Determination of Spectral Parameters in Microwave Fouriertransform Spectroscopy by Analysis of Time-Domain Signals

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Some disadvantages of using the Fouriertransform algorithm to obtain rotational spectra from microwave pulse induced transient signals are demonstrated. To overcome the difficulties, a fitting procedure is suggested which is based on the analysis of time-resolved data.

Microwave Fourier transform (MWFT) spectrometers have proved in the last years to be useful tools in MW spectroscopy because of their high sensitivity and resolution [1]. Utilizing this experimental technique to record time resolved data, spectral parameters such as line center frequencies are commonly obtained with transformation from time to frequency domain by means of a fast Fourier transform algorithm, using the resulting power spectrum to avoid distortions from phase errors. However, unfortunately, the splittings of multiplets with overlapping lines are then in general too large. Comparing the results for molecular parameters as obtained from the analysis of both large and small splittings in recent experimental investigations, has indicated a systematic error up to 20% in the latter case [2, 3]. Theoretical calculations and computer simulations, done by Merke et al. [4], were able to explain these experimental results with the interference of neighbouring lines. Since the phases of the transient emission signals corresponding to different transitions are strongly frequency dependent, such interference effects are particularly critical in case of overlapping lines (for example see Fig. 4 below). In addition, the cut-off of time-resolved data produces wiggles in the power spectrum which contribute to the limitation of the dynamical range of the spectrometer.

A possible method to overcome these difficulties, which has been discussed extensively [4], is based on the subjective comparison of experimental and theoretical power spectra, the latter being calculated with variation of the spectral parameters to be determined. Such computer simulations of spectral line patterns were found to yield satisfactory results in most cases but were somewhat critical for noisy spectra, particularly in presence of close multiplets. Analysing directly the time-domain data as described below, seems to offer some advantage with respect to a reliable determination of spectral parameters and avoids the problem of biassed analysis using power spectra with less information content.

In order to demonstrate the difficulties which may arise from the analysis of power spectra, Fig. 1 shows computer simulations carried out on a triplet with close components. This theoretical example was chosen with reference to an experimental investigation discussed below (see Figure 3). Figure 1 a gives the power spectrum as obtained from the sum of the transient decay signals for all three transitions, whereas the three lines on Fig. 1 b were calculated from each decay signal separately. A comparison of the spectra in Figs. 1 a and 1 b, which were generated by the same spectral parameters, clearly demonstrates the distortion of resonance frequencies, line shapes and amplitudes in the power spectrum of Figure 1 a.

The fitting procedure, which has been developed for analysis of time-domain data provided by MWFT-spectrometers, is organized as follows. The transient signal corresponding to a multiplet with N components is analysed by a least squares fit to the expression

$$S(t) = \sum_{k=1}^{N} A_k \exp\{-t^2/4q^2\} \cdot \exp\{-t/(T_2)_k\} \cos\{\Omega_k t + \phi_k\}, \qquad (1)$$

where $S(t)$ is the value of the signal at time t after the offset of the microwave pulse and A_k, $(1/T_2)_k$, Ω_k and

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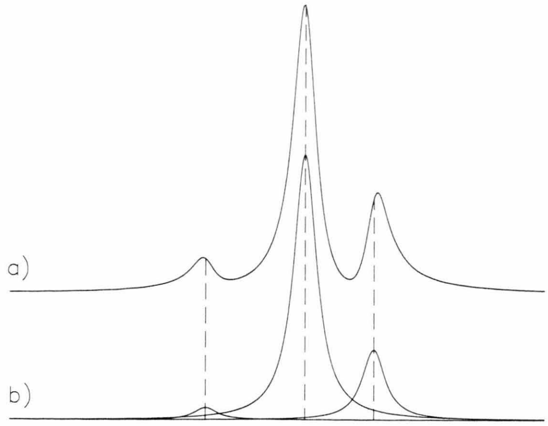

Fig. 1. Theoretical power spectra from computer-simulations with consideration of a triplet. a) Power spectrum from time-domain data including all three lines. b) Power spectra from time-domain data for each line separately.

ϕ_k are fitting parameters. The constant q is related to the Doppler half-width $\Delta\nu_{\mathrm{D}}$ [$= (\ln 2)^{1/2}/2\pi q$].

Fitting such a theoretical expression to the time resolved data is the usual method to obtain rotational relaxation parameters like collision-induced widths and shifts of lines directly from MW-pulse induced transient emission signals [5]. The original motivation to obtain such relaxation data for more than one line, for example in case of nuclear quadrupole hyperfine structures, has lead us to the development of the fitting procedure as described here. Previous attempts with simultaneous variation of all parameters in the least squares fit procedure were not successful in most cases, primarily due to the lack of reliable starting values for the parameters to be fitted. We have therefore chosen a different procedure which is illustrated schematically by the simplified flow diagram in Figure 2.

The spectral parameters are fitted by an iterative procedure, taking into account only the constants in one term of the sum (1) at once. In the first step, we generally fit the constants belonging to the strongest line and then subtract the resulting theoretical values for time-domain data of this line from the experimental signal. The next and all following lines are treated likewise, using each time for the least squares analysis the residuum from the previous fit. This procedure allows to determine parameters of weak lines even close to strong ones. Once all lines have been treated in this way, a new fitting cycle starts to account for effects from the overlap of lines.

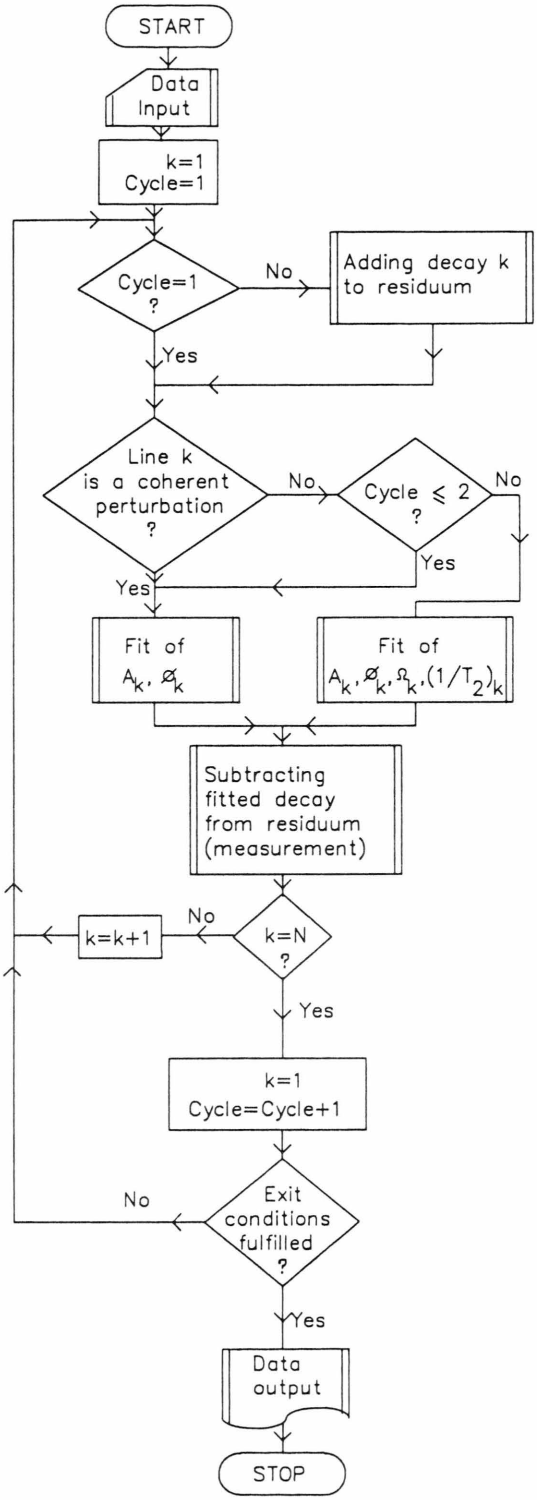

Fig. 2. Simplified flow diagram for the fit procedure to determine spectral parameters by analysis of time-domain signals.

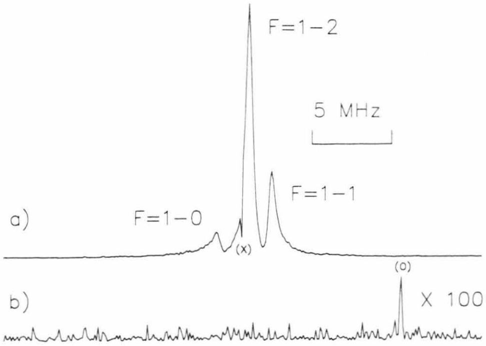

Fig. 3a. Experimental power spectrum for the rotational transition $J, K = 0{,}0 - 1{,}0$ of $CH_3C^{14}N$ at pressure $p = 3.46$ mTorr and temperature $T = 300$ K. Transition frequencies with twice the standard deviations: 18 398.022 (2) MHz ($F = 1 - 2$), 18 396.736 (5) MHz ($F = 1 - 1$) and 18 399.876 (11) MHz ($F = 1 - 0$), obtained from time-domain signal analysis with inclusion of a perturbing CW signal (×) at 30 MHz intermediate frequency. Fig. 3b. Power spectrum of the resulting residuum, enlarged by a factor 100. The perturbing signal (○) at 40 MHz intermediate frequency was not considered in the fit analysis.

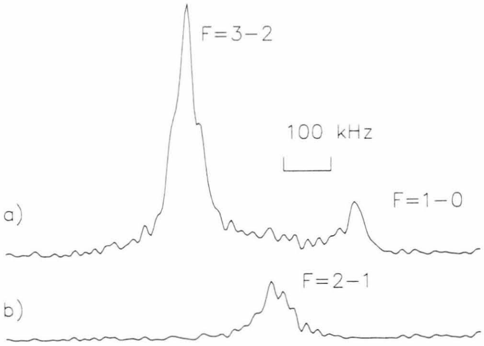

Fig. 4a. Experimental power spectrum for the rotational transition $J(K_-, K_+) = 1(0{,}1) - 2(0{,}2)$ of α-fluoroacetamide at pressure $p = 1.4$ mTorr and temperature $T = 300$ K. Fig. 4b. Power spectrum of residuum from time-domain fit analysis showing an originally hidden line. Transition frequencies with twice the standard deviations, obtained from a fit including all three lines: 13 835.876(2) MHz ($F = 3 - 2$), 13 836.065(5) MHz ($F = 2 - 1$) and 13 836.240(5) MHz ($F = 1 - 0$). – Experimental data provided by Heineking [6].

In the second and all following fitting cycles refined parameter values are then obtained, again treating each line separately. This is done by analysing the experimental data after subtraction of the theoretical data from previous fit results which describe the time dependence of the signal due to all other lines. The procedure stops, usually after several fitting cycles, upon a user defined condition on the relative decrease of the sum of squared defects in consecutive cycles.

The finally resulting residuum in the time domain is useful to indicate transient disturbances, e.g. in case of insufficient suppression of the microwave pulses. With Fourier transformation from time to frequency domain its resulting power spectrum may often reveal per turbing CW signals and/or hidden molecular lines which wer not included in the fit analysis. Examples are given with Figs. 3 and 4 for illustration of these points. Figure 3a gives an experimental result from an investigation on the rotational transition $J, K = 0{,}0 - 1{,}0$ of CH_3CN with ^{14}N-nuclear quadrupole hyperfine structure which was referred to in the introductory remarks on the problem of evaluating molecular parameters from power spectra. Using our fit procedure for analysis of the corresponding transient emission signal with inclusion of all three components of the multiplet and an interfering signal at a 30 MHz intermediate frequency, leads to the power spectrum of the residuum, Figure 3b. The quality of the fit is clearly indicated, as well as the appearance of another disturbance at an intermediate frequency of 40 MHz which does not show up in the original spectrum.

An experimental example for a hidden molecular line in the power spectrum is shown with Figure 4a. The least squares analysis of the time domain data including the two lines results in the residuum, Fig. 4b, which reveals a third line. This line is even stronger than the weaker line in Figure 4a.

It is often useful not to fit all parameters in (1). For a perturbing coherent CW signal the beat frequency Ω is often known, the relaxation parameter $1/T_2$ is zero and the Doppler correction is not used.

In addition, at the start of the fitting procedure, rough values for the resonance frequencies are usually known either from the FT spectra or theoretical predictions from molecular models. We also found that the fitted relaxation parameters were systematically too large until the fit of the other parameters becomes stable. We therefore usually keep the frequencies Ω_k and relaxation parameters $(1/T_2)_k$ fixed during the first two fitting cycles.

The number of variables may be reduced further in many cases with reasonable assumptions on the spectral parameters. In case of fine structures of a rotational line due to intramolecular interaction, the width or $1/T_2$-value for each line is normally the same within the experimental accuracy. In addition, relations between the phases Ω_k for the oscillating decay functions of the investigated transitions may be taken into account. As demonstrated by Heineking [6], a linear frequency dependence of the phases Ω_k results because of the delay between the end of the MW pulse and the beginning of data acquisition. Assuming such a linear phase-frequency relationship approximates also the phase variations due to off-resonant excitation of the transitions for short MW pulses. Thus, the number of variables may be often reduced considerably to get better information out of noisy measurements.

We finally mention that a different approach to spectral analysis by fitting a model to the time-domain data has been worked out recently for application to electron spin-echo (ESE) and NMR pulse experiments [7]. It should be worth to apply this method, which eliminates the need for starting values and the iterative execution in conventional least squares fitting techniques, to MWFT spectroscopy and to compare it with our fit procedure.

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