Investigation of Self- and Foreign Gas Collision-induced Transitions between M-resolved Rotational Levels of OCS

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Four-level MW-MW double resonance experiments on rotational Stark levels $j = 0$, 1, 2 and 3 of OCS have been performed to investigate transfer of rotational energy by collisions of OCS with OCS, He, Ne, Ar, Kr, H_2, N_2, O_2, and CH_3F. Theoretical arguments are given for the interpretation of the experimentally determined η-values by considering Bloch-type equations of an "embedded" four-level system with $\pm$M degeneracy of the energy levels. The results indicate significant deviations from first order dipole collisional interaction.

Introduction

The investigation of gas phase rotational relaxations has been of considerable interest in the past few years and various experimental methods have been developed for these studies using microwave techniques. Both single and multiple resonance experiments have been performed either in the time or in the frequency domain to obtain information about the transfer of rotational energy due to molecular collisions [1—4]. Concerning the space-fixed component M of the angular momentum of the molecules, no explicit information about the M-dependence of rotational relaxation parameters results from measurements in the absence of external electric or magnetic fields. In the case of single resonance experiments, steady-state line-shapes or transient MW-pulse responses have so far been studied only in the field-free case, whereas the transient Stark-switching techniques has given details of the M-dependence of the relaxation rates $1/T_1$ and $1/T_2$ in particular cases [5, 6, 7].

In the case of multiple resonance experiments most of the rotational relaxation studies are based on four level double resonance in the frequency domain which may give the relative change of a signal absorption, $\eta = \Delta I/I$, by collision-induced transitions [1]. The results of such experiments are important for understanding the details of relaxation pathways in the rotational energy manifold of a molecule, in particular if the M-degeneracy of the energy levels has been removed. However, there have been so far only a few reports on M-resolved studies of collision-induced transitions in the microwave range [1, 8—13].

In the present paper we report on the investigation of collision-induced transitions between M-resolved rotational levels of carbonyl sulfide, OCS. This investigation completes our earlier four level double resonance studies of the pure gas [11] and also gives the results for mixtures with polar and nonpolar foreign gases.

Theoretical arguments are given for the interpretation of the experimental results by considering the equation of motion of the density matrix for a system of linear molecules in the presence of an electric field. Bloch-type equations of an "embedded" four-level system are derived with particular emphasis on the $\pm M$ degeneracy of the rotational energy levels.

Experimental

We have studied four level double resonance involving rotational Stark levels of the normal isotopic species of OCS. The energy level diagram for the investigated pump and signal transitions is illustrated in Figure 1. We have pumped the $(j, m = |M|)$: $(0, 0 \rightarrow (1, 0)$ transition and observed the (j, m) : $(1, 1) \rightarrow (2, 1)$, $(2, 0) \rightarrow (3, 0)$, $(2, 1) \rightarrow (3, 1)$ and $(2, 2) \rightarrow (3, 2)$ transitions as indicated on Figure 1. The Stark field up to 2.500 V/cm was produced in a conventional rectangular Stark cell (inner dimension $1.0 \times 4.7 \times 340.0$ cm). The experimental arrangement was such to have the Stark field and both the pump and signal microwave elec-

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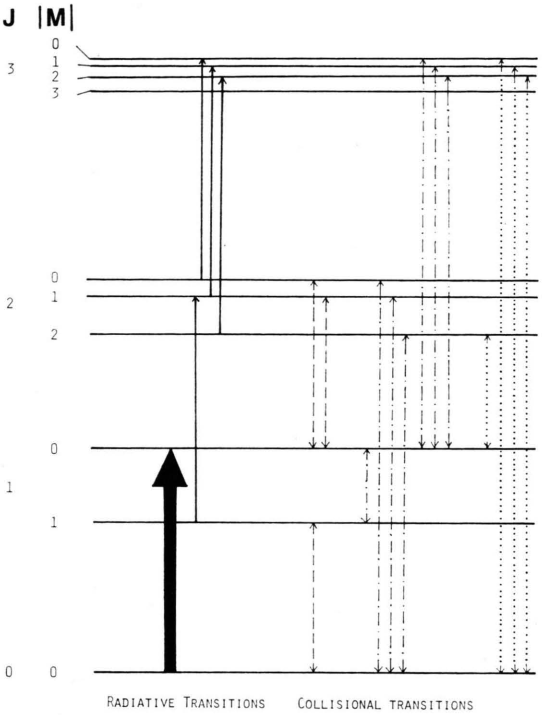

Fig. 1. Energy level scheme of OCS for nonzero Stark field. The energy differences between the levels are not in scale. Zero Stark field frequencies are (j: $0 \to 1$) $= 12162.97$ MHz, (j: $1 \to 2$) $= 24325.93$ MHz, (j: $2 \to 3$) $= 36488.81$ MHz, and Stark splitting are in the order of MHz for the fields used in the experiments.
$\rightarrow$ pump transition $(j, |M|) = (0, 0) \to (1, 0)$;
$\blacktriangleright$ signal transitions $(j, |M|) = (1, 1) \to (2, 1)$, $(2, 0) \to (3, 0)$, $(2, 1) \to (3, 1)$ and $(2, 2) \to (3, 2)$.
The dashed lines indicate collisional channels between pump and signal levels which are classified according to "selection rules" (see text). ---- first order dipole; -·-·- first order quadrupole, second order dipole; ..... higher order.

tric fields parallel, that is only $\Delta M = 0$ radiative transitions were allowed.

The pump and signal microwave radiation was supplied from phase stabilized BWO's. The pump radiation was amplified by an X-band TWT up to 4 W.

The OCS sample gas, used in the experiments, was distilled under vacuum and tested afterwards by gas chromatography for impurities which were found to be insignificant. Foreign gases of research purity were used for the investigation of the mixtures with He, Ne, Ar, Kr, H_2, N_2, O_2, CO_2, and CH_3F. The sample pressure was measured with a MKS Baratron 310 B capacitance manometer. The experiments were predominatly carried out at a gas temperature of about 200 K.

Different experimental setups were used for the present study. The method of pump amplitude modulation and phase sensitive detection, as described earlier [14], has been applied to investigate M-dependencies of collision-induced changes of signal line intensities (ΔI, $j = 2 \to 3$ transition) in a DC electric field. In order to determine the relative change of collision-induced signal line intensity, $\eta = \Delta I / I$, conventional measuring techniques [15, 16] were found to be insufficient for the investigated transitions by sensitivity reasons. Instead, a modification of the recently described sensitive method of double modulation [17] was used in this experiment. The general setup is shown in Figure 2. The pump radiation was on-off modulated at 10 Hz by means of a PIN-diode switch. In addition, Stark modulation at 100 kHz with phase sensitive detection was applied for the observation of the signal line intensities, I and $I + \Delta I$, corresponding to the steady-state absorption of the signal microwave radiation in the absence and presence of the pump, respectively. The modulated (10 Hz) analog output of the PSD was fed into a Fabri-tek 7040 signal averager to obtain S/N-improvement by digital averaging. Then, as result of the averaging, η may be determined from the values for I and $I + \Delta I$ stored in the memory of the averager. This is illustrated in Fig. 3 where the analog representation of the averagers memory content is given for an example ($\eta \simeq 6\%$).

For the M-resolved measurements of η, square wave modulated Stark field amplitudes up to 1500 V/cm with superimposed DC offsets up to 2500 V/cm were used. The sensitivity of the double modulation technique with digital averaging which made the determination of η-values to about 0.1% for the studied systems possible, is demonstrated by the experimental results given below.

Theory

In the following, theoretical expressions are derived to describe the time dependencies of the density matrix elements for an ensemble of four-level systems which may be used to discuss the experimental results. The formalism is developed for a system of four energy levels a, b, c, and d, as

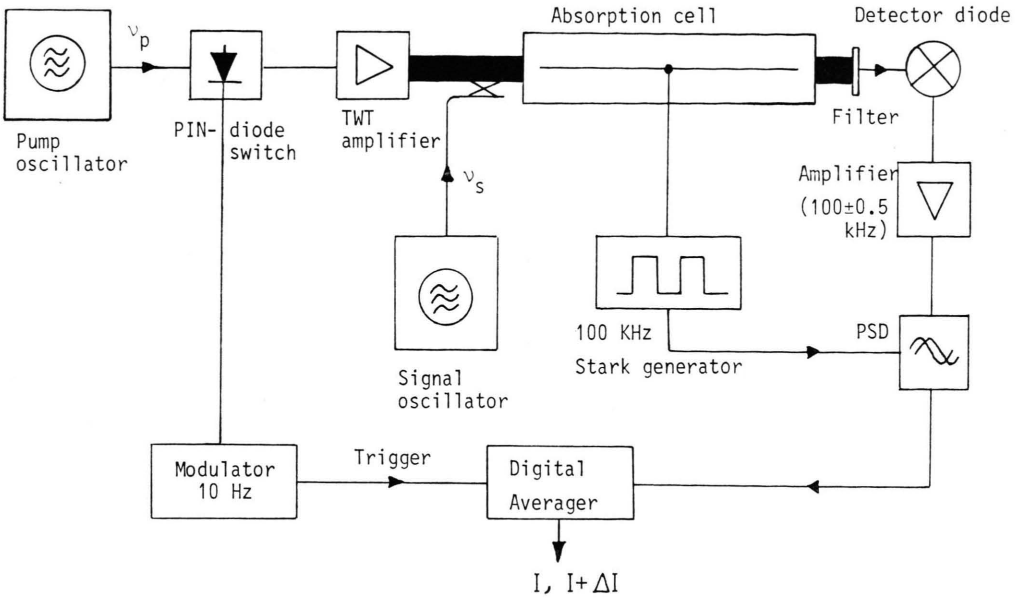

Fig. 2. Schematic block diagram of the experimental arrangement for the determination of relative change of collision-induced signal line intensity η by double modulation. Both pump and signal oscillator are phase stabilized BWO's.

indicated in Fig. 4, which are part of a rigid rotor multi-level system in a static electric field.

The following derivation is closely related to the recently given theoretical treatment for an idealized system of four non-degenerate energy levels [18]. In the presence of a sufficiently strong Stark field when all M-states are well separated such model may be applied if $M=0$ for both the pump and the signal transition. However, in the more general case of states with $M \neq 0$ the two-fold $\pm m$-degeneracy of the energy levels ($m=|M|$) has to be considered.

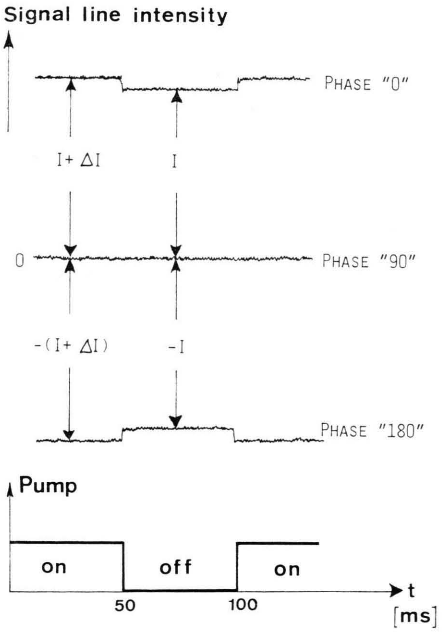

Fig. 3. Scheme of the determination of η with 100 kHz pump amplitude modulation. The signal line intensity (I without pump, $I+\Delta I$ with pump) as obtained by phase sensitive detection is digitally averaged. The averagers memory content is given for the example $\eta \simeq 6\%$. The phase settings of the PSD refer to maximum (phase "0" and phase "180") and zero (phase "90") signal line intensity.

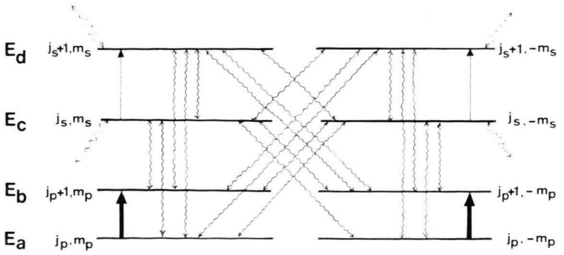

Fig. 4. General energy level scheme of a rigid rotor for non-zero Stark field. Pump transition: $E_a \to E_b$, signal transition: $E_c \to E_d$. The wavy arrows indicate collisional channels within the four level scheme, characterized by first order rate constants; dashed wavy arrows indicate collisional coupling of signal levels and "bath levels". Only such collisional channels are given in the figure which are relevant for the theoretical expression (25) for η (see text).

We first derive the equation of motion for the density matrix ϱ in the absence of collisions. The microwave radiation is given by a superposition of pump and signal microwave radiation, plane polarized along the direction (x) of the static electric field

$$\varepsilon = 2\,\varepsilon_\mathrm{p}\cos\omega_\mathrm{p} t + 2\,\varepsilon_\mathrm{s}\cos\omega_\mathrm{s} t\,. \tag{1}$$

ε_p and ε_s denote the electric field amplitude of the pump and signal radiation with angular frequencies ω_p and ω_s respectively. The equation of motion of ϱ is given by

$$i\hbar\,\dot{\varrho} = [H, \varrho] \tag{2}$$

with H given by

$$H = H_0 - \mu\,\varepsilon_\mathrm{st} - \mu\,\varepsilon\,, \tag{3}$$

where μ is the electric dipole operator with respect to the x-axis and $H_0 - \mu\,\varepsilon_\mathrm{st}$ the time independent Hamiltonian for the molecules in the Stark field with amplitude ε_st. The eigenvalues E_a, E_b, E_c, and E_d of $H_0 - \mu\,\varepsilon_\mathrm{st}$ constitute the considered four-level system.

With parallel directions of the Stark field and the microwave polarisation planes we have the spectroscopic selection rule $\Delta M = 0$ and may assume, according to Figure 4, the pump and signal radiation to be resonant, or near resonant, with the transition a→b $(j_\mathrm{p}, \pm m_\mathrm{p} \to j_\mathrm{p}+1, \pm m_\mathrm{p})$ and c→d $(j_\mathrm{s}, \pm m_\mathrm{s} \to j_\mathrm{s}+1, \pm m_\mathrm{s})$ respectively. For sufficiently different resonance frequencies

$$\begin{aligned} \omega_{\mathrm{p}0} &= (E_\mathrm{b} - E_\mathrm{a})/\hbar \quad \text{and} \\ \omega_{\mathrm{s}0} &= (E_\mathrm{d} - E_\mathrm{c})/\hbar \end{aligned} \tag{4}$$

of pump and signal transition, we may closely follow the procedure given in [18] for non-degenerate energy levels in order to obtain the relevant time development equations for the density matrix elements of the considered system.

Though radiative coupling terms between $+m$ and $-m$ states are missing, it is convenient to introduce for the appropriate treatment of relaxation (see below) the following linear combinations

$$\begin{aligned} \varrho^\pm(jm, j'm) &= \varrho(jm, j'm) \\ &\quad \pm \varrho(j(-m), j'(-m))\,, \\ &\qquad\qquad \text{for} \quad m \neq 0\,, \\ \varrho^+(j0, j'0) &= \varrho(j0, j'0)\,, \quad \text{for} \quad m = 0\,, \end{aligned} \tag{5}$$

where the notation $\varrho(jm, j'm)$ for diagonal $(j = j')$ and off-diagonal $(j' = j \pm 1)$ density matrix elements has been used.

Refering to the four-level system we now define with (5) the variables

$$\begin{aligned} U_\mathrm{p}^\pm &= \varrho^\pm(j_\mathrm{p} m_\mathrm{p}, j_\mathrm{p}+1\,m_\mathrm{p})\,e^{-i\omega_\mathrm{p} t} \\ &\quad + \varrho^\pm(j_\mathrm{p}+1\,m_\mathrm{p}, j_\mathrm{p} m_\mathrm{p})\,e^{i\omega_\mathrm{p} t}, \\ U_\mathrm{s}^\pm &= \varrho^\pm(j_\mathrm{s} m_\mathrm{s}, j_\mathrm{s}+1\,m_\mathrm{s})\,e^{-i\omega_\mathrm{s} t} \\ &\quad + \varrho^\pm(j_\mathrm{s}+1\,m_\mathrm{s}, j_\mathrm{s} m_\mathrm{s})\,e^{i\omega_\mathrm{s} t}, \\ V_\mathrm{p}^\pm &= i(\varrho^\pm(j_\mathrm{p}+1\,m_\mathrm{p}, j_\mathrm{p} m_\mathrm{p})\,e^{i\omega_\mathrm{p} t} \\ &\quad - \varrho^\pm(j_\mathrm{p} m_\mathrm{p}, j_\mathrm{p}+1\,m_\mathrm{p})\,e^{-i\omega_\mathrm{p} t})\,, \\ V_\mathrm{s}^\pm &= i(\varrho^\pm(j_\mathrm{s}+1\,m_\mathrm{s}, j_\mathrm{s} m_\mathrm{s})\,e^{i\omega_\mathrm{s} t} \\ &\quad - \varrho^\pm(j_\mathrm{s} m_\mathrm{s}, j_\mathrm{s}+1\,m_\mathrm{s})\,e^{-i\omega_\mathrm{s} t})\,, \\ W_\mathrm{p}^\pm &= \varrho^\pm(j_\mathrm{p} m_\mathrm{p}, j_\mathrm{p} m_\mathrm{p}) \\ &\quad - \varrho^\pm(j_\mathrm{p}+1\,m_\mathrm{p}, j_\mathrm{p}+1\,m_\mathrm{p})\,, \\ W_\mathrm{s}^\pm &= \varrho^\pm(j_\mathrm{s} m_\mathrm{s}, j_\mathrm{s} m_\mathrm{s}) \\ &\quad - \varrho^\pm(j_\mathrm{s}+1\,m_\mathrm{s}, j_\mathrm{s}+1\,m_\mathrm{s})\,, \\ S_\mathrm{p}^\pm &= \varrho^\pm(j_\mathrm{p} m_\mathrm{p}, j_\mathrm{p} m_\mathrm{p}) \\ &\quad + \varrho^\pm(j_\mathrm{p}+1\,m_\mathrm{p}, j_\mathrm{p}+1\,m_\mathrm{p})\,, \\ S_\mathrm{s}^\pm &= \varrho^\pm(j_\mathrm{s} m_\mathrm{s}, j_\mathrm{s} m_\mathrm{s}) \\ &\quad + \varrho^\pm(j_\mathrm{s}+1\,m_\mathrm{s}, j_\mathrm{s}+1\,m_\mathrm{s})\,. \end{aligned} \tag{6}$$

For the considered R-branch transitions of a linear molecule the quantities U^+ and V^+ are proportional to the in- and out-of-phase component of the macroscopic polarisation [19] due to the superposition of pump and signal states, labelled with p and s, respectively. The difference and sum of total occupation probability of the pump (signal) levels is given by W_p^+ and S_p^+ (W_s^+ and S_s^+)*.

By making use of the rotating wave approximation [20] we obtain with (1), (2), (3), and (6) the following differential equations

$$\begin{aligned} \dot{U}_\mathrm{p}^\pm &= -\,\Delta\omega_\mathrm{p}\,V_\mathrm{p}^\pm\,, \\ \dot{V}_\mathrm{p}^\pm &= \Delta\omega_\mathrm{p}\,U_\mathrm{p}^\pm - \varkappa_\mathrm{p}\,\varepsilon_\mathrm{p}\,W_\mathrm{p}^\pm\,, \\ \dot{W}_\mathrm{p}^\pm &= \varkappa_\mathrm{p}\,\varepsilon_\mathrm{p}\,V_\mathrm{p}^\pm\,, \\ \dot{S}_\mathrm{p}^\pm &= 0\,, \\ \dot{U}_\mathrm{s}^\pm &= -\,\Delta\omega_\mathrm{s}\,V_\mathrm{s}^\pm\,, \\ \dot{V}_\mathrm{s}^\pm &= \Delta\omega_\mathrm{s}\,U_\mathrm{s}^\pm - \varkappa_\mathrm{s}\,\varepsilon_\mathrm{s}\,W_\mathrm{s}^\pm\,, \\ \dot{W}_\mathrm{s}^\pm &= \varkappa_\mathrm{s}\,\varepsilon_\mathrm{s}\,V_\mathrm{s}^\pm\,, \\ \dot{S}_\mathrm{s}^\pm &= 0\,, \end{aligned} \tag{7}$$

* As shown below the equations of motion for the variables labelled with — will not be needed.

where

$$\Delta\omega_{\mathrm{p}} = \omega_{\mathrm{p0}} - \omega_{\mathrm{p}}; \quad \Delta\omega_{\mathrm{s}} = \omega_{\mathrm{s0}} - \omega_{\mathrm{s}}$$

and

$$\varkappa_{\mathrm{p}} = 2\langle j_{\mathrm{p}} m_{\mathrm{p}} | \mu | j_{\mathrm{p}} + 1\, m_{\mathrm{p}}\rangle/\hbar;$$
$$\varkappa_{\mathrm{s}} = 2\langle j_{\mathrm{s}} m_{\mathrm{s}} | \mu | j_{\mathrm{s}} + 1\, m_{\mathrm{s}}\rangle/\hbar$$

with

$$\langle j_{\mathrm{p}} m_{\mathrm{p}} | \mu | j_{\mathrm{p}} + 1\, m_{\mathrm{p}}\rangle = \langle j_{\mathrm{p}}(-m_{\mathrm{p}}) | \mu | j_{\mathrm{p}} + 1(-m_{\mathrm{p}})\rangle$$

and

$$\langle j_{\mathrm{s}} m_{\mathrm{s}} | \mu | j_{\mathrm{s}} + 1\, m_{\mathrm{s}}\rangle = \langle j_{\mathrm{s}}(-m_{\mathrm{s}}) | \mu | j_{\mathrm{s}} + 1(-m_{\mathrm{s}})\rangle$$

the transition dipole matrix element of pump and signal transition, respectively.

The effect of molecular collisions alone is considered next. The intermolecular interaction may be described under the impact approximation by first order differential equations for the elements of the density matrix with use of the relaxation superoperator Λ ($\dot{\varrho}\,|_{\mathrm{coll}} = -\Lambda \cdot \varrho$) [19].

In contrast to the case of radiative interaction, density matrix elements with different sign of m are, in general, coupled by collisional interaction. For example, elements of Λ such as

$$\langle\langle j m, j + 1\, m | \Lambda | j(-m), j + 1(-m)\rangle\rangle$$

describe the coupling of the off-diagonal density matrix elements ($\varrho(jm, j+1m)$ and $\varrho(j(-m), j+1(-m))$). Collisions may also transfer population from states with $+m$ to $-m$, characterized by relaxation matrix elements

$$\langle\langle j m, j m | \Lambda | j'(-m), j'(-m)\rangle\rangle$$

between the diagonal elements of ϱ, $\varrho(jm, jm)$ and $\varrho(j'(-m), j'(-m))$.

It has been shown by Liu et al. [19] that the kinetic equation for an ensemble of two-level systems in uncoupled with introduction of the linear combinations ϱ^{+} and ϱ^{-}, as defined by (5).

An extension to the considered four-level system is straight-forward and we obtain for the time derivatives of $U_{\mathrm{p}}^{\pm}$, $V_{\mathrm{p}}^{\pm}$, $U_{\mathrm{s}}^{\pm}$, and $V_{\mathrm{s}}^{\pm}$

$$\begin{aligned}
\dot{U}_{\mathrm{p}}^{\pm}\,|_{\mathrm{coll}} &= -(1/T_{2\mathrm{p}}^{\pm})\, U_{\mathrm{p}}^{\pm} - \delta_{\mathrm{p}}^{\pm}\, V_{\mathrm{p}}^{\pm}\,,\\
\dot{V}_{\mathrm{p}}^{\pm}\,|_{\mathrm{coll}} &= -(1/T_{2\mathrm{p}}^{\pm})\, V_{\mathrm{p}}^{\pm} + \delta_{\mathrm{p}}^{\pm}\, U_{\mathrm{p}}^{\pm}\,,\\
\dot{U}_{\mathrm{s}}^{\pm}\,|_{\mathrm{coll}} &= -(1/T_{2\mathrm{s}}^{\pm})\, U_{\mathrm{s}}^{\pm} - \delta_{\mathrm{s}}^{\pm}\, V_{\mathrm{s}}^{\pm}\,,\\
\dot{V}_{\mathrm{s}}^{\pm}\,|_{\mathrm{coll}} &= -(1/T_{2\mathrm{s}}^{\pm})\, V_{\mathrm{s}}^{\pm} + \delta_{\mathrm{s}}^{\pm}\, U_{\mathrm{s}}\,.
\end{aligned} \tag{8}$$

The relaxation parameters $T_{2\mathrm{p}}^{\pm}$, $\delta_{\mathrm{p}}^{\pm}$, $T_{2\mathrm{s}}^{\pm}$, and $\delta_{\mathrm{s}}^{\pm}$ are related to the elements of Λ as follows

$$\begin{aligned}
1/T_{2\mathrm{p}}^{\pm} &= \mathrm{Re}\, \lambda_{\mathrm{ba,ba}}^{\pm}\,,\\
\delta_{\mathrm{p}}^{\pm} &= \mathrm{Im}\, \lambda_{\mathrm{ba,ba}}^{\pm}\,,\\
1/T_{2\mathrm{s}}^{\pm} &= \mathrm{Re}\, \lambda_{\mathrm{cd,cd}}^{\pm}\,,\\
\delta_{\mathrm{s}}^{\pm} &= \mathrm{Im}\, \lambda_{\mathrm{cd,cd}}^{\pm}\,,
\end{aligned} \tag{9}$$

where

$$\begin{aligned}
\lambda_{\mathrm{ba,ba}}^{\pm} &= \langle\langle j_{\mathrm{p}} + 1\, m_{\mathrm{p}}, j_{\mathrm{p}} m_{\mathrm{p}} | \Lambda | j_{\mathrm{p}} + 1\, m_{\mathrm{p}}, j_{\mathrm{p}} m_{\mathrm{p}}\rangle\rangle\\
&\quad \pm \langle\langle j_{\mathrm{p}} + 1(-m_{\mathrm{p}}), j_{\mathrm{p}}(-m_{\mathrm{p}}) | \Lambda | j_{\mathrm{p}} + 1\, m_{\mathrm{p}}, j_{\mathrm{p}} m_{\mathrm{p}}\rangle\rangle\\
\lambda_{\mathrm{dc,dc}}^{\pm} &= \langle\langle j_{\mathrm{s}} + 1\, m_{\mathrm{s}}, j_{\mathrm{s}} m_{\mathrm{s}} | \Lambda | j_{\mathrm{s}} + 1\, m_{\mathrm{s}}, j_{\mathrm{s}} m_{\mathrm{s}}\rangle\rangle\\
&\quad \pm \langle\langle j_{\mathrm{s}} + 1(-m_{\mathrm{s}}), j_{\mathrm{s}}(-m_{\mathrm{s}}) | \Lambda | j_{\mathrm{s}} + 1\, m_{\mathrm{s}}, j_{\mathrm{s}} m_{\mathrm{s}}\rangle\rangle
\end{aligned}$$

for m_{p}, $m_{\mathrm{s}} \neq 0$, and

$$\begin{aligned}
\lambda_{\mathrm{ba,ba}}^{\pm} &= \langle\langle j_{\mathrm{p}} + 1\,0, j_{\mathrm{p}} 0 | \Lambda | j_{\mathrm{p}} + 1\,0, j_{\mathrm{p}} 0\rangle\rangle \quad \text{for} \quad m_{\mathrm{p}} = 0\,,\\
\lambda_{\mathrm{dc,dc}}^{\pm} &= \langle\langle j_{\mathrm{s}} + 1\,0, j_{\mathrm{s}} 0 | \Lambda | j_{\mathrm{s}} + 1\,0, j_{\mathrm{s}} 0\rangle\rangle \quad \text{for} \quad m_{\mathrm{s}} = 0\,.
\end{aligned}$$

The relaxation contribution to the differential equations for the linear combinations $W_{\mathrm{p}}^{\pm}$, $S_{\mathrm{p}}^{\pm}$, $W_{\mathrm{s}}^{\pm}$, and $S_{\mathrm{s}}^{\pm}$ of diagonal density matrix elements, see Eqs. (5) and (6), is given by

$$\begin{aligned}
\dot{W}_{\mathrm{p}}^{\pm}\,|_{\mathrm{coll}} = &-(1/T_{1\mathrm{p}}^{\pm})(W_{\mathrm{p}}^{\pm} - W_{\mathrm{p0}}^{\pm}) - \alpha_2^{\pm}(S_{\mathrm{p}}^{\pm} - S_{\mathrm{p0}}^{\pm}) + \gamma_1^{\pm}(W_{\mathrm{s}}^{\pm} - W_{\mathrm{s0}}^{\pm}) + \gamma_2^{\pm}(S_{\mathrm{s}}^{\pm} - S_{\mathrm{s0}}^{\pm})\\
&+ \sum_{j''m''}(k_{j''m'', j_{\mathrm{p}} m_{\mathrm{p}}}^{\pm} - k_{j''m'', j_{\mathrm{p}}+1 m_{\mathrm{p}}}^{\pm})(\varrho^{\pm}(j''m'', j''m'') - \varrho_0^{\pm}(j''m'', j''m''))\,,\\
\dot{S}_{\mathrm{p}}^{\pm}\,|_{\mathrm{coll}} = &-\alpha_3^{\pm}(S_{\mathrm{p}}^{\pm} - S_{\mathrm{p0}}^{\pm}) - \alpha_4^{\pm}(W_{\mathrm{p}}^{\pm} - W_{\mathrm{p0}}^{\pm}) + \gamma_3^{\pm}(W_{\mathrm{s}}^{\pm} - W_{\mathrm{s0}}^{\pm}) + \gamma_4^{\pm}(S_{\mathrm{s}}^{\pm} - S_{\mathrm{s0}}^{\pm})\\
&+ \sum_{j''m''}(k_{j''m'', j_{\mathrm{p}} m_{\mathrm{p}}}^{\pm} + k_{j''m'', j_{\mathrm{p}}+1 m_{\mathrm{p}}}^{\pm})(\varrho^{\pm}(j''m'', j''m'') - \varrho_0^{\pm}(j''m'', j''m''))\,,
\end{aligned}$$

$$\begin{aligned}
\dot{W}_{\mathrm{s}}^{\pm}|_{\mathrm{coll}} = &-(1/T_{1\mathrm{s}}^{\pm})(W_{\mathrm{s}}^{\pm}-W_{\mathrm{s}0}^{\pm})-\beta_2^{\pm}(S_{\mathrm{s}}^{\pm}-S_{\mathrm{s}0}^{\pm})+\gamma_5^{\pm}(W_{\mathrm{p}}^{\pm}-W_{\mathrm{p}0}^{\pm})+\gamma_6^{\pm}(S_{\mathrm{p}}^{\pm}-S_{\mathrm{p}0}^{\pm})\\
&+\sum_{j''m''}{}'(k_{j''m'',j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}-k_{j''m'',j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm})(\varrho^{\pm}(j''m'',j''m'')-\varrho_0^{\pm}(j''m'',j''m'')),\\
\dot{S}_{\mathrm{s}}^{\pm}|_{\mathrm{coll}} = &-\beta_3^{\pm}(S_{\mathrm{s}}^{\pm}-S_{\mathrm{s}0}^{\pm})-\beta_4^{\pm}(W_{\mathrm{s}}^{\pm}-W_{\mathrm{s}0}^{\pm})+\gamma_7^{\pm}(W_{\mathrm{p}}^{\pm}-W_{\mathrm{p}0}^{\pm})+\gamma_8^{\pm}(S_{\mathrm{p}}^{\pm}-S_{\mathrm{p}0}^{\pm})\\
&+\sum_{j''m''}{}'(k_{j''m'',j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}+k_{j''m'',j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm})(\varrho^{\pm}(j''m'',j''m'')-\varrho_0^{\pm}(j''m'',j''m'')).
\end{aligned} \tag{10}$$

The thermal equilibrium values of the variables in (10) which correspond to a Boltzmann distribution of level populations are labelled by zeros ($W_{\mathrm{p}0}^{\pm}$, $S_{\mathrm{p}0}^{\pm}$, etc.). The sums $\sum'$ are extended over all quantum numbers j'', m$''$ differing from those of the considered four levels.

The constants given in (10) are linear combinations of first order rate constants $k_{jm,j'm'}$ describing collisional coupling of diagonal density matrix elements ($\varrho(jm,jm)\rightarrow\varrho(j'm',j'm')$) and are related to the elements of Λ as follows.

$$k_{jm,j'm'} = -\langle\langle j'm',j'm'\,|\,\Lambda\,|\,jm,jm\rangle\rangle\,. \tag{11}$$

Defining the linear combinations

$$\begin{aligned}
k_{jm,j'm'}^{\pm} &= k_{jm,j'm'} \pm k_{jm,j'(-m')} &&\text{for}\quad m' \neq 0\,,\\
k_{jm,j0}^{\pm} &= k_{jm,j'0} &&\text{for}\quad m' = 0\,.
\end{aligned} \tag{12}$$

The constants in (10) are given by

$$\begin{aligned}
(1/T_{1\mathrm{p}}^{\pm}) &= \tfrac{1}{2}\Big(2\,k_{j_{\mathrm{p}}m_{\mathrm{p}},j_{\mathrm{p}}+1mp}^{\pm}+2\,k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j_{\mathrm{p}}m_{\mathrm{p}}}^{\pm}+2\,\gamma_8^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{p}}m_{\mathrm{p}},j''m''}^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j''m''}^{\pm}\Big),\\
\alpha_2^{\pm} &= \tfrac{1}{2}\Big(2\,k_{j_{\mathrm{p}}m_{\mathrm{p}},j_{\mathrm{p}}+1m_{\mathrm{p}}}^{\pm}-2\,k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j_{\mathrm{p}}m_{\mathrm{p}}}^{\pm}+2\,\gamma_7^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{p}}m,j''m''}^{\pm}-\sum_{j''m''}{}'k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j''m''}^{\pm}\Big),\\
\alpha_3^{\pm} &= \tfrac{1}{2}\Big(2\,\gamma_8^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{p}}m_{\mathrm{p}},j''m''}^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j''m''}^{\pm}\Big),\\
\alpha_4^{\pm} &= \tfrac{1}{2}\Big(2\,\gamma_7^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{p}}m_{\mathrm{p}},j''m''}^{\pm}-\sum_{j''m''}{}'k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j''m''}^{\pm}\Big),\\
(1/T_{1\mathrm{s}}^{\pm}) &= \tfrac{1}{2}\Big(2\,k_{j_{\mathrm{s}}m_{\mathrm{s}},j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm}+2\,k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}+2\,\gamma_4^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{s}}m_{\mathrm{s}},j''m''}^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j''m''}^{\pm}\Big),\\
\beta_2^{\pm} &= \tfrac{1}{2}\Big(2\,k_{j_{\mathrm{s}}m_{\mathrm{s}},j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm}-2\,k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}+2\,\gamma_3^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{s}}m_{\mathrm{s}},j''m''}^{\pm}-\sum_{j''m''}{}'k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j''m''}^{\pm}\Big),\\
\beta_3^{\pm} &= \tfrac{1}{2}\Big(2\,\gamma_4^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{s}}m_{\mathrm{s}},j''m''}^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j''m''}^{\pm}\Big),\\
\beta_4^{\pm} &= \tfrac{1}{2}\Big(2\,\gamma_3^{\pm}+\sum_{j''m''}{}'k_{j_{\mathrm{s}}m_{\mathrm{s}},j''m''}^{\pm}-\sum_{j''m''}{}'k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j''m''}^{\pm}\Big),\\
\gamma_1^{\pm} &= \tfrac{1}{2}(k_{j_{\mathrm{s}}m_{\mathrm{s}},j_{\mathrm{p}}m_{\mathrm{p}}}^{\pm}+k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j_{\mathrm{p}}+1m_{\mathrm{p}}}^{\pm}-k_{j_{\mathrm{s}}m_{\mathrm{s}},j_{\mathrm{p}}+1m_{\mathrm{p}}}^{\pm}-k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j_{\mathrm{p}}m_{\mathrm{p}}}^{\pm}),\\
\gamma_2^{\pm} &= \tfrac{1}{2}(k_{j_{\mathrm{s}}m_{\mathrm{s}},j_{\mathrm{p}}m_{\mathrm{p}}}^{\pm}+k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j_{\mathrm{p}}m_{\mathrm{p}}}^{\pm}-k_{j_{\mathrm{s}}m_{\mathrm{s}},j_{\mathrm{p}}+1m_{\mathrm{p}}}^{\pm}-k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j_{\mathrm{p}}+1m_{\mathrm{p}}}^{\pm}),\\
\gamma_3^{\pm} &= \tfrac{1}{2}(k_{j_{\mathrm{s}}m_{\mathrm{s}},j_{\mathrm{p}}m_{\mathrm{p}}}^{\pm}+k_{j_{\mathrm{s}}m_{\mathrm{s}},j_{\mathrm{p}}+1m_{\mathrm{p}}}^{\pm}-k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j_{\mathrm{p}}m_{\mathrm{p}}}^{\pm}-k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j_{\mathrm{p}}+1m_{\mathrm{p}}}^{\pm}),\\
\gamma_4^{\pm} &= \tfrac{1}{2}(k_{j_{\mathrm{s}}m_{\mathrm{s}},j_{\mathrm{p}}m_{\mathrm{p}}}^{\pm}+k_{j_{\mathrm{s}}m_{\mathrm{s}},j_{\mathrm{p}}+1m_{\mathrm{p}}}^{\pm}+k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j_{\mathrm{p}}m_{\mathrm{p}}}^{\pm}+k_{j_{\mathrm{s}}+1m_{\mathrm{s}},j_{\mathrm{p}}+1m_{\mathrm{p}}}^{\pm}),\\
\gamma_5^{\pm} &= \tfrac{1}{2}(k_{j_{\mathrm{p}}m_{\mathrm{p}},j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}+k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm}-k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}-k_{j_{\mathrm{p}}m_{\mathrm{p}},j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm}),\\
\gamma_6^{\pm} &= \tfrac{1}{2}(k_{j_{\mathrm{p}}m_{\mathrm{p}},j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}+k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}-k_{j_{\mathrm{p}}m_{\mathrm{p}},j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm}-k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm}),\\
\gamma_7^{\pm} &= \tfrac{1}{2}(k_{j_{\mathrm{p}}m_{\mathrm{p}},j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}+k_{j_{\mathrm{p}}m_{\mathrm{p}},j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm}-k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}-k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm}),\\
\gamma_8^{\pm} &= \tfrac{1}{2}(k_{j_{\mathrm{p}}m_{\mathrm{p}},j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}+k_{j_{\mathrm{p}}m_{\mathrm{p}},j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm}+k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j_{\mathrm{s}}m_{\mathrm{s}}}^{\pm}+k_{j_{\mathrm{p}}+1m_{\mathrm{p}},j_{\mathrm{s}}+1m_{\mathrm{s}}}^{\pm}).
\end{aligned} \tag{13}$$

The complete set of differential equations describing the dynamical behaviour of the ensemble of four-level systems is given by (7), (8), and (10). Since these equations do not couple the variables with different labels (+ or −) and only the variables labelled by + (U^{+} and V^{+}) are related to observable quantities (macroscopic polarisation components), only the equations for the linear combinations (6) of ϱ^+-matrix elements will be considered in the following*.

We now introduce some approximations to make the remaining system of differential equations applicable to practical problems. With omission of all sums with $\varrho^+(j''m'', j''m'') - \varrho_0^+(j''m'', j''m'')$ in (10) only population changes within the four levels are retained, thereby treating all other levels as thermal bath. The collisional damping of such "embedded" four-level systems does not include feedback of nonthermal bath populations to the pump and signal levels by cascading processes. Further simplification is obtained by assuming that the scattering dynamics of pump and signal levels, respectively, are not much different, such that

$$\begin{aligned} & k^+_{j_\mathrm{p} m_\mathrm{p}, j_\mathrm{s} m_\mathrm{s}} + k^+_{j_\mathrm{p} m_\mathrm{p}, j_\mathrm{s}+1\, m_\mathrm{s}} + \sum_{j''m''}{}' k^+_{j_\mathrm{p} m_\mathrm{p}, j''m''} \\ & \cong k^+_{j_\mathrm{p}+1\, m_\mathrm{p}, j_\mathrm{s} m_\mathrm{s}} + k^+_{j_\mathrm{p}+1\, m_\mathrm{p}, j_\mathrm{s}+1\, m_\mathrm{s}} \\ & \quad + \sum_{j''m''}{}' k^+_{j_\mathrm{p}+1\, m_\mathrm{p}, j''m''}, \end{aligned}$$

and

$$\begin{aligned} & k^+_{j_\mathrm{s} m_\mathrm{s}, j_\mathrm{p} m_\mathrm{p}} + k^+_{j_\mathrm{s} m_\mathrm{s}, j_\mathrm{p}+1\, m_\mathrm{p}} + \sum_{j''m''}{}' k^+_{j_\mathrm{s} m_\mathrm{s}, j''m''} \\ & \cong k^+_{j_\mathrm{s}+1\, m_\mathrm{s}, j_\mathrm{p} m_\mathrm{p}} + k^+_{j_\mathrm{s}+1\, m_\mathrm{s}, j_\mathrm{p}+1\, m_\mathrm{p}} \\ & \quad + \sum_{j''m''}{}' k^+_{j_\mathrm{s}+1\, m_\mathrm{s}, j''m''}, \end{aligned} \tag{14}$$

which gives with (13) $\alpha_4^+ \cong 0$, $\beta_4^+ \cong 0$.

The assumptions (14) are essential for the derivation of two-level Bloch equations [19] and are supported from the results of single resonance experiments which show that the relaxation of population differences may be described within the experimental uncertainties by a simple exponential decay law [21].

In addition, for the considered transitions in the microwave range with $\hbar\omega_{\mathrm{p}0}$, $\hbar\omega_{\mathrm{s}0} \ll kT$ for common temperatures, we may make use of the principle of detailed belancing giving

$$\begin{aligned} & k_{j_\mathrm{p}(\pm m_\mathrm{p}), j_\mathrm{p}+1(\pm m_\mathrm{p})} / k_{j_\mathrm{p}+1(\pm m_\mathrm{p}), j_\mathrm{p}(\pm m_\mathrm{p})} \\ & = \exp(-\hbar\,\omega_{\mathrm{p}0}/kT) \cong 1 \end{aligned}$$

and

$$\begin{aligned} & k_{j_\mathrm{s}(\pm m_\mathrm{s}), j_\mathrm{s}+1(\pm m_\mathrm{s})} / k_{j_\mathrm{s}+1(\pm m_\mathrm{s}), j_\mathrm{s}(\pm m_\mathrm{s})} \\ & = \exp(-\hbar\,\omega_{\mathrm{s}0}/kT) \cong 1 \end{aligned} \tag{15}$$

for pump and signal transition, respectively.

With use of Eq. (4.39) of Ref. [19] and symmetries of the $3j$-symbol, giving $k_{j+1(-m), jm} = k_{j+1m, j(-m)}$ we may also conclude with (12) and (15) that

$$k^+_{j_\mathrm{p} m_\mathrm{p}, j_\mathrm{p}+1\, m_\mathrm{p}} \cong k^+_{j_\mathrm{p}+1\, m_\mathrm{p}, j_\mathrm{p} m_\mathrm{p}}$$

and

$$k^+_{j_\mathrm{s} m_\mathrm{s}, j_\mathrm{s}+1\, m_\mathrm{s}} \cong k^+_{j_\mathrm{s}+1\, m_\mathrm{s}, j_\mathrm{s} m_\mathrm{s}} \tag{16}$$

which with (13), (14) make neglection of terms with α_2^+ and β_2^+ in (10) possible.

With the above assumptions we now have with (7), (8) and (10) the following differential equations

$$\begin{aligned} \dot U^+_\mathrm{p} &= -(\Delta\omega_\mathrm{p} + \delta^+_\mathrm{p})\, V^+_\mathrm{p} - (1/T^+_{2\mathrm{p}})\, U^+_\mathrm{p}, \\ \dot V^+_\mathrm{p} &= (\Delta\omega_\mathrm{p} + \delta^+_\mathrm{p})\, U^+_\mathrm{p} \\ & \quad - (1/T^+_{2\mathrm{p}})\, V^+_\mathrm{p} - \varkappa_\mathrm{p}\,\varepsilon_\mathrm{p}\, W^+_\mathrm{p}, \\ \dot W^+_\mathrm{p} &= \varkappa_\mathrm{p}\,\varepsilon_\mathrm{p}\, V^+_\mathrm{p} - (1/T^+_{1\mathrm{p}})(W^+_\mathrm{p} - W^+_{\mathrm{p}0}) \\ & \quad + \gamma_1^+ (W^+_\mathrm{s} - W^+_{\mathrm{s}0}) + \gamma_2^+ (S^+_\mathrm{s} - S^+_{\mathrm{s}0}), \\ \dot S^+_\mathrm{p} &= -\alpha_3^+ (S^+_\mathrm{p} - S^+_{\mathrm{p}0}) \\ & \quad + \gamma_3^+ (W^+_\mathrm{s} - W^+_{\mathrm{s}0}) + \gamma_4^+ (S^+_\mathrm{s} - S^+_{\mathrm{s}0}), \\ \dot U^+_\mathrm{s} &= -(\Delta\omega_\mathrm{s} + \delta^+_\mathrm{s})\, V^+_\mathrm{s} - (1/T^+_{2\mathrm{s}})\, U^+_\mathrm{s}, \\ \dot V^+_\mathrm{s} &= (\Delta\omega_\mathrm{s} + \delta^+_\mathrm{s})\, U^+_\mathrm{s} \\ & \quad - (1T^+_{2\mathrm{s}})\, V^+_\mathrm{s} - \varkappa_\mathrm{s}\,\varepsilon_\mathrm{s}\, W^+_\mathrm{s}, \\ \dot W^+_\mathrm{s} &= \varkappa_\mathrm{s}\,\varepsilon_\mathrm{s}\, V^+_\mathrm{s} - (1/T^+_{1\mathrm{s}})(W^+_\mathrm{s} - W^+_{\mathrm{s}0}) \\ & \quad + \gamma_5^+ (W^+_\mathrm{p} - W^+_{\mathrm{p}0}) + \gamma_6^+ (S^+_\mathrm{p} - S^+_{\mathrm{p}0}), \\ \dot S^+_\mathrm{s} &= -\beta_3^+ (S^+_\mathrm{s} - S^+_{\mathrm{s}0}) \\ & \quad + \gamma_7^+ (W^+_\mathrm{p} - W^+_{\mathrm{p}0}) + \gamma_8^+ (S^+_\mathrm{p} - S^+_{\mathrm{p}0}). \end{aligned} \tag{17}$$

Equations (17) may be used to analyze both time-resolved and steady-state four-level double resonance experiments on a system of linear molecules in a static electric field.

For the experiments to be discussed here, we are only interested in the steady-state solution $(t \to \infty)$ of (17)**, in particular for $V^+_\mathrm{s}(t \to \infty)$ at low probe power, since the steady-state absorption coefficient of the signal transition is proportional to $V^+_\mathrm{s}(t \to \infty)$ [19, 22]. With the solutions $V^+_\mathrm{s}(t \to \infty)$ at high pump power and $V^+_{\mathrm{s}0}(t \to \infty)$ at zero pump power, the relative change in signal line intensity, $\eta = \Delta I/I$, is then given by

$$\eta = \{V^+_\mathrm{s}(t \to \infty) - V^+_{\mathrm{s}0}(t \to \infty)\} / V^+_{\mathrm{s}0}(t \to \infty). \tag{18}$$

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* It may be noted that these equations are formally equivalent to those for four non-degenerate energy levels as given recently [18]. However, the relaxation parameters which describe collisional phenomena in the two cases, are in general different.

** For resonance, $\Delta\omega_\mathrm{p} + \delta^+_\mathrm{p} = 0$ and $\Delta\omega_\mathrm{s} + \delta^+_\mathrm{s} = 0$.

The steady-state solutions for V_s^+ are found straightforwardly with some algebra by setting all time derivatives in (17) equal to zero. With the assumption of saturating pump power,

$$\varkappa_p^2\,\varepsilon_p^2 \gg (1/T_{1p}^+)\cdot(1/T_{2p}^+)\,,$$

we then obtain for $V_s^+(t\to\infty)$ in the low probe power limit, $\varkappa_s^2\,\varepsilon_s^2 \ll (1/T_{1s}^+)(1/T_{2s}^+)$,

$$\begin{aligned} V_s^+(t\to\infty) &= -(\varkappa_s\,\varepsilon_s)\,(T_{2s}^+) \\ &\cdot\Bigg\{W_{so}^+ - W_{p0}^+ \\ &\cdot\frac{\gamma_5^+(\alpha_3^+\beta_3^+ - \gamma_4^+\gamma_8^+) + \gamma_4^+\gamma_6^+\gamma_7^+}{(1/T_{1s}^+)(\alpha_3^+\beta_3^+ - \gamma_4^+\gamma_8^+) - \beta_3^+\gamma_3^+\gamma_6^+}\Bigg\}. \end{aligned} \tag{19}$$

For zero pump power, $\varkappa_p\,\varepsilon_p = 0$, we have

$$V_{s0}^+(t\to\infty) = -(\varkappa_s\,\varepsilon_s)\,(T_{2s}^+)\,W_{s0}^+ \tag{20}$$

as it follows directly also from the Bloch equations for an ensemble of two-level systems with $\pm M$ degeneracy in the low power limit [22].

With (18), (19), and (20) we then obtain

$$\eta = -\frac{\gamma_5^+(\alpha_3^+\beta_3^+ - \gamma_4^+\gamma_8^+) + \gamma_4^+\gamma_6^+\gamma_7^+}{(1/T_{1s}^+)(\alpha_3^+\beta_3^+ - \gamma_4^+\gamma_8^+) - \beta_3^+\gamma_3^+\gamma_6^+}\cdot\frac{W_{p0}^+}{W_{s0}^+}\,. \tag{21}$$

(21) may be considerably simplified for many cases of practical interest. From (13) we note that the constant α_3^+ (β_3^+) represents a sum over γ_8^+ (γ_4^+) and two "bath constants" for the levels of pump (signal) transition (e.g. $\sum' k_{j_p m_p, j'' m''}$, etc.). For an sufficiently large number of open collisional channels to levels outside the four-level scheme we may assume that the bath constants are considerably larger than any of the constants γ_i^+ ($i = 1, 2, \ldots, 8$) describing collisional energy transfer between pump and signal levels. With neglection of terms $\beta_3^+\gamma_3^+\gamma_6^+$ (using $\beta_3^+ < (1/T_{1s}^+)$, see (13)), the simplified expression for η is given by

$$\eta = \frac{-\gamma_5^+}{(1/T_{1s}^+)}\cdot\frac{W_{p0}^+}{W_{s0}^+}\,. \tag{22}$$

The thermal equilibrium values of W_{p0}^+ and W_{s0}^+, the probability for total occupation difference of pump and signal levels, respectively, are given by

$$W_{p0}^+ = g_{m_p}\cdot\frac{\exp\{-E_a/k\,T\} - \exp\{-E_b/k\,T\}}{Z} \tag{23}$$

and

$$W_{s0}^+ = g_{m_s}\cdot\frac{\exp\{-E_c/k\,T\} - \exp\{-E_d/k\,T\}}{Z} \tag{24}$$

with $g_m = 2$ for $m \neq 0$ and $g_m = 1$ for $m = 0$ ($m = m_p, m_s$) where Z is the molecular partition sum.

For transitions in the microwave range we may expand the exponentials in (23) and (24) according to (15) and then obtain with (22), expressing γ_5^+ in terms of individual rate constants (see (13))

$$\eta = -\frac{g_{m_p}\,\nu_{s0}}{2\,g_{m_s}\,\nu_{s0}}\cdot\frac{k_{j_p m_p, j_s m_s}^+ + k_{j_p+1\,m_s, j_s+1\,m_s}^+ - k_{j_p+1\,m_p, j_s m_s}^+ - k_{j_p m_p, j_s+1\,m_s}^+}{(1/T_{1s}^+)}\exp\{+(E_c - E_a)/k\,T\}, \tag{25}$$

where ν_{p0} and ν_{s0} are the resonance frequencies of pump and signal transition, respectively.

(25) gives an approximative description of the relative change in signal intensity, $\eta = \Delta I/I$, which contains as relaxation parameters the rate constants for collisional transfer of rotational energy between pump and signal levels, as well as the relaxation time T_{1s}^+ for the signal transition. The experimental results, given in the next section, will be discussed on the basis of the theoretical expression (25) for η[*].

Results and Discussion

As described above the η-values have been measured for the pump-signal transition scheme illustrated in Figure 1. The results are given in Table 1, together with the estimated error limits. Less accurate results were obtained for the mixtures with foreign gases since small amounts of OCS with large excess of the foreign gas have been used in order to minimize the effects of the interaction between OCS molecules.

The reliability of the results for η was tested by changing various experimental conditions. No significant dependence of the $\Delta I/I$-ratios on the signal microwave power was found in the available power range (< 100 μW). However, by reducing the

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[*] An expression similar to (25) without explicit consideration of the ± m degeneracy of the energy levels was used by Lees [12] for the discussion of the results from investigations of four-level systems of OCS, other than the present ones.

Table 1. Observed η-values for $^{16}O^{12}C^{32}S$ in the natural isotopic mixture and in mixtures with the foreign gases He, Ne, Ar, Kr, H_2, N_2, O_2, CO_2 and CH_3F. Estimated errors in parantheses are in the last digit given. Temperature $T = 200$ K, pump microwave power $L_p \cong 0.5$ W.

Pump transition P: $(j_p, m_p) = (0, 0) \rightarrow (1, 0)$	η [%] for collision partner									
Signal transition S: $(j_s, m_s) \rightarrow (j_s+1, m_s)$	OCS	He	Ne	Ar	Kr	H_2	N_2	O_2	CO_2	CH_3F
$(1, 1) \rightarrow (2, 1)$	$-1.20\,(10)^a$	$0.0\,(2)^c$	$+1.2\,(7)$	$+0.4\,(3)$	$+0.8\,(4)$	$+0.3\,(2)^d$	$0.0\,(2)$	$+0.4\,(3)$	$-1.6\,(4)$	$-4.2\,(4)^d$
$(2, 0) \rightarrow (3, 0)$	$+0.17\,(4)^b$	$-0.3\,(2)$	$-0.6\,(2)$	$-0.5\,(2)$	$-0.5\,(2)$	$-0.4\,(2)$	$-0.3\,(2)$	$-0.5\,(2)$	$+0.3\,(2)$	$> +0.5^e$
$(2, 1) \rightarrow (3, 1)$	$+0.06\,(3)^b$	$-0.3\,(2)$	$-0.5\,(2)$	$-0.4\,(2)$	$-0.5\,(2)$	$-0.3\,(2)$	$-0.2\,(1)$	$-0.5\,(2)$	$+0.10\,(7)$	$> +0.2^e$
$(2, 2) \rightarrow (3, 2)$	$-0.26\,(4)^b$	$-0.4\,(2)$	$-0.6\,(2)$	$-0.5\,(2)$	$-0.4\,(2)$	$-0.5\,(2)$	$-0.4\,(2)$	$-0.4\,(2)$	$-0.2\,(1)$	$< -0.4^e$

[a] $p_{OCS} = 14.3$ mTorr, [b] $p_{OCS} = 13.8$ mTorr, [c] mixtures with foreign gases with partial pressure ratio $p_{fg} : p_{OCS} \cong 25$ mTorr : 0.3 mTorr,

[d] measured at $T = 298$ K with X-band waveguide (4.7 m length); $p_{H_2} : p_{OCS} = 26$ mTorr : 2 mTorr; $p_{CH_3F} : p_{OCS} = 25$ mTorr : 5 mTorr,

[e] estimated from measurements of ΔI_{fg} with foreign gas admixtures by comparison with the pure gas result ΔI_{OCS} (see Fig. 7) and the η-value of the pure gas (η_{OCS}). From the inequality $I_{OCS} > I_{fg}$ (decrease of signal line intensity with foreign gas admixture) it follows that $|\eta_{fg}| = |\Delta I_{fg}|/I_{fg} > |\Delta I_{fg}|/I_{OCS} = |\Delta I_{fg} \cdot \eta_{OCS}/\Delta I_{OCS}|$, (fg=$CH_3F$).

pump microwave power, in particular below 0.5 W, a variation of the experimental η-values was found, reflecting incomplete saturation of the pump transition. Such reduction of the pumping efficiency* is not only caused by pressure broadening but also by broadening of the pump line due to the inhomogeneity of the Stark field. For comparison with the theory given above the experimental η-values have to be normalized to 100% pumping efficiency, i.e. saturation of the pump transition as assumed for the derivation of (25).

The determination of η is not very critically dependent on the accurate setting of the pump frequency ν_p as illustrated in Fig. 5, where η is plotted against the frequency offset $\nu_p - \nu_{p0}$. The small signal change at $\nu_p - \nu_{p0} \cong -20$ MHz corresponds to a three-level double resonance signal with the pump transition $(j_p, m_p) : (0, 0) \rightarrow (1, 1)$, which is weakly allowed due to components of the Stark field perpendicular to the polarisation plane of the microwave radiation ($\Delta M = \pm 1$ spectroscopic selection rule).

The results for η which were obtained for the m-components of the $j = 2 \rightarrow 3$ transition correspond to collision-induced changes ΔI in the signal line intensity, as observed by means of pump amplitude modulation (100 kHz). In addition to the measurement of η, the investigation of the frequency dependence $\Delta I(\nu_s)$ with application of a DC Stark field is very useful for the observation of m-resolved collision-induced transitions as it has been previously shown for the pure OCS gas [11]. Examples for recordings of $\Delta I(\nu_s)$ for different admixtures of

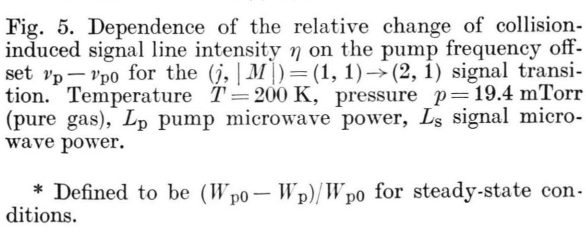

Fig. 5. Dependence of the relative change of collision-induced signal line intensity η on the pump frequency offset $\nu_p - \nu_{p0}$ for the $(j, |M|) = (1, 1) \rightarrow (2, 1)$ signal transition. Temperature $T = 200$ K, pressure $p = 19.4$ mTorr (pure gas), L_p pump microwave power, L_s signal microwave power.

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* Defined to be $(W_{p0} - W_p)/W_{p0}$ for steady-state conditions.

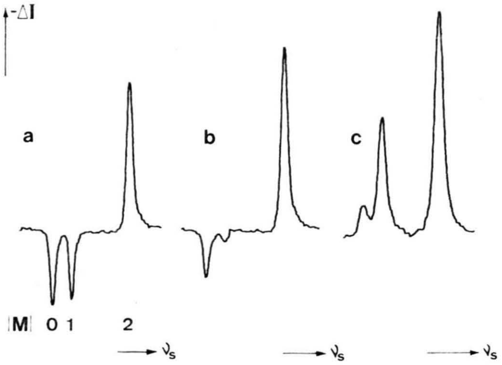

Fig. 6. Observed collision-induced transition pattern for the OCS $j=2 \rightarrow 3$ transition for nonzero Stark field and different admixtures of He. The change of signal line intensity ΔI is given in arbitrary units. Temperature $T=200$ K, partial pressure of OCS $p_{\text{OCS}}=12$ mTorr, He partial pressures: a) 0 mTorr, b) 6 mTorr, c) 26 mTorr.

foreign gases are given in Fig. 6 and 7, demonstrating rather drastic variations with increasing partial pressure of the collision partner. As shown for mixtures with He in Fig. 6, already at small admixtures of He a change of sign in ΔI is observed for the $m=0$ and $m=1$ component of the $j=2 \rightarrow 3$ transition, corresponding to the results for η at higher gas pressures (see Table 1). Line patterns similar to those given in Fig. 6, were found for the mixtures with the other rare gases, as well as H_2, N_2 and O_2. No change of sign but only an increase was found for the signal change ΔI of all three m-components when CO_2 was admixed to the OCS gas probe. Collision-induced signals at different partial pressures of CH_3F are shown in Figure 7, indicating a significant increase of $|\eta|$ for the $m=0$, 1 and 2 component of the $j=2 \rightarrow 3$ transition with increasing amount of CH_3F in the mixture.

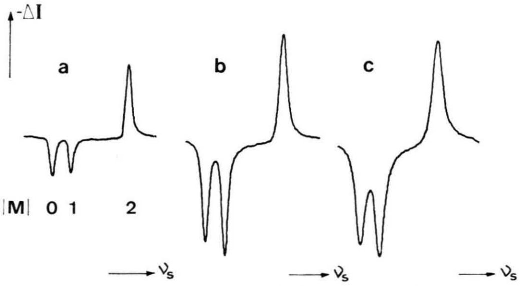

Fig. 7. Observed collision-induced transition pattern for the OCS $j=2 \rightarrow 3$ transition for nonzero Stark field and different admixtures of CH_3F. The change of signal line intensity ΔI is given in arbitrary units. Temperature $T=200$ K, partial pressure of OCS $p_{\text{OCS}}=12$ mTorr CH_3H partial pressures: a) 0 mTorr, b) 6 mTorr, c) 15 mTorr.

We now discuss the results for $\Delta I/I$ of Table 1, indicating various collisional preferences for the investigated systems. In order to compare η with the theoretical expression (25) it was necessary to allow for systematic effects which were not considered in the theoretical treatment. The observed η-values were thus extrapolated to 100% pumping efficiency corresponding to complete equalization of the populations of the pumped levels*, no wall collisious and infinite dilution of the mixtures, by using standard procedures [23] and the data from previous two-level relaxation studies. The corrected η-values are then used together with data for $1/T^+_{1s}$ from two-pulse transient experiments [21, 24]** to evaluate the coefficients of the pressure dependence of $(k^+_{j_p m_p, j_s m_s} + k^+_{j_p+1\, m_p, j_s+1\, m_s} - k^+_{j_p+1\, m_p, j_s m_s} - k^+_{j_p m_p, j_s+1\, m_s})$ in (25). The results are given in Table 2 where the positive coefficients Φ_l have been introduced with the notation

$$k^+_{jm,j'm'} = \Phi_l(j, m \rightarrow j', m') \cdot p \qquad (26)$$

for the linear pressure dependence of the rate constants $k^+_{jm,j'm'}$. p gives either the pressure of the pure gas (p_{OCS}) or the foreign gas partial pressure (p_{FG}) for the mixtures. Though the linear combinations of pressure coefficients in Table 2 are not very accurately determined, the results may be discussed qualitatively with regard to different types of collisional interactions which are characterized by the index l for the coefficients Φ.

The collision-induced transitions will be classified according to "selection rules" which are obtained from consideration of long-range intermolecular forces due to permanent multipole, induction and dispersion interaction [1]. For molecules with $C_{\infty v}$ symmetry (such as OCS) in the ground vibronic state, a first order perturbation treatment of the dipole interaction ($l=1$) gives the preference rules***

$$\Delta j = \pm 1\,, \quad \Delta M = 0, \pm 1\,. \qquad (27)$$

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* Since the pump power distribution within the absorption cell is not very accurately known, the actual pump efficiency was estimated with rather large error limits to be about $(70 \pm 20)\%$ (pump power ≈ 0.5 W).

** Though not explicitely stated in [21], π, τ, $\pi/2$ sequence experiments involving two-level systems with $\pm m$-degeneray result in $1/T^+_{1s}$-values as may be concluded from (17) for $W^+_p \approx W^+_{p0}$, $S^+_p \approx S^+_{p0}$ which holds approximately for $\varepsilon_p = 0$.

*** Not considering mixing of rotational wavefunctions due to the Stark field.

Table 2. Sum of coefficients $1/p\,\{k^{+}_{j_p m_p,\, j_s m_s} + k^{+}_{j_p+1\, m_p,\, j_s+1\, m_s} - k^{+}_{j_p+1\, m_p,\, j_s m_s} - k^{+}_{j_p m_p,\, j_s+1\, m_s}\}$ for the pressure depen-
OCS with OCS, He, Ne, Ar, Kr, H_2, N_2, O_2, CO_2 and CH_3F. The data refer to the η-values of Table 1, extrapolated to

Pump transition P: $(j_p, m_p) = (0, 0) \rightarrow (1, 0)$ Signal transition S: $(j_s, m_s) \rightarrow (j_s + 1, m_s)$	$R = 1/p\,\{k^{+}_{j_p m_p,\, j_s m_s} + k^{+}_{j_p+1\, m_p,\, j_s+1\, m_s} - k^{+}_{j_p+1\, m_p,\, j_s m_s} - k^{+}_{j_p m_p,\, j_s+1\, m_s}$	R [μs^{-1} Torr^{-1}] for collision partner		
		OCS	He	Ne
$(1, 1) \rightarrow (2, 1)$	$\{\Phi_1(0, 0 \rightarrow 1, 1) + \Phi_1(1, 0 \rightarrow 2, 1)\}$ $- \{\Phi_2(0, 0 \rightarrow 2, 1) + \Phi_2(1, 0 \rightarrow 1, 1)\}$	+ 6.8 (26)	0.0 (4)	− 3.8 (26)
$(2, 0) \rightarrow (3, 0)$	$\{\Phi_2(0, 0 \rightarrow 2, 0) + \Phi_2(1, 0 \rightarrow 3, 0)\}$ $- \{\Phi_3(0, 0 \rightarrow 3, 0) + \Phi_1(1, 0 \rightarrow 2, 0)\}$	− 0.7 (4)	+ 0.8 (6)	+ 1.4 (8)
$(2, 1) \rightarrow (3, 1)$	$\{\Phi_2(0, 0 \rightarrow 2, 1) + \Phi_2(1, 0 \rightarrow 3, 1)\}$ $- \{\Phi_3(0, 0 \rightarrow 3, 1) + \Phi_1(1, 0 \rightarrow 2, 1)\}$	− 0.6 (4)	+ 1.4 (10)	+ 2.0 (12)
$(2, 2) \rightarrow (3, 2)$	$\{\Phi_2(0, 0 \rightarrow 2, 2) + \Phi_2(1, 0 \rightarrow 3, 2)\}$ $- \{\Phi_3(0, 0 \rightarrow 3, 2) + \Phi_3(1, 0 \rightarrow 2, 2)\}$	+ 2.2 (10)	+ 2.0 (14)	+ 2.8 (16)

The collisional selection rules due to the molecular quadrupole moment ($l = 2$) are in first order

$$\Delta j = 0, \pm 2, \quad \Delta M = 0, \pm 1, \pm 2 . \tag{28}$$

It should be noted that the rules (28) which are characterized here to be of "quadrupole-type" may also be attributed to second order contributions from dipolar collisional interaction.

Collisional transitions which do not obey the rules (27) or (28) are characterized in Table 2 by the index $l = 3$. From inspection of Table 2 we may conclude that various collisional preferences have to be considered for the studied systems. Whenever the sum of rate coefficients characterizing the collisional pathways between lower pump to lower signal level (a→c, see Figs. 1, 4) and upper pump to upper signal level (b→d) predominates over the sum of rate coefficients for collisional transfer of rotational energy from upper pump to lower signal level (b→c) and lower pump to upper signal level (a→d), we have $R > 0$ (for example

$$\{\Phi_1(0, 0 \rightarrow 1, 1) + \Phi_1(1, 0 \rightarrow 2, 1)\}$$
$$> \{\Phi_2(0,0 \rightarrow 2, 1) + \Phi_2(1, 0 \rightarrow 1, 1)\}$$

for the signal transition $(j, m): (1, 1) \rightarrow (2, 1)$ and the pure OCS gas, see Table 2. The results for the collision partners OCS, CH_3F and CO_2 indicate for these systems the importance of first order dipolar collisional preference corresponding to the rules (27). Whenever a direct dipolar collisional channel ($l = 1$) is present the coefficients Φ_1 give the dominant contribution to R, as found for the (j, m): $(1, 1) \rightarrow (2, 1)$, $(2, 0) \rightarrow (3, 0)$ and $(2, 1) \rightarrow (3, 1)$ signal transition. However, the small magnitude of R for the latter two transitions points to a near balance of dipole-type ($l = 1$) and quadrupole-type ($l = 2$) collisional transitions.

In case of the $(j, m): (2, 2) \rightarrow (3, 2)$ signal transition no direct dipole collisional transitions between pump and signal levels are involved and the coefficients with $l = 2$ which may be attributed to second order dipole effects, clearly dominate. The effects of dipolar collisional interaction are particularly distinct for the polar collision partner CH_3F with a permanent dipole moment of 1.859 D [25] which is larger than that of OCS (0.715 D) [26]. Therefore, the long-range dipole-dipole interaction gives rise to larger cross sections for OCS-CH_3F collisions than for OCS-OCS collisions. For collisions of OCS with the nonpolar molecule CO_2 the results in Table 2 may be interpreted as effect of a dipole (OCS)-quadrupole (CO_2) interaction, which results in the rules (27) for the transfer of population from pump to signal levels [1].

For the interaction of OCS with the nonpolar molecules H_2, N_2 and O_2, as well as with the rare gas atoms, the results in Table 2 indicate the importance of collisional preferences with $l = 2$*. Thus, for the $(j, m): (1, 1) \rightarrow (2, 1)$ signal transition, contributions to R from collisional transfer of rotational energy with $\Delta j = 1$ ($l = 1$) is either balanced ($R \approx 0$) or outweighted ($R < 0$) by collisional processes with $\Delta j = 0$ or $\Delta j = 2$ ($l = 2$). For the signal transitions $j = 2 \rightarrow 3$ ($m = 0, 1, 2$) second order rate constants ($l = 2$) with $\Delta j = 2$ clearly

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* The quadrupole moments of H_2, O_2 and N_2 are smalle. than the quadrupole moment of CO_2 [27]. Therefore, wr may expect less important contributions to the coefficiente Φ_1 from dipole-quadrupole interactions for these moleculess

dence of rate constants characterizing transfer of population between pump and signal levels, induced by collisions of 100% pumping efficiency, no wall collisions and infinite dilution for the mixtures.

Ar	Kr	H_2	N_2	O_2	CO_2	CH_3F
− 1.6 (14)	− 2.8 (20)	− 1.8 (14)	0.0 (4)	− 1.8 (16)	+ 8.4 (22)	+ 42.0 (140)
+ 1.4 (9)	− 1.2 (8)	+ 1.9 (13)	+ 1.0 (8)	+ 0.9 (6)	− 1.2 (9)	< -7.0
+ 1.8 (14)	− 2.4 (16)	+ 2.8 (22)	+ 1.4 (12)	+ 1.2 (8)	− 0.8 (6)	< -6.0
+ 2.4 (16)	− 2.0 (14)	+ 4.4 (28)	+ 2.6 (14)	+ 2.2 (16)	+ 1.6 (12)	$> +10.0$

dominate, whereas contributions from collisions with $\Delta j = 1$ or $\Delta j = 3$ are less important. These results may be attributed to induction and dispersion interactions which, compared to dipolar intermolecular interaction, are of shorter range and often considered to be near twofold symmetric with respect to a rotation of the linear molecule [28, 29]. Then, collisional quantum jumps with even Δj prevail*, in agreement with the results of our measurements. For the OCS-H_2 system, the experimental findings are also supported from recent results of quantum calculations of rate constants at low temperature ($\lesssim 100$ K) [30] which show the importance of collisional channels with $\Delta j = 2$.

The above conclusions about collisional preferences in OCS mixtures are in accordance to the observations made by Lees [12] in a microwave double resonance study on other pump-signal transition schemes of OCS. In these studies it was found that dipole-type $\Delta j = 1$ transitions dominate (if present) the collisional transfer of rotational energy between pump and signal levels for polar collision partners (OCS and CH_3OH), but that $\Delta J = 2$ quadrupole-type transitions are dominant for the mixtures with He and H_2.

Collisional transitions obeying non-dipolar selection rules have also been found in a laser-microwave double resonance study of FCN [31]. From the investigation of collisionally induced double resonance signals on the pure gas it was concluded that quadrupole-type collisional effects dominate for some of the studied transitions, even in presence of dipole-type collisional channels between pump and signal levels. This behaviour is somewhat contrary to the pure gas results of OCS and is possibly due to a different magnitude of the molecular quadrupole moments of OCS and FCN, the latter being about a factor four times larger in magnitude than for OCS**.

In this paper, it has been shown with discussion of the qualitative aspects of collisional transfer of rotational energy of OCS, that collisional channels differing from first order dipole-type are of importance, in particular for mixtures with nonpolar gases. The experiments provide additional information on bulk relaxation data which should be useful to check the reliability of theoretical approaches to collision dynamics.

In addition, such information (on mixtures with He and H_2) may also become important for elucidating nonthermal rotational energy distribution of OCS in the interstellar medium.

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* In case of a linear molecule with $D_{\infty h}$ symmetry (such as CO_2) the collisional selection rules $\Delta j = 0, \pm 2, \pm 4, \ldots$ hold rigorously because of the symmetry of the interaction potential [29].

** From rotational Zeeman effect studies, the molecular quadrupole moments of OCS (normal isotope) and $FC^{15}N$ were determined to be $Q(\text{OCS}) = (-0.88 \pm 0.15) \times 10^{-26}$ esu cm^2 [32] and $Q(\text{FCN}) = (-3.7 \pm 1.0) \times 10^{-26}$ esu cm^2 [33].

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