Investigation of Collision Induced Transitions in the Microwave Range: Ethylene Oxide and Carbonylsulfide

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Collisional energy transfer between rotational levels of ethylene oxide C_2H_4O, its deuterated species C_2D_4O and carbonyl sulfide OCS, has been investigated by means of microwave-microwave four-level double resonance. The results are in agreement with collisional selection rules which can be predicted in the weak collision limit. Collisionally induced transitions up to $\Delta J = 4$ have been detected for C_2D_4O.

Introduction

The increasing interest in energy transfer processes, as has recently been demonstrated in laser and astrophysical problems, encouraged us for a detailed study of collision induced transitions. A review of such studies for the microwave and infrared region was given by Oka [1]. The experiment, as illustrated in Fig. 1, may be briefly described as follows:

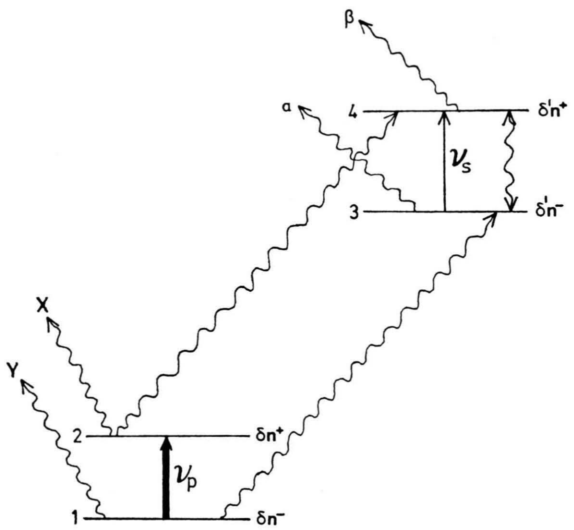

Fig. 1. Scheme of the four-level double resonance experiment;
ν_p = pump radiation,
ν_s = signal radiation,
δn^- = decrease in population due to pump radiation ($\delta n^- < 0$),
δn^+ = increase in population due to pump radiation ($\delta n^+ > 0$),
$\delta n'$ = population variation due to collisions.
The wavy arrows indicate the collisional transfer channels which depend on the collisional selection rules. The channels α and β indicate cascading processes.

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By means of the resonant pump radiation ν_p in the power range of watts the population of the two levels 1 and 2 is changed. This population variation is then transferred by collisions to the levels 3 and 4 and to other levels X and Y. The effect of the collisions is detected by a weak signal radiation ν_s in the power range of μwatts. Usually the Stark modulation double resonance technique (SMDR-technique) has been applied. This method uses Stark effect modulation for the detection of ν_s and continuous pump radiation ν_p. In our experiment we use on-off modulation of the pump radiation by means of a PIN-modulator. This is a kind of microwave modulated double resonance technique (MMDR-method).

Experimental

The experimental set up of the MMDR-spectrograph has been described elsewhere [2, 3]. Both, the pump and the signal microwave sources have been phase stabilised. Usually the pump radiation is on resonance and the signal frequency is swept. The frequency of the on-off modulation of the pump is 100 kHz and the collision induced signal is detected with the help of a phase sensitive detector (PSD). Care should be taken to suppress the harmonics and the noise produced by the TWT, which is used to get a high power level for the pump radiation. The pump frequency could be varied from 8 to 18 GHz and that of the signal between 12,4 and 41 GHz. Presently we are limited to experiments with $\nu_p \leqslant \nu_s - 3$ GHz because of filtering problems. The attenuation of the PIN-modulator should be at least 60 dB. Otherwise the phase sensitive detected collision induced signals will be lowered because of population variations during the pump "off"-period. As shown later, even pump powers in the mW-region can change the Boltzmann distribution.

Table 1. Measured collision induced signals that are allowed by the selection rules.

Pump transition		Signal transition and corresponding change in J			
		$\Delta J = \pm 1$		$\Delta J > 1$	
$J_{K_-K_+} - J'_{K_-'K_+'}$		$J_{K_-K_+} - J'_{K_-'K_+'}$		$J_{K_-K_+} - J'_{K_-'K_+'}$	
C_2H_4O					
$1_{10} - 1_{01}$	11385.71	$2_{21} - 2_{12}$*	34157.13	$3_{30} - 3_{21}$	23134.32
				$3_{21} - 3_{12}$	23611.98
$2_{20} - 2_{11}$	15603.23	$3_{31} - 3_{22}$	39681.63	$4_{40} - 4_{31}$	34150.18
		$1_{11} - 0_{00}$	39581.61		
C_2D_4O					
$1_{10} - 1_{01}$	8855.61	$2_{21} - 2_{12}$*	26566.83	$3_{30} - 3_{21}$	29079.71
				$3_{12} - 3_{03}$	25053.95
$2_{11} - 2_{02}$	14344.06	$1_{11} - 0_{00}$	31941.03	$4_{13} - 4_{04}$	36734.31
		$3_{22} - 3_{13}$	33284.29	$4_{22} - 4_{13}$	21663.59
				$4_{31} - 4_{22}$	25600.69
				$6_{42} - 6_{33}$	34682.14
$2_{20} - 2_{11}$	16401.60	$1_{11} - 0_{00}$	39581.61	$4_{13} - 4_{04}$	36734.31
		$3_{31} - 3_{22}$	35341.83	$4_{22} - 4_{13}$	21633.59
		$3_{22} - 3_{13}$	33284.29	$4_{31} - 4_{22}$	25600.69
$3_{21} - 3_{12}$	16938.84	$4_{32} - 4_{23}$	38867.92	$5_{41} - 5_{32}$	39593.51
				$5_{23} - 5_{14}$	31279.90
$^{16}O^{12}C^{32}S$					
J: 1 – 0	12162.972	J: 3 – 2	36488.813		
$^{16}O^{13}C^{32}S$					
J: 1 – 0	12123.845	J: 3 – 2	36371.390		

* strongest observed collisional signal transitions.
Experimental conditions: pressure about 20 mT, temperature −30 °C, time constant 1.25 s.
Frequencies are given in MHz.

In cases of somewhat higher pump power (1 Watt or more) the high frequency Stark effect [4] (HFStE) produced by the modulated pump radiation demands some attention. Variation of the pump frequency provides a method to distinguish between collision induced and HFStE-signals. By sweeping the pump frequency and keeping the signal frequency on resonance the collision induced signal vanishes for off resonant pump. An offset of 50 MHz generally was sufficient. The HFStE-signal however is rather frequency independent in this range. For strong collision induced signals a reduction of the pump power L_p reduces perturbation by HFStE, as the high frequency Stark field is proportional to $\sqrt{L_p}$.

The MMDR-method can only detect the change in the magnitude of the signal intensity $|\Delta I|$ due to collisions. A referencing of the collision induced signals to get $\eta = \Delta I / I$ [5] with I the intensity of the corresponding Stark transition is not possible with this MMDR-spectrograph. But as the collisional effect is modulated and the absorption cell without a Stark septum can be made rather long (in our case 11,5 m) a high sensitivity is achieved ($^{16}O^{13}C^{32}S$ see Table 1). So the MMDR-method is very suitable for the investigation of collisional selection rules and the dependence of the collisional processes on external parameters such as for instance pump power and sample pressure.

Collisional "Selection Rules"

For the investigation of collisional selection rules we have chosen the molecules ethylene oxide $\underset{\diagdown O \diagup}{H_2C\text{——}CH_2}$, its deuterated species $\underset{\diagdown O \diagup}{D_2C\text{——}CD_2}$ — both asymmetric top molecules of C_{2v}-symmetry with b-type transitions — and the linear carbonyl sulfide molecule OCS. The following selection rules for collision induced dipolar type transitions were predicted on the basis of a bimolecular collision model in the "weak collision limit" [6] that implies small interactions of long range, and under the assumption of a linear path in the first order:

$$\Delta J = J^i - J^f = 0, \pm 1, \quad J^i + J^f \geqq 1\,,$$
$$\Delta M = M^i - M^f = 0, \pm 1\,.$$

Table 2. Investigated signal transitions for "forbidden" collisional processes. For experimental conditions see Table 1. Frequencies are given in MHz.

Pump transition $J_{K_-K_+} - J'_{K_-'K_+'}$		Signal transition $J_{K_-K_+} - J'_{K_-'K_+'}$	
C_2H_4O			
$1_{10} - 1_{01}$	11385.71	$1_{11} - 0_{00}$	39581.61
$2_{20} - 2_{11}$	15603.23	$2_{21} - 2_{12}$	34157.13
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		$3_{30} - 3_{21}$	29079.71
		$4_{32} - 4_{23}$	38867.92
$2_{20} - 2_{11}$	16401.16	$2_{21} - 2_{12}$	34157.13
		$3_{12} - 3_{03}$	25053.93
		$3_{30} - 3_{21}$	29079.71
		$4_{32} - 4_{23}$	38876.92
$3_{21} - 3_{12}$	16938.84	$3_{31} - 3_{22}$	35341.83
		$3_{22} - 3_{13}$	33284.29

For asymmetric top molecules with C_{2v}-symmetry we have in addition [7]:

$$A \leftrightarrow B_b, \quad B_c \leftrightarrow B_a \tag{1}$$

or written in terms of K_- and K_+

$$\Delta K_- = \pm 1, \ \pm 3, \ \pm 5, \dots ;$$
$$\Delta K_+ = \pm 1, \ \pm 3, \ \pm 5, \dots .$$

Here i and f indicate initial and final levels as for example 1 and 3 in Figure 1.

A summary of measured collision induced signals which are predicted by (1) is presented in Table 1. As demonstrated in this table we were able to detect signal transitions involving collision processes not only with $\Delta J = \pm 1$ but also with $\Delta J > 1$, for C_2D_4O with $\Delta J = 4$. The question if these transitions with higher ΔJ processes are due to cascading processes, quadrupole or higher multipole interactions or second order effects as discussed by Verter et al. [8] cannot be answered with confidence presently. Additional experiments have to be performed. As the group theory used for the derivation of the collisional selection rules strictly predicts cases where no collisional transfer in the weak collision limit should occur, a complete check of the theory should care for these strictly forbidden transitions. We tried to measure some of these transitions, which are given in Table 2. In no case a transition has been detected. The MMDR-method with its phase sensitive detection of $|\Delta I|$ and the use of the long absorption cell would have allowed a measurement of lines which are by a factor of thousand weaker than the strongest allowed ones (see * in Table 1). Part of the results of Table 1 and 2 is illustrated by Figure 2.

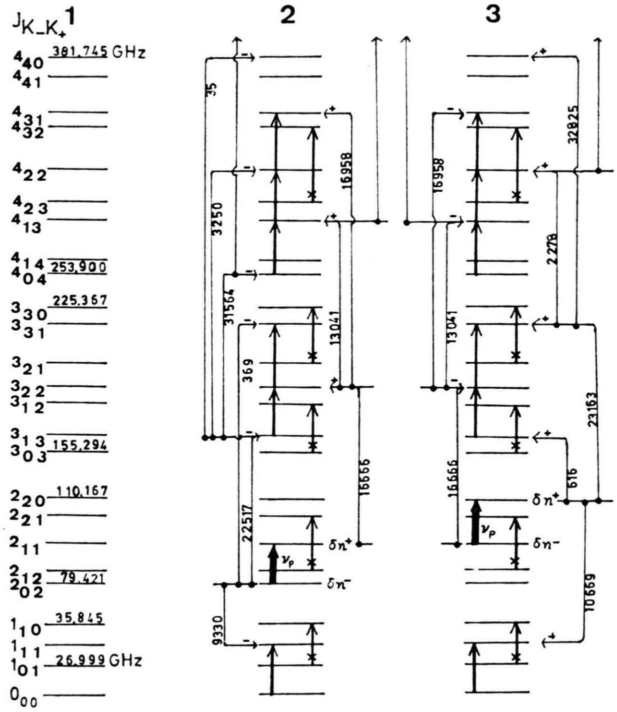

Fig. 2. Investigated collisional transfer for D_2C——CD_2 (bridged by O).
Scheme 1 gives a schematic view of the lower rotational energy levels of C_2D_4O (to the left hand side $J_{K_-K_+}$, on some energy levels energy in GHz). Scheme 2 gives the dipolar type collision scheme with $2_{11} - 2_{02}$ as pumped transition. The measured collision induced signals are indicated by arrows —>. Signal transitions, which should show according to the selection rules no significant intensity changes upon pumping, and which we have investigated with ultimate sensitivity of the present experimental set up without being able to detect a signal are indicated by crossed out arrows —×—>. Their signals, if there should be any, are at least by a factor of 1000 weaker than the strongest allowed ones. The thin arrows -> at left and right hand side represent some of the possible collision channels with the line strength for electric dipole transitions [12] written aside. Scheme 3 gives the corresponding scheme for the pump transition $2_{20} - 2_{11}$. + and − indicate the sign of the population variation transferred by one collisional channel. This sign is dependent on the pump transition selected.

Variation of External Parameters

To get further insight in the collisional processes we made experiments with varied pump power and sample pressure. In Fig. 3 we present some of the results, here obtained for OCS.

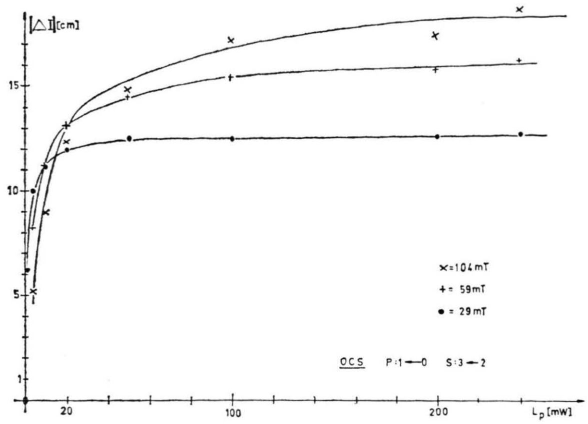

Fig. 3. Dependence of the signal intensity $|\Delta I|$ of the collision induced signal on pump power L_p. The given measurements are for OCS with pressure as parameter $|\Delta I|$ arbitrary unit.

As is seen from Fig. 3 saturation of the pumped transition (as indicated by constant intensity of the signal transition) can be achieved more easily for smaller sample pressure.

The pressure dependence of the signal intensity for fixed pump powers L_p is shown in Figure 4.

For certain pump powers saturation could not be achieved for pressures higher than 50 mT.

Though the formula of Karplus and Schwinger [9]

$$n_l - n_u = (n_l^0 - n_u^0) \cdot \left[1 + \frac{1}{4\pi^2(\nu_p - \nu_p^0)^2 + (1/\tau^2)} \cdot \frac{|\mu_{lu}|^2 E^2}{\hbar^2}\right]^{-1} \tag{2}$$

with

n_l^0 and n_u^0 = Boltzmann population for the lower and upper level,

n_l and n_u = population of the lower and upper level under the influence of the pump radiation,

E = electric field strength of the pump radiation,

μ_{lu} = dipole matrix element of the pump transition,

τ = average time between two collisions,

ν_p^0 = resonant pump frequency,

ν_p = actual pump frequency

describes the deviation of the population difference from Boltzmann distribution under the influence of the pump power only for steady state experiments, it seems to be sufficient to describe qualitatively the observations of Fig. 3 and 4 which are obtained by modulated pump radiation.

Our signal intensity, corresponding to $|\Delta I|$, is proportional to the collision induced population difference of the signal levels 3 and 4 of Figure 1. For $|\Delta I|$ we have [5]:

$$|\Delta I| \sim \delta n_3 - \delta n_4 \,. \tag{3}$$

This difference in turn is proportional to the population variation in the pumped levels introduced by the pump radiation [5], i.e.

$$\begin{aligned} |\Delta I| \sim \delta n_1 - \delta n_2 &= (n_1 - n_1^0) - (n_2 - n_2^0) \\ &= (n_1 - n_2) - (n_1^0 - n_2^0) \,. \end{aligned} \tag{4}$$

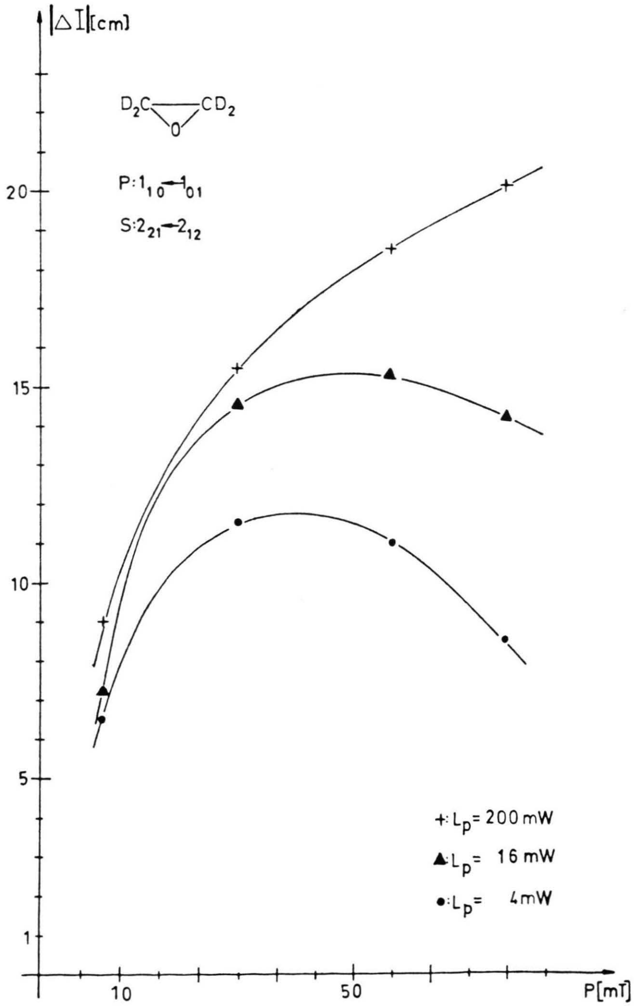

Fig. 4. Dependence of the collision induced signal intensity $|\Delta I|$ on sample pressure p. The given measurements are for C_2H_4O with pump power as parameter.

Insertion of Eq. (2) for the pumped pair of levels gives for resonant pump radiation ($\nu_p = \nu_p{}^0$)

$$|\Delta I| \sim (n_1{}^0 - n_2{}^0) \left\{ \left[1 + \frac{|\mu_{1u}|^2 E^2}{(1/\tau^2)\hbar^2} \right]^{-1} - 1 \right\}. \quad (5)$$

Differentiation of this formula with respect to E^2 for constant pressure p (that is for constant $1/\tau$) results in:

$$\left(\frac{\partial |\Delta I|}{\partial (E^2)} \right)_p \sim \frac{(n_1{}^0 - n_2{}^0) A}{(1 + A E^2)^2}; \quad A = \frac{|\mu_{1u}|^2 \tau^2}{\hbar^2}. \quad (6)$$

For $A E^2 \ll 1$, that is for small pump powers, we have

$$\left(\frac{\partial |\Delta I|}{\partial (E^2)} \right)_p \sim \left(\frac{\partial |\Delta I|}{\partial L_p} \right)_p \sim (n_1{}^0 - n_2{}^0) A$$

which describes the linear rise of $|\Delta I|$ with L_p as shown in Figure 3.

The other limiting case $AE^2 \gg 1$ results in

$$\left(\frac{\partial |\Delta I|}{\partial L_p} \right)_p \to 0$$

explaining the saturation for high pump power.

The decrease in signal intensity in Fig. 4 can be explained in the following way. For saturation $L_p \gg \dfrac{\hbar^2}{\tau^2 |\mu_{1u}|^2}$ is fullfilled. For higher pressure p and constant L_p this condition becomes gradually invalid as $p \sim 1/\tau$. So saturation cannot be achieved anymore, resulting in a decrease of the collision induced signal.

Though, in general the present MMDR-spectrograph permits no accurate comparison of collision induced signals whose transition frequencies are largely different, due to the frequency dependence of the microwave parts of the apparatus, it is in some cases possible to get the relative strength of the collision induced signals. This was demonstrated for M-resolved measurements in a previous publication [10]. Another possibility for comparing collision induced signals gives the following system (see Figure 5). For C_2D_4O we pumped the $2_{11}-2_{02}$ transition and observed a rather strong collision induced signal $3_{22}-3_{13}$ for saturating pump power (PSD-setting 100 mV, time constant 1.25 sec). For this pumping condition δn^+ is transferred to the upper signal level and δn^- to the lower signal level. Then we changed ν_p to the $2_{20}-2_{11}$ transition leaving all other experimental conditions constant except the phase setting of the PSD. The phase was

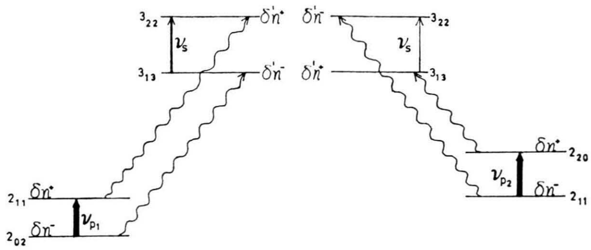

Fig. 5. Collisional scheme for C_2D_4O with the same signal transition ν_s but different pump transitions ν_{p_1} and ν_{p_2}. The change of the pump frequency from ν_{p_1} to ν_{p_2} results in a reversed population variation in the signal levels indicated by δn^+ and δn^-. This means that with ν_{p_1} for pump frequency in the SMDR-method the intensity of the corresponding Stark signal transition ν_s decreases upon pumping whereas for the pump frequency ν_{p_2} the signal intensity increases. For the possible dipolar type transitions of Fig. 5 we have the following line strengths [12]:
$3_{22} - 3_{13}$: 10440;
$2_{20} - 2_{11}$: 15557; $2_{11} - 2_{02}$: 17782;
$3_{22} - 2_{11}$: 16666; $3_{13} - 2_{02}$: 22517; $3_{13} - 2_{20}$: 616.

optimised and the pump power level was adjusted to the same level as for the other pump transition and saturation was achieved again. In this case the collision channels are "crossed", i.e. δn^+ is transferred to the lower signal level and δn^- to the upper signal level. This different way of population transfer results in this and equivalent examples in a decrease of the signal intensity by a factor of 3 to 5 and a change of the phase setting of about 180°. For each case of these crossed collision channels there is one channel with relatively small line strength. The theoretically predicted dependence of the rate constants [11] on the dipole matrix element of the collisional transition under consideration is reflected by this experiment. The relative line strengths which are calculated according to Ref. [12] are given in Figure 5. The change in phase setting is due to the different transport of the population variation caused by the pump power.

Some other examples for collision induced signals with crossed transfer ways are:

C_2D_4O, S: $3_{13} - 3_{22}$, P_1: $2_{20} - 2_{11}$, P_2: $2_{11} - 2_{02}$;
C_2H_4O, S_1: $3_{30} - 3_{21}$, S_2: $3_{21} - 3_{12}$, P: $1_{10} - 1_{01}$.

During our measurements we found that surprisingly low pump power is sufficient to produce a collision induced signal. We were able to record a collision induced signal with less than 4 mW pump power (C_2H_4O, P: $1_{10} - 1_{01}$, S: $2_{21} - 2_{12}$, pressure 20 mT). This suggests that even the weak signal radiation may influence the collisional process. The necessary change in phase setting of the PSD with varying signal power indicates the influence of the signal radiation. A simulation experiment showed that increasing signal power alone without relaxation process cannot change the phase setting [13]. This observation agrees with that of Glorieux, who observed an influence of the signal radiation by time resolved measurements [14].

In order to distinguish single collision with $\Delta J = 2$ and two successive collisions with $\Delta J = 1$, i.e. a cascading process, we undertook some measurements following a proposal of Gordon [15]. He argued that it should be possible to separate these two processes by observing the effects in the low pressure region. A calculation for the used X-Band wave-guide cell (cross section 10.6 mm $\times$ 22.86 mm) shows that one has to reduce pressure to about 1 mT, so that the mean free path of the molecules reaches cell dimension and single collisions should be dominant over cascading collisions. But at these low pressures no sufficient signal could be detected (P: $1_{10} - 1_{01}$, S: $2_{21} - 2_{12}$ and $3_{30} - 3_{21}$ for the molecules C_2H_4O and C_2D_4O). For higher pressures no significant difference between signal (3 and 4 in Fig. 1) and higher transitions (α and β in Fig. 1) ocurred. This is in accordance with a calculation of the pressure dependence of direct and cascading collisional processes.

For the following consideration we neglect wall collisions, which is possible for the pressure region we normally used for our investigations (20–50 mT). For the analysis of the collisional processes one generally uses a system of linear rate equations with rate constants k_{ij} describing a transition from level i to j. For the levels $i \neq 1, 2$ which should be the pumped levels, we have according to Oka [16] for the case of saturation and under steady state conditions

(i.e. $n_1 = n_2$ and $\delta n_1 = -\delta n_2 = (n_2{}^0 + n_1{}^0)/2 = \text{const}$):

$$\sum_j (k_{ji}\,\delta n_j - k_{ij}\,\delta n_i) = \delta\dot{n}_i = 0\,, \qquad i = 3, 4, \ldots; \quad j = 1, 2, \ldots. \tag{7}$$

Actually this equation should have an infinite number of rows and columns. But as according to the Boltzmann distribution the population of the higher levels decreases to zero, one can assume that only a finite number of levels — say n — will contribute to the collisional process. Equation (7) now reads:

$$\begin{pmatrix} \sum\limits_{j\neq 3} k_{3j} & -k_{43} & -k_{53} & \ldots & -k_{n3} \\ -k_{34} & \sum\limits_{j\neq 4} k_{4j} & -k_{54} & \ldots & -k_{n4} \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & & \cdot \\ -k_{3n} & -k_{4n} & -k_{5n} & \ldots & \sum\limits_{j\neq n} k_{nj} \end{pmatrix} \cdot \begin{pmatrix} \delta n_3 \\ \delta n_4 \\ \cdot \\ \cdot \\ \delta n_n \end{pmatrix} = \begin{pmatrix} (k_{13} - k_{23})\,\delta n_1 \\ (k_{14} - k_{24})\,\delta n_1 \\ \cdot \\ \cdot \\ (k_{1n} - k_{2n})\,\delta n_1 \end{pmatrix} = \begin{pmatrix} b_3\,\delta n_1 \\ b_4\,\delta n_1 \\ \cdot \\ \cdot \\ b_n\,\delta n_1 \end{pmatrix}. \tag{8}$$

Collisional selection rules will greatly simplify the rate equation system as certain transitions are then forbidden and the corresponding rate constant vanishes.

A solution of (8) demands the determinant of the coefficient-matrix to be nonzero *, which is generally accepted but not generally proved. As each k_{ij} is directly proportional to pressure [11] we may write: $k_{ij} = p\,k'_{ij}$ and $b_i = p\,b'_i$ where k'_{ij} and b'_i are now independent of pressure. Equation (8) then gives:

$$p \cdot \begin{pmatrix} \sum\limits_{j\neq 3} k'_{3j} & -k'_{43} & -k'_{53} & \ldots & -k'_{n3} \\ -k'_{34} & \sum\limits_{j\neq 4} k'_{4j} & -k'_{54} & \ldots & -k'_{n4} \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & & \cdot \\ -k'_{3n} & -k'_{4n} & -k'_{5n} & \ldots & \sum\limits_{j\neq n} k'_{nj} \end{pmatrix} \begin{pmatrix} \delta n_3 \\ \delta n_4 \\ \cdot \\ \cdot \\ \cdot \\ \delta n_n \end{pmatrix} = p \begin{pmatrix} b'_3\,\delta n_1 \\ b'_4\,\delta n_1 \\ \cdot \\ \cdot \\ \cdot \\ b'_n\,\delta n_1 \end{pmatrix} \tag{9}$$

As $p \neq 0$, p can be cancelled.

Equation (9) can be solved according to Cramers rule, giving

$$\delta n_m = c_m\,\delta n_1\,, \quad m = 3, 4, \ldots, n \tag{10}$$

* The solution of the rate equation system describing the equilibrium Boltzmann distribution, i.e. including the levels 1 an 2 is given by:

$$\sum_j (k_{ji}\,n_j{}^0 - k_{ij}\,n_i{}^0) = \dot{n}_i{}^0 = 0\,, \qquad i = 1, 2, \ldots; \; j = 1, 2, \ldots.$$

As we have a nontrivial solution of this homogenous system — the Boltzmann distribution — the determinant of the coefficientmatrix should be zero. Actually this is the case because the sum of the rows from 2 to n gives the negative of the first row, i.e. the system is linear dependent. (In the notation of Gordon's [15] π-matrix: $\sum_j \pi_{ij} = 0$ for all i.)

with c_m a constant independent of pressure. This result is independent of special selection rules and a general property of the rate equation system.

As

$$\delta n_1 = -\delta n_2 = (n_2{}^0 - n_1{}^0)/2 \sim p \tag{11}$$

all δn_i are directly proportional to pressure. The signal detected by the MMDR-method $|\Delta I|$ is proportional to the difference of the population variation of the two levels. So we have

$$|\Delta I|_{\text{signal}} \sim (\delta n_3 - \delta n_4) \sim p\,, \tag{12a}$$

$$|\Delta I|_{\text{cascade}} \sim (\delta n_5 - \delta n_6) \sim p\,. \tag{12b}$$

Equation (12) means that there should be no significant difference in the pressure dependence of the direct and the cascading collisional process (see for example Figure 6). Assuming $\Delta J = 2$ collisions (i.e. quadrupole instead of dipole collisional selection rules) the pressure dependence of the collision induced signal is again given by Eq. (12) as the derivation is independent of special selection rules.

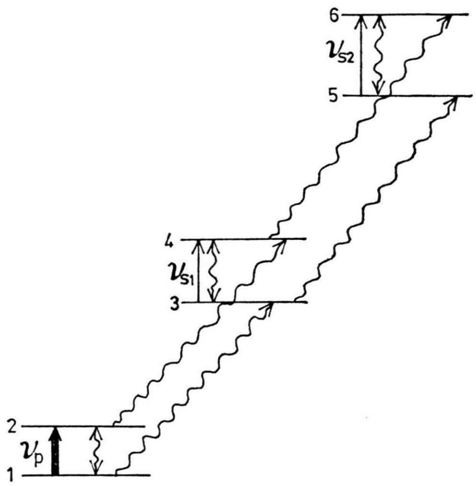

Fig. 6. Collision scheme for the calculation of the pressure dependence of the collision induced signals ν_{S1} and ν_{S2}. ν_{S1} indicates a direct process and ν_{S2} a cascading process.

Discussion

As Table 1 indicates, the MMDR-method is a sensitive tool for the investigation of collisional selection rules. The meaurements are in agreement with predicted dipolar collisional selection rules. The variety of detected collision induced signals shows that for the analysis of the collisional scheme one has to take into account many collisional channels. The influence of the signal power seemed to be not completely neglegible. The influence of the collisional transfer ways has been demonstrated experimentally.

Problems to be solved concerning the MMDR-method are the intensity measurement of the collision induced signals, the separation of pump and signal frequency and the high frequency Stark effect. Until now a principle difficulty of the investigation of collision induced signals is how to differentiate between the various collisional effects which may be caused by different terms of the interaction potential or higher order effects [8].

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