Simplification of Rotational Spectra and Spectral Hole Burning by Selective Excitation Techniques in Microwave Fourier Transform Spectroscopy

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Dedicated to Professor Helmut Dreizler on the Occasion of his Sixtieth Birthday

Selective excitation techniques have been applied to pulsed microwave Fourier transform spectroscopy. The frequency selectivity in excitation has been reached either by a long, weak pulse, or by a DANTE multi-pulse sequence. The corresponding excitation spectra calculated from a density matrix theory are in good agreement with the experimental results. The selective excitation techniques have been combined with double resonance sequences in order to simplify the recorded one- or two-dimensional spectra. Furthermore, selective excitation techniques have been applied to burn 'holes' into rotational transition lines broadened by an inhomogeneous Stark field.

Introduction

In the field of pulsed nuclear magnetic resonance (NMR) spectroscopy, different techniques were developed in order to excite individual resonances selectively. In the 'weak-pulse method', a very long pulse of low intensity is used [1]. In this case, only a very small region around the carrier frequency is excited. A much more general method, called 'tailored excitation' or 'synthesized excitation', was proposed by Tomlinson and Hill [2]. It allows one to 'tailor' the frequency spectrum of the excitation to any desired pattern. The corresponding pulse sequence is calculated from the desired excitation pattern by a Fourier transform. However, it was found to be very difficult to implement the required complicated pulse sequences in practice [3]. A much simpler pulse sequence, which consists of a regular train of identical, short, strong pulses was introduced by Morris and Freeman [3, 4]. The pulse sequence is called 'DANTE' (Delays Alternating with Nutations for Tailored Excitation). It excites the frequencies close to the carrier as well as those close to a series of equally spaced sidebands. The sidebands are symmetrically disposed around the carrier frequency and separated by the pulse repetition rate.

Pulsed microwave Fourier transform (MWFT) spectroscopy proved to be a very powerful method for the observation of rotational spectra. The method is very sensitive [5–7] and shows high resolution [7–9]. However, multi-pulse experiments are much harder to realize than in NMR. This occurs because the relaxation times in rotational spectroscopy are typically five to seven orders of magnitude shorter than in NMR. Therefore, all relevant time intervals have to be much shorter in MWFT experiments than in NMR. However, recently, purely pulsed MWFT double resonance experiments [10, 11] and two-dimensional (2 D) correlation experiments [11–14] were successfully tested. These were based on sequences of only two or three pulses, but indicated that much more complicated pulse trains could, indeed, be applied in the microwave region.

The possibility of applying frequency-selective excitation techniques can be very helpful in the field of MWFT spectroscopy. Rotational spectra are often dominated by different types of strong, unwanted transitions. Selective excitation of the desired resonances should enable one to suppress or at least to reduce the unwanted signals. In spectra recorded with pulsed double resonance methods, different double resonance connections are usually present at the same time. As a result, it is often impossible to identify the individual connections. To solve such assignment problems, it may be helpful to record different spectra of the signal transitions with only one of the candidates for the pump transition being selectively excited. In addition, selective excitation techniques may be useful to simplify complex 2 D spectra. An other valu-

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able experiment is the selective saturation of a narrow region within an inhomogeneously broadened transition line. This effect is well known as 'spectral hole burning' in NMR [3, 15], infrared [16] and optical spectroscopy [17].

In the present paper, solutions of the equations of motion for a two-level quantum system are given. They are used to calculate the behaviour of the molecular systems during single pulses and DANTE pulse trains. The results of these calculations are shown to be in good agreement with experimental data. Furthermore, two MWFT double resonance experiments are performed using a DANTE pulse train. The reaction of the corresponding spectra on the application of the DANTE sequence is demonstrated. In addition, the selective excitation technique is applied to burn a hole into a rotational transition broadened by an inhomogeneous Stark field.

Experimental Details

The experiments were performed using commercial samples of boron trifluoride (Fluka), methyl formate (Fluka), 1-chloro-1-fluoroethene (Fluorochem Ltd.) and carbonyl sulfide (Matheson).

For all experiments, an Ekkers-Flygare type MWFT spectrometer [18] with waveguide cells operating in the frequency range 8–18 GHz was used. Our design is similar to that described by Bestmann et al. [19]. The details of construction and the operation principles of our spectrometer and pulse sequence generator will be published elsewhere [20]. Only a brief description is given here.

The microwave radiation is generated by phase-stabilised klystrons. The microwave pulses or pulse sequences are produced by fast PIN-diode switches, driven by a memory type sequence generator of our own design. The sequence generator is equipped with seven individual programmable sequence channels, each of which contains a 4096 × 16 bit memory. A resolution of 10 ns in generating pulses is reached by a serial memory readout at a rate of 100 MHz. The output pulses are then amplified by a travelling wave tube amplifier up to 40 W peak power. These microwave pulses excite the gaseous sample in the 6 m long waveguide sample cell. The transient molecular emission signals are amplified and down-converted in two steps to the 0–50 MHz band and digitized at a rate of 100 MHz with 512 points. The pulse sequence is repeated at a rate of 55 kHz. The transient signals are summed in a multichannel memory in order to improve the signal-to-noise ratio. After a Fourier transformation of the accumulated data, the frequency-domain magnitude spectrum is recovered over a range of 50 MHz with 256 points.

The extensions of the MWFT spectrometer for the double resonance experiments and for the Stark effect measurements are described in [12–14] and [21], respectively.

Theoretical Background

The dynamical behaviour of an ensemble of identical two-level systems is described by

$$i\hbar\dot{\varrho} = [\hat{H}, \varrho]\,, \tag{1}$$

where ϱ is the density matrix in a space-fixed coordinate system and $\hat{H}$ the total Hamiltonian consisting of a time-independent rotational part and the dipole interaction of the molecules with the time dependent electric field. Relaxation effects are not considered in (1). If it is assumed that the dipole matrix elements $\mu_{aa}=0$ and $\mu_{bb}=0$, the non-zero elements of the corresponding Hamiltonian $\hat{H}$ are given by

$$\begin{aligned} &H_{aa}=E_a\,, \qquad H_{bb}=E_b\,, \\ &\mathrm{H}_{ab}=\mathrm{H}_{ba}=-\mu_{ab}\,\varepsilon\cos(\omega t)\,, \end{aligned} \tag{2a–c}$$

where E_a and E_b are the two molecular energy levels in the absence of the radiation field. ε and ω denote the amplitude and angular frequency, respectively, of the applied microwave radiation. Because the equations are formulated for a certain volume element at the position z in the waveguide, the z-dependence has not been introduced.

By working out the commutator in (1), four coupled differential equations are obtained. They are transformed in a rotating frame by

$$\begin{aligned} &\sigma_{aa}=\varrho_{aa}\,, \qquad &\sigma_{bb}=\varrho_{bb}\,, \\ &\sigma_{ab}=\varrho_{ab}\,e^{-i\omega t}\,, \qquad &\sigma_{ba}=\varrho_{ba}\,e^{i\omega t}\,, \end{aligned} \tag{3a–d}$$

and simplified by dropping the counter-rotating terms (rotating wave approximation). After a second transformation given by

$$\begin{aligned} &s=\sigma_{aa}+\sigma_{bb}\,, \qquad &v=i(\sigma_{ba}-\sigma_{ab})\,, \\ &u=\sigma_{ab}+\sigma_{ba}\,, \qquad &w=\sigma_{aa}-\sigma_{bb}\,, \end{aligned} \tag{4a–d}$$

the equations of motion read as follows

$$\begin{aligned} \dot{s} &= 0\,, & \dot{v} &= \Delta\omega\, u - \alpha\, w\,, \\ \dot{u} &= -\Delta\omega\, v\,, & \dot{w} &= \alpha\, v\,. \end{aligned} \tag{5a–d}$$

The two coherences u and v are proportional to the components of the macroscopic polarization P which are, respectively, in- and out-of-phase with the external radiation. The variable w can be attributed to the difference of occupation probabilities between the two energy levels [7, 22, 23]. $\Delta\omega$ denotes the displacement of the angular frequency of the applied radiation from the molecular resonance angular frequency $\omega_0 = (E_b - E_a)/\hbar$, and α is the Rabi angular frequency. That is

$$\Delta\omega = \omega_0 - \omega\,, \qquad \alpha = \varepsilon\,\mu_{ab}/\hbar\,. \tag{6a, b}$$

The general solutions of the equations of motion (5a–d) during a pulse of duration t are

$$\begin{aligned} s(t) &= s(t=0)\,, \\ u(t) &= \{u(t=0)/\Omega^2\} \cdot \{\Delta\omega^2 \cos(\Omega t) + \alpha^2\} \\ &\quad - \{v(t=0)/\Omega\} \cdot \Delta\omega \sin(\Omega t) \\ &\quad + \{w(t=0)/\Omega^2\} \cdot \alpha\,\Delta\omega\,\{1 - \cos(\Omega t)\}\,, \\ v(t) &= \{u(t=0)/\Omega\} \cdot \Delta\omega \sin(\Omega t) + v(t=0) \cdot \cos(\Omega t) \\ &\quad - \{w(t=0)/\Omega\} \cdot \alpha \sin(\Omega t)\,, \\ w(t) &= \{u(t=0)/\Omega^2\} \cdot \alpha\,\Delta\omega\,\{1 - \cos(\Omega t)\} \\ &\quad + \{v(t=0)/\Omega\} \cdot \alpha \sin(\Omega t) \\ &\quad + \{w(t=0)/\Omega^2\} \cdot \{\alpha^2 \cos(\Omega t) + \Delta\omega^2\}\,, \end{aligned} \tag{7a–d}$$

where Ω is defined by

$$\Omega^2 = \alpha^2 + \Delta\omega^2\,. \tag{8}$$

The solutions for periods of free precession (in absence of external radiation) can be easily derived from (7a–d) and (8) by setting $\alpha = 0$. They are

$$\begin{aligned} s(t) &= s(t=0)\,, \\ u(t) &= u(t=0)\cos(\Delta\omega\, t) - v(t=0)\sin(\Delta\omega\, t)\,, \\ v(t) &= u(t=0)\sin(\Delta\omega\, t) + v(t=0)\cos(\Delta\omega\, t)\,, \\ w(t) &= w(t=0)\,. \end{aligned} \tag{9a–d}$$

The equations (7)–(9) are sufficient to explain the excitation of the system during selective pulses or DANTE pulse trains. After such an excitation, the molecular emission signals are monitored during the detection period t_d. It was demonstrated that in MWFT experiments the signal at the detector is proportional to the macroscopic polarization P [24]. P is defined by

$$P = N\,\mathrm{Tr}\,\{\mu\,\varrho\}\,, \tag{10}$$

where N is the number density of two-level systems, ϱ is the density matrix in the space-fixed system, and μ is the matrix of the dipole moment operator. By working out the trace in (10) and with the transformations (3) and (4), the polarization can be expressed as

$$P(t_d) = N\,\mu_{ab}\,\{u(t_d)\cos(\omega t_d) - v(t_d)\sin(\omega t_d)\}\,. \tag{11}$$

Because no external radiation is present during the detection time, we can combine (11) with (9b, c) to obtain

$$\begin{aligned} P(t_d) &= N\,\mu_{ab}\,\{u(t_d=0)\cos(\omega_0 t_d) - v(t_d=0)\sin(\omega_0 t_d)\} \\ &= A\,N\,\mu_{ab}\cos(\omega_0 t_d - \varphi)\,, \end{aligned} \tag{12}$$

with

$$\begin{aligned} A^2 &= u(t_d=0)^2 + v(t_d=0)^2\,, \\ \varphi &= \arctan\{-v(t_d=0)/u(t_d=0)\}\,. \end{aligned} \tag{13a, b}$$

A can be attributed to the amplitude and φ to the phase of the excitation. Therefore, the excitation function of a single pulse or a pulse train can be directly represented by the variable A, calculated as a function of the off-resonance frequency $\Delta\nu$ (with $\Delta\nu = \Delta\omega/2\pi$).

Results and Discussion

Selective Excitation by a Single Pulse

First, the excitation pattern for single pulses of different durations were calculated from (7b, c), (8) and (13a). It was assumed that the pulses act on the system at thermal equilibrium, with $u(t=0) = v(t=0) = 0$ and $w(t=0) = w_0$. The resulting excitation functions $A(\Delta\nu)$ for pulse durations τ_p of 30, 80, and 200 ns are given in the middle section of Figures 1a–c. Each of these excitation functions has its primary maximum at the frequency of the carrier (at $\Delta\nu = 0$). Each function decreases with increasing frequency offset, and reaches zero at $\Delta\nu = \pm 1/\tau_p$. For larger frequency offsets, the excitation function shows numerous secondary maxima. These secondary maxima are much weaker than the primary ones, and their intensities decrease rapidly for higher frequency offsets. Thus, with a single pulse, high excitation can only be obtained for transition frequencies in the vicinity of the carrier. The frequency range which experiences high excitation is given by the duration of this pulse τ_p. Short pulses are able to excite transitions in a relatively broad range, whereas longer pulses act more frequency selective. This effect can be seen in the MWFT spectra of $^{11}BF_3$, pictured in the lower part of Figures 1a–c. Ten 'for-

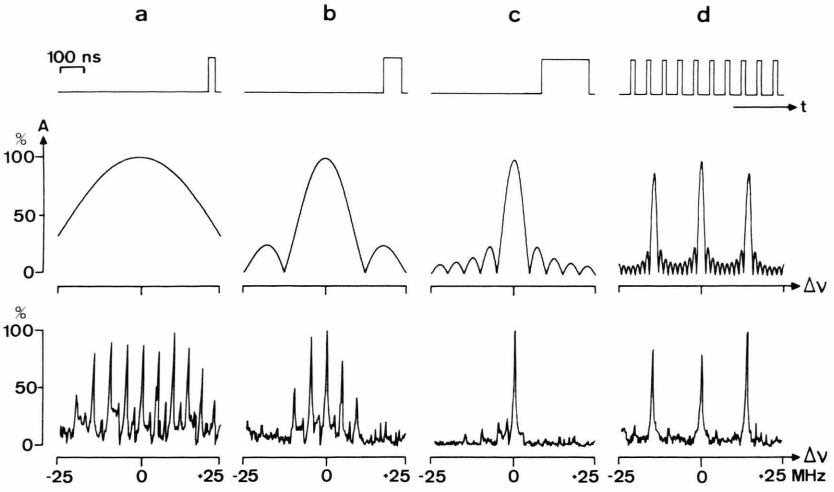

Fig. 1. Broadband and selective excitation in MWFT spectroscopy. Upper part: Applied pulses or pulse sequence. Single pulses with durations of 30 ns (trace a), 80 ns (trace b), and 200 ns (trace c), or a DANTE sequence of 10 pulses (trace d) are used. The pulses of the DANTE sequence have a duration of 20 ns and are spaced by 70 ns. Middle part: Corresponding excitation spectra. All excitation functions are calculated for overall pulse angles of $\pi/4$. Lower part: Corresponding MWFT magnitude spectra of $^{11}BF_3$. Ten 'forbidden' $K = \pm 1 \leftarrow \mp 2$ Q-branch transitions, with J values between 30 (highest frequency) and 39 (lowest frequency) fall in the given frequency range of these spectra. The relative intensities of these transitions agree well with the calculated excitation spectra. The experimental conditions used to record the spectra were: microwave frequency 15461.6 MHz, microwave power 20 W, sample pressure 30 mTorr, sample temperature 200 K, and recording time 60 min (1.8×10^8 cycles) for trace a 10 min (3×10^7 cycles) for trace b, and 5 min (1.5×10^7 cycles) for traces c and d.

bidden' $\Delta K = \pm 3$ Q-branch transitions of $^{11}BF_3$ with J between 30 and 39 fall into the frequency range given in these spectra [25]. These transitions are almost equally spaced and have nearly the same peak absorption coefficients. Therefore, the intensity distribution of these transitions is mainly due to the corresponding excitation functions. Good agreement between the obtained intensities and the predicted excitation spectra in fact was found in all recorded spectra of $^{11}BF_3$. This is clearly visible in the three examples of Figures 1 a–c.

Selective Excitation by a DANTE Sequences

A frequency selective excitation of rotational transitions also can be reached by a DANTE sequence. Such a sequence consists of a regular train of n identical, short pulses, each with a small angle (of $\alpha \tau_p \leq \pi/2n$). Because here the individual pulses are separated by intervals of free precession, the calculation of the excitation function $A(\Delta v)$ is done by a step-wise process. The values of the relevant variables after the first pulse, calculated from (7b–d) and (8), are used as initial values for the calculation of the behavior during the following period of free precession (with equations (9b–d)). The values at the end of this interval then are used as initial values for the second pulse, and so on. The resulting excitation functions for DANTE sequences of 10 and 50 pulses are pictured in Figure 2. In contrast to the single pulse method, not only the frequencies around the carrier, but also those around numerous sidebands are excited to a significant extent. The sidebands are symmetrically disposed with respect to the carrier and separated by the repetition rate of the pulses during the DANTE sequence. The selectivity of this method improves with the length of the sequence τ_s and, therefore, if the pulse repetition rate is fixed, with the number of pulses in the sequence. For the central maximum as well as for each sideband, only a frequency range of less than $2/\tau_s$ is significantly excited.

The nature of the selectivity of the DANTE sequence can be visualized easily. If the pulses are on resonance, their effect will be cumulative, assuming that the relaxation can be neglected. If the pulses are applied off-resonance, the precession during the intervals between the pulses will change the phase of the coherence created, and the net effect of the pulses tend to cancel out. However, if the pulses are off-resonant in frequency precisely by m/τ, where m is an integer

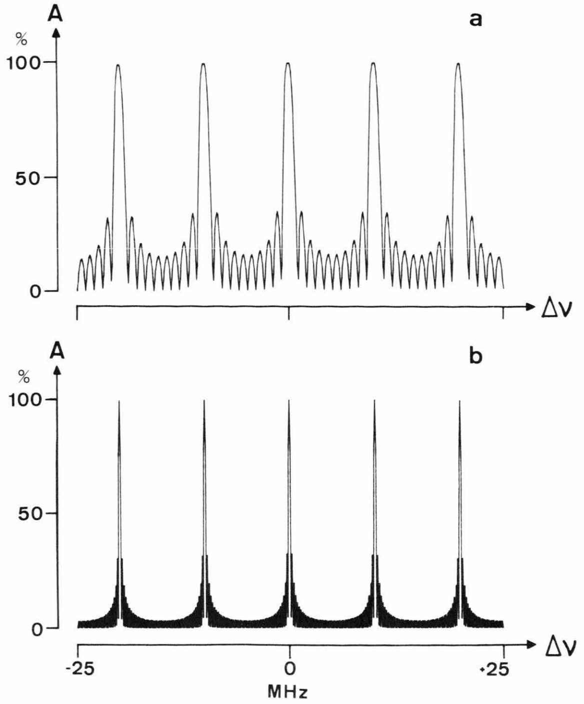

Fig. 2. Calculated frequency domain excitation spectra corresponding to DANTE sequences of 10 (trace a) and 50 pulses (trace b). The conditions are: duration of each pulse 10 ns, spacing between the pulses 100 ns, and overall pulse angle $\pi/2$.

and τ the pulse interval, the coherences precess through a complete number of full rotations in the intervals between the pulses. Thus, the coherence will be in phase with the radiation field for all pulses, and the effect of the pulses again will be cumulative. This leads to the described sidebands in the corresponding excitation spectrum.

A DANTE sequence consisting of ten pulses was applied to record a spectrum of $^{11}BF_3$, as shown in Figure 1 d. In this spectrum, the three transitions with $J=33$, 35 and 37 were excited by the central maximum or by the first sidebands. All other transitions of $^{11}BF_3$, in particular the two lying between the excited ones, do not appear in this spectrum.

Selective Excitation in Double Resonance Experiments

Not only in the 'standard' MWFT spectroscopy, but also in the field of pulsed double resonance or two-dimensional (2 D) spectroscopy, selectivity in the frequency domain often would be a decided advantage. To explore the potential applications of the DANTE sequence in this area, two different double resonance pulse sequences were combined with the selective excitation techniques described above. Both experiments allow one to explore connections between the transitions excited by two pulsed microwave radiations of different frequencies, called signal and pump radiation. Frequency selectivity in the range of the pump can be obtained with the first experiment, whereas the chosen signal transitions are excited exclusively with the second method.

The simplest MWFT double resonance technique is the two-pulse population transfer experiment of Bestmann and Dreizler [10]. The first pulse of the corresponding sequence produces a change of the population differences between the two levels of each pumped transition. A second pulse, now at the signal frequency, is applied immediately after the first and excites the signal transitions. If a signal transition shares a common energy level with a pumped transition, also the population difference between the signal levels is affected by the pump pulse, and the intensity of the signal transition will change. By using double resonance modulation, only this intensity change is detected [13]. An example of such a double resonance modulated spectrum of methyl formate is given in Figure 3 a. The spectrum shows both A and E internal rotation components of the $J(K_a, K_c)=2(1,1)-2(0,2)$ signal transition. The two corresponding components of the connected $J(K_a, K_c)=2(0,2)-1(1,1)$ pump transition are spaced by only 3 MHz and, therefore, they both are affected by the short pump pulse. However, if the pump pulse is replaced by a DANTE sequence, each of the two internal rotation components can be pumped selectively. This is demonstrated in Figures 3 b–c. In these spectra, the second sideband of the excitation produced by a DANTE sequence of 30 pulses was set on-resonance either with the E (Fig. 3 b), or with the A component of the pump transition (Figure 3 c).

The second double resonance technique described here is the double-quantum correlation experiment of Stahl et al. [11]. The three-pulse sequence, supplied with a phase cycle for double resonance modulation, can be applied successfully to record 2 D MWFT spectra [12–14]. The sequence is pictured in the upper part of Figure 4 a. The first pulse excites the coherences of the signal transitions. If a signal transition shares a common energy level with a pump transition, the following pump pulse will transfer the signal coherence into double-quantum coherence. After the evolution

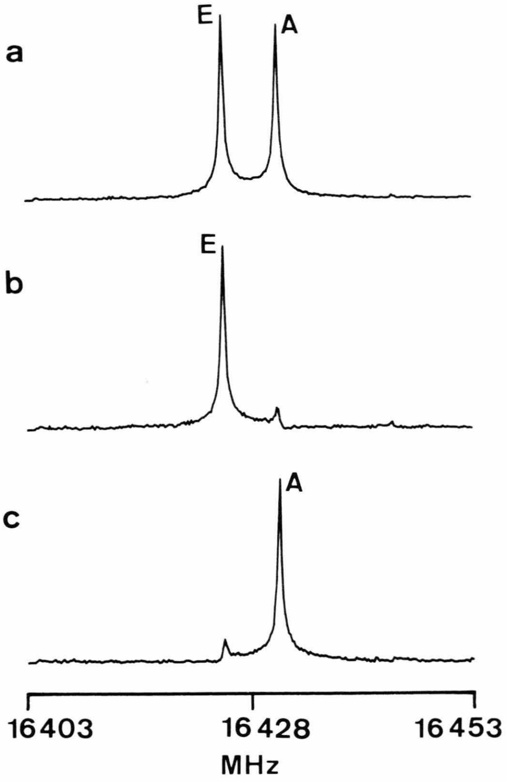

Fig. 3. Selective excitation in double resonance experiments. a) Double resonance modulated spectrum of methyl formate. Signal transition: $J(K_a, K_c)=2(1,1)-2(0,2)$, pump transition: $2(0,2)-1(1,1)$. The spectrum was recorded using the population transfer sequence consisting of a pump pulse of 50 ns duration, immediately followed by a 30 ns signal pulse. Both A and E internal rotation components are pumped in this experiment. b) and c): The single pump pulse of the sequence was replaced by a DANTE train of 30 pulses (with a duration of each pulse of 10 ns and a spacing between the pulses of 100 ns). b) Pump frequency 11 250.7 MHz. The second sideband of the pump interacts selectively with the E component of the pump transition at 11 230.7 MHz. c) Pump frequency 11 247.5 MHz, the A component of the pump transition at 11 227.5 MHz is selectively pumped. The general experimental conditions for all spectra were: signal frequency 16428 MHz, pressure 5 mTorr, temperature 200 K, recording time 1 min (3×10^6 cycles).

time t_1, the second pump pulse converts the double-quantum coherence back into signal coherence, which is monitored during the following detection period t_2. In these studies, t_1 is incremented 256 times in steps of 10 ns. A two-dimensional Fourier transform of the data with respect to t_1 and t_2 yields the 2D frequency domain spectrum. For each double resonance connection, a cross peak appears in the 2D spectrum. This peak is located along $\Delta\nu_2$ at the off-resonance frequency of the signal transition, and along $\Delta\nu_1$ at the off-resonance frequency of the double-quantum transition, respectively. For additional details see [12–14]. A 2D spectrum of the $J(K_a, K_c)=2(0,2)-1(1,1)-2(1,2)$ three-level system of 1-chloro-1-fluoroethene recorded with this sequence is presented in Figure 4a. All seven cross peaks within this spectrum appear because the corresponding hyperfine components of signal and pump transition share a common energy level. From their $\Delta\nu_2$ frequencies, the seven peaks can be assigned to the four hyperfine components of the signal transition $2(1,2)-1(1,1)$ at $\Delta\nu_2=-8.23$ MHz, -2.10 MHz, 1.44 MHz, and 10.00 MHz. All these frequencies lie within the excitation range of the signal pulse of 30 ns duration used in this experiment. However, replacing the signal pulse by a DANTE pulse train allows selective excitation of only one hyperfine component. This is demonstrated in Figure 4b. The applied DANTE sequence consisting of twelve pulses excited only frequencies in the immediate vicinity of $\Delta\nu_2=0$, ± 10 MHz, ± 20 MHz, ... Therefore, only the two cross peaks which correspond to the hyperfine component at $\Delta\nu_2=10.00$ MHz remain in the 2D spectrum. This off-resonance signal frequency in fact coincides with the first sideband of the excitation spectrum.

Spectral Hole Burning

As known from other types of spectroscopy [3, 15–17], 'holes' only can be burned into inhomogeneously broadened transitions. In the field of rotational spectroscopy, inhomogeneous broadening may occur by the Doppler effect or by applying inhomogeneous electric or magnetic fields. In such 'hole burning' experiments, a narrow region of the inhomogeneously broadened transition is saturated selectively, whereas the remainder is left essentially unaffected. This means that the radiation only interacts with the molecules in a restricted region within the sample cell or, in case of Doppler broadening, with the molecules having a velocity in a restricted range. All other molecules are off-resonance with respect to the applied radiation and do not interfere. This leads to a 'dip' or a 'hole' in the lineshape of this transition. Such a hole may never be narrower than the 'natural' homogeneous linewidth [3].

Because the Doppler broadening is small in the frequency range of our MWFT spectrometer, the 'hole burning' effect is demonstrated on a transition broadened by an inhomogeneous Stark field. Figure 5a

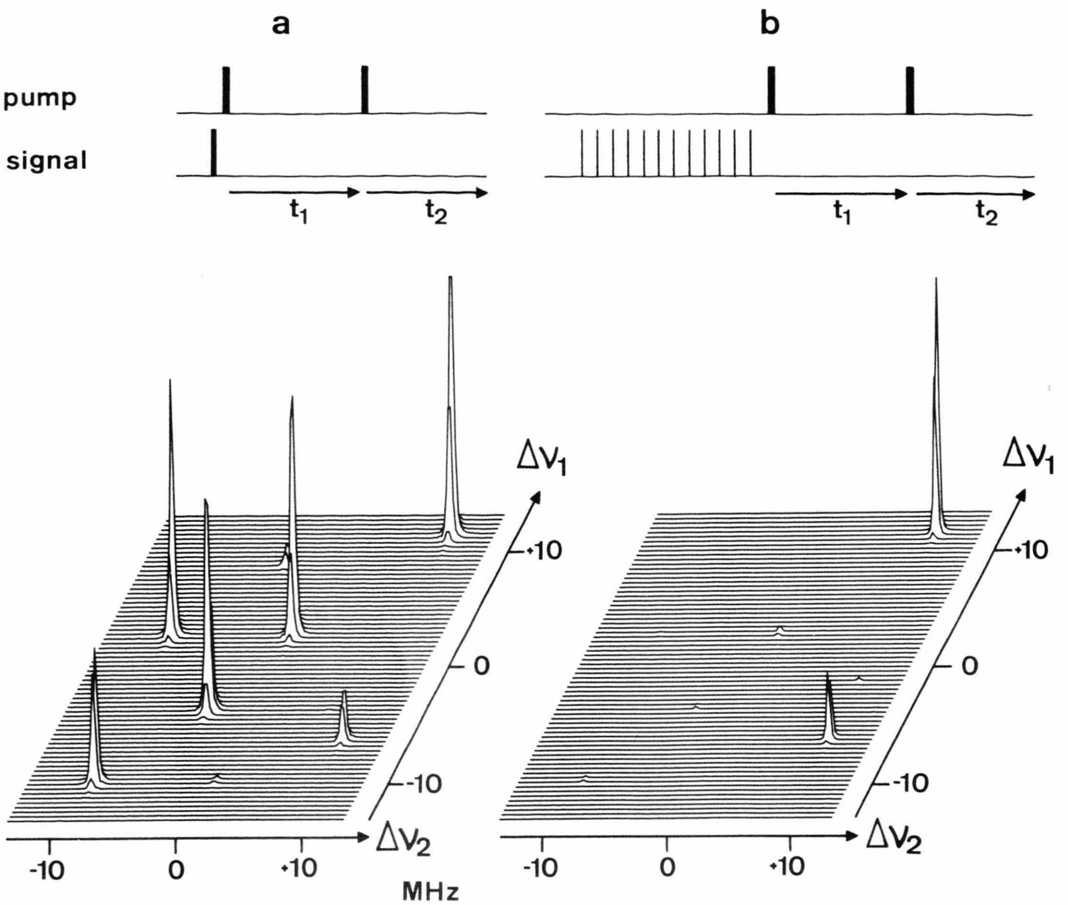

Fig. 4. Selective excitation in two-dimensional MWFT experiments. The applied pulse sequences are shown in the upper part of the figure. a) 2 D spectrum of 1-chloro-1-fluoroethene recorded with the double-quantum correlation sequence. Four different hyperfine components of the signal transition are excited by the first pulse of the sequence. They give rise to seven cross peaks in spectrum. For additional details see Fig. 6 of [14]. b) The single signal pulse of the sequence is replaced by a DANTE pulse train consisting of 12 pulses. As a result, only one hyperfine component of the signal transition is excited. In the corresponding 2 D spectrum, only the two cross peaks at $\Delta\nu_2 = 10$ MHz remain, whereas all other resonances disappear. Both 2 D spectra were recorded under the following conditions: signal frequency 15441.1 MHz, pump frequency 11196 MHz, durations of the pump pulses 40 ns, pressure 8 mTorr, temperature 200 K, and total recording time 90 min (256 scans, each of 10^6 cycles). For trace a, a 30 ns long signal pulse was used, whereas for trace b a DANTE sequence with pulse durations of 10 ns and a spacing between the pulses of 100 ns was applied.

shows the standard MWFT spectrum of the $J = 1 \leftarrow 0$ transition of OCS at a static Stark field of 2920 V/cm. At this field, the frequency of the transition is shifted by 48.5 MHz, and its linewidth of 2.5 MHz is increased by a factor of five, as compared to the value of 0.5 MHz determined in absence of the field. Each of the spectra given in Figs. 5 b–d shows a 'hole' in the line profile. These 'holes' were burned by the second sideband of the excitation produced by a DANTE sequence of 50 pulses. The DANTE sequence was applied prior to the detection pulse. The pulses of the DANTE sequence and the excitation pulse were produced from two individual microwave radiations, differing both in power and frequency. In the three spectra of Figs. 5 b–d, the DANTE excitation was set on different frequencies within the transition linewidth, so that different regions of the transition line experienced a selective saturation. The width of the hole is with approximately 0.6 MHz only slightly larger than the width of the transition in absence of the field.

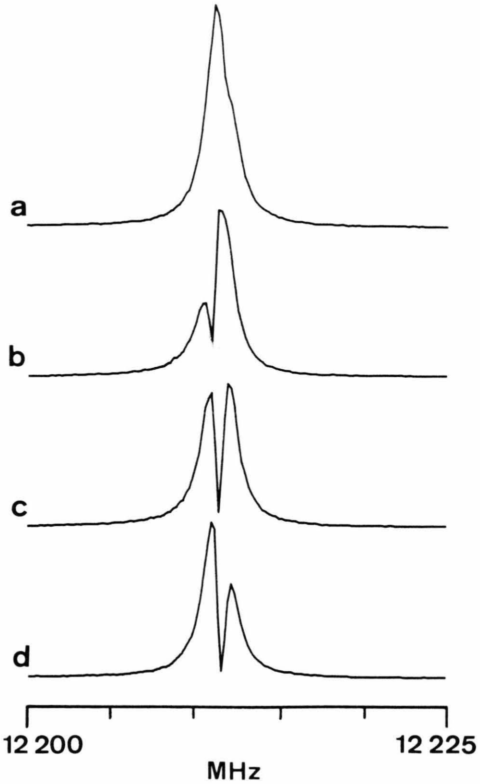

Fig. 5. Spectral hole burning. a) Standard MWFT spectrum of the $J=1-0$ transition of OCS at a DC Stark field of 2920 V/cm. The transition line is broadened by the inhomogeneity of the applied field. A 30 ns long detection pulse of 5 W peak power and a frequency of 12210 MHz was used to polarize the sample. b–d) A DANTE sequence of 50 pulses was applied prior to the detection pulse. The 'holes' appeared because the corresponding regions of the transition were selectively saturated. The pulses of the DANTE sequence were 10 ns long, had a peak power of 0.5 W, and were spaced by 100 ns. The carrier frequency for the DANTE sequence was 12231.1 MHz for trace b, 12231.4 MHz for trace c, and 12231.6 MHz for trace d. The second sideband of the DANTE excitation which was used to burn the 'holes' appears 20 MHz below the carrier frequency.

Conclusions

In the present paper, the general principles of frequency selective excitation in MWFT spectroscopy have been discussed, and some experiments based on selective excitation techniques have been performed. The excitation spectrum of a DANTE pulse train has been compared with that of a single pulse. Whereas with a long, weak pulse only a small frequency range around the carrier can be excited to a significant extent, also numerous sidebands are excited if a DANTE multi-pulse sequence is applied. The use of a sideband rather than the central maximum for the excitation may be favourable, because in MWFT spectra a coherent disturbance usually is present at the frequency of the carrier.

Selective excitation can suppress unwanted signals in the recorded spectra. Unfortunately, this methods fails if the transition moment of the unwanted peak is much larger than that of the interesting transition. In particular, it will be nearly impossible to remove the transitions of polar impurities from the MWFT spectra of nonpolar molecules only by selective excitation techniques.

The application of frequency selective excitation in pulsed double resonance and 2D experiments gives more detailed information about connections between the irradiated transitions. This simplifies the assignment of the MWFT spectra. It is obvious that the DANTE sequence also can be combined with double resonance sequences different from those described here.

As demonstrated in this work, 'spectral hole burning' experiments, well known from optical spectroscopy, can also be performed now in the microwave range. This experiment is a useful test for inhomogeneous broadening.

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