T_2-Measurement on a Dipole-forbidden Transition of OCS

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A double resonance pulse sequence experiment is described allowing the determination of the rotational relaxation time T_2 of certain dipole-forbidden transitions. Measurements on the pressure dependence of T_2 for the dipole-forbidden transition $J = 0$, $M = 0 \rightarrow J = 2$, $M = 0$ of OCS have been performed using a superhet bridge type transient spectrometer. No significant difference of the results is found compared with measurements on the dipole-allowed transitions $J = 0$, $M = 0 \rightarrow J = 1$, $M = 0$ and $J = 1$, $M = 0$, $\pm 1 \rightarrow J = 2$, $M = 0$, ± 1.

I. Introduction

Investigations of the rotational relaxation time T_2 are often performed by analysis of transient emission signals. These can be observed after the interaction of the molecular ensemble with the polarizing MW-radiation has been switched off. In most experiments either the Stark-switch technique [1] or a PIN-switch method [2, 3] is used. The Stark-field tunes the molecular transition frequency into and out of resonance with the MW-radiation. With a PIN-switch, resonant MW-pulses are produced which polarize the molecular ensemble. The signals are superheterodyne detected and may be converted to a nonzero intermediate frequency [2], giving the observed molecular response an oscillatory appearance, or may be converted to DC [3] resulting in zero beat signals. A PIN-switch method allowing the observation of both transient absorption- and emission signals by means of a superheterodyne bridge type spectrometer was described recently [4].

T_2-measurements from investigation of transient emission can only give information about dipole-allowed rotational transitions and the connected off-diagonal elements of the density matrix. The behaviour of off-diagonal elements of the density matrix that correspond to dipole-forbidden transitions is not described by the two-level theory [5] which only implies the dipole interaction between an ensemble of two-level systems and a single MW-radiation.

A sufficient model is that of a three-level system with the energy levels $E_a < E_b < E_c$ and the two dipole-allowed transitions between E_a and E_b (pump transition) and between E_b and E_c (signal transition). By introducing both a pump- and a signal-MW it can be shown that off-diagonal elements of the density matrix corresponding to the transition between E_a and E_c can be generated. According to the theory of three-level systems given by Bottcher, Baker and Feuillade [6, 7] this transition does not have to be dipole-allowed.

In this paper we describe a pulse sequence experiment. It was performed with our bridge type superheterodyne spectrometer allowing the determination of a T_2-type relaxation time for a forbidden transition of the type $E_a \leftrightarrow E_c$. The experiment required the application of pulsed pump- and signal-MW radiation with adjustable pulse lengths and variable delay time between the pulses. The forbidden transition $J = 0$, $M = 0 \rightarrow J = 2$, $M = 0$ of Carbonylsulfide, OCS, was chosen in our experiment.

II. Theory

We consider an ensemble of three-level systems with the energy levels $E_a < E_b < E_c$ perturbed by a pump-MW radiation with the electric field strength ε_p and a signal-MW radiation with ε_s*:

$$\varepsilon_p(Z, t) = 2\,\varepsilon_{ab} \cos(\omega_{ab} t - k_{ab} Z)\,, \tag{1}$$

$$\varepsilon_s(Z, t) = 2\,\varepsilon_{bc} \cos(\omega_{bc} t - k_{bc} Z)\,. \tag{2}$$

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* The definitions of signal- and pump-transition are arbitrary. Our definition refers to the experimental setup. The transition the polarisation of which is detected in the experiment will be called the signal transition.

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Plane wave propagation in Z-direction is assumed. By time dependent perturbation theory "three-level Bloch equations" have been derived [6, 7] describing the time dependent behaviour of the macroscopic polarisation of the ensemble and the population differences between the energy levels:

$$-\dot{\boldsymbol{L}} = \mathbf{A}\,\boldsymbol{L} - \boldsymbol{C} \tag{3}$$

with the column vectors:

$$\boldsymbol{L} = \{\Delta N_{bc}, \Delta N_{ab}, P_{bc}, Q_{bc}, P_{ac}, Q_{ac}, P_{ab}, Q_{ab}\}, \tag{4}$$

$$\boldsymbol{C} = \{\Delta N^0_{ab}\gamma_w + \Delta N^0_{bc}\gamma_x, \Delta N^0_{ab}\gamma_y + \Delta N^0_{bc}\gamma_z, 0, 0, 0, 0, 0, 0\} \tag{5}$$

and the matrix $\mathbf{A}$:

$$\mathbf{A} = \begin{pmatrix}
\gamma_x & \gamma_w & 0 & -4\frac{\varepsilon_{bc}}{\hbar} & 0 & 0 & 0 & 2\frac{\varepsilon_{ab}}{\hbar} \\
\gamma_z & \gamma_y & 0 & 2\frac{\varepsilon_{bc}}{\hbar} & 0 & 0 & 0 & -4\frac{\varepsilon_{ab}}{\hbar} \\
0 & 0 & \frac{1}{T_2^{bc}} & \Delta\omega_{bc} & 0 & \frac{\varepsilon_{ab}}{\hbar} & 0 & 0 \\
\mu_{bc}^2\frac{\varepsilon_{bc}}{\hbar} & 0 & -\Delta\omega_{bc} & \frac{1}{T_2^{bc}} & -\frac{\varepsilon_{ab}}{\hbar} & 0 & 0 & 0 \\
0 & 0 & 0 & \mu_{ab}^2\frac{\varepsilon_{ab}}{\hbar} & \frac{1}{T_2^{ac}} & \Delta\omega_{ac} & 0 & -\mu_{bc}^2\frac{\varepsilon_{bc}}{\hbar} \\
0 & 0 & -\mu_{ab}^2\frac{\varepsilon_{ab}}{\hbar} & 0 & -\Delta\omega_{ac} & \frac{1}{T_2^{ac}} & \mu_{bc}^2\frac{\varepsilon_{bc}}{\hbar} & 0 \\
0 & 0 & 0 & 0 & 0 & -\frac{\varepsilon_{bc}}{\hbar} & \frac{1}{T_2^{ab}} & \Delta\omega_{ab} \\
0 & \mu_{ab}^2\frac{\varepsilon_{ab}}{\hbar} & 0 & 0 & \frac{\varepsilon_{bc}}{\hbar} & 0 & -\Delta\omega_{ab} & \frac{1}{T_2^{ab}}
\end{pmatrix}. \tag{6}$$

The physical quantities in this set of coupled differential equations are:

$$\begin{aligned}
\Delta N_{ab} &= N_b - N_a \\
&= N(\langle b|\varrho|b\rangle - \langle a|\varrho|a\rangle), \qquad (7\text{a}) \\
\Delta N_{bc} &= N_c - N_b \\
&= N(\langle c|\varrho|c\rangle - \langle b|\varrho|b\rangle) \qquad (7\text{b})
\end{aligned}$$

the population differences between the pairs of energy levels E_a, E_b and E_b, E_c respectively and:

$$\begin{aligned}
P_{ab} &= \operatorname{Re}(N\langle b|\mu|a\rangle\langle a|\varrho|b\rangle), \\
Q_{ab} &= \operatorname{Im}(N\langle b|\mu|a\rangle\langle a|\varrho|b\rangle), \\
P_{bc} &= \operatorname{Re}(N\langle c|\mu|b\rangle\langle b|\varrho|c\rangle), \qquad (7\text{c}—\text{h}) \\
Q_{bc} &= \operatorname{Im}(N\langle c|\mu|b\rangle\langle b|\varrho|c\rangle), \\
P_{ac} &= \operatorname{Re}(N\langle c|\mu|b\rangle\langle b|\mu|a\rangle\langle a|\varrho|c\rangle), \\
Q_{ac} &= \operatorname{Im}(N\langle c|\mu|b\rangle\langle b|\mu|a\rangle\langle a|\varrho|c\rangle)
\end{aligned}$$

with N the total number of three-level systems, μ the space fixed Z-component of the dipole moment operator and ϱ the density matrix in the interaction representation. The quantities P_{ab}, Q_{ab}, P_{bc} and Q_{bc} represent real and imaginary parts of the macroscopic dipole polarisation in the interaction representation. In contrast to that P_{ac} and Q_{ac} depending on the off-diagonal element $\langle a|\varrho|c\rangle$ of the density matrix, do not correspond to a dipole polarisation, if $\langle a|\mu|c\rangle = 0$ is assumed. For the selected levels of OCS $a \triangleq J = 0$, $b \triangleq J = 1$ and $c \triangleq J = 2$ this assumption is fulfilled.

The other symbols used in Eqs. (4) to (6) are:

ΔN^0_{ab}, ΔN^0_{bc} the population differences in thermal equilibrium,

$\Delta\omega_{ab}$, $\Delta\omega_{bc}$ and $\Delta\omega_{ac}$ the deviations of the incident radiations from resonance defined by*:

$$\begin{aligned}
\Delta\omega_{ab} &= \frac{E_b - E_a}{\hbar} - \omega_{ab}, \\
\Delta\omega_{bc} &= \frac{E_c - E_b}{\hbar} - \omega_{bc}, \qquad (8\text{a}—\text{c}) \\
\Delta\omega_{ac} &= \frac{Ec - E_a}{\hbar} - (\omega_{ab} + \omega_{bc}),
\end{aligned}$$

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* The effect of collision induced lineshift is neglected in our treatment.

and the transition moments

$$\begin{aligned} \mu_{ab}^2 &= |\langle a|\mu|b\rangle|^2 , \\ \mu_{bc}^2 &= |\langle b|\mu|c\rangle|^2 . \end{aligned} \qquad (8\text{d}-\text{e})$$

To allow for collisional relaxation a set of relaxation times for the different elements of the density matrix is introduced into the equations.

γ_x, γ_y, γ_z, and γ_w (see [6] for definition) concern the relaxation of population, T_2^{ab}, T_2^{bc} and T_2^{ac} are the relaxation times for the polarisation of the indicated pair of levels.

If only one MW-radiation is applied to the ensemble, e.g. only a pump-MW (i.e. $\varepsilon_{ab} \neq 0$, $\varepsilon_{bc} = 0$) and if this radiation is in resonance with the molecular transition frequency $\omega_{ab} = (E_b - E_a)/\hbar$ (or $\Delta\omega_{ab} = 0$) then the equation system splits into four separate subsystems*:

$$\begin{aligned} &\Delta\dot{N}_{bc} + 2\,(\varepsilon_{ab}/\hbar)\,Q_{ab} + \gamma_w(\Delta N_{ab} - \Delta N_{ab}^0) \\ &\qquad + \gamma_x(\Delta N_{bc} - \Delta N_{bc}^0) = 0 , \\ &\Delta\dot{N}_{ab} - 4\,(\varepsilon_{ab}/\hbar)\,Q_{ab} + \gamma_z(\Delta N_{bc} - \Delta N_{bc}^0) \\ &\qquad + \gamma_y(\Delta N_{ab} - \Delta N_{ab}^0) = 0 , \quad (9\text{a}) \\ &\dot{Q}_{ab} + \mu_{ab}^2(\varepsilon_{ab}/\hbar)\,\Delta N_{ab} + Q_{ab}/T_2^{ab} = 0 , \\ &\qquad\qquad \dot{P}_{ab} + P_{ab}/T_2^{ab} = 0 , \quad (9\text{b}) \end{aligned}$$

$$\begin{aligned} &\dot{Q}_{bc} - (\varepsilon_{ab}/\hbar)\,P_{ac} && + Q_{bc}/T_2^{bc} = 0 , \\ &\dot{P}_{ac} + \mu_{ab}^2(\varepsilon_{ab}/\hbar)\,Q_{bc} && + P_{ac}/T_2^{ac} = 0 , \quad (9\text{c}) \end{aligned}$$

$$\begin{aligned} &\dot{P}_{bc} + (\varepsilon_{ab}/\hbar)\,Q_{ac} && + P_{bc}/T_2^{bc} = 0 , \\ &\dot{Q}_{ac} - \mu_{ab}^2(\varepsilon_{ab}/\hbar)\,P_{bc} && + Q_{ac}/T_2^{ac} = 0 . \quad (9\text{d}) \end{aligned}$$

The first two systems (9a–b) correspond to the Bloch-equations for the two-level case with one resonant MW-radiation (ε_{ab}) applied. The important difference is that the more detailed model of a three level system used here gives rise to an additional equation describing the time dependent behaviour of ΔN_{bc}.

The other two systems (9c–d) concern the coupling of *b*, *c*-elements with *a*, *c*-elements of the density matrix ϱ under the influence of a resonant pump-MW between the energy levels E_a and E_b. For our experiment it is important, that with (9c) Q_{bc} and P_{ac} are coupled together and decoupled from the other quantities of (7).

The solutions of (9c) are:

$$\begin{aligned} Q_{bc}(t) &= P_{ac}(0)\,\frac{\varepsilon_{ab}}{\hbar}\exp\{-t/T\}\,\frac{\sin\Omega t}{\Omega} \\ &\quad + Q_{bc}(0)\exp\{-t/T\} \\ &\quad \cdot\left\{\cos\Omega t + \frac{1}{T^*}\,\frac{\sin\Omega t}{\Omega}\right\} , \end{aligned} \qquad (10\text{a})$$

$$\begin{aligned} P_{ac}(t) &= P_{ac}(0)\exp\{-t/T\} \\ &\quad \cdot\left\{\cos\Omega t - \frac{1}{T^*}\,\frac{\sin\Omega t}{\Omega}\right\} \qquad (10\text{b}) \\ &\quad - Q_{bc}(0)\,\mu_{ab}^2\,\frac{\varepsilon_{ab}}{\hbar}\exp\{-t/T\}\,\frac{\sin\Omega t}{\Omega} \end{aligned}$$

with

$$\begin{aligned} \frac{1}{T} &= \frac{1}{2}\left(\frac{1}{T_2^{ac}} + \frac{1}{T_2^{bc}}\right) , \\ \frac{1}{T^*} &= \frac{1}{2}\left(\frac{1}{T_2^{ac}} - \frac{1}{T_2^{bc}}\right) , \\ \Omega &= \left[\mu_{ab}^2\,\frac{\varepsilon_{ab}^2}{\hbar^2} - \frac{1}{T^{*2}}\right]^{1/2} . \end{aligned} \qquad (10\text{c}-\text{e})$$

Considering short pulses of radiation: $t \ll T_2^{ac}$, T_2^{bc} with sufficient MW-power to fulfill: $\mu_{ab}(\varepsilon_{ab}/\hbar) \gg (1/T^*)$ we get the approximate solutions:

$$\begin{aligned} Q_{bc}(t) &= P_{ac}(0)\,(1/\mu_{ab})\sin\mu_{ab}(\varepsilon_{ab}/\hbar)\,t \\ &\quad + Q_{bc}(0)\cos\mu_{ab}(\varepsilon_{ab}/\hbar)\,t , \end{aligned} \qquad (11\text{a})$$

$$\begin{aligned} P_{ac}(t) &= P_{ac}(0)\cos\mu_{ab}(\varepsilon_{ab}/\hbar)\,t \\ &\quad - Q_{bc}(0)\,\mu_{ab}\sin\mu_{ab}(\varepsilon_{ab}/\hbar)\,t . \end{aligned} \qquad (11\text{b})$$

Similar to the treatment of transient absorption of an ensemble of two-level systems based on the two-level Bloch equations [5] we can define also in this case $\pi/2$- and π-pulses by the conditions $\mu_{ab}(\varepsilon_{ab}/\hbar)\,t_{\pi/2} = \pi/2$ and $\mu_{ab}(\varepsilon_{ab}/\hbar)\,t_\pi = \pi$ respectively.

Thus considering the initial conditions:

$$Q_{bc}(0) \neq 0, \quad P_{ac}(0) = 0 \qquad (12)$$

we get at the end of a "$\pi/2$-pulse":

$$Q_{bc}(t_{\pi/2}) = 0 , \qquad (13\text{a})$$

$$P_{ac}(t_{\pi/2}) = -\,\mu_{ab}\,Q_{bc}(0) . \qquad (13\text{b})$$

If we apply a second $\pi/2$-pulse starting at $t_{\pi/2}$, Eq. (13a, b) must be used as initial conditions. At the end of the second $\pi/2$-pulse we have:

$$Q_{bc}(t_{\pi/2} + t_{\pi/2}) = Q_{bc}(t_\pi) = -\,Q_{bc}(0) , \qquad (14\text{a})$$

$$P_{ac}(t_{\pi/2} + t_{\pi/2}) = P_{ac}(t_\pi) = 0 . \qquad (14\text{b})$$

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* $\Delta\omega_{bc}$ and thus $\Delta\omega_{ac}$ are chosen to be zero. Thus the interaction representation is referred to the molecular transition frequency ω_{bc}.

(14) gives the results for Q_{bc} and P_{ac} obtained directly after a sequence of two $\pi/2$-pump pulses without delay between the pulses which is equivalent to a single π-pulse with the initial condition (12).

For the determination of the relaxation time T_2^{ac} the following pulse sequence of the pump-MW (ε_{ab}) may be used (see Figure 1):

initial conditions:

$$Q_{bc}(0) \neq 0, \quad P_{ac}(0) = 0, \tag{15}$$

at the end of the first $\pi/2$-pulse:

$$\begin{aligned} Q_{bc}(t_{\pi/2}) &= 0, \\ P_{ac}(t_{\pi/2}) &= -\mu_{ab}\, Q_{bc}(0), \end{aligned} \tag{16}$$

at the end of the delay τ (no MW applied):

$$\begin{aligned} Q_{bc}(t_{\pi/2}+\tau) &= 0, \\ P_{ac}(t_{\pi/2}+\tau) &= -\mu_{ab}\, Q_{bc}(0) \\ &\quad \cdot \exp\{-\tau/T_2^{ac}\}, \end{aligned} \tag{17}$$

at the end of the second $\pi/2$-pulse:

$$\begin{aligned} Q_{bc}(t_{\pi/2}+\tau+t_{\pi/2}) &= -Q_{bc}(0) \\ &\quad \cdot \exp\{-\tau/T_2^{ac}\}, \\ P_{ac}(t_{\pi/2}+\tau+t_{\pi/2}) &= 0. \end{aligned} \tag{18}$$

Varying the delay τ the relaxation time T_2^{ac} may be determined by measurement of $Q_{bc}(t_{\pi/2}+\tau+t_{\pi/2})$ as a function of τ. Thus the relaxation of P_{ac} is measured indirectly by observation of transient signals (Q_{bc}) corresponding to the dipole-allowed transition between the energy levels E_b and E_c.

The second MW-pulse of the sequence described above may have a pulse length $t_p > t_{\pi/2}$ if the amplitude of Q_{bc} is recorded at the time $t_{\pi/2}$ in the experiment (see Section III). The situation is similar to that of the "$\pi-\tau-\pi/2$"-experiment for measurement of T_1 of an ensemble of two-level systems [8]. In that experiment the pulses actually applied usually form a "$\pi-\tau-\pi$"-sequence.

The initial condition $Q_{bc}(0) \neq 0$ (see Fig. 1) can be provided by means of a resonant pulse of the signal-MW which has to be applied prior to the first pulse of the pump sequence, i.e. prior to $t=0$. The equation system valid under these experimental conditions ($\varepsilon_{ab}=0$, $\varepsilon_{bc} \neq 0$ and $\omega_{bc}=(E_c-E_b)/\hbar$) is completely analogous to (9). Q_{bc} can then be calculated by means of the subsystem corresponding to (9a). If we again neglect relaxation (for short signal-MW pulses) the two-level Bloch equations for the pair of energy levels E_b, E_c result. Although the value of $Q_{bc}(0)$ has no influence on the experiment in principle, it should be made as large as possible to give maximum observable signal. This is obtained by choosing the signal pulse length $t_{\pi/2}$ with: $2\mu_{bc}(\varepsilon_{bc}/\hbar)t_{\pi/2}=\pi/2$ ($\pi/2$-pulse, as defined in the two-level theory [5]).

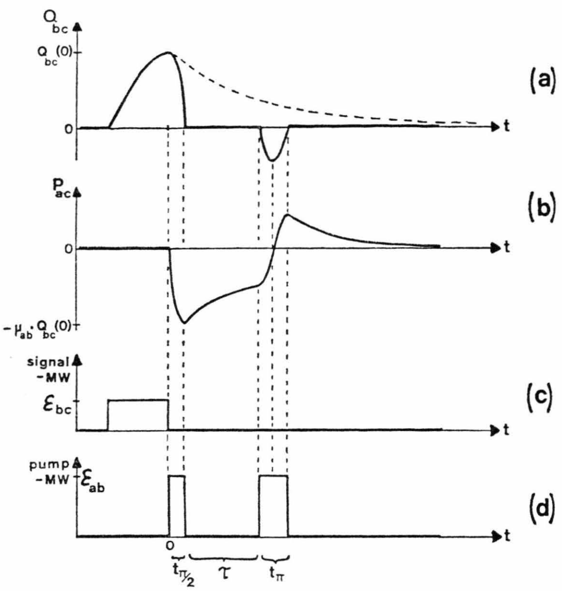

Fig. 1. DR-pulse sequence for the determination of T_2^{ac}. (a) observable polarisation Q_{bc} (signal transition) and (b) unobservable quantity P_{ac}. Prior to $t=0$: Q_{bc}: transient absorption due to the resonant signal-MW pulse shown in (c), $P_{ac} \equiv 0$ (Equation (15)); after $t=0$: If no pump-MW is applied: Q_{bc}: transient emission, relaxation time T_2^{bc} (dotted line). $P_{ac} \equiv 0$. If the pump pulse sequence (d) is applied: 1) $0<t<t_{\pi/2}$: Q_{bc} is completely converted into P_{ac} (Equation (16)); 2) $t_{\pi/2}<t<t_{\pi/2}+\tau$: decay of P_{ac}, relaxation time T_2^{ac}, $Q_{bc} \equiv 0$ (Equation (17)); 3) $t_{\pi/2}+\tau<t<t_{\pi/2}+\tau+t_\pi$: P_{ac} is converted back into Q_{bc} (Eq. (18)) (first half to the pulse) and arises again with opposite sign (second half). Q_{bc} should be recorded at $t=t_{\pi/2}+\tau+t_{\pi/2}$ to give information about the relaxation of P_{ac} during τ.

The second initial condition required for our pump pulse sequence $P_{ac}(0)=0$ is also fulfilled since the signal-MW pulse does not affect P_{ac}. This can be seen from the subsystem corresponding to (9c) that describes the coupling of Q_{ab} and P_{ac} under the influence of ε_{bc}:

$$\begin{aligned} \dot{Q}_{ab} + \frac{\varepsilon_{bc}}{\hbar} P_{ac} + \frac{Q_{ab}}{T_2^{ab}} &= 0, \\ \dot{P}_{ac} - \mu_{bc}^2 \frac{\varepsilon_{bc}}{\hbar} Q_{ab} + \frac{P_{ac}}{T_2^{ac}} &= 0. \end{aligned} \tag{19}$$

The solutions of (19) are analogous to (10).

Since both Q_{ab} and P_{ac} are assumed to be zero at the beginning of the experiment (thermal equilibrium) they will not change during the signal-MW pulse.

III. Experimental and Results

The spectrometer we used for our experiments is shown in Figure 2. The arrangement basically consists of the superhet bridge type DR-spectrometer a detailed description of which we gave in a previous paper [4]. The spectrometer can be used for X-band pump and K-band signal frequencies respectively. The required triple pulse sequence (one signal and two pump pulses) is provided by two pulse generators. A commercial one (19)* the output of which drives the PIN switch for the signal-MW pulse generation and a home-made double pulse generator (18) providing the pump pulse sequence with variable delay time τ.

The spectrometer has to be operated in the "absorption mode" [4] thus allowing the observation of the imaginary part of the macroscopic polarisation (Q_{bc}) that corresponds to the signal transition. This is assumed in the theoretical treatment above.

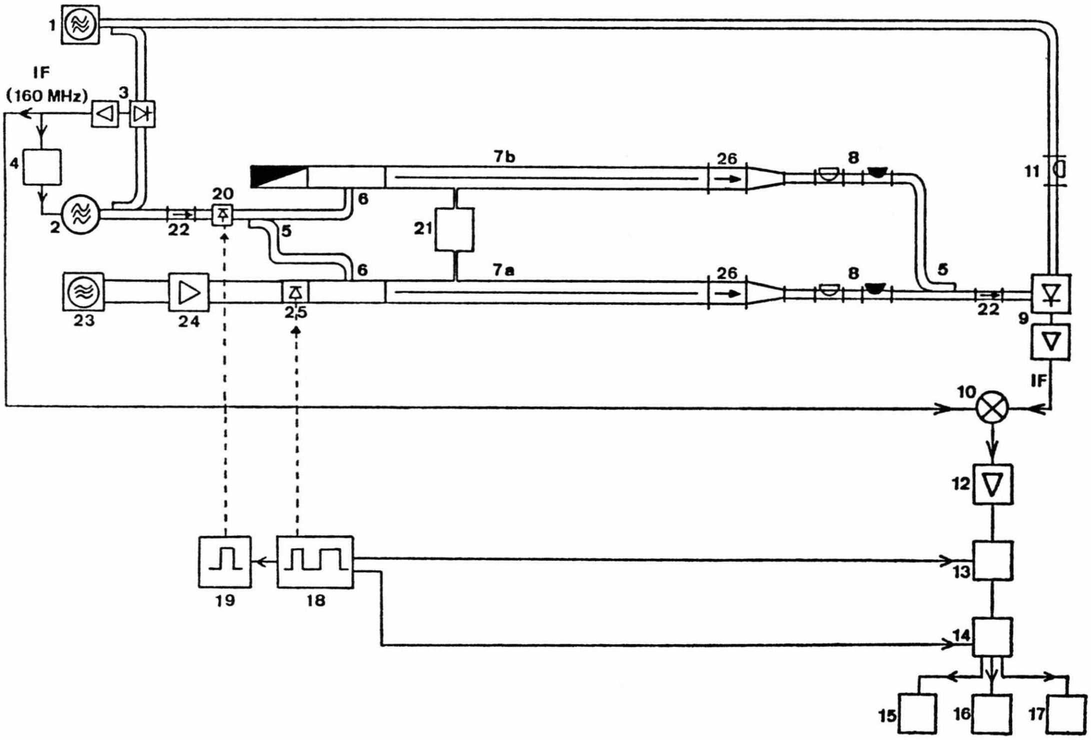

Fig. 2. Experimental setup. 1. Phase stabilized local oscillator: BWO (hp-Sweeper 8696 A), K-band (18—26.5 GHz). 2. Signal oscillator: Klystron: OKI 24 V 11 (22—26 GHz). 3. MW-mixer (double balanced) Norsal DBM 1—26 with IF-amplifier. 4. Phase stabilisation of the signal oscillator including 130 MHz quartz. 5.—8. MW-bridge: (carrier suppression >40 dB over a bandwidth of ~ 1 MHz). 5. Directional couplers, K-band: hp K 752 A, 3 dB. 6. Directional couplers, ~ 10 dB for X-band pump MW. 7. Sample (7a) and reference (7b) cell, X-band, length: 4.7 m, including Stark septum. 8. Phase shifters and attenuators. 9. Balanced mixer with integrated broadband IF-preamplifier: Spacekom FK-U. 10. IF-mixer (double balanced): Mini Circuits ZAD-3. 11. Phase shifter. 12. Broadband amplifier: PAR mod. 115, DC-70 MHz. 13. Boxcar integrator: PAR mod. 162/164. 14. Digital averager: Fabri-Tek 1072. 15. PDP 11 Computer. 16. X-Y-recorder. 17. Oscilloscope. 18. Double-pulse generator (home made) providing: TTL-pulses of adjustable length with automatic advance of the second pulse, various trigger pulses (gate advance (to 13), address advance (to 14), pretrigger (to 19)). 19. Pulse generator: Anritsu MG 412 A. 20. PIN switch: Arra H 8753-80 D. 21. Vacuum system including 20 *l* bulb and capacitance manometer: MKS-Baratron 310 B. 22. Waveguide isolators (K-band). 23. Phase stabilized pump-MW: YIG-tuned FET-oscillator. 24. TWT-amplifier: Hughes 1177 H (X-band.) 25. PIN switch: Arra 8753-80 D. 26. Waveguide isolators (X-band).

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* Numbers refer to Figure 2.

The amplitude of the molecular signal due to the probe pulse (second pump pulse) is recorded by means of a boxcar integrator (13) in connection with a digital averager (14) (see Figure 2). The principles of operation of this detection arrangement are described in detail in [8] where the apparatus was used for measurement of the population relaxation time T_1 in an ensemble of two-level systems.

The delay time τ is varied automatically in steps of 70 nsec in the experiment and the corresponding signal amplitude is stored in the memory of the digital averager. Thus for each recording carried out with fixed sample pressure a digitized exponentially decaying curve is obtained. The corresponding relaxation time T_2^{ac} is then evaluated by means of a computer performing a least squares fit procedure with the function $A \exp\{-\tau/T_2^{ac}\} + B$.

Using the experimental technique described above we carried out measurements of the relaxation time T_2^{02} for the dipole-forbidden transition $J=0$, $M=0 \rightarrow J=2$, $M=0$ of the molecule OCS. The frequencies of the corresponding dipole allowed transitions $J=0 \rightarrow J=1$ (X-band, pump transition) and $J=1 \rightarrow J=2$ (K-band, signal transition) fit in with the frequency regions covered by our spectrometer.

The time dependence of the observed polarisation component Q_{bc} (i.e. Q_{12}) under the influence of pump-MW pulses (MW-amplitude $\varepsilon_{ab} = \varepsilon_{01}$) schematically shown in Fig. 1 is illustrated by some experimental curves in Figure 3. 3a shows the signal of transient emission after resonant polarisation of the transition $J=1 \rightarrow J=2$ by means of a preceding (not shown) signal-MW pulse. Due to the frequency conversion of the emitted molecular signal radiation to DC [4] an exponential decay without oscillatory behaviour is observed. In 3b a $\pi/2$-pump pulse ($J=0 \rightarrow J=1$) of about 500 mW power terminates the observed emission signal by converting Q_{bc} (i.e. Q_{12}) into P_{ac} (i.e. P_{02}) as described above. 3c shows the molecular response to a sequence of two pump pulses being separated in time by a fixed value of the delay τ. The amplitude of the molecular response to the second (probe) pulse is the quantity to be recorded by means of the boxcar integrator in the T_2^{02}-experiment. In order to obtain the illustrations of the transient behaviour shown in Fig. 3 and Fig. 4 the boxcar integrator was replaced by a fast A/D-converter (Biomation 6500) recording the molecular signal in a time range of some μseconds. Figure 4 again shows the pulse sequence. Several recordings with different values of the delay are shown simultaneously in one plot. The sample pressure was 16 mTorr (4a) and 6 mTorr (4b) respectively.

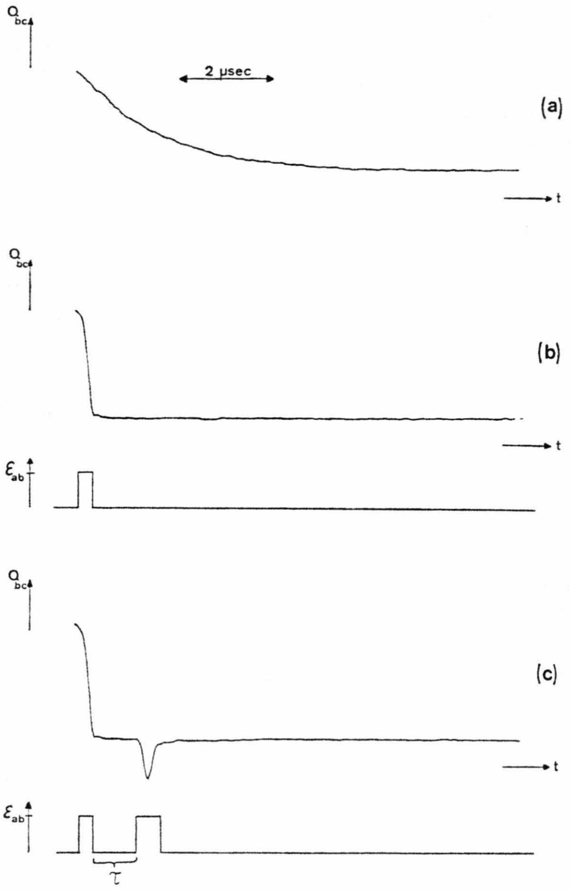

Fig. 3. Transient signals after resonant polarisation of OCS: $J=1 \rightarrow 2$ by a preceding (not shown) signal-MW pulse. $p \sim 12$ mTorr, (a) without pump-MW, (b) application of a single resonant $\pi/2$-pump pulse shown below. (Power ~ 500 m W), (c) application of a resonant $\pi/2-\tau-\pi$-pump pulse sequence with a fixed delay τ. The curves are measured, the pulses have been drawn for illustration.

The three-level system under consideration only consists of the $M=0$ components of the energy levels $J=0$, $J=1$ and $J=2$, the polarizing signal-MW pulse (preparation of Q_{12}) on the other hand acts on both the $M=0$- and the $M=\pm 1$-component of the transition $J=1 \rightarrow J=2$. Thus an interfering additional molecular signal (transient emission of the $M=\pm 1$-component) is observed together with the pump pulse response shown in

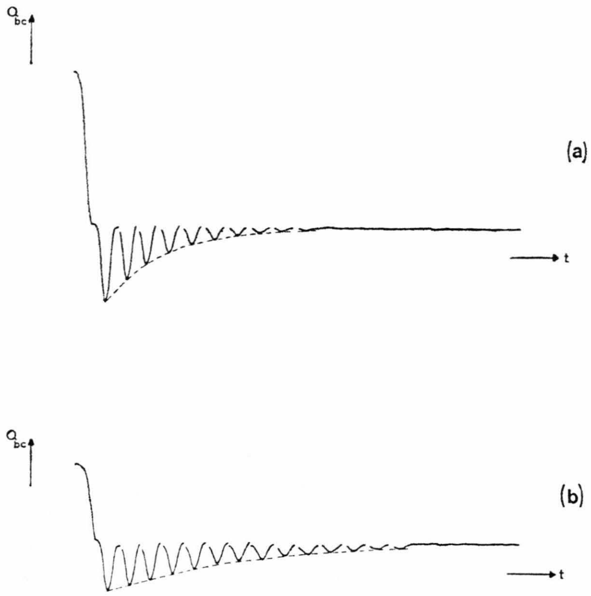

Fig. 4. Transient signals as in Figure 3c. Recordings with different values of the delay τ are shown in one plot. (a) $P \sim 16$ mTorr, (b) $P \sim 6$ mTorr.

Figs. 3 and 4. Of course there is no direct influence of the pump-MW on this emission signal due to the selection rule $\Delta M = 0$. In order to eliminate the interference a baseline subtraction method had been used while recording the molecular signals shown in Figs. 3 and 4. For that purpose a single $\pi/2$-pump pulse like the first one in the double pulse sequence described above was applied after the polarizing signal pulse. The pump pulse quenches the emission signal of the $M = 0$-component while the $M = \pm 1$-component is not affected. This provides a method of separating the interfering signal which can thus be subtracted from the total signal within the memory of the digital averager giving the remaining $M = 0$-component alone.

Similarly while measuring T_2^{02} with the boxcar integrator arrangement described above we had to carry out a baseline subtraction sweep after each measurement. For that purpose the second pump-MW pulse (probe pulse) was suppressed and thus the baseline was detected alone and afterwards subtracted from the total signal.

The alternative method of performing M-resolved measurements applying a static Stark-field is not useful in this kind of experiment due to the fact that field inhomogeneities always present in the cell would cause the molecular resonance frequencies to spread over a large frequency range. This effect leads to an incorrect increase of the measured T_2-values [9].

The pressure dependence of the T_2^{02}-values measured in our experiments may be described by the expression: $1/T_2^{02} = \alpha + \beta p$ (see Fig. 5) where p is the sample pressure.

We obtained the following values of the parameters α and β:

$$\alpha = 0.16 \pm 0.01 \ \mu\text{sec}^{-1},$$
$$\beta = 0.0350 \pm 0.0008 \ \mu\text{sec}^{-1}\ \text{mTorr}^{-1}.$$

The given errors are twice the standard deviations of the linear fit shown in Figure 5. These errors do not reflect systematic inaccuracies of the experiment. A more realistic estimate of the reliability of these measurements will limit it to about 10% due to the effects of MW-field inhomogeneities (damping and mode inhomogeneities), difficulties in adjustment as well as reflections of the $\pi/2$- and π-pump pulses and pressure instabilities. In order to minimize interference caused by reflections of the pump-MW pulses at the tapered outlet of the absorption and the reference cell (tapers from X-band to K-band) we used two waveguide isolators (see Figure 2). The inhomogeneity of the pump-MW field on the other hand restricts the validity of the theoretical considerations described in Chapter II, these being derived under the assumption that the MW-amplitude is constant all over the cell dimensions. Thus in

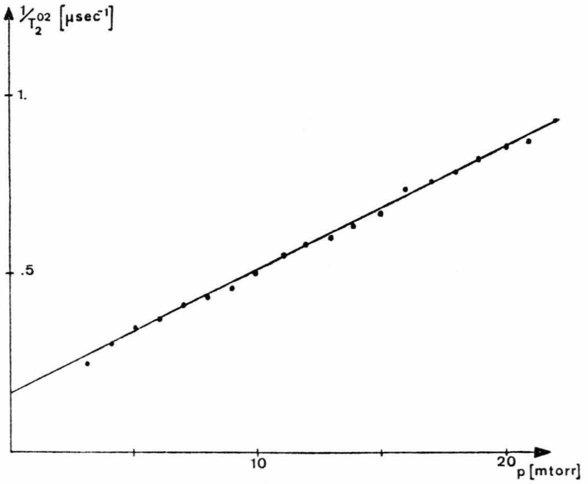

Fig. 5. Pressure dependence of $1/T_2^{02}$ of OCS: $J = 0 \to 2$, $M = 0$ at room temperature.

reality the observed $\pi/2$- and π-pulses have to be regarded as averages.

Considering the estimated uncertainty of 10% mentioned above the obtained pressure dependence parameter β of T_2^{02} for the dipole-forbidden transition $J=0 \rightarrow J=2$, $M=0$ of OCS does not show a significant deviation compared with the corresponding results for the dipole-allowed transitions $J=0 \rightarrow J=1$ [10] and $J=1 \rightarrow J=2$ [4, 11]. The value we found for the intercept (parameter α) seems to be relatively high (> 0.1 μsec^{-1}) as compared to the results of conventional T_2-experiments as well as theoretical considerations given elsewhere [12]. We regard this deviation to be due to the different experimental inaccuracies especially the pump field inhomogeneity mentioned above, these problems being not present in conventional transient emission T_2-experiments.

IV. Conclusion

Considering the theory of the three-level Bloch equations it can be deduced that information about the relaxation behaviour of density matrix elements may be obtained even if these correspond to dipole-forbidden molecular transitions. In this case interaction with external MW-fields can only concern the remaining two (allowed) transitions in the three-level system. It could be shown experimentally that by observation of the dipole polarisation corresponding to an allowed transition an indirect method for the determination of a relaxation parameter corresponding to a dipole forbidden transition can be provided. For that purpose both pump- and signal-MW have to be applied in a special pulse sequence. Similar experiments concerning diagonal elements (population relaxation) are of interest too because they can give a more detailed information about the transfer of population compared with two-level (T_1) experiments. It appears that pulse sequence methods are especially suitable for that kind of investigations. On the one hand solutions of the three-level Bloch equations are more easily obtained if relaxation can be neglected (during application of short MW-pulses) and on the other hand in such experiments relaxation of the observed system usually occurs when no interfering MW-field is present. Thus the advantage of experimental conditions which are reasonably well-defined can be combined with that of easy methods for the interpretation of the measurements.

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