

Investigation of T_1 -Relaxation by a Microwave Pulse Technique for HCCC¹⁵N Rotational Transitions

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The pressure dependence of $1/T_1$ has been measured with a bridge type superhet spectrometer at room temperature for the rotational transitions $(J, |M|) = (1, 0) - (2, 0)$, $(1, 1) - (2, 1)$, $(2, 0) - (3, 0)$, $(2, 1) - (3, 1)$ and $(2, 2) - (3, 2)$ of cyanoacetylene, HCCC¹⁵N, by using a π , τ , $\pi/2$ microwave pulse sequence method. In addition to the measurements on the pure gas, T_1 -relaxation has also been investigated for mixtures with H₂, He, Ne and Ar. The results are used to derive linear combinations of rate constants for collision-induced transfer of rotational energy between $|M|$ -resolved rotational levels of HCCC¹⁵N.

I. Introduction

Gas phase rotational relaxation data may be roughly classified according to two different types of collision-induced effects, characterized either by coherence decay rates or population transfer rates. Microwave single and multiple resonance techniques have proved to be very useful for the investigation of both types of collisional phenomena in molecular gas samples. For example, the study of spectral lineshapes at low microwave power provides information about coherence decay rates and has a long tradition in microwave spectroscopy [1]. During the past decade, such rates have also been determined with use of more recent techniques in coherent transient microwave spectroscopy, in particular with study of T_2 -relaxation by the transient emission technique [2]. Another pulse technique has also been applied to obtain information about T_1 -relaxation, describing population transfer behaviour in two-level systems [3]. Besides these single resonance experiments in both frequency and time domain, four-level double resonance experiments have proved to be particularly well suited for the determination of rotational relaxation data involving population transfer rates between different rotational states [4].

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The experimental results from various types of investigation on rotational relaxation are important for understanding the collision dynamics of molecules. Relating different rates to binary collision events might not only be useful to check the reliability of theoretical scattering calculations but also to get more detailed information about intermolecular potential parameters. Furthermore, bulk relaxation data on population transfer are especially important for the derivation of inelastic rate constants, in particular with combination of the results from single and four-level double resonance experiments [5–7]. Such rotational excitation rates are essential for the interpretation of diverse phenomena, like the establishment of excitation temperatures of molecules in interstellar clouds due to collisions with H₂ and to lesser extent He [8].

In the present paper we report on the study of T_1 -relaxation of several $|M|$ -resolved rotational transitions of the linear molecule cyanoacetylene, HCCC¹⁵N*, by means of a π , τ , $\pi/2$ pulse sequence method which employs – instead of the earlier Stark-switching technique [9] – a microwave pulse technique to induce nonthermal population distribution within the molecular sample. This investigation complements a recent four-level double resonance study on collision-induced transitions of this molecule [10], giving results for the pure gas and mixtures with H₂, He, Ne and Ar.

* The ¹⁵N-isotope has been chosen to avoid complications caused by the nuclear quadrupole hyperfine structure.

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In the next section, we give details of the experimental setup for the pulse sequence experiment to determine T_1 -relaxation times which was performed with our bridge type superheterodyne spectrometer. The theory to describe the observed transient phenomena is extended to include $\pm M$ degeneracy of the rotational energy levels of linear molecules in static Stark fields and is briefly outlined in Section III. In the last section, we report on the results for the pressure dependence of T_1 for the studied systems. With inclusion of η -values as obtained from earlier double resonance studies on this molecule [10], linear combinations of rate constants for collision-induced transfer of rotational energy are also derived.

Experimental

The method which has been employed here to determine T_1 -relaxation times is very similar to the earlier π , τ , $\pi/2$ -pulse sequence using the Stark-switching technique [3, 9]. The first pulse creates a population inversion, and the second pulse probes the T_1 -decay of population difference back to equilibrium with changing delay time τ between the pulses. However, the radiation field-molecule interaction has been pulsed here by switching on and off the microwave radiation, instead of shifting the rotational energy difference by means of Stark-modulation. The principle of the pulse sequence experiment is illustrated in Figure 1. It shows the time dependence of the electric field amplitude of the incoming microwave radiation and the transient molecular signals in both emission and absorption periods, the latter being indicated by dashed lines and not observed with our experimental setup (see text below).

The MW-pulse technique offers advantages over the Stark-switching technique in many respects. Firstly, high voltage Stark pulses often severely contribute to coherent pickup signals and limit the sensitivity of the Stark-switch method. These high voltage pulses do not appear in the PIN-switching technique. Secondly, PIN-switching times (< 10 ns) are considerably shorter than Stark-pulse rise and fall times which better approximates the neglect of relaxation phenomena during the switching periods in the theoretical description of the experiments. In addition, shorter pulse widths may then be achieved at higher microwave powers (sufficient attenuation

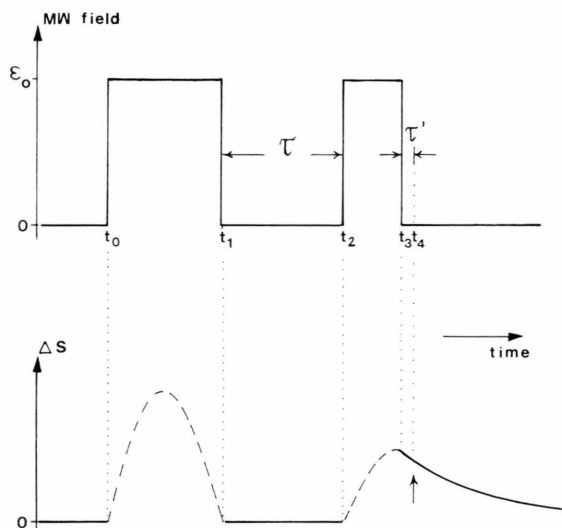


Fig. 1. Scheme of π , τ , $\pi/2$ -pulse sequence for determination of T_1 -relaxation times. ϵ_0 MW electric field amplitude. Transient molecular signal ΔS : Full line: observed change in signal. Dashed line: transient absorption signal, not observed in the experiment (see text). τ variable delay time. The arrow indicates the gate position of the Boxcar integrator which remains at a fixed delay τ' with respect to the end of the second pulse.

of the PIN-switches provided) which might not be possible with the Stark-switch method due to disturbing effects of off-resonant absorption [11]. Short pulses are essential for a well defined sample preparation by the radiative interaction and also simplify the discussion and analysis of molecular velocity effects on the observations [12, 13]. Furthermore, difficulties of the Stark-switch method by fast passage effects [14] do not occur with the microwave pulse method. In addition to investigations with DC Stark fields for $|M|$ -resolved rotational transitions, this method offers also the possibility to observe T_1 -relaxation in the absence of an external electric field which is in principle different from the static field case [15]. Relaxation studies in zero field by microwave pulse methods are also very useful for the investigation of transitions with high rotational quantum numbers J [16] where Stark-switching is not feasible.

The apparatus which was used for the experiments basically consists of the K-band bridge-type superheterodyne spectrometer which has been described in detail earlier [17]. Its schematic block diagram is given in Fig. 2 and only the modifications for the π , τ , $\pi/2$ -pulse sequence experiments are reported here. The microwave signal radiation

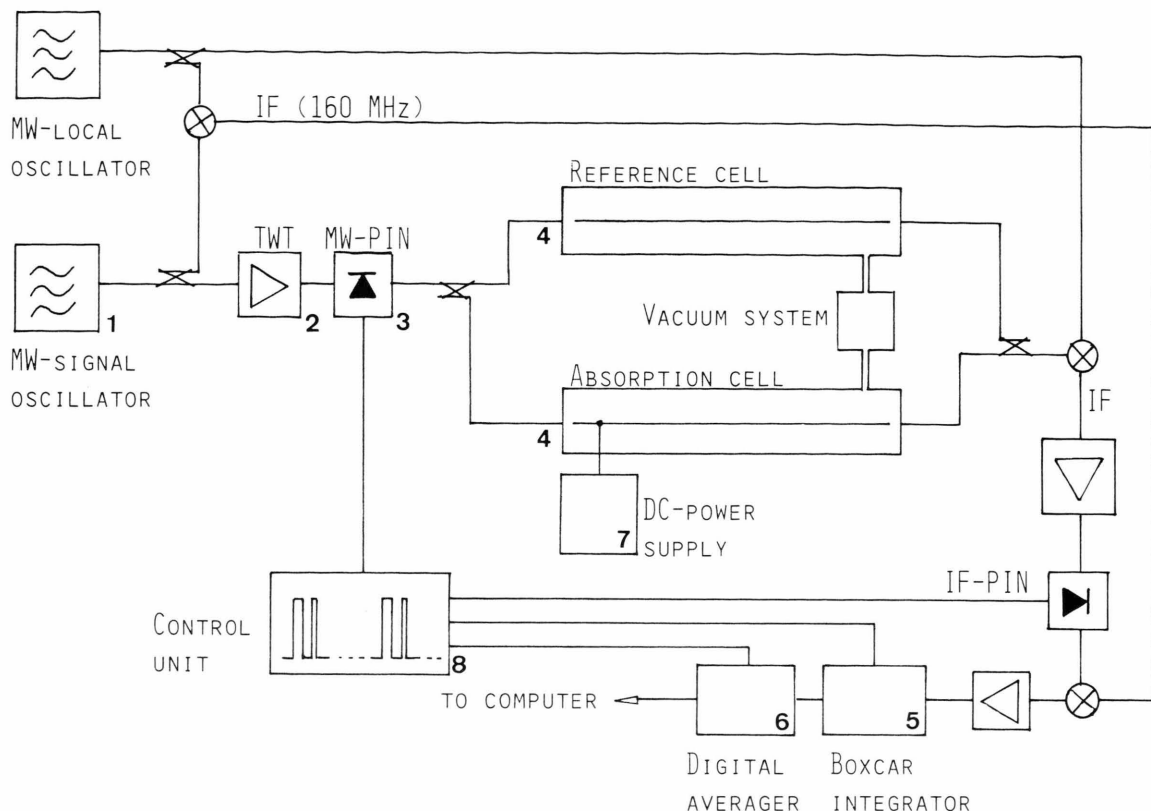


Fig. 2. Block diagram of experimental arrangement.

1. Signal oscillator: BWD Varian VA 163 M (18–26.5 GHz).
 2. TWT-amplifier: Hughes 1077 H (K-band).
 3. MW PIN-switch: α -Industries MT 3486 H.
 4. X- to K-band waveguide transitions.
 5. Boxcar integrator: PAR Mod. 162/164.
- For details of other parts see Fig. 1 of [17] and text.

6. Digital averager: Fabri Tek 1072.
7. DC-power supply (0–2000 V): Fluke 4156.
8. Modulation unit for control of π , τ , $\pi/2$ -pulse sequence experiment (TTL).

was supplied from a phase stabilized BWO, amplified to about 200 mW by means of a TWT amplifier, appropriately PIN-switched according to the adjustable pulses of the sequence (see Fig. 1) and then coupled through K- to X-band waveguide transitions into both cells of the MW-bridge. The power modulating PIN-switch was placed behind the TWT amplifier in order to cut off the TWT noise for the periods of absent microwave power, in particular to enhance the signal-to-noise ratio during the detection period after the second pulse. The bridge was balanced for carrier suppression with both cells evacuated as described in [17]. Thus apart from a small residual signal, rejection of the MW-pulses could be obtained without a MW-PIN-switch protecting the detection system. The latter arrangement is employed in MW Fourier transform spectrometers without a MW bridge [18–20], which have the

disadvantage that only transient molecular emission signals can be detected after the microwave radiation has been switched off. In addition, with use of a MW bridge, pulse reflections may be suppressed more effectively allowing shorter delay times for acquiring data after the end of pulses.

Having brought the bridge out of balance by filling one cell with sample gas, the only microwave radiation reaching the MW-mixer is the molecular signal (ideal carrier suppression assumed) which is frequency converted downwards to DC in two steps according to the superheterodyne detection principle [17]. Then, transient emission signals exhibit pure exponential decay behaviour with zero beat frequency if the polarizing MW radiation is chosen to be exactly resonant with the transition under investigation. As no dispersion phenomena are present in the resonant case, the spectrometer was used

in the absorption mode and only emission signals were observed in our experiments. This was achieved by interrupting the IF-signals during the pulse periods to reject unwanted spikes with application of IF-gate pulses which were slightly longer than the corresponding MW-pulses of the sequence (see Figs. 2 and 3 of [17]).

Detection of transient absorption signals is also possible with the bridge spectrometer and would be more closely related to earlier Stark-switch T_1 -experiments [3, 9] where the signal absorption during the second pulse of the sequence is measured as a function of the delay between the pulses. However, due to instabilities of the bridge balance which influence the signal amplitudes only during the absorption periods, such method was found to be considerably less reliable than the investigation scheme which used the detection of transient emission signals and is described in more detail next.

The length of the first pulse of the sequence (see Fig. 1) was adjusted to yield no observable emission signal during the delay period between the pulses. This procedure may be used to define an "effective π -pulse" giving near population inversion of the levels of interest. After a certain delay time τ the second MW-pulse was applied, its length chosen to result in maximum transient emission signal after the end of the pulse ("effective $\pi/2$ -pulse"). The value of absorption at a fixed delay after the beginning of the second pulse is thus measured by acquiring the following emission signal.

In our experiments, typical pulse lengths of about 1 μ s and 0.5 μ s for π - and $\pi/2$ -pulses, respectively, were used. The information about T_1 -relaxation was obtained by changing the delay time τ which, starting with an adjustable minimum delay time, was increased in steps of 71.43 ns as controlled by a 14 MHz oscillator. For a fixed delay time the two-pulse sequence was repeated 1024 times with a repetition rate of about 4 kHz which was low enough to guarantee restored equilibrium conditions at the beginning of a pulse sequence. To enhance sensitivity, the detection of the transient emission signal was performed with a Boxcar integrator driven in single-point analysis mode which gives sufficient information for analysis of T_1 -relaxation in the π , τ , $\pi/2$ -pulse sequence [9]. For this purpose the integrators aperture position was held fixed with respect to a trigger signal which was synchronized to the second pulse of the pair, taking

data after a short delay time τ' with respect to the end of that pulse (see Figure 1). Due to synchronization, always the same portion of the emission signal is probed and averaged, independent of delay time τ . The analog output of the Boxcar integrator is thus proportional to the initial amplitude of the transient emission signal, damped exponentially in the present study (zero beat frequency, see discussion above) and thereby probes the decay of non-thermal population difference as achieved by the first pulse. The output of the Boxcar integrator was A/D converted and the results from a scan over delay times τ were stored in the memory of a digital averager which made additional averaging for repeated experiments possible. For further analysis the data were transferred to a TI-990/10 minicomputer and a DEC-10 computer system.

The sample of HCCC¹⁵N was prepared by the method of Miller and Lemmon [21] and after vacuum distillation used in the experiments. No impurities caused by foreign substances could be detected with analysis by gas chromatography. Pressure measurements were made using a MKS Baratron 310 B capacitance manometer. A 20 l bulb was attached to the system in order to stabilize the pressure and to minimize the influence of selective adsorption of the mixture components on the walls of the sample cell. The pressure range was from 1 mTorr to 4 mTorr for the pure gas. For the mixtures, the partial pressure of cyanoacetylene was held fixed at about 2.5 mTorr and the partial pressures of the foreign gases (H_2 , He, Ne and Ar) were varied in the range from 0 to 20 mTorr. Details of the method to determine the partial pressures have been described earlier [3]. All measurements were done at room temperature.

III. Theory

In the following, the theory to analyze the above described pulse sequence experiments is briefly outlined. The formalism is closely related to earlier discussions of time domain T_1 -experiments which have treated the electric dipole interaction of the microwave radiation with molecules by considering an idealized system of two non-degenerate energy levels [3, 9]. We extend these treatments to the presently investigated case of $\pm M$ -degenerate rotational energy levels of a linear molecule in a static Stark field.

The considered energy levels are specified by the quantum numbers J and $\pm m$ for the rotational angular momentum and its component with respect to a fixed axis in space ($m = |M|$). For the radiation induced transition we have the dipole selection rule $J \rightarrow J+1$ and $\pm m \rightarrow \pm m$ ($\Delta M = 0$) according to the experimental arrangement of parallel directions of the static Stark field and the MW electric field component, i.e. the levels of interest may be denoted by $J(\pm m)$ and $J+1(\pm m)$, respectively.

Following the formulation of Liu and Marcus [15] for the derivation of two-level Bloch equations, it is necessary to consider the equations of motion for off-diagonal and diagonal density matrix elements, respectively, for the system of absorber molecules described here,

$$\begin{aligned} \frac{\partial}{\partial t} Q_{J(\pm m), J+1(\pm m)} &= i \omega_m Q_{J(\pm m), J+1(\pm m)} \\ &+ i \chi_m \varepsilon_0 \cos \omega t \{Q_{J+1(\pm m), J+1(\pm m)} - Q_{J(\pm m), J(\pm m)}\} \\ &- A_{J(\pm m), J+1(\pm m); J(\pm m), J+1(\pm m)} \cdot Q_{J(\pm m), J+1(\pm m)} \\ &- A_{J(\pm m), J+1(\pm m); J+1(\pm m), J(\pm m)} \cdot Q_{J+1(\pm m), J(\pm m)} \\ &- A_{J(\pm m), J+1(\pm m); J(\mp m), J+1(\mp m)} \cdot Q_{J(\mp m), J+1(\mp m)} \\ &- A_{J(\pm m), J+1(\pm m); J+1(\mp m), J(\mp m)} \cdot Q_{J+1(\mp m), J(\mp m)}, \quad (1) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial t} Q_{J(\pm m), J(\pm m)} &= i \chi_m \varepsilon_0 \cos \omega t \{Q_{J+1(\pm m), J(\pm m)} - Q_{J(\pm m), J+1(\pm m)}\} \\ &- \sum_{J' M'} A_{J(\pm m), J(\pm m); J' M', J' M'} \\ &\cdot \{Q_{J' M', J' M'} - Q_{J' M', J' M'}^0\}, \quad (2) \end{aligned}$$

and corresponding equations for $\partial Q_{J+1(\pm m), J(\pm m)} / \partial t$ and $\partial Q_{J+1(\pm m), J+1(\pm m)} / \partial t$.

Equations (1) and (2) are based on the Hamiltonian

$$H = H_0 - \mu \varepsilon_0 \cos \omega t \quad (3)$$

for an isolated absorber molecule where H_0 is the time-independent Hamiltonian whose Stark-shifted eigenvalues include the energy levels of the considered two-level system with angular transition frequency ω_m . μ is the electric dipole operator along the electric field component of the microwave radiation with amplitude ε_0 and angular frequency ω . The transition dipole matrix elements ($\mu_{J(\pm m), J+1(\pm m)} = \mu_{J+1(\pm m), J(\pm m)}$) do not depend on the sign of M and are given in units of \hbar by χ_m in (1) and (2).

The effects of molecular collisions are taken into account by elements of the relaxation supermatrix A describing first order relaxation of density matrix elements in the absence of external radiation, assumed to be diagonal in thermal equilibrium and then denoted by Q^0 . The sum in (2) is extended over all quantum numbers $J' M'$ for the two-level system, which makes use of the “heath bath” approximation with neglect of nonthermal population of all states outside the considered manifold [22].

In general, to account for a dependence of the measured rates on the absolute velocity (speed) of absorber molecules [12], the matrix elements of A might also be labelled by a single absorber speed if velocity-changing collisions are negligible [23, 24]. However, for the sake of simplicity, such speed dependence has been ignored in the present treatment. Accordingly, the effects of translational motion of molecules, which introduce additional velocity dependence of density matrix elements due to the radiative interaction [9], are not taken into account here. For example, with derivation of (1) and (2), Doppler shifts in resonance frequencies have been neglected by omitting in (3) the phase contribution to the microwave field which depends on the direction of wave propagation [25]. Molecular motion along perpendicular directions, which might become effective due to MW field inhomogeneities and wall collisions [9], is also not considered to simplify the following discussion. The extension to a more general treatment with inclusion of such velocity effects is straightforward, following the same line of thoughts given earlier with discussion of the $\pi, \tau, \pi/2$ -pulse sequence, applied to a system of two non-degenerate energy levels [9].

With reference to the earlier derivation of four-level Bloch-equations for the case of static Stark fields [6], we give some extended treatment here and proceed by introducing the variables

$$\begin{aligned} U^\pm &= Q_{Jm, J+1m}^\pm \exp(-i \omega t) + Q_{J+1m, Jm}^\pm \exp(i \omega t) \\ V^\pm &= i [Q_{J+1m, Jm}^\pm \exp(i \omega t) - Q_{Jm, J+1m}^\pm \exp(-i \omega t)], \\ W^\pm &= Q_{Jm, Jm}^\pm - Q_{J+1m, J+1m}^\pm, \\ S^\pm &= Q_{Jm, Jm}^\pm + Q_{J+1m, J+1m}^\pm, \end{aligned} \quad (4)$$

where the linear combinations Q^\pm of density matrix elements are given by

$$\begin{aligned} Q_{Jm, J' m'}^\pm &= Q_{Jm, J' m'}^\pm \pm Q_{Jm, J'(-m')}^\pm \quad \text{for } m' \neq 0, \\ Q_{J0, J' 0}^\pm &= Q_{J0, J' 0} \quad \text{for } m' = 0 \end{aligned} \quad (5)$$

with $J' = J$ for diagonal and $J' = J + 1$ for off-diagonal elements of the density matrix, respectively.

With use of (1) and (2), we obtain differential equations for the variables introduced in (4). Using symmetries of the matrix elements of μ and A [15], it can be shown that these equations do not couple the variables with different labels (+ or -). For the considered R-branch transitions of a linear molecule, we may also conclude that only the quantities U^+ and V^+ are related to the macroscopic polarization of the sample which is the observable quantity in our experiments. Explicitly, the polarization is given by [7]

$$P = N \mu_{Jm, J+1m} (U^+ \cos \omega t - V^+ \sin \omega t) \quad (6)$$

where N is the number density of molecules. With use of a MW bridge spectrometer, the polarization components in phase ($\sim U^+$) and in quadrature ($\sim V^+$) to the external radiation, respectively, may both be observed [17].

According to the above statements, we will consider only the time-development equations for ρ^{\pm} -matrix elements of (4) in the following. We then obtain with (1), (2), (4) and (5) by making use of the rotating wave approximation [26]

$$\begin{aligned} \dot{U}^+ &= -(\Delta\omega + \delta^+) V^+ - (1/T_2^+) U^+, \\ \dot{V}^+ &= (\Delta\omega + \delta^+) U^+ - (1/T_2^+) V^+ - xW^+, \\ \dot{W}^+ &= xV^+ - \alpha_1^+ (W^+ - W^{+0}) - \alpha_2^+ (S^+ - S^{+0}), \\ \dot{S}^+ &= -\alpha_3^+ (S^+ - S^{+0}) - \alpha_4^+ (W^+ - W^{+0}), \end{aligned} \quad (7)$$

where $\Delta\omega = \omega_m - \omega$ and $x = \gamma_m \varepsilon_0$ is the Rabi angular frequency of the transition.

The thermal equilibrium values of the variables W^+ and S^+ which correspond to population difference and sum of the $\pm M$ -degenerate levels, respectively, are labelled by zero. With retention of a time-development equation for S^+ in (7), a more general treatment of population relaxation is possible when the Bloch-type description of isolated two-level systems [22] is invalid.

It may be noted that the equations (7) are formally equivalent to those for two non-degenerate energy levels given earlier [2].

However, the relaxation parameters which describe collisional phenomena in the two cases are in general different. Here, the constants $1/T_2^+$, δ^+ , α_1^+ ,

α_2^+ , α_3^+ and α_4^+ are given by linear combinations of A -matrix elements as follows

$$\begin{aligned} 1/T_2^+ &= \text{Re} \{ A_{J+1m, Jm; J+1m, Jm} \\ &\quad + (1 - \delta_{m0}) A_{J+1(-m), J(-m); J+1m, Jm} \} \\ \delta^+ &= \text{Im} \{ A_{J+1m, Jm; J+1m, Jm} \\ &\quad + (1 - \delta_{m0}) A_{J+1(-m), J(-m); J+1m, Jm} \}, \\ \alpha_1^+ &= \frac{1}{2} \{ 2k_{Jm, J+1m}^+ + 2k_{J+1m, Jm}^+ \\ &\quad + \sum_{J''m''} k_{Jm, J''m''}^+ + \sum_{J''m''} k_{J+1m, J''m''}^+ \}, \\ \alpha_2^+ &= \frac{1}{2} \{ 2k_{Jm, J+1m}^+ - 2k_{J+1m, Jm}^+ \\ &\quad + \sum_{J''m''} k_{Jm, J''m''}^+ - \sum_{J''m''} k_{J+1m, J''m''}^+ \}, \\ \alpha_3^+ &= \frac{1}{2} \{ \sum_{J''m''} k_{Jm, J''m''}^+ + \sum_{J''m''} k_{J+1m, J''m''}^+ \}, \\ \alpha_4^+ &= \frac{1}{2} \{ \sum_{J''m''} k_{Jm, J''m''}^+ - \sum_{J''m''} k_{J+1m, J''m''}^+ \}, \end{aligned} \quad (8)$$

where

$$k_{Jm, J'm'}^+ = k_{Jm, J'm'} + (1 - \delta_{m'm}) k_{Jm, J'(-m')} \quad (9)$$

is in general a sum of two rate constants for population transfer between different J, m -states ($k_{Jm, J'(\pm m')} = -A_{J'(\pm m'), J'(\pm m'); Jm, Jm}$) and the sums \sum' are extended over all quantum numbers J'', m'' differing from those of the considered two levels.

The principles of our MW-pulse sequence experiment are easily explained by the appropriate solutions of (7) as shown in the following. Because of the aforementioned formal equivalence of these equations to those for non-degenerate two-level systems, extended theoretical discussions on the latter systems [3, 9] may be applied to the present treatment, keeping in mind that other relaxation parameters have to be considered for interpretation of the data.

The times involved in the sequence are given in Fig. 1 and each experiment starts at t_0 in thermal equilibrium conditions ($U^+(t_0) = V^+(t_0) = 0$, $W^+(t_0) = W^{+0}$, $S^+(t_0) = S^{+0}$). According to the experimental conditions, only the resonant solutions of (7) ($\Delta\omega + \delta^+ = 0$) will be considered. Then, as checked experimentally using the bridge spectrometer in dispersion mode, U^+ remains zero during the sequence and is therefore omitted in the following.

For further simplification we assume short pulses to make the concept of π - and $\pi/2$ -pulses with neglect of relaxation during the pulse periods applicable. Then the length of the first pulse is defined by $t_\pi = \pi/x$ which gives the following solution of (7) at $t_1 = t_0 + t_\pi$, the end of the pulse

$$V^+(t_1) = 0, \quad W^+(t_1) = -W^{+0}, \quad S^+(t_1) = S^{+0}. \quad (10)$$

During the delay period of length τ no external radiation field is present and nonthermal population is relaxing back to equilibrium. With the initial conditions (10) we have at $t_2 = t_1 + \tau$ for W^+ and S^+ ($V^+(t_2) = 0$)

$$W^+(t_2) = W^{+0} - 2W^{+0} \exp(-\alpha^+ \tau) \cdot [\cosh \gamma^+ \tau - (\beta^+/\gamma^+) \sinh \gamma^+ \tau], \quad (11)$$

$$S^+(t_2) = S^{+0} + 2W^{+0} (\alpha_4^+/\gamma^+) \exp(-\alpha^+ \tau) \sinh \gamma^+ \tau,$$

where $\alpha^+ = \frac{1}{2}(\alpha_1^+ + \alpha_3^+)$, $\beta^+ = \frac{1}{2}(\alpha_1^+ - \alpha_3^+)$ and $\gamma^+ = (\beta^{+2} + \alpha_2^+ \alpha_4^+)^{1/2}$. Only the solution for W^+ will be needed in the following since there is no coupling of S^+ to the observables through the radiative interaction, see (7). Conversion of population difference ($\sim W^+$) to polarization ($\sim V^+$) is achieved through the second pulse with length $t_{\pi/2} = \pi/2x$, giving with neglect of relaxation terms in (7) at $t_3 = t_2 + t_{\pi/2}$

$$V^+(t_3) = -W^+(t_2), \quad W^+(t_3) = 0. \quad (12)$$

We are interested here in solutions for V^+ after the end of the second pulse, which may be related to the transient emission signal as observed in our experiments. With (12) we have for times $t > t_3$

$$V^+(t) = -W^+(t_2) \exp[-(t - t_3)/T_2^+]. \quad (13)$$

With solution (13) the basic principle of the microwave pulse sequence are easily explained. As discussed in Sect. II, the detected transient emission signal $\Delta S (\sim V^+)$ is recorded at a fixed delay time τ' after the end of the $\pi/2$ -pulse (see Figure 1). With (11) and (13) ΔS may then be given as a function of τ

$$\Delta S(\tau) = D [1 - 2 \exp(-\alpha^+ \tau) \cdot \{\cosh \gamma^+ \tau - (\beta^+/\gamma^+) \sinh \gamma^+ \tau\}] \quad (14)$$

where $D (\sim \exp(-\tau'/T_2^+))$ is independent of τ .

Equation (14) generally describes a decay in signal intensity which is the sum of two exponential terms with decay rates $\alpha^+ + \gamma^+$ and $\alpha^+ - \gamma^+$, respectively. It has been shown previously, that single exponential decay behaviour is approximately ob-

tained for the limiting cases $\alpha_1^+ \approx \alpha_3^+$ or $\alpha_2^+ \alpha_4^+ \ll \beta^{+2}$, but deviates from it on a time scale of the order of $1/\alpha^+$ [22]. In particular, we have $\alpha_4^+ = 0$ when the rates out of the two connected levels are not different (see (8)) and (14) is reduced to

$$\Delta S(\tau) = D [1 - 2 \exp(-\tau/T_1^+)], \quad (15)$$

where $1/T_1^+ = \alpha_1^+$ according to the usual notation for the relaxation rate of population difference in the Bloch-type description of two level systems. For the considered system which includes a $\pm M$ -degeneracy of energy levels, the corresponding Bloch-type equations (i.e. using $S^+ = S^{+0}$ in (7)) would have resulted directly in the solution (15) to describe our pulse sequence which is formally equivalent to the inversion recovery method in NMR [27].

Both (14) oder (15) may be used for analysis of the experiments as discussed in the next section, depending on the accuracy of the data and the validity of the previously made assumptions. However, as pointed out in the beginning of this section, we emphasize that additional non-exponentialities in the observed decays may be caused by other effects which are due to the velocity distribution of absorber molecules.

IV. Results and Discussion

With use of the previously described pulse sequence, population relaxation has been investigated for the rotational transition ($J, |M|$): (1, 0)–(2, 0), (1, 1)–(2, 1), (2, 0)–(3, 0), (2, 1)–(3, 1) and (2, 2)–(3, 2) of HCCC¹⁵N in the ground vibrational state for the pure gas and mixtures with H₂, He, Ne and Ar. In addition to the $|M|$ -shifted transitions in presence of a DC Stark field, the M -unresolved transitions in zero Stark field have also been investigated but not treated theoretically here (see below).

The observed decay signal $\Delta S(t)$ for a fixed pressure and mixture composition was analyzed by a least squares fit program according to the following expression

$$\Delta S(t) = A + B \exp(-Ct) \quad (16)$$

with A , B and C as fitting parameters. Equation (16) corresponds to the theoretical expression $\Delta S(\tau)$,

(15), with arbitrary offset A and $t = \tau - \tau_{\min}$, where τ_{\min} is the minimum delay time, chosen to be about 1 μ s for data analysis. With increase of this initial delay time the validity of the assumed single exponential decay behaviour was tested. No significant changes in the fitting constant C were obtained, which indicates that more complicated theoretical predictions, e.g. by (14) and [9, 23], cannot be confirmed with the results of our experiments.

From the results for $1/T_1^+$ corresponding to the fit parameter C at different sample pressures, the coefficients for the linear pressure dependence were then evaluated by using a linear least squares fit, weighting the $1/T_1^+$ data points with their standard deviation in the following expression

$$1/T_1^+ = \alpha + \beta p. \quad (17)$$

For the pure gas, p is the total sample pressure and the intercept α is primarily due to wall collisions [9]. For the mixtures, α contains a contribution from self-collisions of HCCCN molecules in a fixed amount and p is the partial pressure for the foreign gas.

The results for the rate coefficients β are given in Table 1 together with the resonance frequencies of the investigated transitions. The error limits for β which are given as twice the standard deviation do not reflect systematic deviations which are primarily caused by shifts in pressure (< 0.1 mTorr) and temperature (< 1 K), and by additional partial pressure inaccuracies of the mixtures. Thus, these additional errors may add up to about 3% of the values given in Table 1 for the pure gas and to about 5% of the results for the mixtures.

The reliability of the results was tested by changing various experimental conditions. Thus, a decrease in MW power was only restricting the range of pressures for which “effective π -pulses” could be achieved. No change of the results was noticed when the gate position of the Boxcar integrator was varied with respect to the end of the second pulse, only affecting the amplitude of the decay signal. Changes of the Stark field strength resulting in different resonance frequencies for the $|M|$ -resolved transitions were found to be not critical as long as the separation from the other $|M|$ -lobes of the line was sufficient ($\gtrsim 10$ MHz) to avoid complications from off-resonance absorption effects at the applied MW power (~ 100 mW). In addition to these tests, the experimental method was also checked by investigation of T_1 -relaxation of OCS normal isotopic species with measurements on the $|M| = 1$ component of the $J = 1 \rightarrow 2$ rotational transition. The result for the rate coefficient was found to be in agreement within its error limits with earlier results as obtained from the Stark-switching technique ($\beta = 0.0359 \pm 0.004 \mu\text{s}^{-1} \text{ mTorr}^{-1}$, [9]).

As seen from Table 1, the $|M|$ -dependence of the values for the studied systems is small and mainly hidden in the experimental uncertainties. The small differences for the pure gas results as obtained from measurements in zero and non-zero Stark fields may indicate some significant change in relaxation rates for the two types of experiments. Such differences might be explained theoretically by treating the relaxation behaviour of spherical tensor combinations of density matrix elements with use of the proper linear combinations of rate constants [28].

Table 1. Coefficients β for the linear pressure dependence of measured decay rates for population difference in HCCC¹⁵N rotational transitions at room temperature in the range from 298 K to 303 K. Errors in parantheses are in the last digit given and twice the standard deviations.

Transition $J - J'$ M	Transition Frequency [MHz]	Stark field strength [V cm ⁻¹]	β [$\mu\text{s}^{-1} \text{ mTorr}^{-1}$] for collision partner				
			HCCC ¹⁵ N	H ₂	He	Ne	Ar
1 – 2							
$M = 0$	17659.650	349	0.213 (6)	0.057 (4)	0.028 (4)	0.027 (3)	0.028 (3)
$M = \pm 1$	17673.300	355	0.215 (4)	0.067 (7)	0.030 (2)	0.026 (3)	0.029 (4)
M -unresolved	17667.000	0	0.230 (3)	0.057 (3)	0.028 (1)	0.026 (3)	0.033 (2)
2 – 3							
$M = 0$	26485.461	1209	0.223 (7)	0.058 (5)	0.024 (4)	0.026 (4)	0.028 (3)
$M = \pm 1$	26496.658	1454	0.225 (8)	0.054 (2)	0.024 (1)	0.024 (2)	0.030 (2)
$M = \pm 2$	26510.460	727	0.210 (7)	0.054 (2)	0.026 (2)	0.024 (2)	0.030 (3)
M -unresolved	26500.561	0	0.231 (7)	0.058 (3)	0.026 (1)	0.025 (1)	0.031 (1)

Table 2. Sum R of coefficients for the pressure dependence of rate constants characterizing transfer of population in four-level system of HCCC¹⁵N, induced by collisions with HCCC¹⁵N, H₂, He, Ne and Ar. The data refer to the η -values of [10], extrapolated to 100% pumping efficiency, now wall collisions and infinite dilution for the mixtures.

Pump transition ($J_p m_p$) = (0, 0) → (1, 0) Signal transition ($J_s m_s$) → ($J_s + 1 m_s$)	$R = \{k_{J_p m_p, J_s m_s}^+ + k_{J_p+1 m_p, J_s+1 m_s}^+ - k_{J_p+1 m_p, J_s m_s}^+ - k_{J_p m_p, J_s+1 m_s}^+\} / p$	R [$\mu\text{s}^{-1} \text{Torr}^{-1}$] for collision partner				
		HCCC ¹⁵ N	H ₂	He	Ne	Ar
(1, 1) → (2, 1)	$\{\Phi_1(0, 0 \rightarrow 2, 2) + \Phi_1(1, 0 \rightarrow 2, 1)\}$ $-\{\Phi_2(0, 0 \rightarrow 2, 1) + \Phi_2(1, 0 \rightarrow 1, 1)\}$	55.0(62)	-2.1(23)	-4.1(17)	-2.5(11)	-2.3(12)
(2, 0) → (3, 0)	$\{\Phi_2(0, 0 \rightarrow 2, 0) + \Phi_2(1, 0 \rightarrow 3, 0)\}$ $-\{\Phi_3(0, 0 \rightarrow 3, 0) + \Phi_1(1, 0 \rightarrow 2, 0)\}$	-10.7(30)	+2.4(16)	+1.4(9)	+1.7(10)	+1.4(10)
(2, 1) → (3, 1)	$\{\Phi_2(0, 0 \rightarrow 2, 1) + \Phi_2(1, 0 \rightarrow 3, 1)\}$ $-\{\Phi_3(0, 0 \rightarrow 3, 1) + \Phi_1(1, 0 \rightarrow 2, 1)\}$	-10.7(31)	+4.5(27)	+2.9(13)	+3.2(11)	+3.2(14)
(2, 2) → (3, 2)	$\{\Phi_2(0, 0 \rightarrow 2, 2) + \Phi_2(1, 0 \rightarrow 3, 2)\}$ $-\{\Phi_2(0, 0 \rightarrow 3, 2) + \Phi_3(1, 0 \rightarrow 2, 2)\}$	+15.0(55)	+5.2(15)	+3.1(15)	+2.9(8)	+2.5(13)

However, because of the limited accuracy of the experimental results and the lack of more reliable data, no attempt has been made here to extend the analysis with application of the general relaxation theory [15] to the π , τ , $\pi/2$ -pulse sequence under zero field conditions.

Besides the present study, only the molecules OCS and NH₃ have been investigated by time domain techniques to yield information about the M -dependence of T_1 -relaxation rates [9, 29]. Minor variations of these rates with $|M|$ were found for OCS rotational transitions [9], whereas a distinct M -dependence of T_1 was observed for NH₃ inversion lines with $1/T_1$ strongly increasing with $|M|$ [29]. The latter result was explained theoretically by a modified Anderson theory [29] and is primarily caused by the predominance of collision-induced transitions between the probed levels. Such collisions which are twice as effective in contributing to the decay rates for population differences than all other collisions, see (8) for α_1^+ , are believed to be less important for the linear molecules OCS and HC₃N. Such assumption is strongly supported by the experimental results of coherence decay rates ($1/T_2$) similar to $1/T_1$ for these systems [30–32], if one assumes that phase-changing collisions are negligible [2]. It is then also expected that the M -dependence of T_1 -relaxation rates is small, provided that many collisional channels are open to outside levels.

More detailed information about rates for state-to-state collisional transitions has been obtained with recent $|M|$ -resolved four level double re-

sonance investigations on HCCC¹⁵N [10]. The resulting η -values for the relative change in intensity of signal lines, ($J, |M|$) = (1, 1)–(2, 1), (2, 0)–(3, 0), (2, 1)–(3, 1) and (2, 2)–(3, 2) when pumping the (J, M) = (0, 0)–(1, 0) transition were used for a qualitative discussion in terms of collisional selection rules. With the data on $1/T_1^+$ of this paper a more detailed analysis for the studied system is possible. For this purpose we use the approximate expression for η as derived earlier [6]

$$\eta = - (g_{m_p} v_{p0} / 2 g_{m_s} v_{s0}) \exp \{ (E_c - E_a) / kT \} \cdot \quad (18)$$

$$\times \frac{k_{J_p m_p, J_s m_s}^+ + k_{J_p+1 m_p, J_s+1 m_s}^+ - k_{J_p+1 m_p, J_s m_s}^+ - k_{J_p m_p, J_s+1 m_s}^+}{1/T_{1s}^+}$$

where $g_m = 2$ for $m \neq 0$ and $g_m = 1$ for $m = 0$ ($m = m_p, m_s$). v_{p0} and v_{s0} are the resonance frequencies of pump and signal transition with lower level energy E_a and E_c , respectively, the rates $k_{J, J', m, m'}^+$ are defined by (9), and $1/T_{1s}^+$ corresponds to the relaxation rate $1/T_1^+$ for the signal transition.

The sum of rate constants in the numerator of (18) was evaluated after extrapolating the observed η -values with standard procedures to 100% pumping efficiency*, no wall collisions and infinite dilution of the mixtures [33]. The results are given in Table 2 where the positive coefficients Φ_l have been introduced with the notation

$$k_{J, J', m, m'}^+ = \Phi_l (J, m \rightarrow J', m') p \quad (19)$$

* The actual pump efficiency was estimated to be about $(90 \pm 10)\%$ from experimental conditions given in [10].

for the linear pressure dependence of the rate constants k_{J_m, J'_m}^+ where p gives either the pressure of the pure gas or the foreign gas partial pressure. The index l classifies different types of collisional interaction as discussed previously [10]. Collisional channels which may be characterized to be of first order dipole-type in a perturbation treatment of the electric multipole interaction of colliding molecules [4] are denoted by $l = 1$, first order quadrupole-type (or second order dipole-type) collisional channels are labelled by $l = 2$ and all others by $l = 3$.

With the results in Table 2, previous conclusions about collisional preferences in the studied systems [10] are supported more quantitatively. Comparing the given linear combinations of rate constants with the predictions of theoretical methods to calculate rotational relaxation parameters can be useful in many respects. Thus, our results may provide a base to test the reliability of existing scattering theories which have not yet been applied to the systems

studied here. Improvements of the theoretical methods may then become necessary with consideration of the M -dependencies in our results. For atom-rotor systems, the accuracy of nonperturbative methods to calculate scattering cross sections is expected to be sufficient to evaluate reliable relaxation rates [23]. With this capability, assumptions about the intermolecular potentials may be ruled out by the experimental results on rotational relaxation.

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