A Microwave Study of Collision-Induced Transitions between M-Resolved-Rotational levels of OCS

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Four-level MW-MW-double resonance experiments on the rotational Stark-levels $J=0$, 1, 2 and 3 of OCS have been performed employing both frequency and time domain techniques. The results indicate significant deviations from first order dipole collisional interaction.

We have undertaken four-level MW-MW-double resonance experiments on OCS by using phase-stabilized BWOs as radiation sources for pump and signal transitions. The pump radiation was on-off modulated by means of a Pin-modulator and amplified with a TWT microwave amplifier. In both frequency and time domain experiments the pump radiation frequency was held fixed at the resonance of the pump transition.

In the frequency domain, a phase sensitive detection technique was used to observe the change of signal line intensity with frequency; the details of the experimental set up have been described elsewhere[1, 2].

Pump modulation and phase sensitive detection provides a sensitive tool to measure small intensity changes of the signal transition due to collisional energy transfer as has been demonstrated recently[3]. In obtaining collisional "selection rules" this method has some advantage over steady-state four-level double resonance techniques with Stark modulation[4, 5] which is used to give the fractional change of signal line intensity due to the pump radiation.

In our experiment it is in general difficult to compare quantitatively signal line intensities over a wide frequency range because of the frequency dependence of cell transmission and detector crystal characteristics. However in the present investigation of M-resolved collisional induced transitions are close enough in frequency to allow for intensity comparison.

There have only been a few reports so far on M-resolved collisional induced transitions in the microwave range[6–9]. We have investigated collisional induced transitions on rotational Stark levels of OCS (normal isotopes). The sample gas was tested gas chromatographically and no significant impurities were detected. The Stark field was pro-

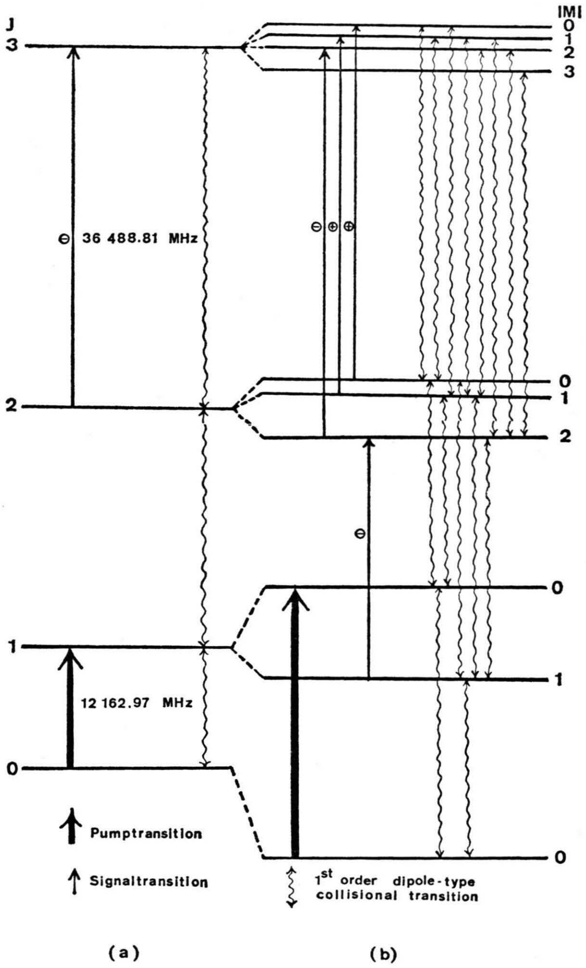

Fig. 1. Energy level scheme of OCS for zero (a) and nonzero (b) Stark field. The energy differences between the levels are not in scale. Frequencies are given for the normal isotope $O^{16}C^{12}S^{32}$. Wavy arrows indicate "selection rules" due to first order dipolar interaction. The signal transitions are labelled with ⊕ (⊖) for an intensity increase (decrease) when the $J=0 \rightarrow 1$ transition was "pumped".

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duced in a conventional rectangular Stark absorption cell (inner dimension 10×47 mm) with DC voltages up to 1200 volts. We have pumped the $(J, M) = (0, 0) \rightarrow (1, 0)$ transition and observed the

$$(J, M) = (1, \pm 1) \rightarrow (2, \pm 1), \; (2, 0) \rightarrow (3, 0), \; (2, \pm 1) \rightarrow (3, \pm 1), \; (2, \pm 2) \rightarrow (3, \pm 2)$$

as indicated on Figure 1. The M-resolved components of the $J = 2 \rightarrow 3$ collisional induced transition as recorded at the output of the PSD are shown on Figure 2. It should be noted that these transitions have not been observed by using Stark modulated MW-MW double resonance technique as reported in [8].

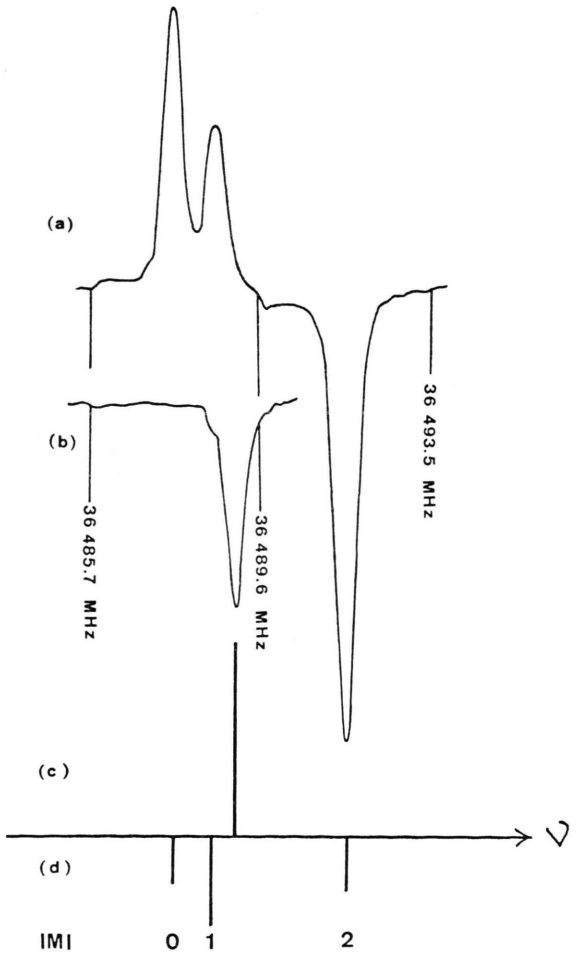

Fig. 2. Observed collision-induced transition pattern for the OCS $J = 2 \rightarrow 3$ transition for nonzero (a) and zero (b) Stark field. Pump: $J, M = (0, 0) \rightarrow (1, 0)$, ~1 W; Signal-power <0.1 mW; Temperature −50 °C, presure: 10 mTorr. The intensity ratio of unresolved (c) and Stark-split lines (d) as obtained in conventional Stark-modulated MW-spectroscopy is given for comparison.

The recorded relative intensities of the individual M-components do not agree with the normal Stark-pattern of this rotational line (see Fig. 2) where the $|M| = 1$ transition is dominant in intensity. As shown in Fig. 2 the four level double resonance experiment results in a rather different pattern where the $|M| = 2$ component is the most intense transition. In addition, when considering the phase adjustments of the PSD to give maximum line intensity, the $|M| = 2$ component is about 180° phase changed with respect to the other two M-components. This indicates different effects of the pump radiation on the population changes of the different M-substates of the $J = 2 \rightarrow 3$ transition. The individual M-components sum up approximately to the weaker unresolved line for zero Stark field condition. The optimal phase adjustment for this line was found to be removed about 110° and −70° from those for the $|M| = 0$, 1 and $|M| = 2$ components respectively (see also Figure 4).

For further experimental analysis we have performed time-resolved four level double resonance experiments. To do this we have used a different experimental set up for signal detection by combining analog and digital signal averaging as shown on Figure 3. The crystal detectors output signal was broadband amplified and integrated with a

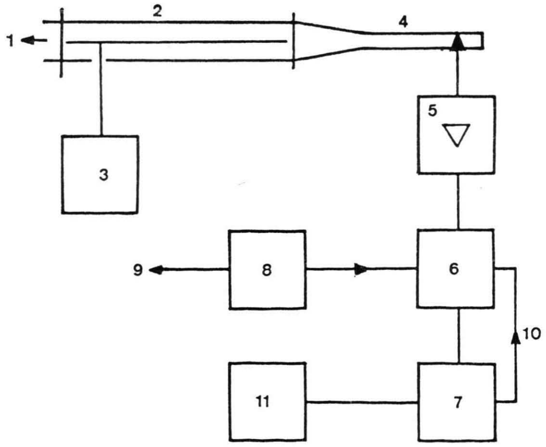

Fig. 3. Schematic block diagram of part of the MW-MW-double resonance spectrograph for time resolved measurements. 1. Radiation sources with stabilisation, PIN-modulation and TWT amplification see Ref. 1, 2. 2. Stark absorption cell. 3. DC-Voltage power supply (Fluke 3038). 4. Suitable waveguide cut off filter and detector. 5. Broadband amplifier (60 db, 1 kHz–70 MHz: Avantek GPD 461, 462, 463 (40 db) and PAR Mod. 115 (20 db)). 6. PAR Mod. 162/164 Boxcar integrator. 7. Fabri-tek Ser. 1070 Signal Averager. 8. Pulse-generator (E–H Res. Labs. Mod. 137 NV). 9. 5 V, 100 kHz square wave to PIN-diode driver. 10. 0–4 V ramp. 11. X-Y-recorder.

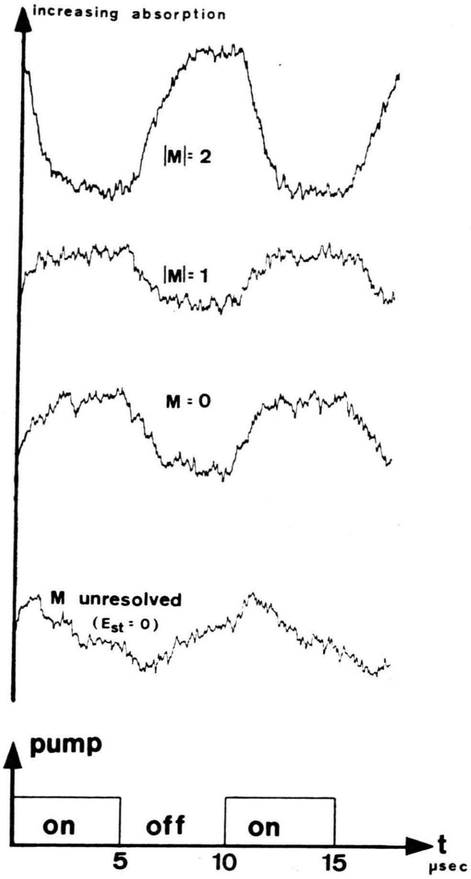

Fig. 4. Time resolved recordings of the M-component of the $J=2 \rightarrow 3$ collision-induced transition. Pressure: 20 mTorr, other experimental conditions see Figure 2.

PAR 162/164 Boxcar integrator of which the aperture delay range time base was triggered by means of the PIN-diode switch pulses. The integrators output signal was fed into a Fabri-tek 7040 signal averager to allow for further digital averaging and manipulating of the data. The gate position of the integrator was scanned externally with a $0-4$ volts ramp which was provided by the digital averager synchronously to its memory adress advance.

Figure 4 shows the recording as obtained for the M sublevels of the $J=2 \rightarrow 3$ transition in the presence of an electric field. The corresponding zero field measurement is also given. Though no quantitative analysis has been done so far, the time resolved four-level double resonance experiments confirm the results for signal amplitude and relative phase as obtained in frequency domain by phase sensitive detection.

In addition, the time domain experiments gives direct information about the absolute sign of signal change due to population transfer from the saturated pump transition. Thus the $|M|=2$ component of the $J=2 \rightarrow 3$ transition is less absorptive if the pump is on, whereas the $|M|=1$ and $|M|=0$ components show up increasing absorption.

In order to qualitatively describe the observation on OCS it is not sufficient to consider only first order dipole type collisional interaction. This interaction type would not lead directly to population changes of the $|M|=2$ sublevels of the $J=2 \rightarrow 3$ transitions and not even predict the intensity ratio of the $|M|=1$ and $|M|=0$ component correctly. The present results suggest the importance of collisional interactions involving higher multipole order and/or second and higher order effects of dipole type. The significance of second order dipole-dipole collisional interaction for OCS has been pointed out by Verter and Rabitz [10].

Summarizing we state that we have observed significant M-dependence of collisional transfer of rotational energy of OCS, which could not be explained by first order dipole-dipole interaction. More quantitative measurements and analysis of the M-dependence of the collision-induced transitions may lead to a better understanding of the collisional process. It is also important to explicitly consider M-dependence of collision induced transitions whenever the M-degeneracy of the rotational levels of the colliding molecules is removed.

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