A Four-Level Double Resonance Experiment on HCCC^{15}N with a Bridge Type Superheterodyne Microwave Spectrometer

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A four-level double resonance method has been developed allowing the determination of the relative collision induced change in signal intensity η without application of the Stark modulation technique. The method is based on certain properties of the bridge type superheterodyne spectrometer and may be applied to molecular transitions showing strong microwave absorption. η-values have been determined for various four-level systems consisting of $|M|$-resolved rotational levels of the linear molecule HCCC^{15}N. In addition to the measurements on the pure substance the influence of foreign gas admixtures with H_2, He, Ne and Ar on the results has been investigated.

Introduction

In order to obtain information about the transfer of rotational energy in a molecular ensemble due to collisions four-level double resonance experiments are often performed. Measurements of the relative collision-induced change in steady state signal intensity due to the pump microwave radiation $\eta = \Delta I/I$ are of special interest since they may give details about the relative significance of different collisional channels [1]. Various experimental techniques for the determination of η are described in literature [1–6], the most accurate of them being based on the principle of "double modulation" [7]. In that kind of experiment the line intensity of the signal transition is measured by means of high frequency Stark modulation (e.g. 100 kHz). Additionally a low frequency modulation (e.g. 1–10 Hz) of the pump microwave amplitude is applied such that the measured intensity gives the value I when the pump is switched off and $I + \Delta I$ when it is switched on. For the determination of ΔI a phase sensitive detector being adjusted to the pump modulation frequency [6] or a digital averager [3] may be used.

Besides the advantage of high sensitivity there is also one major problem that normally arises in the double modulation experiment. As a result of the Stark modulation molecular transient effects occur concerning the signal as well as the pump transition. Especially the required saturation of the pump transition does not persist continously as long as the pump microwave is switched on but is destroyed and reestablished again in any non-resonant and resonant period of the Stark-modulation respectively. That behaviour has not been taken into account in the theoretical expression for η [8], the derivation of which is based on steady state considerations only. Thus an inaccuracy may arise in the determination of η-values and the influence of this effect on the interpretation of the results can hardly be estimated.

In this paper an experimental method is described allowing the measurement of η without application of the Stark modulation technique and thus avoiding the problems associated with molecular transient effects mentioned above. The method is based on the operation principles of a bridge type superheterodyne microwave spectrometer and may be applied to molecular transitions showing strong microwave absorption as described below. It has been employed for the investigation of several four-level systems consisting of the $|M|$-resolved rotational transitions $J = 0-1$, $J = 1-2$ and $J = 2-3$ of the linear molecule cyanoacetylene, HCCC^{15}N *. The corresponding four-level systems of the linear molecule OCS have been investigated earlier using Stark modulation and the results of these measurements given elsewhere [3] will be compared with the η-values obtained here. In this context it has to be

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* The isotope ^{15}N has been chosen to avoid complications caused by nuclear quadrupole hyperfine structure.

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taken into account that the molecular dipole moment of HCCCN ($\mu \cong 3.7$ D) [9] as well as its molecular quadrupole moment ($Q = 2.385 \cdot 10^{-26} \cdot \mathrm{esu} \cdot \mathrm{cm}^2$) [10] exceed the corresponding quantities for OCS.

Experimental Setup

The experimental arrangement we used for our investigations is shown in Figure 1. It basically consists of the K-band bridge type superheterodyne spectrometer, a detailed description of which we gave in a previous paper [11]. In order to carry out the η-experiment some modifications were necessary. The measurement of molecular absorption intensities required for the determination of η is based on the detection of the difference in microwave power present at the output of the two waveguide cells (7a, b) if one of the cells is filled with

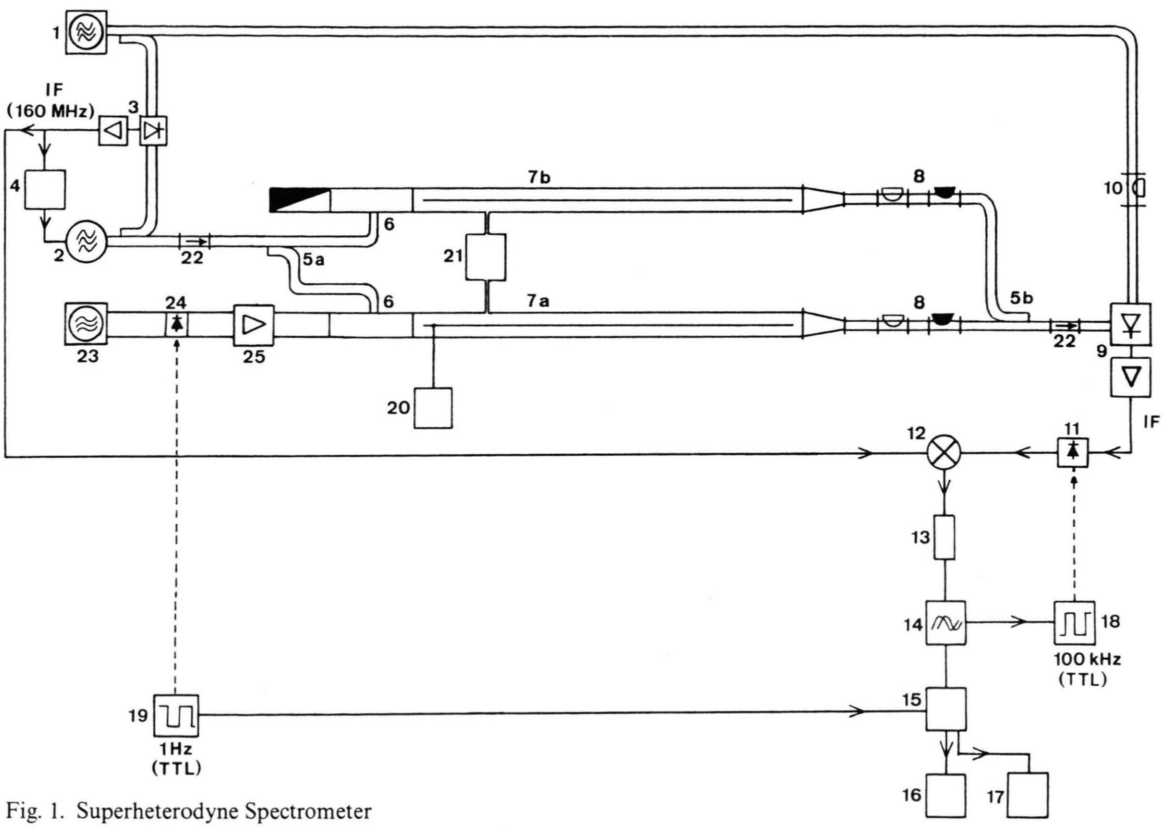

Fig. 1. Superheterodyne Spectrometer

1. Phase stabilized local oscillator: BWO (hp-Sweeper 8696A), K-band (18 – 26.5 GHz).
2. Signal oscillator: BWO Varian VA 163M (18 – 26.5 GHz).
3. MW-mixer (double balanced): RHG DM18-1B with IF-amplifier 160 MHz.
4. Phase stabilisation of the signal oscillator including 130 MHz quartz [12].
5. – 8. MW-bridge: (Carrier suppression > 40 dB over a band-width of ~ 1 MHz).
5. Directional couplers, K-band: Hp K 752A, 3 dB.
6. Directional couplers, ~ 10 dB for X-band pump MW.
7. Sample (7a) and reference (7b) cell, X-band, length 4.7 m, including Stark septum.
8. Phase shifters and attenuators, K-band.
9. Balanced mixer with integrated broadband IF-preamplifier: Spacekom FK-U and second IF-amplifier: RHG ICFH 160 LN.
10. Phase shifter, K-band.
11. IF-PIN-switch: Lorch ES 351.
12. IF-Mixer (double balanced): Mini Circuits ZAD-3.
13. Lowpass filter 5 MHz.
14. Phase sensitive detector: Ithaco Dynatrac 391 A.
15. Digital averager: Fabri Tek 1072.
16. X/Y-recorder.
17. Oscilloscope.
18. TTL-pulse generator (100 kHz).
19. TTL-pulse generator (1 Hz).
20. DC-power supply (0 – 2000 V): Fluke 415b.
21. Vacuum system including 20 l-bulb and capacitance manometer: MKS-Baratron 310B.
22. Unilines.
23. Phase stabilized pump oscillator (hp-Sweeper 8694A), X-band (8 – 12.4 GHz).
24. MW-PIN-switch: Arra 8753-80D.
25. TWT-amplifier: Hughes 1177H (X-band).

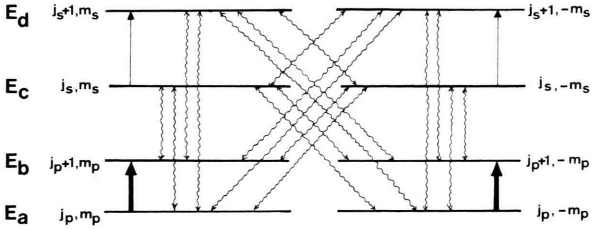

Fig. 2. Part of an energy level scheme in the presence of a Stark field. – The straight vertical arrows indicate the transitions affected by the pump ($E_a - E_b$) and signal microwave ($E_c - E_d$) respectively. Collisional channels within the level scheme that are taken into account in the theoretical expression (2) for η are designated by wavy arrows.

the substance under investigation while the other one is evacuated.

The principles of this method may be understood as follows. The frequency of the signal oscillator (2) radiation ν_s has to be tuned in resonance with the signal transition ($E_c - E_d$, see Fig. 2) of the considered four-level scheme whereas the whole pump microwave system (23–25) can be ignored or regarded to be switched off at the moment. Furthermore the absorption cell (7a) shall be filled with substance and (7b) held under vacuum. Now the bridge has to be balanced by means of the phase shifters and attenuators (8) as described in [11]. The transparency of the gas required for that adjustment process is achieved by means of a static Stark voltage (20) which is applied to the septum of (7a). Thus apart from a small residual signal the MW-carrier is suppressed and no microwave radiation reaches the signal input of the MW-mixer (9)*. If the static Stark voltage is now tuned back to the value corresponding to resonance of the signal transition the balance of the bridge is destroyed due to the molecular absorption in (7a). The resulting radiation amplitude at the input of (9) is a measure of the steady state absorption intensity I** since no modulation of the resonance is applied. After frequency conversion to 160 MHz (IF) the molecular signal is amplified in (9) and then fed into the IF-Mixer (12) to be converted to DC in a second step. In order to determine the signal amplitude as precise as possible the following modulation method is employed. By means of the PIN-diode switch (11) the IF-radiation at the input of (12) is interrupted periodically at a frequency of 100 kHz and with a 1:1 duty cycle. Thus at the low frequency output of (12) a 100 kHz square wave voltage appears the amplitude of which is measured with a phase sensitive detector (PSD) (14). Its internal reference signal controls the TTL-pulse generator (18) driving the PIN-switch. Provided the spectrometer is adjusted to "absorption mode" [11] the PSD-output can be regarded as a measure of the steady state signal intensity I and thus as one of the quantities necessary for the determination of $\eta = \Delta I / I$. The other one is the signal intensity $I + \Delta I$ in the presence of a pump microwave being

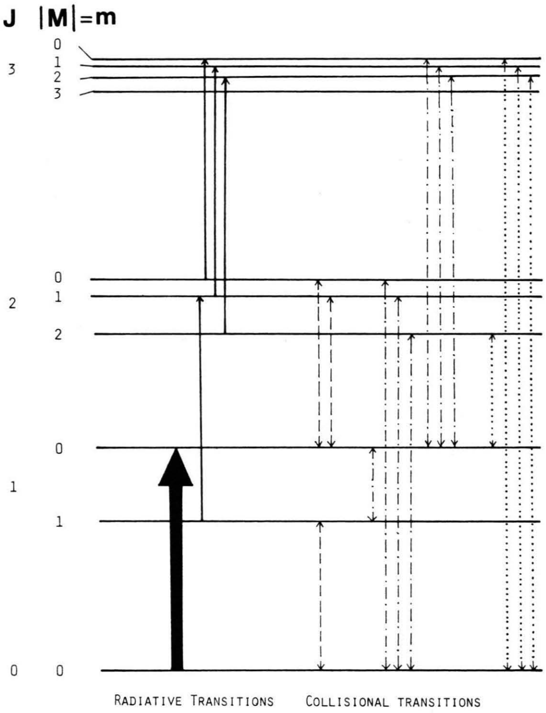

Fig. 3. Energy levels of HCCC^{15}N in the presence of a Stark field. The level differences are not in scale. Pump and signal transitions are indicated on the left hand side: pump transitions: $(J, m) = (0, 0) - (1, 0)$, Zero Stark field frequency [8]: 8833.545 MHz signal transitions: $(J, m) = (1, 1) - (2, 1)$, Zero Stark field frequency: 17667.000 MHz; $(J, m) = (2, 0) - (3, 0)$, Zero Stark field frequency: 26500.461 MHz; $(J, m) = (2, 1) - (3, 1)$, Zero Stark field frequency: 26500.461 MHz; $(J, m) = (2, 2) - (3, 2)$, Zero Stark field frequency: 26 500.461 MHz. The dashed arrows refer to collisional channels which are relevant for the theoretical expression (2) for η and are classified according to "collisional selection rules": first order dipole type channels: – – –, first order quadrupole (second order dipole) type channels: –·–·–, other channels: · · · · .

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* With our bridge we achieved a maximum carrier suppression of about 80 dB.

** Apart from the first few microseconds after switching on the resonance.

in resonance with the pump transition of the four-level system. In order to measure $I + \Delta I$ an X-band MW-source (23) in connexion with a TWT-amplifier (25) is used to provide the pump radiation which can be switched on and off by means of the PIN-switch (24).

Consequently the PSD-output gives $I + \Delta I$ when the pump is switched on whereas it gives I when it is switched off as described above. In both cases no molecular modulation is applied and the use of the PSD is just a formal analogy to the method of Stark spectroscopy. In the same sense the concept of "double modulation" which is described in detail elsewhere [7] may be utilized as a convenient technique for the determination of η. For that purpose the pump radiation has to be on/off amplitude modulated with a low frequency (e.g. 1 Hz). Consequently the PSD-output voltage alternates between the value corresponding to I and the one belonging to $I + \Delta I$. The pulse generator (19) driving the PIN-switch (24) also triggers a digital averager (15) such that the time dependent PSD-output signal is stored in its memory for evaluation. In order to increase the signal-to-noise-ratio many output cycles of (14) are added synchronously. The mean values for I and $I + \Delta I$ determined from the resulting curve stored in the digital memory of (15) are then used for the calculation of η.

Employing the experimental technique described above the problems due to molecular transient effects associated with the application of the Stark modulation method may be avoided. On the other hand one major problem arises that restricts the applicability of our method to strongly absorbing rotational transitions. Since it is the deviation from bridge balance caused by molecular absorption that is detected in our experiment the corresponding signal cannot be distinguished from a residual carrier resulting from an incorrect adjustment of the bridge. Thus the molecular signal amplitude has to exceed that of the residual carrier always appearing in a bridge type arrangement by at least one order of magnitude. However, an incompletete balance decreases the experimental accuracy of the intensity measurement. In order to minimize the interferring influence the following baseline subtraction method was applied in our experiments. After adding n cycles of the low frequency (1 Hz) modulated PSD-output signal in the memory of the digital averager the next n sweeps are used for baseline subtraction. For that purpose the molecular absorption is suppressed by means of a static Stark voltage driving the transition frequency out of resonance. Thus the MW-signal at the output of the bridge consists of the residual carrier alone and only the non-molecular part of the DC-signal (baseline) appears at the output of the PSD. Utilizing this subtraction method the influence of the residual MW-carrier is significantly decreased, the remaining interference being caused by its drift in phase and amplitude during the experiment due to thermal effects and mechanical vibrations. Thus our method of η-measurement is still restricted to molecular transitions showing sufficiently strong microwave absorption.

Furthermore there are some experimental conditions that have to be satisfied in any kind of η-measurement in order to get correct results [7]. The pump as well as the signal microwave radiation have to be exactly in resonance with the corresponding molecular transitions. The MW-power levels have to be adjusted in a way that saturation of the pump transition is provided and that only small deviations from thermal equilibrium occur concerning the population difference of the signal transition. Apart from that the gas pressure applied in the experiment has to be sufficiently high to avoid complications caused by the influence of wall collisions and the spectrometer has to be adjusted to "absorption mode" exactly as mentioned above.

The correct experimental conditions can be found by changing the individual parameters and observing the corresponding effect on the result of the measurement. If sufficiently small deviations in the individual parameters do not affect the measured η-values the settings of the apparatus can be regarded to be satisfactory.

Experimental and Results

A general treatment concerning a system of four molecular energy levels each of them being twofold degenerate is given elsewhere [3]. Thus we only quote the results as far as they apply to our η-experiment. The energy level scheme together with the effect of the two radiation fields and the different collisional channels is illustrated in Figure 2. Due to the assumed twofold $\pm M$-degeneracy which corresponds to the fact that our measurements are carried out in a static Stark field many more collisional channels appear as compared to the nondegenerate case. They may in first order be classified to be of dipole, quadrupole and higher moment type as described below and the corresponding rate constants are denoted by $k_{JM,J'M'}$ with $J, J' = J_S, J_S + 1, J_P, J_P + 1$ and $M, M' = |M_S|, -|M_S|, |M_P|, -|M_P|$.

Introducing the notation $m_S = |M_S|$, $m_P = |M_P|$ and defining linear combinations of rate constants

$$k^{\pm}_{Jm,J'm'} = k_{Jm,J'm'} \pm k_{Jm,J'(-m')} \quad \text{for} \quad m' \neq 0\,,$$
$$K^{+}_{Jm,J'0} = k_{Jm,J'0} \tag{1}$$

an approximate expression for the relative collision-induced change in signal intensity η is derived [3]

$$\eta = -\frac{g_{m_P}}{2\,g_{m_S}}\frac{\nu_{P_0}}{\nu_{S_0}}\,\frac{k^{+}_{J_P m_P, J_S m_S} + k^{+}_{(J_P+1)m_P,(J_S+1)m_S} - k^{+}_{(J_P+1)m_P,J_S m_S} - k^{+}_{J_P m_P,(J_S+1)m_S}}{1/T^{+}_{1S}} \cdot \exp\{(E_c - E_a)/kT\}\,, \tag{2}$$

where $g_m = 2$ for $m \neq 0$ and $g_m = 1$ for $m = 0$ ($m = m_S, m_P$).

$$\nu_{P_0} = (E_b - E_a)/\hbar \quad \text{and} \quad \nu_{S_0} = (E_d - E_c)/\hbar$$

(see Figure 2).

T^{+}_{1S}: corresponds to population relaxation time T_{1S} concerning the signal transition as introduced in the treatment of two-level schemes [13]. T^{+}_{1S} is obtained by substituting all rate constants k_{ij} involved by the linear combinations k^{+}_{ij} as defined above. k is the Boltzmann constant and T the absolute temperature.

As can be seen from (2) the measurement of η provides information about the relative magnitude of four rate constants for collisional energy transfer k^{+}_{ij}. If the relaxation time T^{+}_{1S} is known the linear combination of rate constants in the numerator of (2) can be calculated explicitly. Even if this is not the case the collisional channels which are of predominating influence may be found by interpretation of sign and value of the quantity alone.

By means of the experimental technique described above η-experiments have been carried out concerning various four-level systems of the molecule HCCC^{15}N in the ground vibrational state. The pump and signal transitions together with the collisional channels affecting the η-measurements respectively are classified according to the collisional selection rules [1]:

$$\Delta J = \pm 1\,; \quad \Delta M = 0, \pm 1 \tag{3a}$$

and

$$\Delta J = 0, \pm 2\,; \quad \Delta M = 0, \pm 1, \pm 2 \tag{3b}$$

being obtained in a frist order perturbation treatment. (3a) describes the dipole interaction between a linear dipolar absorber and an arbitrary perturber molecule with a permanent electrical moment of any order whereas (3b) corresponds to an interaction induced by a molecular quadrupole moment of the absorber*.

Those which do not belong to the types described by (3a) and (3b) are summarized to be of higher order.

The investigated four-level schemes consisted of the following pump and signal transitions respectively.

Pump transition:

$(J, m) = (0, 0) - (1, 0)$, = 8833.545 MHz, $g_{m_P} = 1$ [9];

signal transitions:

$(J, m) = (1, 1) - (2, 1)$, = 17667.000 MHz, $g_{m_S} = 2$,

$(J, m) = (2, 0) - (3, 0)$, = 26500.461 MHz, $g_{m_S} = 1$,

$(J, m) = (2, 1) - (3, 1)$, = 26500.461 MHz, $g_{m_S} = 2$,

$(J, m) = (2, 2) - (3, 2)$, = 26500.461 MHz, $g_{m_S} = 2$.

The frequencies given refer to the case of zero Stark field and the g_m-values describe the degeneracy of the energy levels for nonzero Stark field as introduced in (2). Field strengths of the order of several hundred Volts/cm were applied during the measurements to provide a sufficient frequency splitting of different m-components. In order to assure that the results we obtained from our investigations are largely independent from the properties and exact settings of our spectrometer, the experimental conditions had to be checked carefully as already mentioned above. The following adjustments were found out to be correct in the sense discussed above: Measurements carried out on pure HCCCN:

signal-MW-power:	~ 10 µW,
pump-MW-power:	~ 50 mW,
substance pressure:	~ 8 mTorr.

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* A second order perturbation treatment of the dipole case yields the same result.

Mixtures with foreign gases H_2, He, Ne and Ar:

signal-MW-power: ~ 50 μW,
pump-MW-power: ~ 250 mW,
substance pressure: HCCN: ~ 4 mTorr,
foreign gas: ~ 100 mTorr.

Furthermore the used HCCCN sample was tested gaschromatographically. No impurities caused by foreign substances could be detected. The percentage of the ^{15}N isotope should have been higher than 95% according to the specification given by the manufacturer of the $^{15}NH_3$ sample utilized for the synthesis of HCCC^{15}N.

The results of our η-measurements together with the estimated error limits are given in Table 1. Due to the smaller signal-to-noise-ratio the experimental uncertainty of the results concerning foreign gas admixtures is larger compared with that of η-values measured on pure HCCCN. According to the classification of collisional channels described above the four rate constants entering the expression (2) for η which are also given in Table 1 are denoted by their corresponding selection rules as follows:

k_1^+ first order dipole type collisional channel (see (3a))
k_2^+ first order quadrupole type, second order dipole type collisional channel (see (3b)),
k_3^+ higher order collisional channel.

In addition to our m-resolved investigations concerning the signal transition $J = 2 - 3$ we carried out measurements in the absence of a Stark field the results of which may be compared with the intensity-weighted average of the η-values found for the individual m-components.

This average can be calculated by the equation

$$\bar{\eta} = \frac{I_{m=0}\,\eta_{m=0} + I_{m=1}\,\eta_{m=1} + I_{m=2}\,\eta_{m=2}}{I_{m=0} + I_{m=1} + I_{m=2}}, \quad (4)$$

where the quantities denoted by I are the relative line intensities of the m-components of the signal transition respectively. Introducing numerical values into (4) gives

$$\bar{\eta} = 0.257\,\eta_{m=0} + 0.457\,\eta_{m=1} + 0.286\,\eta_{m=2}. \quad (5)$$

As can be seen from Table 1 the results obtained for $\bar{\eta}$ are in good agreement with those of the m-unresolved measurements.

In the following a qualitative discussion of the measured η-values in terms of collisional selection rules is given. Since no investigations yielding the rotational relaxation time T_1 have so far been performed on HCCCN the linear combination of rate constants appearing in (2) cannot be calculated numerically.

However, an interpretation of the results that is based on the sign and the relative magnitude of the η-values in connection with the type of collisional channels concerned is possible. Furthermore our observations may be compared to those made on the corresponding four-level systems of the linear molecule OCS [3] although the latter investigations were performed by applying the Stark modulation method. A significant difference between the results obtained by means of the two experimental techniques is expected in a more precise treatment only.

Table 1. η-values measured at room temperature for pure HCCC^{15}N and for mixtures with the foreign gases H_2, He, Ne and Ar. The sum of rate constants $-\sum k_{ij}^+$ appearing in the expression (2) for η is given for each four-level system, the individual rate constants being classified according to "collisional selection rules" (see text). Estimated error limits always concern the last digit given.

Pump transition: $J = 0 - 1$, $m = 0$		η [%]				
Signal transition	$-\sum k_{ij}^+$	HCCC^{15}N	H_2	He	Ne	Ar
$J = 1 - 2$, $m = 1$	$-(k_1^+ + k_1^+ - k_2^+ - k_2^+)$	$-2.8(2)$	$\pm 0.0(5)$	$+0.4(4)$	$\pm 0.0(4)$	$\pm 0.0(3)$
$J = 2 - 3$, $m = 0$	$-(k_2^+ + k_2^+ - k_3^+ - k_1^+)$	$+0.7(1)$	$-0.4(2)$	$-0.5(2)$	$-0.5(2)$	$-0.4(2)$
$J = 2 - 3$, $m = 1$	$-(k_2^+ + k_2^+ - k_3^+ - k_1^+)$	$+0.33(5)$	$-0.5(1)$	$-0.6(2)$	$-0.6(1)$	$-0.5(1)$
$J = 2 - 3$, $m = 2$	$-(k_2^+ + k_2^+ - k_3^+ - k_3^+)$	$-0.5(1)$	$-0.7(1)$	$-0.8(2)$	$-0.8(1)$	$-0.6(2)$
$J = 2 - 3$, m-unresolved		$+0.23(5)$	$-0.55(10)$	$-0.65(10)$	$-0.68(6)$	$-0.58(6)$
$\bar{\eta}$ $(J = 2 - 3)$		$+0.19$	-0.53	-0.63	-0.63	-0.5

As far as measurements on pure HCCCN are concerned the sign of η shows the same dependence on the signal transition as in the case of pure OCS. If dipole type collisional channels (rate constants $k_1^\dagger$) contribute to η they will be of predominant influence as can be seen from the results corresponding to the signal transitions $J = 1 - 2$, $m = 1$ and $J = 2 - 3$, $m = 0{,}1$. If on the other hand only rate constants of the types $k_l^\dagger$ with $l \geqslant 2$ appear in (2) (signal transition $J = 2 - 3$, $m = 2$) the effect of the quadrupole type collisional channel ($k_2^\dagger$) exceeds that of the higher order ones.

Because of the large dipole moment of HCCCN we limited our investigations on mixtures with foreign gases to the nonpolar substances H_2, He, Ne and Ar. As already observed in the study of mixtures of these gases with OCS the influence of the dipole type rate constants $k_1^\dagger$ significantly decreases. Thus considering the signal transition $J = 1 - 2$, $m = 1$ the effect of the dipole and the quadrupole type selection rules approximately compensate giving $\eta \sim 0$ apart from the slightly positive η-value measured on mixtures with He. Similarly we found that our measurements concerning the signal transition $J = 2 - 3$ are in qualitative agreement with those carried out on OCS. In the cases $m = 0{,}1$ the sign of η changes under the influence of the nonpolar foreign gases. This again refers to a decreasing significance of the rate constants $k_1^\dagger$ as compared to $k_2^\dagger$. On the other hand no change in sign of η is observed as far as the component $m = 2$ is concerned. Since in that case no first order dipole type rate constant contributes to η ($l \geqslant 2$) the excess of nonpolar collision partners does not alter the conditions significantly compared with those of pure HCCCN or OCS respectively.

Conclusion

Employing a superhet bridge type spectrometer an experimental technique for the determination of η was developed which is free from Stark modulation and thus excludes uncertainties caused by molecular transient effects. The method proved to be applicable to the measurement of η-values down to 0.5% provided the microwave absorption of the signal transition is sufficiently strong. Considering the determination of rate constants for collision-induced energy transfer another feature of our experiment can be advantageous. The measurements may be carried out using waveguide cells without Stark septum. In that kind of cell an electromagnetic field distribution of pump and signal microwave radiation may be generated in which the two electric field vectors are perpendicular to one another [14]. Due to the spectroscopic selection rule $\Delta M = 1$ that has to be taken into account in this case the measurement of η may yield linear combinations of rate constants which can not be obtained in a conventional type of η-experiment.

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