across the wavenumber region, or for the signal scan (i.e. $\sigma = \sqrt{N}$). However, this needs to be carefully scaled from both the FTIR measurement and certainly not using the Absorbance scale. That is, an assumption of a normal distribution is only valid if N represents the number of particles and if these approximate a normal distribution, which a scaled absorbance does not. In principle, the three measures should be consistent. While our methodology involves some assumptions, it is verified both by self-consistency and robustness to within a factor of two, and by later investigation.
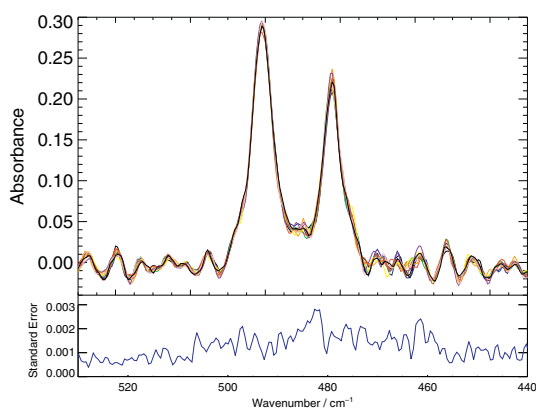
We have generated a plausible error field providing a functional with energy or channel (Methods A and B) which is very different from $\sqrt{N}$ on the derived signal; but which appears to model the data well. This provides a methodology for allowing hypothesis testing. Our modelling also supports the conclusion that these estimates of uncertainty are generally valid to a factor of two.

In the dilute solution temperature series spectra, the maximum absorbance varied from 0.228(2) to 0.353(3) for the IR spectra of dilute Fc in wax, and from 0.813(1) to 0.303(2) for dilute dFc in wax. Maximum absorbances in the IR spectra (over 300 K to 7 K) of concentrated Fc in wax varied from 0.766(4) to 1.495(5); for concentrated dFc, those varied from 1.653(4) to 3.003(5). For the IR spectra with solid KBr pellet samples, maximum absorbances varied from 1.007(3) to 1.184(4) for Fc at temperatures from 300 K to 7 K, and from 2.506(4) to 4.731(5) for dFc at temperatures from 300 K to 80 K.
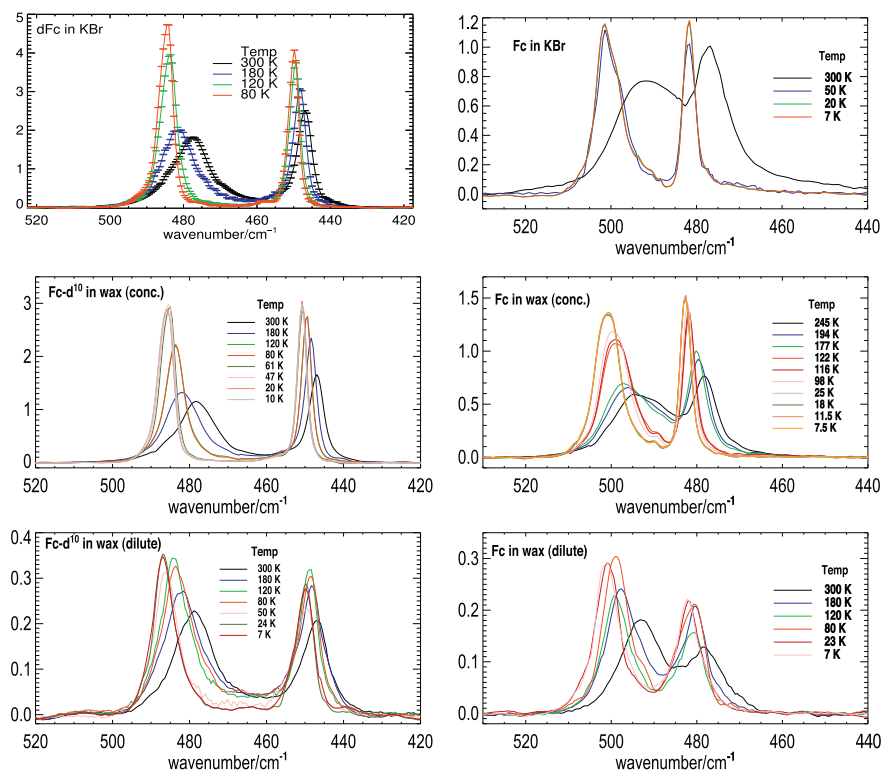
Fig. 6. Corrected IR spectra of Absorbance ($\ln(I_0/I)$) for the Fc and dFc in solid (frozen) solutions over a range of temperatures ranging from room temperature down to 7 K. The complex temperature dependence of peak energy, centroid, band location, amplitude and area, and asymmetric broadening require advanced physical models and advanced theory. Uncertainties, defined by the noise signal, were found within the range $\sigma \in [7.00 \times 10^{-4}, 6.07 \times 10^{-3}]$. Although unobservable, the uncertainties are illustrated in the first plot. The minimum uncertainty occurs for the data for dilute Fc in wax at 23 K (dilute system, low absorbance, low temperature) and the maximum uncertainty occurs for the data for dFc in KBr at 180 K (high temperature, higher concentration, high absorbance) as perhaps might be expected; but the actual values vary by large factor depending upon the quality of the spectral conditions of the individual data set.

Hence, uncertainties were generally stable around 0.001 to 0.003 for the temperature series IR spectra, corresponding to 0.1% to 1% of the absorbance, or a signal-to-uncertainty value in the range of 100–1000. This axis and point uncertainty leading to this peak amplitude and correspondingly integrated area uncertainty is then a clear statement of the quality of the data, which can be compared across data sets in a beam-line or experimentally-independent manner, and utilised for robust hypothesis testing of chemical, physical, dynamic and structural models.

Processed IR spectra of both Fc and dFc temperature series in dilute wax are summarised in Fig. 6. In both Fc and dFc, the theoretical predictions based on isolated molecule and zero Kelvin temperature for the positions and separations of the components differ from all of the experimental spectra. Hence, we would expect possibly distortions due to clustering, Fc–Fc bonding and the environment in both of the concentrated systems. However, we observe dramatic variation with temperature even for the dilute systems in wax. For dilute solutions in wax, the molecules should be relatively isolated, and independent of interactions with other molecules. However, the profile, peak energy and centroid positions, separations and relative intensities all vary with temperature implying that a single DFT theoretical prediction of any type is unable to predict the IR spectroscopy. Profiles also become increasingly asymmetric with increasing temperature.

4. Conclusions

Methods for measurement of low temperature solution spectra from lipophilic solutes as independent molecules; for removing low-MW contaminant bands; for processing channel spectra and interference removal; and for determining the data quality, are effective and prove a high quality of the data sets as explicitly observed by independent measures of variance.

Fig. 7. Point-wise variance from 10 repeated scans across the spectrum for dilute Fc solutions at 23 K. Notice that the repeated point variance in the wings of the spectrum even prior to Butterworth filtering is very well predicted by the measure used to estimate overall uncertainty. Rather than being perfectly flat (i.e. a constant variance across the fitting region) we do observe some variation across the spectrum and for concentrated samples we find commonly an increased variance near the peak, corresponding to a weak counting statistic. In other words, there is slightly greater σ at an absorbance peak compared to over the background region, but in fact the measure demonstrates that the dominant statistic is given by the large σ uncertainty arising from the reference uncertainty which is of course fairly uniform over any sample peak profile region.

The dilute spectra in paraffin wax are particularly interesting and with complex variations in disagreement with current DFT theory for the zero Kelvin, isolated molecule and theoretical conformation, separately and inconsistently for the gas-phase data, Fc, dFc, the dilute system in wax Fc, dFc, high temperatures and low temperatures. This is caused by the need for a more advanced quantum mechanical modelling of the system with dynamics, as we introduce in the Reaction Coordinate Method (RCM) analysis [1]. It remains to be seen as to whether quantitative analysis with the RCM approach will reveal deeper insight and consistency of the highly sensitive profile shapes. The higher-quality data with strong signatures and well-defined uncertainty allows a careful investigation of these signatures and the development of novel complex theory to investigate these issues; and we have high quality DFT theory to interrogate and resolve these questions.

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