Triple Resonance Experiments in Microwave Fourier Transform Spectroscopy

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Two-dimensional (2 D) correlation techniques in microwave Fourier transform spectroscopy have been extended to study triple resonance phenomena. Dipole-forbidden double- and triple-quantum transitions have been observed with a five-pulse sequence. The introduction of a phase cycle acting as a triple-quantum filter has simplified the recorded spectra. Experimental results on trifluoromethylacetylene are given as an example.

Introduction

Pulsed microwave Fourier transform (MWFT) spectroscopy proved to be a very powerful method for the observation of pure rotational spectra [1–3]. Compared with conventional microwave spectrometers, the sensitivity [1–3] and resolution [4] of waveguide MWFT spectrometers were improved considerably. The development of two-dimensional (2 D) correlation techniques [5–11] further extended the potential of the MWFT method. Appropriate 2 D techniques made it possible to simplify complex spectra [6, 10, 11], to indicate connections between different resonances [6–11], and to separate transitions which overlapped in one-dimensional spectra [10, 11]. In addition, relaxation processes [8] were investigated and dipole-forbidden transitions [5–7, 10–12] were observed with 2 D techniques. The frequencies of pumped transitions in the broad region from radio frequencies [10] up to millimeter-waves [11] were accurately determined, thereby extending the accessible frequency range of the MWFT method considerably.

Whereas all previously reported experiments were based on three- and four-level double resonance, the present work applies the 2 D MWFT method to triple resonance in a four-level system. Dipole-forbidden double- and triple-quantum transitions were observed with a five-pulse sequence of three different microwave radiations. This technique demonstrated triple resonance connections and provided all transition frequencies in a consecutive four-level quantum system. Figure 1 depicts this system with the dipole-allowed excitation of the three transitions $a \rightarrow b$ ('signal'), $b \rightarrow c$ ('pump 1'), and $c \rightarrow d$ ('pump 2').

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Experimental

A commercial sample of trifluoromethylacetylene (3,3,3-trifluoropropyne, SCM PCR Inc.) was used in the experiments without further purification. The rotational spectrum of this compound was reported in [13].

An Ekkers-Flygare type MWFT spectrometer [1] with a *P*-band waveguide cell operating in the frequency range 11–18 GHz was used to record the spectra. The basic MWFT spectrometer was extended for triple resonance operation. Details of the construc-

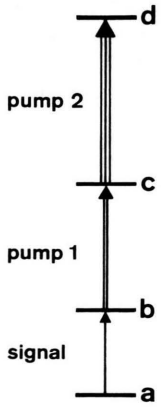

Fig. 1. Energy level scheme for triple-resonance. The three dipole-allowed transitions $a \rightarrow b$ ('signal'), $b \rightarrow c$ ('pump 1'), and $c \rightarrow d$ ('pump 2') are indicated.

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tion and operation were given elsewhere [7] and are summarized here only briefly.

The multi-pulse sequence was produced in a computer controlled memory type sequence generator of our own design. This instrument drove all switches, the phase modulator and the A/D converter. The sequence generator was equipped with seven individual programmable sequence channels, each of which contained a 4096×16 bit memory. A resolution of 10 ns in generating pulses was reached by a serial memory readout at a rate of 100 MHz.

All three radiations ('signal' at 11.5 GHz, 'pump 1' at 17.3 GHz, and 'pump 2' at 23.0 GHz) were generated by phase-stabilized microwave tubes. The microwave pulses of 10 to 100 ns duration were formed by fast PIN-diode switches. The phase of each 'pump 2' pulse was set by a fast 0/180° biphase modulator. The two radiations with lower frequency ('signal' and 'pump 1') were added together by a coaxial power combiner and amplified by a travelling wave tube amplifier (TWTA) up to 20 W peak power. The radiation of highest frequency ('pump 2') was amplified in a separate TWTA and combined with the other two radiations by a tunable waveguide power combiner of our own design [14]. This combiner was located at the entrance of the waveguide cell of 6 m length. The microwave pulse sequence excited the gaseous sample in the cell. After each pulse sequence, the weak molecular emission signals were amplified and downconverted with a superheterodyne detection scheme to the frequency band of 0–50 MHz. These transient signals, corresponding to the time domain t_2, were then digitized at a rate of 100 MHz by means of a 3-bit A/D converter with 512 channels. Each individual pulse sequence was repeated 0.5×10^6 times in order to enhance the signal. The accumulated data were then stored in a LSI-11/73 processor. To record 2 D spectra the above procedure was repeated 256 times incrementing the evolution time t_1 in 10 ns steps. A two-dimensional Fourier transform of the data with respect to t_1 and t_2 yielded the 2 D frequency domain MWFT spectrum with bandwidths of 100 MHz in ν_1 and of 50 MHz in ν_2 [11].

Results and Discussion

The features of the experiment are explained in terms of a four-level quantum system $a-b-c-d$, corresponding to the $J = 1-2-3-4$ energy levels in trifluoromethylacetylene. The five-pulse sequence applied to this system is shown in Figure 2. The initial 'signal' pulse of frequency ν_{ab} acts on the system in thermal equilibrium and generates the single-quantum coherence σ_{ab} of the 'signal' transition [11]. This coherence is transferred by the following pulse of 'pump 1' frequency ν_{bc} into the double-quantum coherence σ_{ac}. The 'pump 2' pulse of frequency ν_{cd} converts σ_{ac} into the triple-quantum coherence σ_{ad}. During the evolution time t_1 the triple-quantum coherence experiences free precession with the sum of the off-resonance frequencies of the three transitions $\Delta\nu_{ad} = \Delta\nu_{ab} + \Delta\nu_{bc} + \Delta\nu_{cd}$. This means that the phase of this coherence rotates with frequency $\Delta\nu_{ad}$ in a rotating frame. The amplitude of σ_{ad} is exponentially damped during t_1 with the relaxation time $T_{ad}^{(2)}$. At the end of the evolution period the triple-quantum coherence σ_{ad} is transferred back into observable signal coherence σ_{ab} in two steps by the two last pulses of the sequence. This coherence transfer depends directly on phase and amplitude of the triple-quantum coherence beeing present at the end of the evolution period. Therefore, incrementation of t_1 leads to modulation of the back-transferred single-quantum coherence. Finally, the coherence σ_{ab} is monitored exclusively during the detection time t_2. The signals of other coherences are prevented from reaching the detector by bandpass filters. The recorded signal is modulated both with respect to t_1 and t_2. The modulation with respect to t_1 yields information about frequency and relaxation time of the dipole-forbidden triple-quantum transition $a \rightarrow d$, whereas the t_2 modulation gains the respective information about the signal transition $a \rightarrow b$.

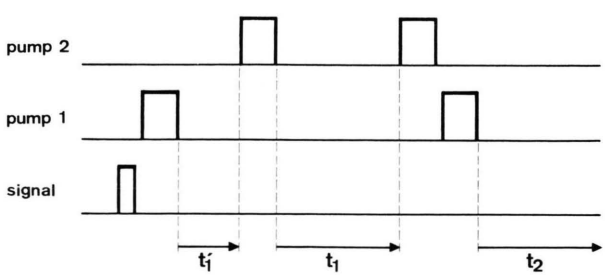

Fig. 2. Pulse sequence for the 2 D triple-quantum (TQ) and triple-quantum filtered double-quantum (TQF-DQ) correlation experiments. In case of the 2 D TQ correlation sequence, the evolution time t_1 is incremented, whereas t'_1 is fixed. For the 2 D TQF-DQ correlation sequence, t'_1 is incremented, whereas t_1 is fixed. The narrow rectangle refer to a $\pi/2$ pulse, the wide ones to π pulses.

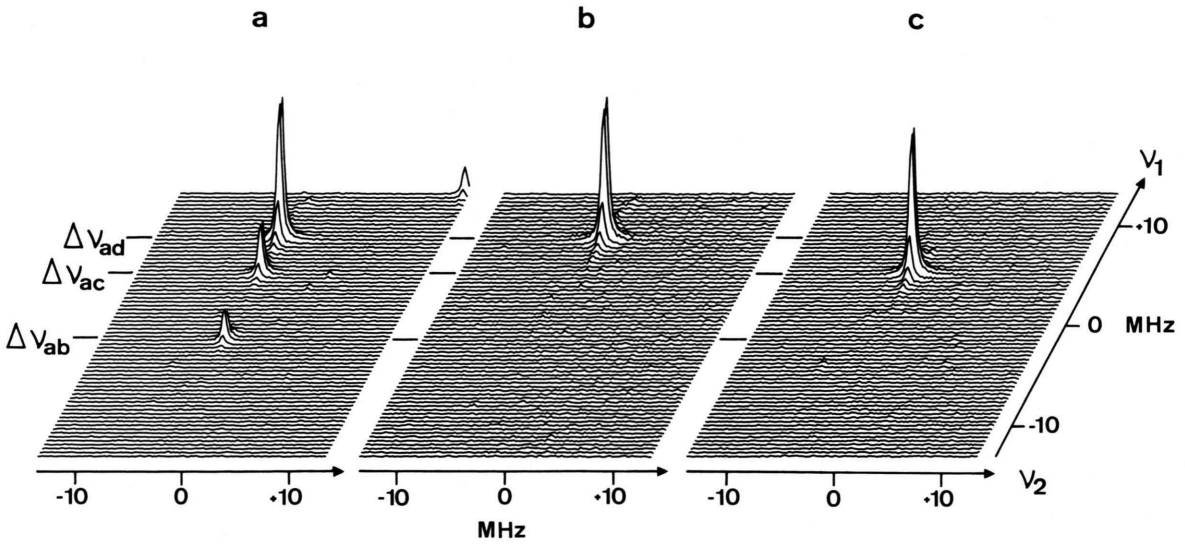

Fig. 3. 2D spectra of the $J = 1-2-3-4$ four-level system of trifluoromethylacetylene, recorded with the pulse sequence of Figure 2. 25 × 25 MHz traces out of the 100 × 50 MHz magnitude spectra are shown. The peaks are located at frequencies $\Delta\nu_{ab}$, $\Delta\nu_{ac}$ or $\Delta\nu_{ad}$ along ν_1 and at $\Delta\nu_{ab}$ along ν_2. a) 2D TQ correlation spectrum, recorded without phase cycle. Three peaks appear. They can be traced back to different coherence transfer pathways. b) 2D TQ correlation spectrum, recorded with a two-step phase cycle on the 'pump 2' pulses. The cycle selects the peak at $\nu_1 = \Delta\nu_{ad}$. c) 2D TQF-DQ correlation spectrum, recorded with a two-step phase cycle on the 'pump 2' pulses. Here the selected resonance appear at $\nu_1 = \Delta\nu_{ac}$. All spectra were recorded under the following conditions: 'signal' frequency 11 514 MHz, 'pump 1' frequency 17 261 MHz, 'pump 2' frequency 23 020 MHz, durations of 'signal' and 'pump 1' pulses 20 ns, durations of 'pump 2' pulses 50 ns, microwave peak power at TWTA output 2 W ('signal' and 'pump 1') and 10 W ('pump 2'), sample pressure 4 mTorr, temperature 210 K, and total recording time 50 min (256 scans, each of 0.5×10^6 cycles).

A 2D triple-quantum (TQ) correlation spectrum of trifluoromethylacetylene recorded with the pulse sequence of Fig. 2 is shown in Figure 3a. The strongest peak within this spectrum is located along ν_1 at $\Delta\nu_{ad}$ and along ν_2 at $\Delta\nu_{ab}$. This resonance corresponds to the coherence transfer pathway described above. Two additional peaks which due to incomplete coherence transfer during the sequence are present in the spectrum. The resonance at $\nu_1 = \Delta\nu_{ac}$, $\nu_2 = \Delta\nu_{ab}$ arise from remaining double-quantum coherence σ_{ac} during t_1, whereas the diagonal peak at $\nu_1 = \nu_2 = \Delta\nu_{ab}$ can be traced back to signal coherence σ_{ab} during t_1. These two unwanted signals can be suppressed efficiently by a two-step phase cycle, as demonstrated in Figure 3b. Thereby, the relative phases between the two 'pump 2' pulses are inverted in two consecutive experiments, synchronized with addition and subtraction of the detected signals. In this way only signals affected by the 'pump 2' pulses are accumulated and other unwanted signals are suppressed. Such phase-cycling procedures which select certain coherence transfer pathways [15, 16] have been successfully applied in 2D MWFT spectroscopy [6–11] several times.

If information about the double-quantum transition is required, minor changes of the TQ correlation sequence have to be done: t_1 has to be fixed at a small value and t_1', the time between the second and third pulse of the sequence, has to be incremented instead of t_1. In this case, double-quantum coherence σ_{ac} instead of σ_{ad} precesses during the evolution time. The coherence σ_{ac} is then transferred in three steps via σ_{ad} and σ_{ac} into the detectable signal coherence σ_{ab}. A two-step phase cycle on the 'pump 2' pulses as described above selects the pathways leading to triple-quantum coherence σ_{ad}. In the resulting 2D spectrum a single peak appears at $\nu_1 = \Delta\nu_{ac}$ and $\nu_2 = \Delta\nu_{ab}$. This experiment, correlating double-quantum with single-quantum coherence and 'filtering' over triple-quantum coherence may be called triple-quantum filtered double-quantum (TQF-DQ) correlation experiment. A 2D spectrum of trifluoromethylacetylene, recorded with the TQF-DQ correlation sequence is given in Figure 3c.

Conclusion

The present work on trifluoromethylacetylene demonstrates that 2D MWFT experiments can be applied successfully to study triple resonance phenomena. The results were confirmed by additional measurements on the $J(K_a, K_c) = 0(0,0) - 1(1,1) - 2(0,2) - 2(1,1)$ system of methyl formate. From both 2D TQ and TQF-DQ correlation experiments, the frequencies of all possible transitions within molecular four-level systems can be determined. The information about the relaxation times of dipole-allowed and dipole-forbidden transitions is included in linewidth and lineshape parameters and can be extracted by fitting the time-domain data [12, 17]. Unfortunately, recording and analysis of 2D spectra are very time-consuming. The one-dimensional analog of the described TQ correlation sequence is well suited to demonstrate the presence of triple-resonance connections, but does not yield precise information about frequencies and relaxation times except for the signal transition.

Triple-resonance experiments may be very useful in cases where the simpler double-resonance methods fail: 2-D MWFT double-resonance techniques require a modulation scheme using a phase-cycle on the pump pulses [6–11]. If in a four-level system $a-b-c-d$ the dipole allowed transition $b-c$ lies in a frequency range where no phase modulators are available, e.g. in the millimeter-wave or infrared region, the required modulation can be reached with a triple resonance technique, but not with a double resonance method. Thus, the TQ and TQF-DQ correlation sequences may be useful to perform MW-MW-laser triple resonance experiments.

Furthermore, it should be possible to record even three-dimensional (3 D) spectra with the five-pulse sequence of Figure 2. By incrementing both t_1' and t_1 and detecting during t_2, the information about the transitions $a \rightarrow c$, $a \rightarrow d$, and $a \rightarrow b$ would be acquired. A triple Fourier-transform of the transient data with respect to t_1', t_1, and t_2 would gain a 3D spectrum, containing the frequency information of the three transitions simultaneously.

Acknowledgements

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