Microwave Double Resonance Investigation of Rotational Relaxation of Methyl Iodide-d_3

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For a study of rotational relaxation of methyl iodide, CD_3I, the method of microwave modulated four-level double resonance has been used. The manifold of the $J = 1, 2$ and 3 levels has been investigated and the η-values have been determined. An experimental procedure to overcome disturbancies produced by the dynamic Stark-effect is described. The sign of the η-values is interpreted in terms of first order dipole and quadrupole type rate constants. The experimental results are in accordance with theoretical results of Rabitz et al. Further a derivation of collisional selection rules for molecules with a nuclear quadrupole moment is given.

I. Introduction

In order to investigate the influence of a nuclear quadrupole moment on rotational relaxation, we choose for our measurements the symmetric top molecule CD_3I because of the large separation of nuclear hyperfine components in its rotational spectrum. To our knowledge, there is only little information in the literature concerned with relaxation problems of molecules with nuclei of spin $I \geqq 1$. Cohen et al. [1] reported on measurements of cyanogen iodide, ICN. Theoretical considerations dealing with the reorientation of the rotational angular momentum during molecular interactions with respect to the nuclear spin I were given by Rabitz et al. [2].

II. Experimental

The methyl iodide-d_3 was purchased from E. Merck, Darmstadt, in a purity of 99.5%. The frequencies of the $K = 0$-transitions investigated are given in Table 1.

Double resonance measurements of rotational relaxation use an intense pump radiation ν_p that alters the population of the pump transition levels. This deviation from Boltzmann equilibrium is then transferred by molecular interactions to other levels and monitored by the signal radiation ν_s. Examples of the transitions investigated are given in Figure 1. As can be seen from Table 1, the hyperfine components of the $J = 0 \leftrightarrow 1$ transition are well separated so that there arises no difficulty in pumping only single transitions. In general an offset of 30 to 50 MHz is sufficient for a pressure of about 10 mT to neglect an alteration of the population difference by the pump radiation in other transitions.

The double resonance apparatus used is shown in Figure 2. In principle the set up is similar to a

Table 1. Frequencies given in MHz for the transitions investigated (CD_3I, $K = 0$ lines).

$J = 0 \leftrightarrow 1$	$F = 5/2 \leftrightarrow 7/2$	12178.81
	$F = 5/2 \leftrightarrow 5/2$	11774.25
	$F = 5/2 \leftrightarrow 3/2$	12353.85
$J = 1 \leftrightarrow 2$	$F = 7/2 \leftrightarrow 9/2$	24203.03
	$F = 7/2 \leftrightarrow 7/2$	23831.04
	$F = 7/2 \leftrightarrow 5/2$	23931.64
	$F = 5/2 \leftrightarrow 7/2$	24135.59
	$F = 5/2 \leftrightarrow 5/2$	24336.19
	$F = 5/2 \leftrightarrow 3/2$	24608.58
	$F = 3/2 \leftrightarrow 5/2$	23756.60
	$F = 3/2 \leftrightarrow 3/2$	24028.98
	$F = 3/2 \leftrightarrow 1/2$	24177.09
$J = 2 \leftrightarrow 3$	$F = 9/2 \leftrightarrow 11/2$	36264.61
	$F = 9/2 \leftrightarrow 9/2$	35910.87
	$F = 9/2 \leftrightarrow 7/2$	35913.01
	$F = 7/2 \leftrightarrow 9/2$	36282.86
	$F = 7/2 \leftrightarrow 7/2$	36285.00
	$F = 7/2 \leftrightarrow 5/2$	36464.90
	$F = 5/2 \leftrightarrow 7/2$	36184.40
	$F = 5/2 \leftrightarrow 5/2$	36364.30
	$F = 5/2 \leftrightarrow 3/2$	36588.55
	$F = 3/2 \leftrightarrow 5/2$	36091.92
	$F = 3/2 \leftrightarrow 3/2$	36316.17
	$F = 3/2 \leftrightarrow 1/2$	36489.44

$B = 6040.228$ MHz, $\mu = 1.65$ Debye, $eqQ = -1928.83$ MHz, for $CD_3{}^{127}I$: nuclear spin $I = 5/2$, molecular electric quadrupole moment for $CH_3{}^{127}I$ according to Ref. [3]: $Q_{aa} = -2\,Q_{cc} = Q = 5.35 \pm 0.85 \times 10^{-26}$ e.s.u.cm^2.

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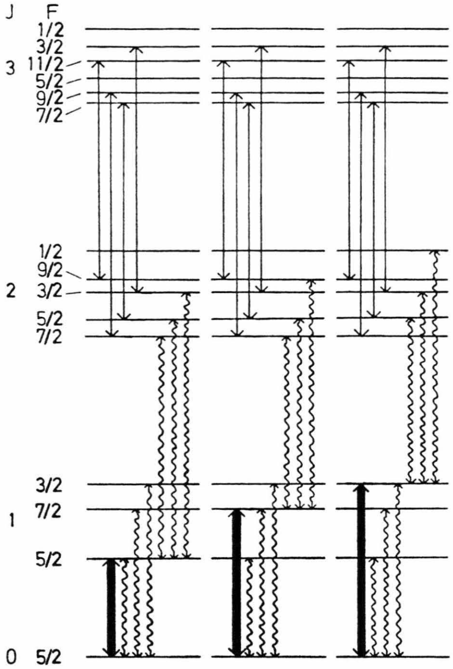

Fig. 1. Level scheme of CD$_3$I ($K=0$ lines). For example some four-level double resonances and first order dipolar collision channels are given. For line frequencies see Table 1. ↔ = pump transition, ↔ = signal transition, ↭ = collisional transition in first order.

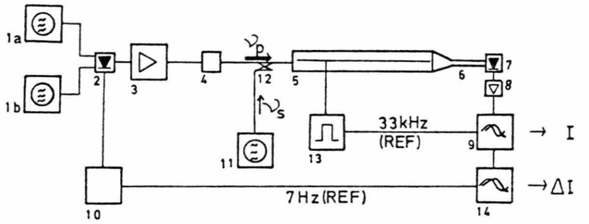

Fig. 2. Scheme of the double resonance spectrometer. 1a pump source for $\nu_p{}^0$, phase stabilized; 1b pump source for ν_p', phase stabilized with respect to 1a; 2 SPDT-switch; 3 TWT-amplifier (Hughes TWT 1177H, X-Band); 4 low pass filter; 5 Stark-cell; 6 waveguide cut off filter; 7 detector for ν_S; 8 preamplifier; 9 PSD 1 (I); 10 switch driver and power supply; 11 signal source ν_S, phase stabilized; 12 directional coupler; 13 Stark-generator; 14 PSD 2 (ΔI).

Stark-spectrometer (parts 5, 7, 8, 9, 11, 13 of Fig. 2) with 33 kHz-modulation giving I, the intensity of the signal transition. The change ΔI in signal intensity due to molecular collisions is determined by the microwave double resonance part of the apparatus. For further details see Reference [4].

The use of amplitude modulated high pump powers in the order of watts leads to two effects: the collision induced transitions, which are rather sensitive to resonance conditions ($\nu_p=\nu_p{}^0$) and the dynamic Stark effect [5] which compared to the collisional effects is rather insensitive to frequency changes of ν_p. In the case of the investigated transitions of CD$_3$I especially for $J=1 \leftrightarrow 2$ the dynamic Stark effect superimposes the signal line produced by collision induced transitions. Cohen et al. [1] also noticed these difficulties in their work.

To overcome this disturbance a "frequency modulated" double resonance experiment was performed. As the reduction of the pump power is limited by the saturation condition for the pump transition, the dynamic Stark-effect could not be

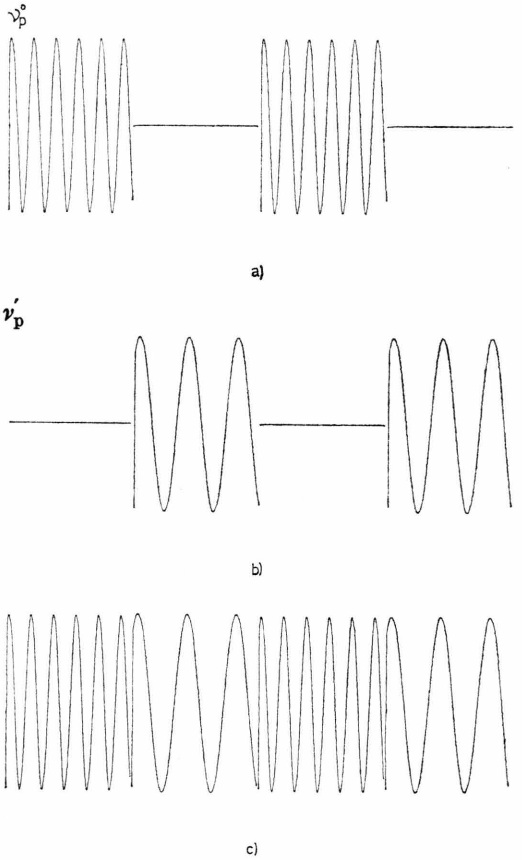

Fig. 3. "Frequency modulation" with the help of a *s*ingle *p*ole *d*ouble *t*hrow (SPDT) switch used in reverse direction. a), b): The microwaves of BWO 1a and 1b are on-off modulated. c): shows the combination of the two radiations The transient regions are in the order of 50 ns. The microwave of frequency $\nu_p{}^0$ is resonant to the pump transition. $\nu_p'=\nu_p{}^0+70$ MHz. The power of the two radiations has to be adjusted, that equal amplitudes are in the absorption cell (schematic drawing).

eliminated by using low pump powers. The saturation condition should be fulfilled to simplify the correlation of $\eta = \Delta I/I$ to the rate constants [6]. For the "frequency modulated" pump source we used two phase stabilized BWO's (1a) and (1b) of Fig. 2, BWO (1b) with a frequency difference of ± 70 MHz to (1a).

The two microwave radiations $\nu_p{}^0$ and $\nu_p{}' = \nu_p{}^0 \pm 70$ MHz were on-off modulated with 180° phase shift at a modulation frequency of 7 Hz, combined with a SPDT-switch as indicated in Fig. 3 and amplified by a TWT-amplifier. In the 7 Hz-PSD (14) the dynamic Stark-effect is eliminated as its signals are nearly equal for a frequency difference of 70 MHz. The use of two BWO's allows an independent adjustment of the MW power to account for different transmission at both frequencies $\nu_p{}^0$ and $\nu_p{}'$. A comparison of a dynamic Stark-effect signal measured by on-off modulated pump, and of the hidden collision induced signal is given in Figure 4.

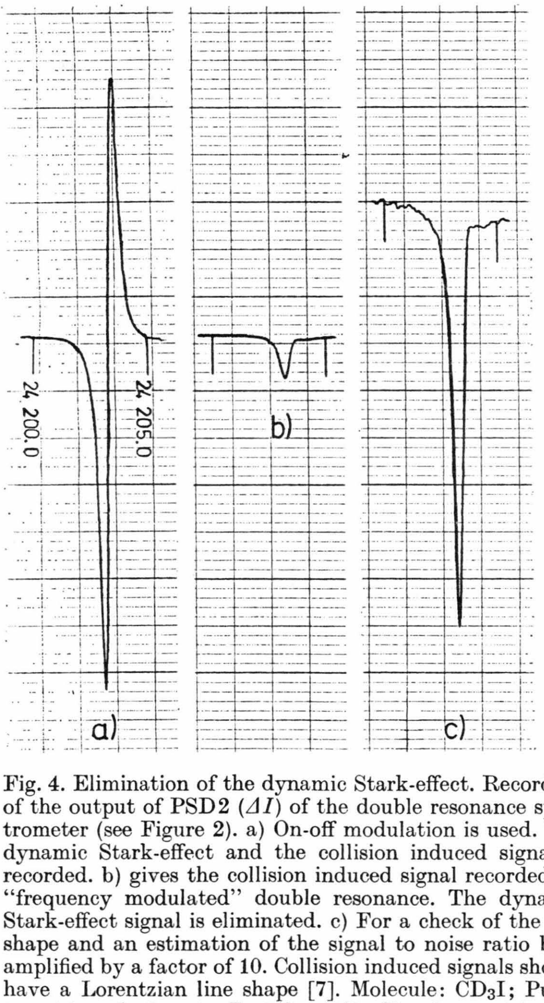

Fig. 4. Elimination of the dynamic Stark-effect. Recording of the output of PSD2 (ΔI) of the double resonance spectrometer (see Figure 2). a) On-off modulation is used. The dynamic Stark-effect and the collision induced signal is recorded. b) gives the collision induced signal recorded by "frequency modulated" double resonance. The dynamic Stark-effect signal is eliminated. c) For a check of the line shape and an estimation of the signal to noise ratio b) is amplified by a factor of 10. Collision induced signals should have a Lorentzian line shape [7]. Molecule: CD$_3$I; Pump transition J: $0 \leftrightarrow 1$; F: $5/2 \leftrightarrow 3/2$; Signal transition J: $1 \leftrightarrow 2$; F: $7/2 \leftrightarrow 9/2$. Frequencies are given in MHz, markers are the same in Figures 4a) to c).

III. Results and Discussion

The measured η-values for CD$_3$I are given in Table 2. The first oder dipolar type collisional selection rules (see appendix) for a molecule with nuclear quadrupole hyperfine structure of rotational transitions are:

$$\begin{aligned} &\Delta J = 0, \pm 1; \quad \Delta K = 0; \quad \Delta I = 0; \\ &\quad (0 \not\leftrightarrow 0) \\ &\Delta F = 0, \pm 1; \quad \Delta M_F = 0, \pm 1 . \end{aligned} \tag{1}$$

The results given in Table 2 indicate that higher order collisional effects or/and cascaded transitions play a significant role in the relaxation behaviour of CD$_3$I. Attempts to detect $\Delta K = 1$ collision induced signals were not successful. This is in agreement with the collisional selection rules (1).

We always used the $J = 0 \leftrightarrow 1$ transitions for pumping. As can be seen from Table 2, the η-values for the collision induced signal transitions $J = 1 \leftrightarrow 2$ are negative, whereas for $J = 2 \leftrightarrow 3$ they are positive or negative. A complete analysis in terms of first order rate constants as we have given for a four-level system of ethylene oxide [4] can not be given here, because the experimental information is too limited. Table 2 contains 51 η-values. 37 first order rate and 15 bath constants besides a higher number of second order rate constants are unknowns.

However the experimentally determined signs of the η-values can be rationalized by using the steady state equations connecting η to the rate constants [6]. For simplification we consider four-level subsystems consisting of the two pump and the two signal levels. A general example and the corresponding first order rate constants k_{ij} describing the collisional transfer from level i to level j, is given in Figure 5a. All collisional processes connecting the four-level system to other levels are summarized by the bath constants k_1, k_2, k_3, k_4. There are also collision induced signals, which cannot be explained by direct first order dipolar collision channels. So we need first order quadrupole or second order

Table 2. η-values in % for CD$_3$I (Temperature: 233 K; pressure 10 mT). DR indicates three-level double resonance. In these cases no η-value can be determined. $\Delta\theta$ gives the reorientation angle (see text). • Collisional signal can not be explained by simple first order dipolar collisional channels. Experimental uncertainties: $J = 1 \leftrightarrow 2$, $\Delta\eta = \pm 0.1$–0.2%; $J = 2 \leftrightarrow 3$, $\Delta\eta = \pm 0.1$%. * indicates deviations from theoretical prediction (see text) — not measured.

Signal transition		Pump transition					
		$J = 0 \leftrightarrow 1$; $F = 5/2 \leftrightarrow 3/2$		$J = 0 \leftrightarrow 1$; $F = 5/2 \leftrightarrow 5/2$		$J = 0 \leftrightarrow 1$; $F = 5/2 \leftrightarrow 7/2$	
		η	$\Delta\theta$	η	$\Delta\theta$	η	$\Delta\theta$
$J = 1 \leftrightarrow 2$	$F = 3/2 \leftrightarrow 1/2$	DR		− 1.3	47	− 1.9	87
	$F = 3/2 \leftrightarrow 3/2$	DR		− 2.9	2*	− 2.9	42
	$F = 3/2 \leftrightarrow 5/2$	DR		− 3.0	18	− 3.1	26
	$F = 5/2 \leftrightarrow 3/2$	− 4.0	36	DR		− 1.7	42
	$F = 5/2 \leftrightarrow 5/2$	− 1.5	52	DR		− 4.1	26
	$F = 5/2 \leftrightarrow 7/2$	− 1.3	70	DR		− 4.3	8
	$F = 7/2 \leftrightarrow 5/2$	− 2.6	52	− 4.4	18	DR	
	$F = 7/2 \leftrightarrow 7/2$	− 1.0	70	− 4.3	32	DR	
	$F = 7/2 \leftrightarrow 9/2$	− 1.4	92*	− 1.7	54	DR	
$J = 2 \leftrightarrow 3$	$F = 1/2 \leftrightarrow 1/2$	+ 2.1		− 0.3•		− 0.5•	
	$F = 1/2 \leftrightarrow 3/2$	+ 2.0		− 0.3•		− 0.4•	
	$F = 3/2 \leftrightarrow 1/2$	+ 0.7		0		− 0.3•	
	$F = 3/2 \leftrightarrow 3/2$	+ 0.7		+ 0.2		− 0.4•	
	$F = 3/2 \leftrightarrow 5/2$	+ 1.0		+ 0.1		− 0.4•	
	$F = 5/2 \leftrightarrow 3/2$	—		—		—	
	$F = 5/2 \leftrightarrow 5/2$	+ 0.2		+ 0.7		− 0.3	
	$F = 5/2 \leftrightarrow 7/2$	+ 0.4		+ 0.6		− 0.3	
	$F = 7/2 \leftrightarrow 5/2$	—		—		—	
	$F = 7/2 \leftrightarrow 7/2$	− 0.1•		+ 0.6		+ 0.1	
	$F = 7/2 \leftrightarrow 9/2$	− 0.2•		+ 0.5		+ 0.1	
	$F = 9/2 \leftrightarrow 7/2$	—		—		—	
	$F = 9/2 \leftrightarrow 9/2$	− 0.1•		− 0.7•		+ 0.5	
	$F = 9/2 \leftrightarrow 11/2$	− 0.3•		− 0.3•		+ 1.6	

dipole channels too, as symbolized in Fig. 5b by k_{14} and k_{23}. The relation between η and the rate constants can be obtained by using the network analogue of the collisional system [8] resulting in the following expressions for the case of first order dipolar type collisional channels**.

$$\eta = -\frac{\nu_p^0}{2\,\nu_s^0}\exp[(E_3 - E_1)/k\,T]\,\frac{k_{13}\,k_4 + k_{24}\,k_3 + 2\,k_{13}\,k_{24}}{k_3(k_{24} + k_{34}) + k_4(k_{13} + k_{34}) + k_3\,k_4 + k_{24}\,k_{34} + k_{13}\,k_{34} + k_{13}\,k_{24}}; \quad (2)$$

ν_p^0	frequency of the pump transition,	T	temperature,
ν_s^0	frequency of the signal transition,	k_{ij}	rate constant connecting level i to level j (see Fig. 5a),
E_i	energy of level i,	k_l	"bath constant", connecting level l to the bath;
k	Boltzmann constant,		pump transition $1 \leftrightarrow 2$, signal transition $3 \leftrightarrow 4$.

When the rate constants k_{14} and k_{23} are also taken into account, we obtain:

$$\eta = -\frac{\nu_p^0}{2\,\nu_s^0}\exp[(E_3 - E_1)/k\,T]\,\frac{(k_{24} - k_{14})(k_{13} + k_{23} + k_3) + (k_{13} - k_{23})(k_{24} + k_{14} + k_4)}{k_3(k_{24} + k_{34}) + k_4(k_{13} + k_{34}) + k_3\,k_4 + k_{24}\,k_{34} + k_{13}\,k_{34} + k_{13}\,k_{24}\cdots}$$

$$\cdots\frac{}{k_{13}\,k_{14} + k_{14}\,k_{34} + k_{14}\,k_{23} + k_{23}\,k_{24} + k_{14}\,k_3 + k_{23}\,k_4 + k_{23}\,k_{34}}. \quad (3)$$

If collision induced transitions connecting the levels $1 \leftrightarrow 4$ and $2 \leftrightarrow 3$ are unimportant, (3) reduces to (2). The derivation of (2) and (3) implicitely assumes saturation of the pump transition, negligible influence

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** The bath constants are not necessarily restricted to be of dipolar type.

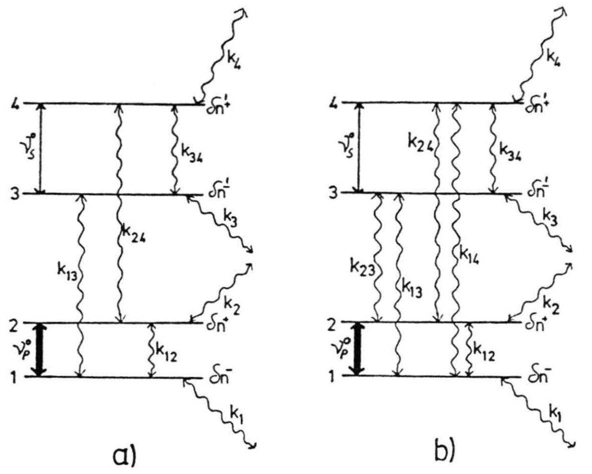

Fig. 5. General level scheme for the four-level double resonance experiments. Figure 5 shows a four-level subsystem of rotational levels 1 to 4 of the general multi-level system. The intense pump radiation $\nu_p{}^0$ gives rise to the deviations δn^+ and δn^- from Boltzmann equilibrium. δn^+ indicate an increase in population, δn^- a decrease. These alterations are transferred to the signal levels 3 and 4 ($\delta n^{+'}$, $\delta n^{-'}$) and are detected by the weak signal radiation $\nu_s{}^0$. The k_{ij} are inelastic rate constants, describing the collisional transfer between levels i and j. k_1 to k_4 describe the coupling of the four levels to the "thermal bath".

Which of the two cases 5a or 5b applies, depends on the four-level system under consideration (see discussion in the text and collisional selection rules).

of the signal radiation on the populations, $k_{ij} = k_{ji} \geqq 0$, $k_{ij} = k_{ji}$ following from the principle of detailed balance for rotational energies ($\ll kT$), neglection of transfer of population changes from levels outside the four levels (thermal bath), and the achievement of the steady state. The last condition means, that the modulation period should be long enough to ascertain steady state conditions for the alteration of the population. It has been checked that a modulation period of 33 kHz is sufficient to fulfil this limitation.

From (2) it can be concluded, that all η-values corresponding to the case of Fig. 5a, should be negative. This is truly observed for the $J = 1 \leftrightarrow 2$ signal transitions (see Table 2), meaning that first order dipolar type collision channels dominate.

Formula (3) allows a change in sign of the η-values, depending on the magnitude of the rate constants k_{24} and k_{14} as well as k_{13} and k_{23}. For the signal transitions $J = 2 \leftrightarrow 3$ the relative magnitude of these rate constants must play an important role, as the sign of η is dependent on the subsystem under consideration.

The double resonance experiments for the $J = 2 \leftrightarrow 3$ signal transitions may be classified roughly into two groups.

In the first one, there is a first order dipolar collisional channel between levels 2 and 3 of Figure 5b*. For example we may consider the pump transition $J = 0 \leftrightarrow 1$; $F = 5/2 \leftrightarrow 3/2$ and the signal transition $J = 2 \leftrightarrow 3$; $F = 3/2 \leftrightarrow 5/2$ of CD_3I (see Fig. 6a; channels connecting the system to the thermal bath are omitted). Possible higher order and cascaded channels are indicated in Figure 6b. If the collision channel $2 \leftrightarrow 3$ dominates the interaction behaviour, then according to (3) the η-value should be positive, as it is actually found. This implies for the given choice of levels that competitive processes like quadrupolar collision induced transitions $1 \leftrightarrow 3$ or cascading transitions are relatively unimportant for the four-level system under consideration. All remaining η-values which have positive sign may be interpreted in the same way for the pump transitions $J = 0 \leftrightarrow 1$; $F = 5/2 \leftrightarrow 3/2$ and $J = 0 \leftrightarrow 1$; $F = 5/2 \leftrightarrow 5/2$.

In the second case, given for example by the subsystems with $J = 0 \leftrightarrow 1$; $F = 5/2 \leftrightarrow 3/2$ for pump transition and $J = 2 \leftrightarrow 3$; $F = 7/2 \leftrightarrow 7/2$ for signal transition, no first order dipolar collision channels exist between pump and signal levels, as shown in Figure 6c. So the collision processes should be determined by quadrupolar or second order dipolar collisional transitions $1 \leftrightarrow 3$, $2 \leftrightarrow 3$, $2 \leftrightarrow 4$ or cascading effects, resulting if k_{23} is small, in negative η-values, as they are found experimentally.

The four-level double resonance results for the pump transition $J = 0 \leftrightarrow 1$; $F = 5/2 \leftrightarrow 7/2$ should be discussed separately. As can be seen from Table 2 the sign of η is just opposite to the $J = 0 \leftrightarrow 1$; $F =$

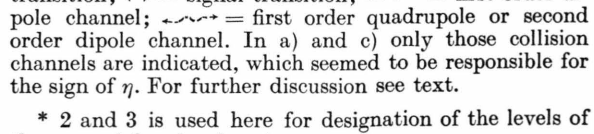

Fig. 6. Examples of four-level systems for CD_3I. ⟷ = pump transition; ↔ = signal transition; ⟵∿⟶ = first order dipole channel; ⇠⇢ = first order quadrupole or second order dipole channel. In a) and c) only those collision channels are indicated, which seemed to be responsible for the sign of η. For further discussion see text.

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* 2 and 3 is used here for designation of the levels of the general four-level system.

$5/2 \leftrightarrow 3/2$ selection of the pump transition. So the relative weight of the competitive collisional processes should be reversed. For explanation let us consider one case of Table 2. The η-value for the pump transition $J=0 \leftrightarrow 1$; $F=5/2 \leftrightarrow 3/2$ is positive for the signal $J=2 \leftrightarrow 3$; $F=1/2 \leftrightarrow 1/2$, indicating that the dipolar type collisional transition $2 \leftrightarrow 3$ is dominant, whereas in the case of pumping $J=0 \leftrightarrow 1$; $F=5/2 \leftrightarrow 7/2$ the quadrupolar or second order dipole collisional channel $1 \leftrightarrow 4$ should be responsible for the negative η. Other collisional channels except the bath constants should be of minor importance. The sign of the other η-values may be interpreted in a similar way.

Up to this point, we have only discussed the sign of the η-values. Following theoretical considerations of Rabitz et al. [2], it is also possible to understand the relative magnitude of the η-values. According to Ref. [2], page 1842, the collisional transition probability may be expressed by a product of two terms. One ($P_1(J_1{}^i \leftrightarrow J_1{}^j)$) depends only on the rotational quantum number J, the other ($P(\Delta F)$) is determined by the reorientation of the total angular momentum F. So, by keeping the rotational quantum numbers J^i and J^j for the collisional transitions fixed, it becomes possible to compare the collision induced signals for the F components only from that part depending on the total angular momentum ($P(\Delta F)$). The results of the calculations may be summarized in the following way:

The nuclear angular momentum I is assumed to be constant, resulting in the collisional selection rule $\Delta I=0$. So the vector I is regarded to constitute an internal pointer during the collision process. The changes in angular momentum can be referred to this pointer. According to Rabitz et al. [2] those collision channels should be preferred, for which the smallest change in magnitude of the angle θ between J and F occurs (see Figure 7). The length of the vectors is taken as $|\boldsymbol{l}|=(l(l+l))^{1/2}$. The $\Delta\theta$ values with $\Delta\theta=|\theta_0-\theta|$ where θ gives the angle for the situation following the interaction are given in Table 2. For collisional transitions from the lower pump level $J=0$ these considerations cannot be applied, as we then have $J=0$, allowing no definition of the angle θ. Therefore it is only possible to compare η-values for which the collisional transition $1 \leftrightarrow 3$ is the same, that is only those signal transitions for fixed pump transition, which originate from the same level 3. We consider the signal transitions $J=1 \leftrightarrow 2$. For the example of Fig. 7 with collision induced transitions originating from the $J=1$; $F=7/2$ level, we get for a θ_0 value of 42° the following changes $\Delta\theta$ for the F sublevels of $J=2$: $F=7/2:8°$; $F=9/2:14°$; $F=5/2:26°$; $F=3/2:42°$ and $F=1/2:87°$. From the $\Delta\theta$ values we should expect for the pump transition $J=0 \leftrightarrow 1$; $F=5/2 \leftrightarrow 7/2$ the following behaviour of the η-values, which here are indicated by the J and F values of the signal transition. In brackets we give η from Table 2 ($\eta_{\text{signal}:\,J',F \leftrightarrow J',F'}$):

$$|\eta|_{1,3/2\leftrightarrow 2,5/2} > |\eta|_{1,3/2\leftrightarrow 2,3/2} > |\eta|_{1,3/2\leftrightarrow 2,1/2}: \quad (3.1\% > 2.9\% > 1.9\%)$$

and

$$|\eta|_{1,5/2\leftrightarrow 2,7/2} > |\eta|_{1,5/2\leftrightarrow 2,5/2} > |\eta|_{1,5/2\leftrightarrow 2,3/2}: \quad (4.3\% > 4.1\% > 1.7\%).$$

The collisional channels $1 \leftrightarrow 3$, here $J=0$; $F=5/2 \leftrightarrow J=1$; $F=3/2$ and $J=0$; $F=5/2 \leftrightarrow J=1$; $F=5/2$ respectively are equal for each series. In the same way the relation between the other η-values can be explained. For two examples indicated by * in Table 2, there is a discrepancy. But with respect to the experimental uncertainties, a clear decision is not possible for these cases. Perhaps quadrupolar collisional transitions from pump levels with $J=0$ play a more important role in these two systems.

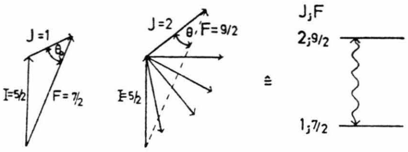

Fig. 7. Geometrical illustration of angular momenta involved in the collisional process. The left part of a) symbolizes the molecular state before interaction, the right part the possible states after collision. Further comments are given in the text. b) shows one of the collisional channels symbolized by diagram a).

Signal transitions with $J=2 \leftrightarrow 3$ we would not like to discuss, because a variety of higher order effects surely will complicate the analysis within this simple model.

As the foregoing discussion shows, the sign of the η-values and in some cases the relative magnitude can be interpreted in terms of rate constants and relative collisional transition strenghts for the CD_3I molecule. Especially, the sign of η on the basis of the Eqs. (2) and (3) allows an estimation of the relative influence of different collision channels.

In general from time dependent measurements, giving the relaxation times for the population T_1 and for the polarisation T_2, such conclusions are not possible a priori since these parameters are connected only to sums of rate constants (see Ref. [4] and references cited there).

Appendix

Collisional selection rules for molecules with a nucleus having spin $I \geqq 1$

For completion we will give a derivation of collisional selection rules for the molecular system under investigation. In terms of first order perturbation theory and under the assumption of the impact approximation we get for the transition probability [6, 9]:

$$P_{R_1{}^\mathrm{i} R_2{}^\mathrm{i} \to R_1{}^\mathrm{f} R_2{}^\mathrm{f}} = \left| \int\limits_{-\infty}^{\infty} \langle R_1{}^\mathrm{i} R_2{}^\mathrm{i} | V(t) | R_1{}^\mathrm{f} R_2{}^\mathrm{f} \rangle \, e^{i \Delta E_R t/\hbar} \, \mathrm{d}t \right|^2 , \tag{A.1}$$

where R designates the rotational states of the colliding molecules 1 and 2 undergoing a transition from the states with total energy $E_{R_1{}^\mathrm{i}} + E_{R_2{}^\mathrm{i}}$ to $E_{R_1{}^\mathrm{f}} + E_{R_2{}^\mathrm{f}}$ and

$$\Delta E_R = E_{R_1{}^\mathrm{f}} + E_{R_2{}^\mathrm{f}} - E_{R_1{}^\mathrm{i}} - E_{R_2{}^\mathrm{i}} \leqq kT . \tag{A.2}$$

Introducing the expansion of the interaction potential $V(t)$ and following the derivation of [9], one gets for the essential part of the matrix element $\langle R_1{}^\mathrm{i} R_2{}^\mathrm{i} | V(t) | R_1{}^\mathrm{f} R_2{}^\mathrm{f} \rangle$ analogous to Eq. (8) of [9] with $M_{lm'}$ the permanent molecular multipole moments:

$$\begin{aligned} & M_{l_1 m_1'} \langle J_{1\mathrm{i}} K_{1\mathrm{i}} I_1 F_{1\mathrm{i}} M_{F_{1\mathrm{i}}} | D^{l_1}_{m_1' m_1} | \\ & \qquad J_{1\mathrm{f}} K_{1\mathrm{f}} I_1 F_{1\mathrm{f}} M_{F_{1\mathrm{f}}} \rangle \\ & \cdot M_{l_2 m_2'} \langle J_{2\mathrm{i}} K_{2\mathrm{i}} I_2 F_{2\mathrm{i}} M_{F_{2\mathrm{i}}} | D^{l_2}_{m_2' m_2} | \\ & \qquad J_{2\mathrm{f}} K_{2\mathrm{f}} I_2 F_{2\mathrm{f}} M_{F_{2\mathrm{f}}} \rangle \end{aligned} \tag{A.3}$$

In (A.3) $\langle R_1{}^\mathrm{i} R_2{}^\mathrm{i} |$ has been specified by

$$\langle J_{1\mathrm{i}} K_{1\mathrm{i}} I_1 F_{1\mathrm{i}} M_{F_{1\mathrm{i}}} | \langle J_{2\mathrm{i}} K_{2\mathrm{i}} I_2 F_{2\mathrm{i}} M_{F_{2\mathrm{i}}} | ,$$

where J is the quantum number of angular momentum, M for its projection to space fixed and K for its projection to molecule fixed Z resp. z axes. I indicates the nuclear spin momentum, F and M_F the total angular momentum and its projection to the space fixed axis Z. For the derivation of the selection rules it is sufficient to consider one factor of (A.3), rewritten in the form:

$$M_{lm'} \langle J_\mathrm{i} K_\mathrm{i} I F_\mathrm{i} M_{F_\mathrm{i}} | D^l_{m'm} | J_\mathrm{f} K_\mathrm{f} I F_\mathrm{f} M_{F_\mathrm{f}} \rangle . \tag{A.4}$$

We remark, that the nuclear spin momentum I does not change in the collisions considered here.

The Wigner-Eckart-Theorem for spherical tensors results in (compare Eq. (5.4.1) of Edmonds [10]

$$\begin{aligned} & \langle J_\mathrm{i} K_\mathrm{i} I F_\mathrm{i} M_{F_\mathrm{i}} | D^l_{m'm} | J_\mathrm{f} K_\mathrm{f} I F_\mathrm{f} M_{F_\mathrm{f}} \rangle \\ & = (-1)^{F_\mathrm{i} - M_{F\mathrm{i}}} \begin{pmatrix} F_\mathrm{i} & l & F_\mathrm{f} \\ -M_{F_\mathrm{i}} & m & M_{F_\mathrm{f}} \end{pmatrix} \\ & \quad \cdot \langle J_\mathrm{i} K_\mathrm{i} I F_\mathrm{i} \| D^l_{m'm} \| J_\mathrm{f} K_\mathrm{f} I F_\mathrm{f} \rangle ; \end{aligned} \tag{A.5}$$

$\begin{pmatrix} F_\mathrm{i} & l & F_\mathrm{f} \\ -M_{F_\mathrm{i}} & m & M_{F_\mathrm{f}} \end{pmatrix}$ is a $3j$-symbol and $\langle \| \| \rangle$ a reduced matrix element. Following (7.1.7) of [10] the reduced matrix element in the coupled basis can be written:

$$\begin{aligned} & \langle J_\mathrm{i} K_\mathrm{i} I F_\mathrm{i} \| D^l_{m'm} \| J_\mathrm{f} K_\mathrm{f} I F_\mathrm{f} \rangle \\ & = (-1)^{J_\mathrm{i} + I + F_\mathrm{f} + l} (2F_\mathrm{i} + 1)^{1/2} \\ & \quad \cdot (2F_\mathrm{f} + 1)^{1/2} \begin{Bmatrix} J_\mathrm{i} & F_\mathrm{i} & I \\ F_\mathrm{f} & J_\mathrm{f} & l \end{Bmatrix} \\ & \quad \cdot \langle J_\mathrm{i} K_\mathrm{i} \| D^l_{m'm} \| J_\mathrm{f} K_\mathrm{f} \rangle . \end{aligned} \tag{A.6}$$

Here { } indicates a $6j$-symbol. Using the fact, that the eigenfunctions for symmetric top molecules may be written in terms of elements of the rotation matrix [9]:

$$| JKM \rangle = \left(\frac{2J+1}{8\pi} \right)^{1/2} D^J_{KM} \tag{A.7}$$

we get, using formula (4.2.7) and (4.6.2) of Ref. [10]:

$$\begin{aligned} & \langle J_\mathrm{i} K_\mathrm{i} M_\mathrm{i} | D^l_{m'm} | J_\mathrm{f} K_\mathrm{f} M_\mathrm{f} \rangle \\ & = (-1)^{K_\mathrm{i} - M_\mathrm{i}} [(2J_\mathrm{i} + 1)(2J_\mathrm{f} + 1)]^{1/2} \\ & \quad \cdot \begin{pmatrix} J_\mathrm{i} & l & J_\mathrm{f} \\ -K_\mathrm{i} & m' & K_\mathrm{f} \end{pmatrix} \begin{pmatrix} J_\mathrm{i} & l & J_\mathrm{f} \\ -M_\mathrm{i} & m & M_\mathrm{f} \end{pmatrix} \end{aligned} \tag{A.8}$$

From (A.8) and

$$\begin{aligned} & \langle J_\mathrm{i} K_\mathrm{i} \| D^l_{m'm} \| J_\mathrm{f} K_\mathrm{f} \rangle = (-1)^{M_\mathrm{i} - J_\mathrm{i}} \\ & \quad \cdot \langle J_\mathrm{i} K_\mathrm{i} M_\mathrm{i} | D^l_{m'm} | J_\mathrm{f} K_\mathrm{f} M_\mathrm{f} \rangle \Big/ \begin{pmatrix} J_\mathrm{i} & l & J_\mathrm{f} \\ -M_\mathrm{i} & m & M_\mathrm{f} \end{pmatrix} \end{aligned} \tag{A.9}$$

which results from the Wigner-Eckart-Theorem, we obtain:

$$\begin{aligned} & \langle J_\mathrm{i} K_\mathrm{i} \| D^l_{m'm} \| J_\mathrm{f} K_\mathrm{f} \rangle = (-1)^{K_\mathrm{i} - J_\mathrm{i}} \\ & \quad \cdot [(2J_\mathrm{i} + 1)(2J_\mathrm{f} + 1)]^{1/2} \begin{pmatrix} J_\mathrm{i} & l & J_\mathrm{f} \\ -K_\mathrm{i} & m' & K_\mathrm{f} \end{pmatrix} . \end{aligned} \tag{A.10}$$

Combining (A.10), (A.6) and A.5) results in the following expression for the relevant matrix element:

$$\begin{aligned} & M_{lm'} \langle J_\mathrm{i} K_\mathrm{i} I F_\mathrm{i} M_{F_\mathrm{i}} | D^l_{m'm} | J_\mathrm{f} K_\mathrm{f} I F_\mathrm{f} M_{F_\mathrm{f}} \rangle \\ & = M_{lm'} (-1)^{F_\mathrm{i}+F_\mathrm{f}-M_{F\mathrm{i}}+I+K_\mathrm{i}+l} \\ & \quad \cdot [(2F_\mathrm{i}+1)(2F_\mathrm{f}+1)(2J_\mathrm{i}+1)(2J_\mathrm{f}+1)]^{1/2} \\ & \quad \cdot \begin{Bmatrix} J_\mathrm{i} & F_\mathrm{i} & I \\ F_\mathrm{f} & J_\mathrm{f} & l \end{Bmatrix} \begin{pmatrix} F_\mathrm{i} & l & F_\mathrm{f} \\ -M_{F_\mathrm{i}} & m & M_{F_\mathrm{f}} \end{pmatrix} \\ & \quad \cdot \begin{pmatrix} J_\mathrm{i} & l & J_\mathrm{f} \\ -K_\mathrm{i} & m' & K_\mathrm{f} \end{pmatrix} . \end{aligned} \tag{A.11}$$

For nonvanishing multipole moments $M_{lm'}$ the collisional selections rules follow from the properties of the two $3j$-symbols in (A.11) to:

$$\begin{aligned} \Delta M_F &= M_{F_\mathrm{f}} - M_{F_\mathrm{i}} = m, \quad |m| \leqq l \qquad \text{(A.12)} \\ \Delta K &= K_\mathrm{f} - K_\mathrm{i} = m', \quad |m'| \leqq l \\ \Delta J &= |J_\mathrm{f} - J_\mathrm{i}| \leqq l, \text{ and } J_\mathrm{f} + J_\mathrm{i} \geqq l, \\ \Delta F &= |F_\mathrm{f} - F_\mathrm{i}| \leqq l, \text{ and } F_\mathrm{f} + F_\mathrm{i} \geqq l. \end{aligned}$$

Only those m' values have to be considered, for which the $M_{lm'}$ are belonging to the totally symmetric species of the molecular point group [6]. Dipolar collisional selection rules result from $l = 1$, quadrupolar selection rules from $l = 2$.

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