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THE σ-STARK EFFECT OF ROTATIONAL TRANSITIONS

PART I: EXPERIMENTAL ASPECTS

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Synopsis

A method is described for the automatic recording of the Stark-splitting patterns of microwave transitions corresponding to $\Delta M = \pm 1$. Potentialities and limitations of the method are shown in the application to the $J = 1 \rightarrow 2$ rotational transition of the $^{16}O^{12}C^{32}S$ molecule in the ground and in the excited bending (l-doublet) vibrational state. Generally, splitting patterns could be recorded automatically over frequency intervals up to 400 MHz. Slight distortion of the line shapes and of the relative intensities could not be avoided, however.

1. *Introduction.* The removal of the spatial (M) degeneracy of quantum transitions by an externally applied electric field and the resulting shift of the resonance frequency or splitting of a line into a number of components is known as Stark effect. The allowed transitions in a uniform applied field correspond with $\Delta M = 0$ (π-Stark effect) or with $\Delta M = \pm 1$ (σ-Stark effect) if the electric vectors of the Stark field and of the exciting electromagnetic field are parallel or perpendicular, respectively.

In the Stark-waveguide cells widely used in microwave spectroscopy for the application of an electric field to the absorbing gas the Stark- and microwave fields are parallel. As a consequence only the π-Stark effect is observed with these cells. The rather difficult experimental problem of obtaining "pure" perpendicular fields has been solved in the recent past by using cavity- and parallel-plate techniques. The σ-Stark effect of rotational transitions was observed and recorded by Dymanus in the K-band region with a TE_{0m1} Stark cavity absorption cell [1)2)], and by Bhattacharya and Gordy in the 3-mm region with a parallel-plate cell fed by a horn whose E-vector tapered to the larger cross section of the cell [3)].

The Stark-splitting pattern of the σ-effect is generally much more complicated and the amount of splitting for a given applied field considerably less than that of the π-effect. From the point of view of applications, the study of the σ-effect will thus be limited to problems which cannot be solved by the

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π-effect. This is the case, for example, when using Stark effect for the identification of rotational transitions (J and ΔJ values) in asymmetric top molecules. The π-effect of many transitions is such that the weakest components are displaced farthest from the unsplit line and, especially with the high-J transitions, become eventually obscured by the noise. It is not possible then to determine the total number of components and hence of the lower J-value of the transition [4]).

In the present paper a method is described for the automatic recording of the σ-type splitting patterns, including an application to the $J = 1 \rightarrow 2$ rotational transition of carbonyl sulphide (OCS) in the ground- and in the bending (l-doublet)-vibrational states. A forthcoming paper (Part II) [5]) will report the results of investigation on the σ-Stark effect of a number of both known and unknown transitions in the microwave spectrum of methyl alcohol (CH_3OH).

2. *Experimental techniques.* The basis component of the experimental set-up is the high-Q Stark cavity which serves both as absorption cell of the spectrometer and as reference cavity of a Pound-Zaffarano klystron frequency stabilizer. It is a pill-box shaped (diameter $\sim$ 15 cm) transmission cavity operating in a cylindrical TE_{0ml} mode, with m ranging from 5 to 12. The details of construction and performance of this cavity are given in ref. 2. The Stark voltage is applied between the bottom and the plunger. As the resulting Stark field is perpendicular to the microwave field of the cavity only $\Delta M = \pm 1$ transitions are detected. Owing to the large diameter to length ratio (15–20) and uniform spacing between the bottom and the plunger the applied Stark field is well homogeneous.

For the recording of the splitting patterns square wave Stark modulation at the frequency of 10 kHz was used throughout the present investigation. Fields up to 2000 V/cm could be obtained with the maximum available square wave voltage of 1400 V. For stronger fields the modulating square-wave voltage was superimposed on a DC voltage. At pressures below about 0.02 mm Hg fields up to 4 kV/cm could be maintained in the cavity. Unfortunately, with the superimposed fields, at its best, only the first derivative of the pattern was recorded.

The part of the experimental set-up (Fig. 1) starting with klystron and running through magic-T and Stark cavity to the output crystal detector X_3, comprises the spectrometer. The signal components at the modulation frequency were first amplified in a low-noise narrowband amplifier, then demodulated in a phase-sensitive detector, and finally applied to a recorder through a low-pass filter. The overall sensitivity of the spectrometer was about 10^{-9} cm^{-1} with a time constant of 1 sec. and loaded-Q factor of 5000–10000.

The magic-T, Stark cavity, uniline (U_2), phase shifter, mixer crystal (X_1),

and the modulator crystal (X_2) with the associated electronic circuitry comprise the Pound-Zaffarano klystron frequency stabilizer [6]). The present stabilizer differs only on minor points from conventional designs. It operates at the modulation frequency of 455 kHz instead of at the conventional 30–60 MHz. It has been found that with the Zaffarano discriminator the loss in ultimate frequency stability is very small on lowering the modulation frequency to the 1 MHz region while a low modulation frequency considerably simplifies the electronic instrumentation. The uniline U_2 matches the mixer arm of the magic-T and thus eliminates multiply reflected and modulated waves. This results in a considerable simplification of the adjustment procedure and in an increased bandwidth of stabilization.

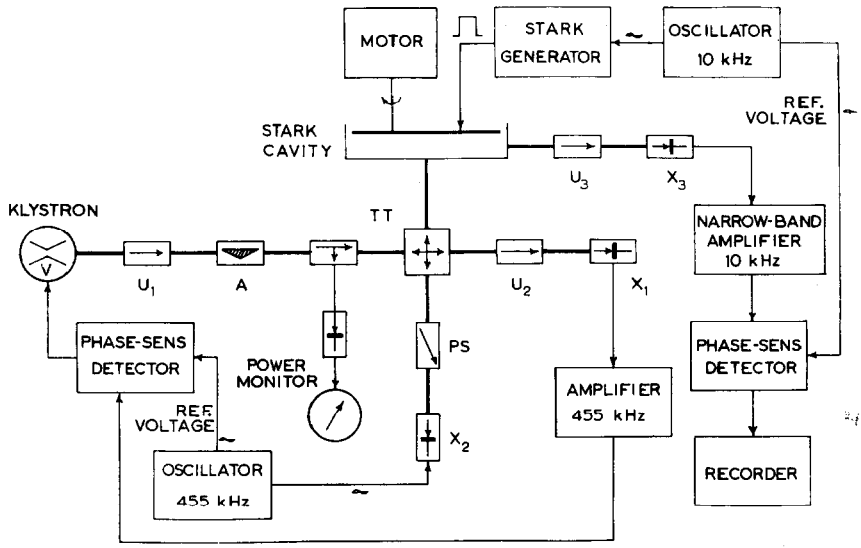

Fig. 1. Simplified diagram of the experimental set-up: TT = magic-T, U_{1-3} = unilines, A = attenuator, PS = phase shifter, X_1 = mixer crystal, X_2 = modulator crystal, X_3 = output-detector crystal.

To record the splitting pattern of a line the resonance frequency of the Stark cavity is varied continuously by a slow-drive motor coupled to the plunger of the cavity. By the action of the stabilizer the klystron frequency follows automatically the resonance frequency of the cavity with a nominally zero frequency difference. Patterns could be recorded in this way over frequency intervals up to 400 MHz in a non-stop run. However, considerable care is required for the coverage of frequency intervals larger than about 50 MHz if distortion of the recorded pattern has to be avoided as far as possible. Generally, three requirements have to be met: (i) sensitivity of the spectrometer and hence also the klystron output power independent of

microwave frequency; (ii) large bandwidth of the stabilizer; (iii) zero frequency difference between the klystron and the cavity frequencies.

The third requirement is the hardest to satisfy mainly because of the unavoidable and often very strong reflections within the microwave discriminator circuit (magic T, mica windows of the cavity, modulator crystal, etc.). These reflections destroy the proper phase relation between the carrier and the sidebands at the mixer crystal, cause a 455 kHz signal to appear also at the resonance frequency of the cavity, and finally exert a pulling-effect on the cavity frequency. The result of all these effects is that the klystron oscillates at a frequency which is slightly different from the cavity frequency. As the latter frequency is varied the klystron frequency follows it leading or lagging by an amount depending on frequency and strength of reflections. This causes distortion of the recorded line widths and relative intensities especially when working with narrow lines, as one usually does. Since reflections cannot be avoided or eliminated completely over a wide frequency region some distortion of the patterns will usually be present in the recordings.

The recorded relative intensities will be distorted farther if, in addition to the effects mentioned above, the klystron power and the sensitivity of the crystal detector X_3 vary with frequency (the first requirement). Obviously, the detector X_3 should be broadbanded and the input power to the cavity kept constant, preferably automatically to eliminate also relatively fast variations [7]). The main cause of these variations is the shift of the operating point of the klystron along the mode pattern as the klystron frequency is forced to follow the resonance frequency of the cavity. This difficulty can be avoided easily by readjusting the mechanical tuner of the klystron such that the point of operation remains on top of the mode. In the present investigation this was done by hand.

To satisfy the second requirement the crystal mounts of both X_2 and X_1 should be broadbanded and at the same time of low reflectivity and (X_2 only) of high efficiency for the generation of side-band power over a wide frequency region. Moreover, the nominal 90° phase difference between the carrier and the sidebands at the mixer crystal should be satisfied as close as possible and the operating point of the klystron should be kept off the edge of the mode (see above). The crystal mounts usually do not meet all requirements mentioned above at the same time. The mounts used in the present investigation were essentially of the tunable type but with broadband tuning properties. They were built at the laboratory. In the absence of reflections within the discriminator the problem of maintaining proper phase difference at the mixer is practically unimportant over intervals of 400 MHz if the lengths of the wavepaths from the mixer crystal to the cavity and to the modulator crystal differ by a quarter of the guide wavelength as it is usually the case. For a shift in frequency of 400 MHz at 24 GHz

the change in the phase is then only about 3°. In the presence of reflections the actual change in phase for the same change in frequency is much larger and, unfortunately, strongly dependent on frequency. It was not possible to cover intervals larger than about 50 HMz without an additional phase correction during the recording. Usually, this phase correction was applied by hand, by having the tuning plunger of the modulator crystal follow a previously established calibration curve of 90° phase difference *vs.* position of the plunger. The calibration curve was obtained from the oscilloscope displays of the well-known discriminator curves at a number of frequencies [8]).

3. *Application to OCS.* (a) The ground-state line. Carbonyl sulphide is a linear molecule and the Stark effect of rotational transitions in the vibrational ground state (000) is essentially of the second order. The frequency displacement $\Delta\nu_M$ of the M-th Stark component from the unsplit line is readily obtained from the well-known [9]) expression for the second-order Stark energies of the J-th rotational level by applying the selection rules: $\Delta J = +1$, $\Delta M = \pm 1$. The result is:

$$\Delta\nu_M = -\frac{(C_s pE)^2}{\nu_0} \cdot \left\{\frac{3M^2(J+2)(2J+1)(2J+5) - 3(M\pm 1)^2 J(2J-1)(2J+3) - 8J(J+1)^2(J+2)}{J(J+2)(2J-1)(2J+1)(2J+3)(2J+5)}\right\}, \quad (1)$$

where p is the electric dipole moment of the molecule, E the applied Stark field, ν_0 the resonance frequency of the transition, J – the rotational quantum number, M – the magnetic quantum number, and C_s is the Stark splitting constant. For p in Debye units, E in V/cm and ν_0 and $\Delta\nu_M$ in MHz, the value of C_s is:

$$C_s = 0.50348.$$

The expression (1) is valid only for $J \neq 0$. For $J = 0$, $\Delta\nu_M$ is given by:

$$\Delta\nu_M = \frac{7}{30}\frac{(C_s pE)^2}{\nu_0} \cdot \quad (2)$$

The upper (+) sign and the lower (−) sign in Eq. (1) correspond with the $\Delta M = +1$ and with the $\Delta M = -1$ transitions, respectively.

The relative intensities of the Stark components and the unsplit line are given by the ratios of the corresponding direction cosine matrixelements (Ref. 9, Chap. 4). For linear molecules the intensity ratio R_M of the M-th component and the unsplit line is given by:

$$R_M = \frac{3(J \pm M + 1)(J \pm M + 2)}{2(J+1)(2J+1)(2J+3)} \cdot \quad (3)$$

The sign convention in eq. (3) is the same as in eq. (1).

The splitting pattern of the $J = 1 \rightarrow 2$ transition calculated from eqs. (1) and (3) using for p and ν_0 the values of 0.712 Debye [10]) and 24.326 MHz, respectively, is shown in fig. 2*a* for $E = 1000$ V/cm. The pattern recorded with the present set-up is given in fig. 2*b* for $E \simeq 1000$ V/cm and in fig. 2*c* for $E \simeq 2000$ V/cm. These recordings show clearly the expected relative displacements and intensities of the individual components. The causes of a slight distortion of line shapes and relative intensities have been discussed above.

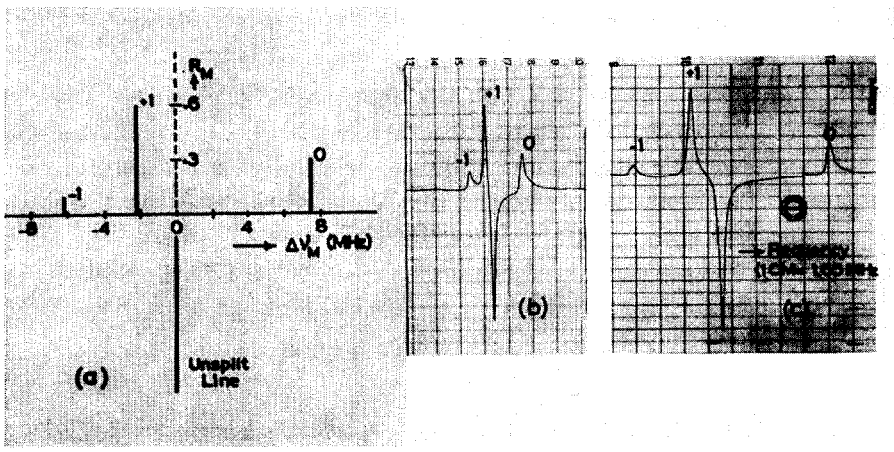

Fig. 2. The σ-type Stark splitting pattern of the $J = 1 \rightarrow 2$ rotational transition of OCS in the ground vibrational state calculated (a) from eqs. (1) and (3) for a field of 1000 V/cm and recorded (b, c) at fields of about 1000 and 2000 V/cm, respectively. As a result of the phase-sensitive demodulation used for the recording the Stark-components (also in fig. 4) are pointing upward and the unsplit lines downward. The labelling of components by their lower-state M-value corresponds to the $\Delta M = +1$ transitions. For the $\Delta M = -1$ transitions M should be replaced by $-M$.

(b) The l-doublet. It is well known that a linear molecule in the degenerate bending vibrational state can be considered as a slightly a-symmetric top. The double degeneracy of the state is removed by the rotation-vibration interaction leading to the splitting of the energy levels known as l-type doubling.

The Stark effect of a slightly asymmetric top has been treated by Penney [11]) and his expression for the energy of a Stark perturbed state can be used to calculate the σ-Stark effect of the l-doublet. In the absence of a Stark field the energies of the l-doublet levels are W_1^0 and W_2^0, where the subscripts 1 and 2 refer to the lower and higher energy level, respectively. When the Stark field is applied the perturbed energies of the two levels are given by:

$$(W_{1,2})_J = \tfrac{1}{2}(W_1^0 + W_2^0)_J \pm \tfrac{1}{2}[(W_1^0 - W_2^0)^2_J + 4E^2 p_{12}^2(J, M)]^{\frac{1}{2}} \quad (4)$$

where:

$$p_{12}(J, M) = p\frac{Ml}{J(J+1)} \tag{5}$$

is the dipole moment matrix element for the transition between the two degenerate levels; l is the quantum number of the angular momentum due to excited degenerate vibration and takes the values

$$l = v_2, v_2 - 2, v_2 - 4, \ldots, -v_2$$

with $|l| \leqq J$ and v_2 the vibrational quantum number.

The resonance frequency ν_0 of the $J \to J+1$ rotational transition in the bending vibrational state and in the presence of a Stark field ($\Delta M = \pm 1$) is obtained from eqs. (4, 5). The result is:

$$\begin{aligned} h\nu_0 = W_{J+1,M\pm1} - W_{J,M} = \tfrac{1}{2}(W_1^0 + W_2^0)_{J+1} - \tfrac{1}{2}(W_1^0 + W_2^0)_J \pm \\ \pm \tfrac{1}{2}[(W_1^0 - W_2^0)^2_{J+1} + 4E^2p_{12}^2(J+1, M\pm1)]^{\frac{1}{2}} \mp \\ \mp \tfrac{1}{2}[(W_1^0 - W_2^0)^2_J + 4E^2p_{12}^2(J, M)]^{\frac{1}{2}} \end{aligned} \tag{6}$$

This expression can be simplified somewhat by noting that:

$$\tfrac{1}{2}(W_1^0 + W_2^0)_{J+1} - \tfrac{1}{2}(W_1^0 + W_2^0)_J = \tfrac{1}{2}h(\nu_1 + \nu_2) \tag{7}$$

where ν_1 and ν_2 are the resonance frequencies of the lower and higher-frequency components of the l-doublet at zero Stark-field, respectively. Moreover, the energy difference $W_1^0 - W_2^0$ is for $|l| = 1$ given by (Ref. 9, Chap. 2):

$$(W_1^0 - W_2^0)_J = \frac{h}{2}q_l(v_2 + 1)\,J(J+1) \tag{8}$$

Here, q_l is the l-type doubling constant. The expression for the frequency displacement of the M-th component from the centre frequency of the l-doublet obtained from eqs. (6–8) is:

$$\begin{aligned} \Delta\nu_M = \pm\tfrac{1}{2}\left[\{\tfrac{1}{2}q_l(v_2+1)(J+1)(J+2)\}^2 + \frac{4E^2p^2(M\pm1)^2l^2}{h^2(J+1)^2(J+2)^2}\right]^{\frac{1}{2}} \\ \mp\tfrac{1}{2}\left[\{\tfrac{1}{2}q_l(v_2+1)\,J(J+1)\}^2 + \frac{4E^2p^2M^2l^2}{h^2J^2(J+1)^2}\right]^{\frac{1}{2}} \end{aligned} \tag{9}$$

This expression describes the well known type of the Stark effect which is of the second order at low fields and of the first order at high fields.

For the $J = 1 \to 2$ transition in OCS the various constants in eq. (9) have the following values:
$J = 1, M = \pm 1, 0; v_2 = 1, l = 1, p = 0.700$ Debye units, $q_l = 6.125$ MHz. By substituting these values into eq. (9) one obtains for $\Delta\nu_M$:

$$\Delta\nu_M = \pm\tfrac{1}{2}[1350 + 0.0138(M\pm1)^2E^2]^{\frac{1}{2}} \pm [150 + 0.124M^2E^2]^{\frac{1}{2}} \tag{10}$$

where E is in V/cm. The relative intensities of the components are given by eq. (3).

In fig. 3 are shown the frequency displacements $\Delta\nu_M$ of the three components of the l-doublet lines as a function of the applied Stark field both

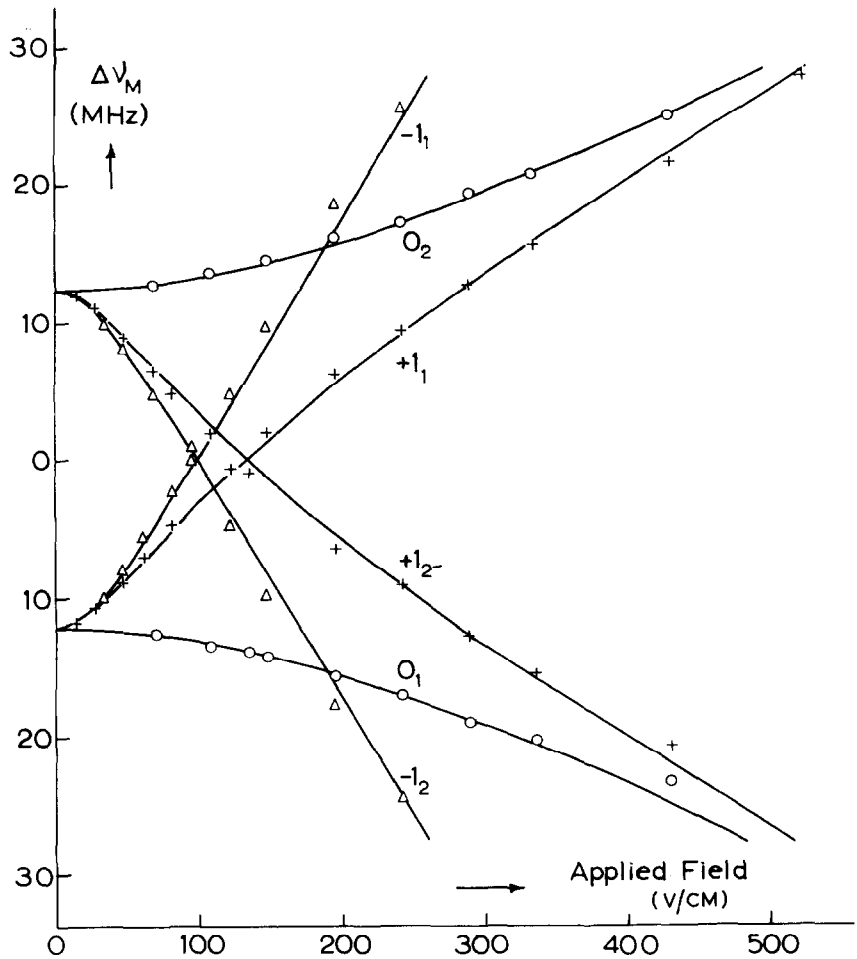

Fig. 3. The calculated (curves) and the measured (points) frequency displacements $\Delta\nu_M$ of the σ-components of the l-doublet of OCS from the centre frequency of the doublet as a function of the applied Stark field. The components are labelled by the M-value of the lower state of the transition corresponding to the $\Delta M = +1$ transitions. The subscripts 1 and 2 attached to the M-values denote the lower-and the higher-frequency member of the doublet, respectively.

calculated (curves) from eq. (10) and measured (points) with the present set-up. Taking into account the relatively large error (2–5%, largely due to line distortion and error in the strength of the applied field) in measuring

relative frequency displacements the agreement between theory and experiment is very good. The recordings of the splitting patterns obtained at the fields of 40, 145 and 270 V/cm are reproduced in figs. 4*a*, 4*b* and 4*c*, respectively. The frequency region covered in recording 4*c* is about 70 MHz and it also shows the ground-state line at 24.326 MHz.

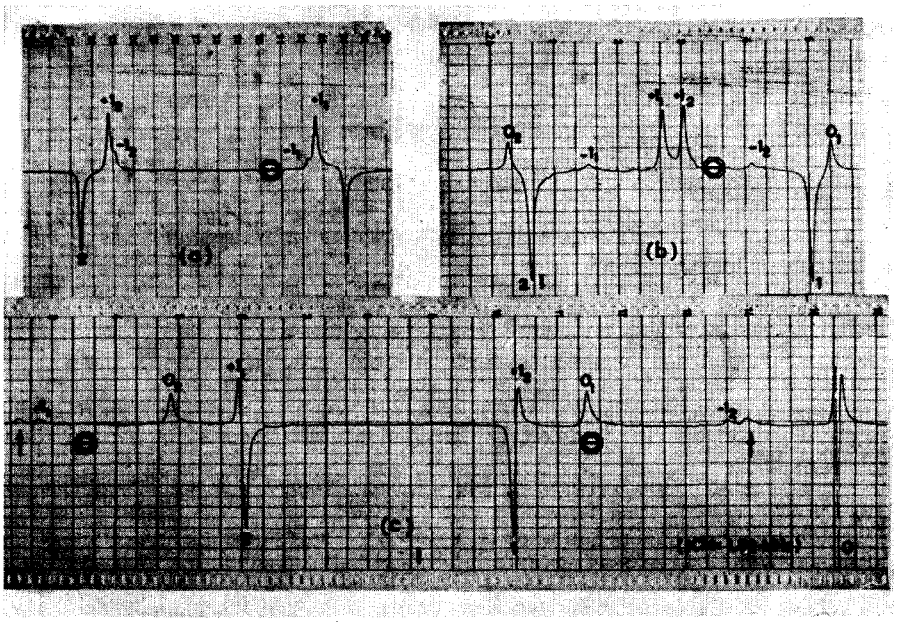

Fig. 4. The σ-type Stark splitting pattern of the l-doublet recorded with the present set-up at the fields of about 40 V/cm (recording (a)), 145 V/cm (recording (b)), and 270 V/cm (recording (c)). The labelling of the unsplit lines (pointing downward) is: 0 for the ground-state line; 1 and 2 for the lower-and the higher-frequency members of the l-doublet, respectively. The labelling of the Stark components is the same as in figure 3. The two weak lines indicated by the arrows are probably the anomalous lines first observed by Shulman and Townes (Phys. Rev. **77** (1950) 500). These lines correspond to transitions which are allowed only in the presence of an electric field.

In view of the results as presented in figs. 2–4, the rather small distortion of the line shapes and relative intensities in the recordings, the good sensitivity, and the large bandwidth permitting recording over frequency intervals up to 400 MHz in a single run, the present method looks quite convenient for the study of the σ-type Stark effect. The limitations of the present method have been discussed at some length in the preceeding section. Two points should be mentioned still: the set-up cannot be used also for the study of the π-type effect, and the Stark field is not constant during a recording but varies inversely as the length of the Stark cavity at the rate

of roughly 1% per 300 MHz. This rate is quite low but may become important for second -order lines at very high fields.

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