INT 190/97 March 1997

FOURIER TRANSFORM INFRARED (FTIR) ABSORPTION SPECTROSCOPY ANALYSIS FOR PLASMA EXPERIMENTS

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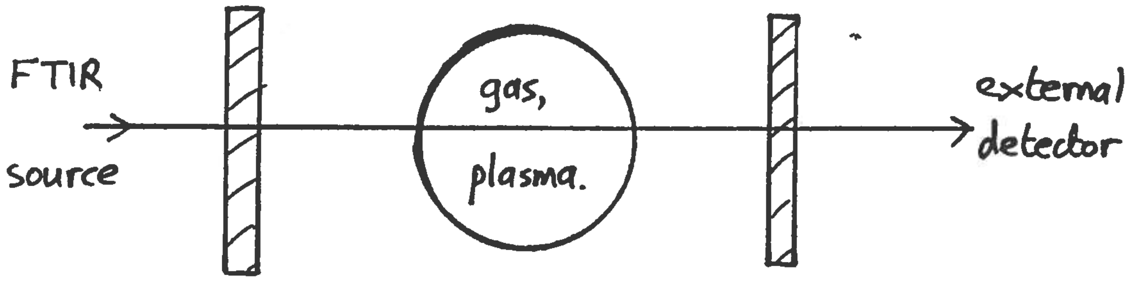


t = true (perfect) data
a = apparent (real measurement) data

Basic Definitions:

True transmitted intensity signal in vacuum = $I_o^t(\nu)$,
which includes source spectrum, window and atmospheric absorption.
True transmitted intensity in presence of gas or plasma = $I^t(\nu)$.

*Check that $I_o^t(\nu)$ is the same before and after experiment (problem of deposition on windows).
*Check that $I^t(\nu) = I_o^t(\nu)$ in the spectral regions without absorption (problem of source intensity variation); if not, normalise $I^t(\nu)$.
*Beware baseline drift due to Mie scattering.

Define: Transmittance $T^t(\nu) = I^t(\nu)/I_o^t(\nu)$

*Check that baseline $T^t(\nu) = 1$ in absence of absorption.

Lambert (Beer) law: $I^t(\nu) = I_o^t(\nu)\ \exp(-k(\nu)d)$
where $k(\nu)$ = absorption coefficient per unit pressure and unit path length and d = "optical depth" = pl = pressure x path length.

Therefore $T^t(\nu) = \exp(-k(\nu)d) = \exp(-k(\nu)pl)$ and $0 \leq T^t(\nu) \leq 1$

Define: Absorbance $A^t(\nu) = k(\nu)pl = -\ln T^t(\nu)$, $A^t(\nu) \geq 0$.

Plasma Measurement $T^t_{pl}(\nu)$ Corrected for Gas Background $T^t_g(\nu)$:

- correction for gas depletion because the source gas pressure p_g is reduced (assuming constant pressure feedback control) in presence of plasma.

Let the partial source gas pressure in the plasma be p'_g -
and so the total pressure with plasma is $p'_g + \sum_i p_{pl_i}$ (= p_g with feedback)
(where p_{pl_i} is the pressure of the i^{th} species created in the plasma).

The transmission with source gas only is $T^t_g(\nu) = \exp(-k_g(\nu)\, p_g\, l)$.
The transmission with plasma is $T^t_{pl}(\nu) = \exp(-k_g(\nu)\, p'_g\, l - \sum_i k_{pl_i}(\nu) p_{pl_i} l)$

The absorbance of the plasma species is $A_{plasma}(\nu) = \sum_i k_{pl_i}(\nu) p_{pl_i} l$

Define: Depletion $D = (p_g - p'_g)/p_g = 1 - p'_g/p_g = 1 - \alpha$, ie $p'_g = \alpha\, p_g$

Therefore $\left[T^t_g(\nu)\right]^\alpha = \exp(-k_g(\nu)\, p'_g\, l)$.

Divide out the residual source gas absorption lines from the plasma transmittance (where α is chosen for the optimal elimination):

$$T^t_{plasma}(\nu) = T^t_{pl}(\nu) \Big/ \left[T^t_g(\nu)\right]^\alpha = \exp(-\sum_i k_{pl_i}(\nu) p_{pl_i} l) = \exp(-A_{plasma}(\nu)).$$

To Compare Model Absorbance Calculations and Real Measurements:

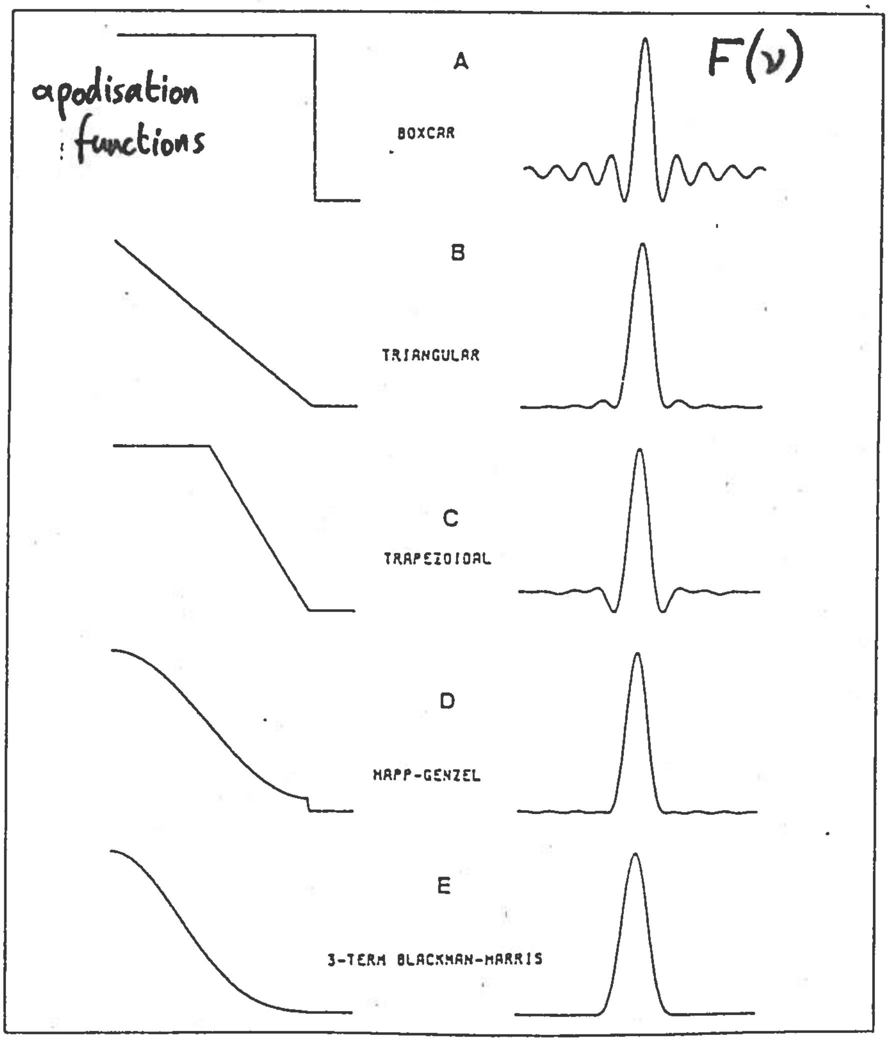
Calculation gives $k^{model}(\nu)$ values for the absorption peaks (Attn. units!).
The calculated transmittance is $T^{model}(\nu) = \exp(-k^{model}(\nu) p l)$.

The real transmittance measurement $T^a(\nu)$ is convolved by the instrumental resolution function $F(\nu)$.

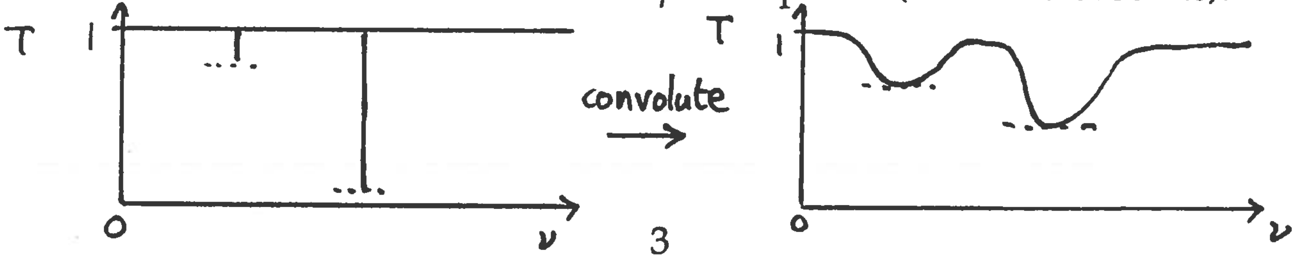
Therefore, we must compare $T^a(\nu)$ with $\int_0^\infty F(\nu'-\nu).T^{model}(\nu).d\nu'$.

For convenience, write $\int_0^\infty F(\nu'-\nu).T(\nu).d\nu'$ as $F \otimes T$ from now on.

Instrumental Resolution:
The experimentally-obtained interferogram is measured for $-L<x<L$ only.
The inverse Fourier Transform therefore convolutes the result by a sinc function = $\sin(x)/x$.
Apodization envelopes applied to the interferogram yield 'smoother' transforms - see Gronholz and Herres (also Champeney, "Fourier Transforms and Their Physical Applications")
(Note: the inverse transform of a Gaussian is a Gaussian; the 3-term Blackman-Harris apodisation function approximates closely to a Gaussian).



The Effect of Convolution on Real Data:
See Cleland and Hess, J. Appl. Phys. 64, 1068 (1988) Figure 2:
Convolution results in a non-linear relation between true and measured peak heights; the minority isotope relative abundances are over-estimated. This is due to the convolution of *absorption* spectra (non-zero baseline).



(Dropping the explicit frequency dependences:)
We could calculate $T^a = I^a / I_o^a = F \otimes I^t / F \otimes I_o^t = F \otimes I_o^t T^t / F \otimes I_o^t$,
but unfortunately, $T^a \neq T^t$; furthermore, $T^a \neq F \otimes T^t$.

Also, $A^a = -\ln T^a = -\ln(F \otimes I_o^t T^t / F \otimes I_o^t) \neq -\ln T^t$, and so $A^a \neq A^t$.

<u>Neither the experimental transmission nor absorbance gives the true value!</u>

<u>First Approximation for Convolution Problem:</u>
Assume that the vacuum spectrum, $I_o(v)$, is approximately invariant over the width of the convolution function F(v); this assumes that there are no atmospheric absorption lines at the spectral region of interest.
Then $F \otimes I_o^t \sim I_o^t(v)$ and $F \otimes I_o^t T^t \sim I_o^t(v) F \otimes T^t$ and so:
$T^a = I^a / I_o^a = F \otimes I^t / F \otimes I_o^t \sim F \otimes T^t$ (OK) however $A^a \sim -\ln F \otimes T^t \neq F \otimes A^t$.
Therefore, we can reasonably work with the experimental transmission, but <u>not</u> with the experimental absorbance.

<u>Problem of Correction for Gas Depletion:</u>

$$\left[T^a(p)\right]^\alpha = \left[F \otimes I_o^t T^t(p) / F \otimes I_o^t\right]^\alpha \sim \left[F \otimes T^t(p)\right]^\alpha \text{ (for 'flat vacuum' approxn.)}$$

$$\neq F \otimes \left[T^t(p)\right]^\alpha = F \otimes T^t(\alpha p) \quad \text{ie } \left[T^a(p)\right]^\alpha \neq F \otimes T^t(\alpha p).$$

Therefore $\left[T^a(p)\right]^\alpha$ cannot be accurately used as a substitute for $T^a(\alpha p)$.

Moral: it is better to acquire gas transmittances for several different pressures over the expected range of the partial pressure with plasma (and even then, the elimination by division as on p2 would still not be applicable).

Note: an empirically-optimum 'α-value' for gas absorption line elimination would not necessarily correspond to the true α value.

The problem is that the gas absorption line transmittance signal varies strongly over the width of the convolution function, ie the FTIR does not resolve gas lines well enough.

Elimination of Background Gas Absorption Lines from Solid Plasma Species

Solid plasma species implies that $k_{pl}(v) \sim$ invariant over the width of F(v).
From p2: The transmission of the gas/powder mixture in the plasma is

$$T^a_{pl}(p_{tot}) = F \otimes T^t_{pl}(p_{tot}) = F \otimes \exp(-k_g(v)\, p'_g\, l - k_{pl}(v)\, p_{pl}\, l)$$

$$\sim \exp(-k_{pl}(v)\, p_{pl}\, l)\; F \otimes \exp(-k_g(v)\, p'_g\, l) = \exp(-k_{pl}(v)\, p_{pl}\, l)\; F \otimes T^t_g(p'_g),$$

ie: $T^a_{pl}(p_{tot}) \sim \exp(-k_{pl}(v)\, p_{pl}\, l)\; F \otimes T^t_g(p'_g)$.

If we have acquired a gas transmission signal (no plasma) at the correct pressure p'_g, then we have $T^a_g(p'_g) = F \otimes T^t_g(p'_g)$, and we directly obtain

The plasma solid species transmission, corrected for gas background:

$$T^a_{plasma}(p_{pl}) = \exp(-k_{pl}(v)\, p_{pl}\, l) \sim T^a_{pl}(p_{tot}) / T^a_g(p'_g). \quad *$$

[If the $T^a_g(p'_g)$ measurement is not available, then the poor approximation $\left[T^a_g(p)\right]^\alpha$ must be used as a substitute for $T^a_g(p'_g) = T^a_g(\alpha p)$ (see pp 2 and 4), where α is chosen for 'optimal' elimination of the gas background signal].

Elimination of Background Gas by Degrading the Resolution (Solid Species)

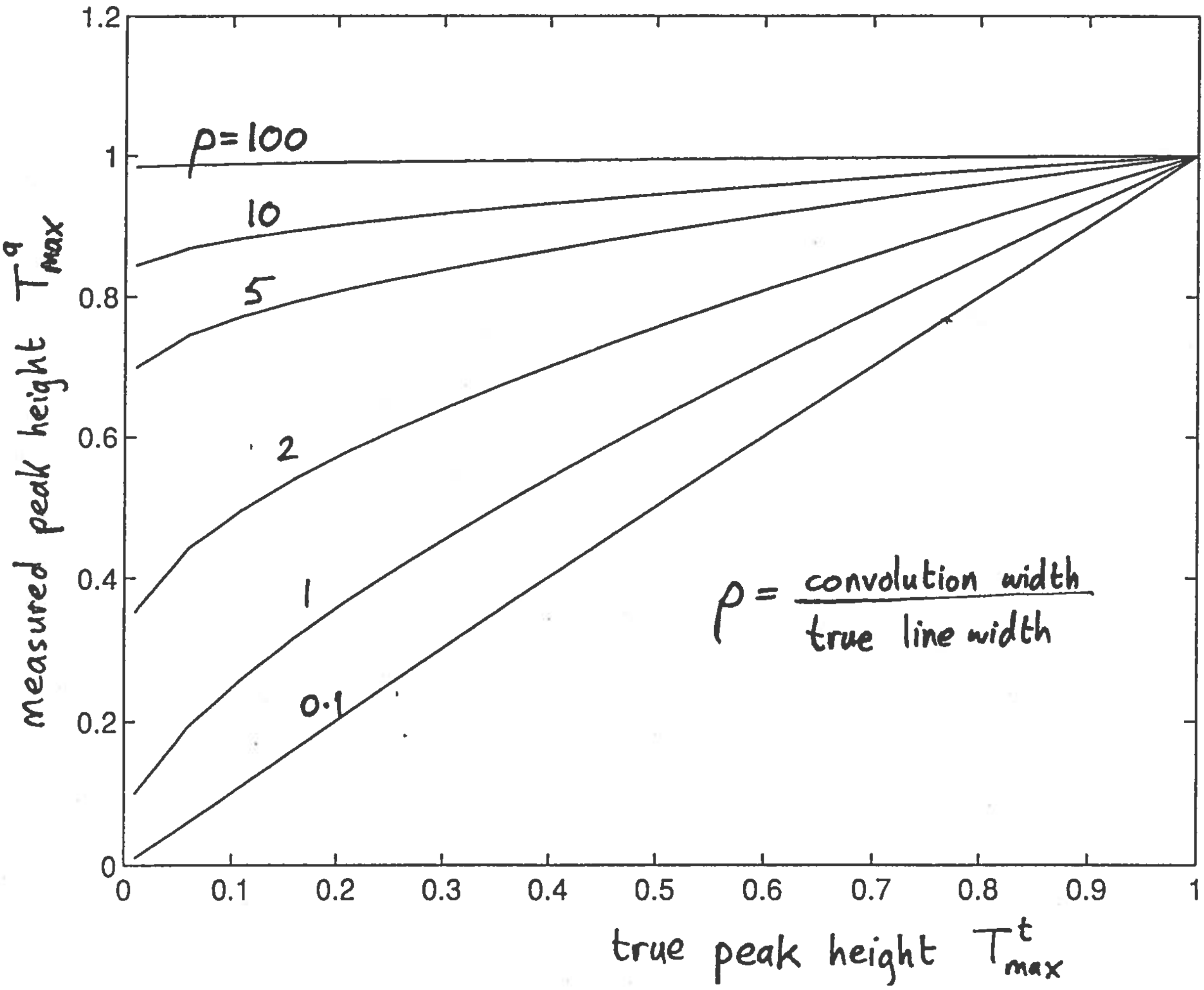
The non-linear relation between the true and measured transmission peak heights (strictly, the peak depths) (p3) depends on the ratio ρ of the convolution width (the resolution) to the true peak width (intrinsic line-width) - see graph on p6, where Gaussian convolution and lineshapes are used.

The larger the ratio ρ, the more the transmission peak is attenuated. Since the intrinsic linewidth of the plasma solid species is very much greater than the gas linewidth, any convolution discriminates in favour of the plasma solid species transmission signal.

The instrumental convolution F(v) already discriminates in favour of the broad, solid species transmission signal: $T^a \sim F \otimes T^t$ and this can be further enhanced by additional digital convolution (Matlab) with a Gaussian G: $T^{conv} = G \otimes T^a = (G \otimes F) \otimes T^t$, having a net convolution of the true data with effective linewidth equal to the sum of G and F Gaussians.

(To preserve the solid species lineshape, the width of G should nevertheless be smaller than the solid species linewidth).

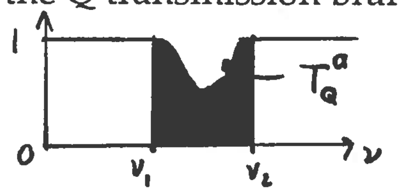
Finally, obtain the solid species transmission T^{conv}_{plasma} by replacing T^a with T^{conv} everywhere in * above.



Measurement of Partial Gas Pressure (eg, for Estimating the Depletion)

"The area under the Q branch can be used to estimate the gas pressure".
Define $\overline{T}_Q$ by the normalised area under the Q transmission branch:

$$\overline{T}_Q = \frac{1}{\nu_2 - \nu_1}\int_{\nu_1}^{\nu_2} T_Q^a \, d\nu = \frac{1}{\nu_2 - \nu_1}\int_{\nu_1}^{\nu_2} T_Q^t \, d\nu$$



using $\int_{-\infty}^{\infty} g(\nu)d\nu = \int_{-\infty}^{\infty} F \otimes g(\nu)d\nu$ for normalised convolution fn. $\int_{-\infty}^{\infty} F(\nu)d\nu = 1$.

(provided that the convolution is not so wide that significant peaks outside the Q branch are added onto the integral range $\nu_2 \rightarrow \nu_1$)

$$\therefore \; \overline{T}_Q = \frac{1}{\nu_2 - \nu_1}\int_{\nu_1}^{\nu_2} \exp(-k(\nu)pl)d\nu = f(p), \text{ unaffected by instrumental resolution.}$$

*the integral could be extended across the P and R branches also, but this would simply deteriorate the signal:noise ratio since the peak spectral density is much lower outside the nearly-degenerate Q branch.

Lambert's law does <u>not</u> apply: $-\ln \overline{T}_Q$ is <u>not</u> simply proportional to pressure!
Therefore, must <u>calibrate</u> $-\ln \overline{T}_Q$ *vs* gas pressure.

*check the Q branch form, at given partial pressure, is the same with/without plasma.