

## High Resolution Stark Spectroscopy of H<sub>2</sub>CO at 3.51 $\mu\text{m}$ by Saturated Absorption

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Precise measurements were carried out on the Stark effect of the vibration-rotation transition  $5_{1,5}(v=0)-6_{0,6}(v_5=1)$  in H<sub>2</sub>CO using a low-noise, stable He-Xe laser at 3.51  $\mu\text{m}$ . The intracavity saturated absorption technique was employed to improve the resolution.

Eight of the allowed transitions were resolved and the small Stark coefficients were determined with high accuracy under a maximum applied field strength of 4.39 kV/cm. Furthermore, the first observation of six cross resonance lines in this transition is reported.

### §1. Introduction

Stark spectroscopy in the optical as well as the microwave region has been widely used as a potential tool for the study of molecular structure.<sup>1-9)</sup> As an example, the Stark effects of the vibration-rotation transitions of H<sub>2</sub>CO have been studied in the wavelength region between 3 and 10  $\mu\text{m}$ .<sup>10-16)</sup> The transition at 3.51  $\mu\text{m}$  ( $5_{1,5}(v=0)-6_{0,6}(v_5=1)$ ) in H<sub>2</sub>CO has been studied using a Zeeman-tuned He-Xe laser.<sup>10)</sup> However, the Stark coefficient of this transition has not yet been determined because it is too small to be measured by the conventional linear absorption technique. Recently, the saturated absorption signal of this transition has been studied, and the frequency of the Zeeman-tuned He-Xe laser has been stabilized using this line as a frequency reference.<sup>17,18)</sup> Furthermore, a highly-stabilized frequency offset locked He-Xe laser system has been constructed for ultrahigh resolution laser spectroscopy.<sup>19)</sup> As a result of this progress, it became possible to measure the Stark spectrum of this transition with higher resolution using the saturated absorption technique.

In this experiment, the Stark effect of this transition was studied with high resolution to assign the lines and to measure the Stark coefficient with higher accuracy using the intracavity saturated absorption technique.

### §2. Experimental Apparatus

The experimental apparatus is shown in Fig. 1. The

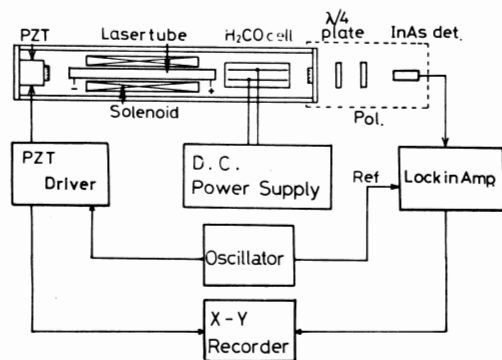


Fig. 1. Experimental apparatus.

low-noise He-Xe laser tube used in this study is of the same type as in the previous work.<sup>19)</sup> It has a discharge section of 5.8 mm inner diameter and 750 mm length, and is excited by a d.c. discharge current of 3.8 mA. Since the frequency of the transition  $5_{1,5}(v=0)-6_{0,6}(v_5=1)$  is about 180 MHz higher than the center of the gain curve of the He-Xe laser, an axial magnetic field of 124G was applied to the laser tube to compensate for this frequency gap. Between two oppositely circularly-polarized Zeeman components oscillated simultaneously,<sup>20)</sup> a higher-frequency component (the  $\sigma_+$  mode) was used for the experiment. Its intensity was measured after being separated from the lower-frequency component (the  $\sigma_-$  mode) by a quarter-wave plate and a polarizer.

The laser cavity was 155 cm long, corresponding to a longitudinal mode separation of 96.6 MHz. One of the cavity mirrors was mounted on a piezoelectric transducer (PZT) for frequency tuning and modulation. An a.c. voltage of 500 Hz was applied to the PZT for frequency modulation, and the maximum frequency deviation was 190 kHz. The first derivatives of the saturated absorption signal were measured by phase-sensitive detection and were displayed on an X-Y recorder. The value of the tuned frequency was estimated from the d.c. voltage applied to the PZT and the longitudinal mode separation.

The intracavity H<sub>2</sub>CO absorption cell contained a pair of Stark electrodes made of aluminum plates, which were 330 mm long and faced each other with a separation of 6.38 mm. Since the flatness of the electrodes was better than 20  $\mu\text{m}$ , the inaccuracy of the Stark field strength was estimated to be less than 0.3%. The maximum d.c. voltage applied in this experiment was 2.8 kV, corresponding to an electric field strength of 4.39 kV/cm.

### §3. Experimental Results and Assignment

Figure 2 shows the derivative signals of the saturated absorption lines observed under a Stark field of 4.39 kV/cm. The H<sub>2</sub>CO pressure was 10 mTorr. The signal obtained using a single scan of the laser frequency had a very high signal-to-noise ratio. As seen from Fig. 2, sixteen separate lines (Nos. 0-15) were clearly observed. Number 0 was assigned to the strongest line, which exhibits the lowest Stark shift. The width of each line was about 500 kHz. Figure 3 shows the relation between the fre-

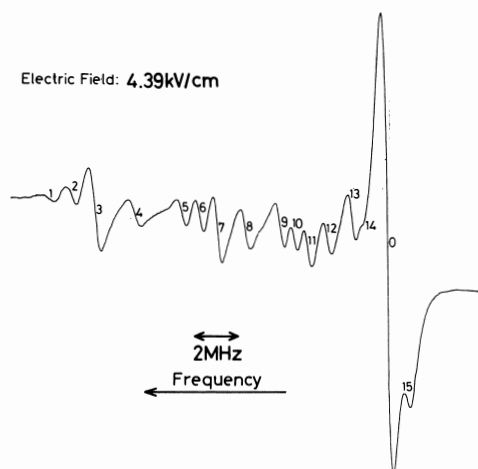


Fig. 2. Derivative of saturated absorption lines observed under Stark field of 4.39 kV/cm.  $\text{H}_2\text{CO}$  pressure was 10 m Torr. Sixteen lines (Nos. 0–15) were observed with high sensitivity in this measurement.

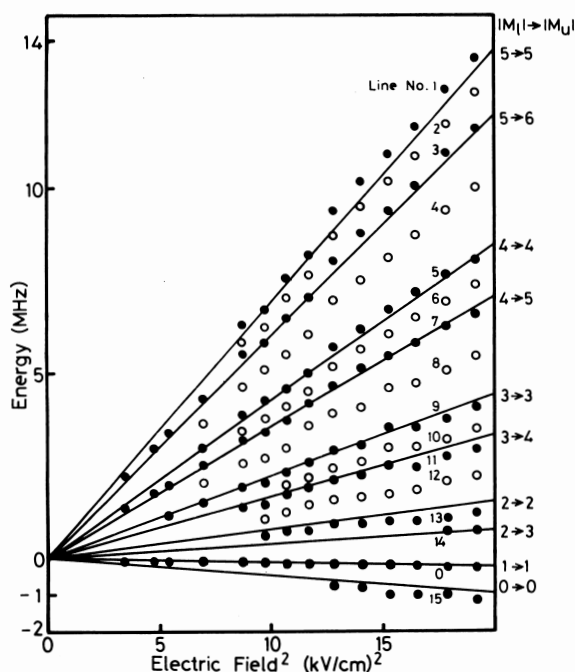


Fig. 3. Relation between frequency shifts of sixteen observed lines and square of Stark field strength. Circles and solid lines represent experimental and calculated results, respectively. Solid circles correspond to allowed transitions, and open circles to six cross-resonance lines. Solid lines are calculated results, where  $M_l$  and  $M_u$  represent magnetic quantum numbers of lower and upper levels of transitions, respectively.

quency shifts of the sixteen lines and the square of the Stark field strength. The solid and open circles in this figure show the experimental results. The solid lines represent the results of the assignment described below, for which a rigid asymmetric rotor model was employed.

The second-order perturbation due to the Stark effect for the nondegenerated rigid asymmetric rotor is expressed as<sup>21)</sup>

$$\mathcal{H}(J\tau M) = W_{J\tau}^0 + E^2 \sum_{J',\tau',g} \frac{\mu_g^2 [(\Phi_{Zg})_{J\tau M; J'\tau' M'}]^2}{W_{J\tau}^0 - W_{J'\tau'}^0}, \quad (1)$$

where  $J$  is the total angular momentum,  $M$  is the magnetic quantum number,  $\tau$  is the identification number for sub-

levels of the asymmetric rotor belonging to the same  $J$ ,  $E$  is the applied electric field,  $\mu$  is the electric dipole moment and  $\Phi_{Zg}$  is the direction cosine between the space-fixed  $Z$  and molecular-fixed  $g$  axes.<sup>22)</sup> Since only one component of  $\mu_g$  has a value in  $\text{H}_2\text{CO}$ , summation over  $g$  can be eliminated. By using the formula in Table I of ref. 22, eq. (1) can be transformed as follows:

$$\mathcal{H}(J\tau M) = W_{J\tau}^0 + \mu_A^2 E^2 [A_{J,\tau} + M^2 B_{J,\tau}]. \quad (2)$$

In this equation, the value of the coefficients  $A_{J,\tau}$  and  $B_{J,\tau}$  for the lower and upper levels of the transition i.e.,  $5_{1,5}(v=0)$  and  $6_{0,6}(v_5=1)$  can be obtained from the values in Table I, which are expressed as follows:

$$A_{5,-4} = 2.7645 \times 10^{-8} \quad \text{and} \\ B_{5,-4} = -6.7914 \times 10^{-9} \quad \text{for } 5_{1,5}(v=0), \quad (3)$$

$$A_{6,-6} = 2.0943 \times 10^{-8} \quad \text{and} \\ B_{6,-6} = -1.5142 \times 10^{-9} \quad \text{for } 6_{0,6}(v_5=1). \quad (4)$$

The Stark shifts of the sublevels in levels  $5_{1,5}(v=0)$  and  $6_{0,6}(v_5=1)$  can be derived from eqs. (2), (3) and (4). Figure 4 shows the results. Since the  $\text{H}_2\text{CO}$  molecules interact with the circularly-polarized laser beam (the  $\sigma_+$  mode), the selection rules of the transition are  $\Delta M = \pm 1$  and 0. Following these rules, seventeen lines should appear. The third column of Table II shows the calculated

Table I. Molecular constants of  $\text{H}_2\text{CO}$  used for calculations.

	Ground state	Excited state ( $v_5=1$ ) <sup>c</sup>
$A$ ( $\text{cm}^{-1}$ )	9.406 171(105) <sup>a</sup>	9.227 87(34)
$B$ ( $\text{cm}^{-1}$ )	1.295 430 4 <sup>a</sup>	1.293 49(49)
$C$ ( $\text{cm}^{-1}$ )	1.134 192 7 <sup>a</sup>	1.130 61(56)
$\mu_A$ (D)	2.331 5(5) <sup>b</sup>	2.284 4(47)

<sup>a</sup>References 24, 15.

<sup>b</sup>Reference 25.

<sup>c</sup>Reference 16.

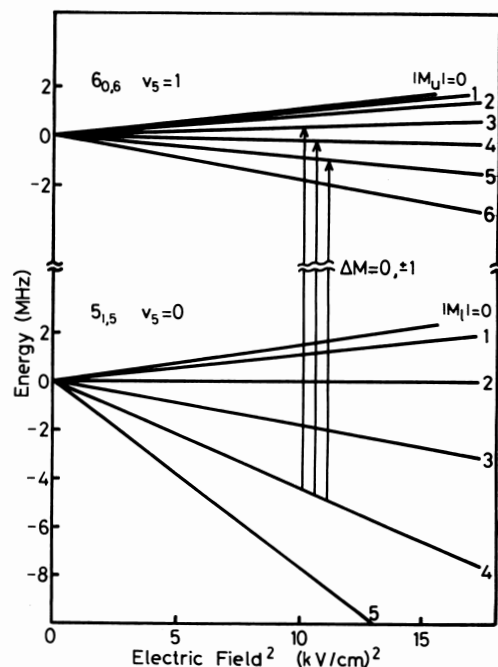


Fig. 4. Stark shifts of sublevels in  $5_{1,5}(v=0)$  and  $6_{0,6}(v_5=1)$  estimated using a rigid asymmetric rotor model.

Table II. Observed and calculated frequencies of H<sub>2</sub>CO Stark spectrum.

Line number	Assignment $ M_l - M_u $	Stark coef. (kHz/(kV/cm) <sup>2</sup> )	
		Calc. <sup>c</sup>	Obs.
0	1-1	-12.0	-12.
	1-0 etc. <sup>a</sup>	- 4.1	
15	0-0	-41.0	-59.
	0-1	-48.9	
	1-2 etc. <sup>a</sup>	-35.7	
14	2-3	35.6	45.
13	2-2	75.1	57.
12	2-3 and 3-3 <sup>b</sup>	128.	108.
11	3-4	165.	145.
10	3-3 and 3-4 <sup>b</sup>	193.	175.
9	3-3	220.	207.
8	4-4 and 3-4 <sup>b</sup>	294.	283.
7	4-5	352.	341.
6	4-4 and 4-5 <sup>b</sup>	388.	385.
5	4-4	423.	421.
4	5-5 and 4-5 <sup>b</sup>	518.	528.
3	5-6	597.	615.
2	5-5 and 5-6 <sup>b</sup>	641.	667.
1	5-5	684.	717.

<sup>a</sup>Overlapped lines.<sup>b</sup>Cross resonance components.<sup>c</sup>Calculated from the molecular constants shown in Table I.

Stark coefficients for some of these lines. The solid lines in Fig. 3 were drawn using these results, where  $M_l$  and  $M_u$  represent the magnetic quantum numbers of the lower and upper levels of the transitions, respectively.

Because no frequency reference was used in this experiment, only the separations between lines were measured, i.e., the absolute values of the Stark shifts were not determined. Therefore, the position of frequency origin had to be found by least-squares fitting so that the experimental results of all the Stark coefficients consistently agreed with that of the calculated ones.\* As a result of the fitting, it can be seen from the third and fourth columns in Table II that the experimental results agree well with the calculated ones without any contradiction in the assignment. It became clear from the results of assignment that the solid circles of Nos. 1, 3, 5, 7, 9, 11, 13 and 14 in Fig. 3 correspond to eight of the allowed transitions. The transitions between the levels of  $|M_l| < 2$  were not clearly resolved because their Stark shifts were too small, i.e., their estimated values were less than 10% of the value of the line width. Lines Nos. 0 and 15 correspond to this case, being composed of several unresolved lines as shown in Table II. In the resolved case of  $|M_l| \geq 2$ , on the other hand, the lines of the transition  $\Delta|M| = -1$  were not observed because their intensities  $I_M$ , estimated from the following formula,<sup>1)</sup> were lower than 10% of those of  $\Delta|M| = 0$  and  $+1$ .

$$I_M = I_0 \{(J+1)^2 - M^2\} \quad \text{for } M \rightarrow M \text{ and}$$

$$I_M = \frac{1}{4} I_0 \{(J \pm M + 1)(J \pm M + 2)\} \quad \text{for } M \rightarrow M \pm 1. \quad (5)$$

The lines shown by open circles in this figure correspond

to cross-resonances<sup>2,3)</sup> which are specific to saturated absorption spectroscopy. These resonances occur when two transitions inside the Doppler width share a common level. The cross-resonance appears at a frequency halfway between the two usual transitions and has an intensity proportional to the geometric mean of the two parent lines. As shown in Table II and Fig. 3, lines Nos. 2, 6, 10, 4, 8 and 12 appeared because of cross-resonance between the pairs of levels Nos. 1-3, 5-7, 9-11, 1-7, 5-11 and 9-14, respectively. These pairs share the common levels  $|M_l| = 5, 4, 3$ , and  $|M_u| = 5, 4, 3$ , respectively. This is, to the authors' knowledge, the first observation of cross-resonance in the transition  $5_{1,5}(v=0) - 6_{0,6}(v_5=1)$  in H<sub>2</sub>CO.

Higher resolution can be expected by decreasing the H<sub>2</sub>CO pressure, expanding the beam width, improving the flatness of the Stark electrodes, and so on.

Furthermore, precise direct frequency readout will be possible if a highly-stabilized frequency offset locked He-Xe laser system<sup>19)</sup> is used. Further experiments are now in progress to improve the resolution and to determine the molecular constants with higher accuracy.

#### §4. Conclusions

Precise measurements were carried out on the Stark spectrum of the vibration-rotation transition  $5_{1,5}(v=0) - 6_{0,6}(v_5=1)$  in H<sub>2</sub>CO using the intracavity saturated absorption technique. Eight of the allowed transitions were resolved and their small Stark coefficients were determined with high accuracy, the results agreeing well with the estimated values. Furthermore, the first observation of six cross-resonance lines in this transition and the result of their assignment are reported.

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\*The fitting was done considering also the cross-resonance lines mentioned later.

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