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# Measurement of the centrifugal-distortion dipole moment of $GeH_4$ using a $CO_2$ laser

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The small dipole moment of $GeH_4$ induced by centrifugal distortion of the tetrahedral structure is measured by three experimental techniques using coincidences between the $\nu_2$ $Q(11)E$ transition of $GeH_4$ and infrared $CO_2$ laser lines: (1) the Stark shift of the infrared-microwave double resonance, (2) infrared-infrared double resonance using modulation sidebands, and (3) laser Lamb-dip Stark spectroscopy. The observed results demonstrate the power of these methods in measuring small Stark shifts. From the observed shifts, Watson's centrifugal dipole moment has been determined to be $\theta_z^{xy} = (3.33 \pm 0.05) \times 10^{-5}$ D for the ground vibrational state. For the excited state the Stark shift was found to be smaller than the ground state by a factor of 9, indicating approximate cancellation between rotation- and vibration-induced dipole moments for the rotational level in the $\nu_2$ vibrational state of $GeH_4$.

## I. INTRODUCTION

Although a tetrahedral molecule is nondipolar in its equilibrium configuration, a small electric-dipole moment is produced by centrifugal distortion when the molecule rotates. The weak pure-rotational transitions caused by such a small dipole moment have recently been studied extensively by various experimental methods (see Ref. 1 for a summary).

Direct measurement of the very small Stark shift due to the distortion-induced dipole moment was reported for $CH_4$ by Ozier,[2] using a molecular-beam magnetic-resonance apparatus; this provided the first experimental evidence for the theory of distortion-induced spectra.[3-6] Subsequently, Kagann, Ozier, and Gerry[7] measured the Stark shift for $SiH_4$ by using a very sensitive microwave spectrometer.

In this paper we report our measurements of the distortion-induced dipole moment of $GeH_4$ using three techniques of laser spectroscopy. In each experiment we have made use of the coincidences between the $^{12}CO_2$ $P(26)$ and $^{13}CO_2$ $R(36)$ lines at 10.65 μm and the $Q(11)$ line of the $\nu_2$ band of $GeH_4$.

The result is analyzed by using the theoretical formula for the first-order Stark shift $\Delta E(J, \kappa)$ given by Dorney and Watson[8]:

$$\Delta E(J, \kappa) = C(J, \kappa)\theta_z^{xy} m \epsilon , \qquad (1)$$

where $C(J, \kappa)$ is a numerical factor (8.393 and −2.882 for the $E^{(2)}$ and $E^{(1)}$ levels studied in this paper), $m$ is the magnetic quantum number, $\theta_z^{xy}$ is Watson's distortion-induced dipole moment, and $\epsilon$ is the applied dc electric field.

## II. STARK SHIFT OF INFRARED-MICROWAVE DOUBLE RESONANCE

### A. Method

Infrared-microwave double-resonance spectroscopy in the laser cavity provides a very powerful means of observing weak distortion-induced rotational transitions. This method has been exploited for $CH_4$ by using the He-Ne laser,[9,10] for $SiH_4$ by using the $N_2O$ laser,[11] and for $GeH_4$ by using the $CO_2$ laser.[12] A coaxial microwave cell containing a sample at low pressure is placed inside the $CO_2$ laser cavity and high-power microwave radiation (~10 W) is applied. The high microwave electric field $E_m$ (~150 V/cm) compensates for the very small distortion-induced dipole moment $\mu$ (~$10^{-4}$ D), so that the Rabi frequency $\mu E_m/h$ is sufficiently large that the microwave transition is saturated. The frequency of the microwave radiation is modulated at 15 kHz and swept; as it passes through resonance a sharp change of the laser output power is observed. A more detailed description of this operation and explanation of the high sensitivity will be found elsewhere.[13]

In order to observe a Stark pattern, we used a coaxial cell made of $X$-band microwave waveguide in which a central Stark plate is supported by Teflon spacers in a fashion normally used for a Stark-modulation microwave spectrometer.[14] The microwave radiation at ~2356 MHz, the wavelength of which is much larger than the cutoff of the waveguide, was fed to the cell through the connection to the Stark electrode. Such a method of coupling generally has poor impedance-matching characteristics for microwave radiation, but worked effectively in this particular frequency range, corresponding to the $J=11$ $E^{(2)} \leftarrow E^{(1)}$ transition of $GeH_4$ in the ground vibrational state. An experimental configuration was used in which both the dc and microwave electric fields were perpendicular to the electric field of the infrared laser radiation.

The energy-level diagram of $GeH_4$ used in the double resonance is given in Fig. 1. The 10.65-μm $^{12}CO_2$ $P(26)$ line pumps molecules in the $E^{(1)}$ $J=11$ rotational level of the ground vibrational state. The zero-field double-resonance signal $\nu_0$ appears

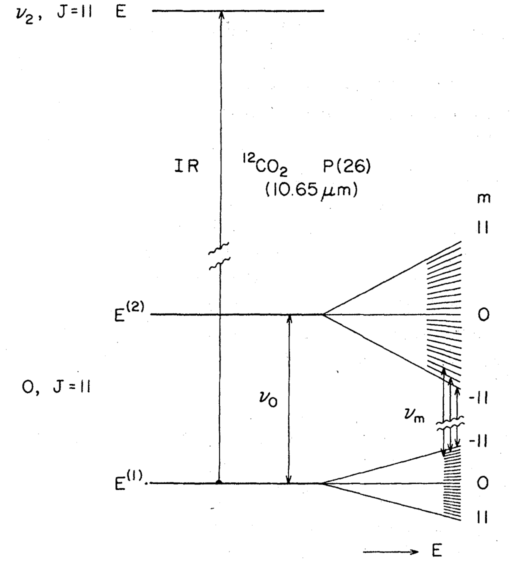

FIG. 1. Energy diagram for Stark shift of infrared-microwave double resonance.

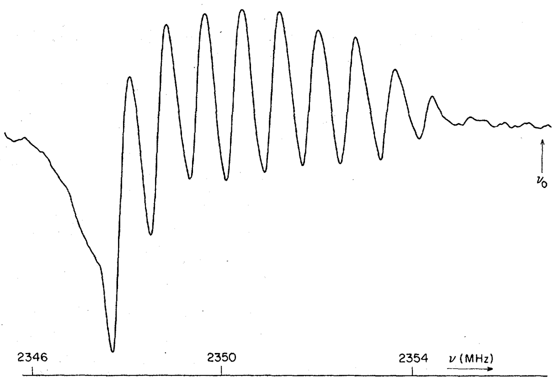

FIG. 2. An example of the observed Stark pattern for the $J = 11$ $E^{(2)} \leftarrow E^{(1)}$ double resonance of $GeH_4$. Only lower half of the symmetric first-order Stark pattern is shown. The arrow $\nu_0$ indicates zero-field position of the double resonance. Pressure of the gas is 15 mTorr and the time constant of detection is 1 sec. The $^{12}CO_2$ $P(26)$ laser line is used.

at 2356.68 MHz.[12] When the dc electric field is applied, both the $E^{(2)}$ and $E^{(1)}$ levels with double parity[15] show a first-order Stark shift,[16] and the resonance is split into a multiplet.

### B. Results

An example of the observed Stark pattern is given in Fig. 2. This multiplet structure represents the lower half (corresponding to minus $m$) of the total first-order Stark pattern, which is symmetric about the zero-field frequency $\nu_0$. The shift and the number of the Stark components establish that the assignment of the resonance is $J = 11$. The relative intensities of the individual $m$ components are expected to be proportional to the product of the radio-frequency transition moment ($\Delta m = 0$), which is proportional to $m^2$, and of the infrared transition moment ($\Delta m = \pm 1$), which is proportional to $(J+1)^2 - m^2$. Although various saturation effects and the variation of laser matching produce complications, the observed relative intensity can be explained semiquantitatively with this simple picture. The large signal-to-noise ratio observed in Fig. 2 demonstrates the high sensitivity of the double-resonance method.

The $m$ components were further resolved at the cost of signal-to-noise ratio by increasing the dc electric field $\epsilon$, allowing us to measure them individually. They showed consistent linear Stark shifts. Observed frequencies of the Stark components and the values of distortion-induced dipole moments are listed in Table I. From these measurements the dipole moment was determined to be

$$\theta_z^{xy} = (3.30 \pm 0.09) \times 10^{-5}\ \mathrm{D}.$$

TABLE I. Stark-shifted frequencies observed by infrared-microwave double resonance.[a]

| | Higher-frequency $m$ components | | | Lower-frequency $m$ components | | |
|---|---|---|---|---|---|---|
| $m$ | $\nu_{rf}$ (MHz) | $\Delta\nu$ (MHz)[b] | $\theta_z^{xy}$ ($10^{-5}$ D) | $\nu_{rf}$ (MHz) | $\Delta\nu$ (MHz)[b] | $\theta_z^{xy}$ ($10^{-5}$ D) |
| 11 | 2366.32 | +9.62 | 3.30 | 2347.09 | −9.61 | 3.30 |
| 10 | 2365.50 | +8.80 | 3.32 | 2347.97 | −8.73 | 3.30 |
| 9 | 2364.59 | +7.89 | 3.31 | 2348.81 | −7.89 | 3.31 |
| 8 | 2363.69 | +6.99 | 3.30 | 2349.69 | −7.01 | 3.31 |
| 7 | 2362.82 | +6.12 | 3.30 | 2350.58 | −6.12 | 3.30 |
| 6 | 2361.93 | +5.23 | 3.29 | 2351.49 | −5.21 | 3.28 |
| 5 | 2361.06 | +4.36 | 3.29 | 2352.32 | −4.38 | 3.31 |
| 4 | 2360.22 | +3.52 | 3.32 | 2353.14 | −3.56 | 3.36 |
| 3 | 2359.35 | +2.65 | 3.34 | 2354.05 | −2.65 | 3.34 |

[a] The applied electric field was 4.665 kV/cm, and the $^{12}CO_2$ $P(26)$ line was used.

[b] A center frequency of 2356.68 MHz was used.

## III. INFRARED DOUBLE RESONANCE USING MODULATION SIDEBANDS

### A. Method

As originally indicated by Brewer[17,18] and Luntz and Brewer,[19] the infrared-infrared double resonance between split $m$ components is a useful technique for accurately measuring first-order Stark shifts. This is because the equal spacing between many $m$ components yields simple double-resonance spectra. In addition to its high resolution and high sensitivity, this method has the special advantage of giving separate shifts for the upper and lower levels of the transition. This characteristic is particularly important in our application to $GeH_4$ because we do not have sufficient theoretical understanding of the Stark shift in the vibrationally excited state. This point will be discussed further in Sec. III C.

A CdTe electro-optic modulator, driven at a single radio frequency $\nu$, was used to create the sidebands ($\nu_L \pm \nu$) needed for the infrared-infrared double-resonance experiment using a single $CO_2$ laser. Either the 10.65-$\mu$m $P(26)$ $^{12}CO_2$ line or the 10.65-$\mu$m $R(36)$ $^{13}CO_2$ line was used. The modulated infrared radiation was passed through a Stark cell containing low-pressure (1–10 mTorr) $GeH_4$ and was detected. The Stark electrodes were separated by 1-mm quartz spacers, and a dc field up to 7 kV and an ac modulation field at 10 kHz were applied. The double-resonance signals were observed when $\nu/2$ or $\nu$ equaled the spacing between $m$ levels in the upper or the lower state. More details of the apparatus and operation have been discussed elsewhere.[20]

### B. Results

Representative double-resonance signals corresponding to the Stark shift in the ground state are shown in Fig. 3. The signal marked 0 is the zero-field level crossing signal.[21] The double-resonance signal marked $2\nu$ is caused by the two sidebands $\nu_L \pm \nu$ ($\nu = 1.2290$ MHz). In the upper trace in Fig. 3, the angular settings of the linear polarizer $\theta$ and of the retardation axis of the waveplate $\phi$ were adjusted such that all of the radiation reaching the Stark cell was concentrated at the two sideband frequencies and polarized perpendicular to the dc electric field. The resonance condition for the $2\nu$ signal is

$$2C(J,\kappa)\theta_z^{xy}\epsilon = 2\nu . \tag{2}$$

In the lower trace, the waveplate orientation $\phi$ is shifted from zero so that now the laser radiation with frequency $\nu_L$ reaches the detector and the $\nu$ signal appears. The resonance condition for this signal is

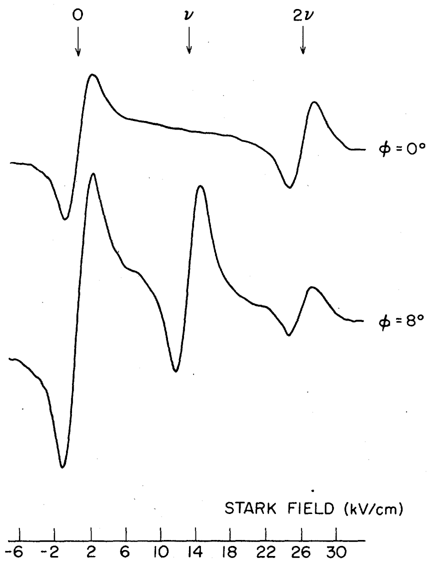

FIG. 3. Examples of infrared-infrared double-resonance signals using modulation sidebands $\nu_L \pm \nu$ with $\nu = 1.2290$ MHz. The signals marked 0 are caused by the zero-field level crossing. The signals marked $2\nu$ are caused by the two side bands $\nu_L \pm \nu$, while the signal marked $\nu$ is caused by $\nu_L$ and $\nu_L \pm \nu$. The pressure of the gas is 5 mTorr and the time constant of detection is 3 sec. The $^{12}CO_2\,P(26)$ laser line is used. The two traces differ in the angular setting $\phi$ of the waveplate in the electro-optic modulator.

$$2C(J,\kappa)\theta_z^{xy}\epsilon = \nu . \tag{3}$$

The observed resonance fields are given in Table II together with the effective Stark coefficient $(C\theta)_{\text{eff}}$. By using the numerical factors given by Dorney and Watson,[8] the dipole moments for the vibrational ground state were determined to be

$$(3.33 \pm 0.04)\times 10^{-5}\ \text{D}$$

and

$$(3.33 \pm 0.05)\times 10^{-5}\ \text{D},$$

respectively, by using the $^{12}CO_2$ $P(26)$ line and the $^{13}CO_2$ $R(36)$ line. We believe these values are more accurate than the value given earlier because the plate spacing was calibrated by double-resonance studies of $CH_3F$.[20]

### C. Resonance in the excited state

Using a lower value of radio frequency (0.5300 MHz) and applying a higher dc electric field, we could observe double-resonance signals corresponding to the Stark shift in the excited vibrational state. These are shown in Fig. 4, together with the ground-state double-resonance signals for the

TABLE II. Observed resonance electric fields for infrared-infrared double resonance.[a]

| | $^{12}CO_2$ $P(26)$ | | | $^{13}CO_2$ $R(36)$ | | |
|---|---|---|---|---|---|---|
| | $\nu$ | $2\nu$ | $10^4(C\theta)_{\rm eff}$ (D) | $\nu$ | $2\nu$ | $10^4(C\theta)_{\rm eff}$ (D) |
| $\nu = 1.2290$ MHz (ground state) | $1.27 \pm 0.01_5$ | $2.55 \pm 0.02$ | $0.960 \pm 0.012$ | $1.26_5 \pm 0.01_5$ | $2.56 \pm 0.02$ | $0.960 \pm 0.015$ |
| $\nu = 0.5300$ MHz (excited state) | $4.95 \pm 0.10$ | ... | $0.106_5 \pm 0.002$ | $5.00 \pm 0.10$ | ... | $0.105_5 \pm 0.002$ |

[a] Entries in this table under the headings $\nu$ and $2\nu$ are the voltages (in kV) applied to the Stark electrodes at resonance. The corresponding Stark field (in kV/cm) may be obtained by dividing by the effective electrode gap ($0.1000_6 \pm 0.0001_5$ cm).

lower modulation frequency. The observed resonance fields and the effective value of Stark-shift coefficient $(C\theta)_{\rm eff}$ are summarized in Table II. It is seen that the Stark shift in the excited state is about 10 times smaller than that in the ground state. The assignment of the rotational level in the excited state cannot uniquely be made from the available infrared spectrum,[22] but it is definitely $J = 11$ and most likely $E^{(2)}$. The fact that the two laser lines [$^{13}CO_2$ $R(36)$ at 938.77765 cm$^{-1}$ (Ref. 23) and $^{12}CO_2$ $P(26)$ at 938.688 26 cm$^{-1}$ (Ref. 24)] are separated by 2680 MHz and yet still show the same Stark pattern, indicates that these two laser lines are in coincidence with the same vibration-rotation transition of different isotopic forms of $GeH_4$.

The Stark shift in the excited state due to the rotation-induced dipole moment should be similar to that in the ground state if the rotational level is $E^{(1)}$ $[C(J,\kappa) = -2.882]$ and larger if it is $E^{(2)}$ $[C(J,\kappa) = 8.393]$. The observed smaller Stark shift indicates that the vibration-induced dipole moment must be cancelling the rotation-induced dipole moment. Such a dipole moment was observed by Uehara, Sakurai, and Shimoda[24] and by Luntz and Brewer[19] to be 0.02 D for the $\nu_3$ state of $CH_4$. Although a vibration-induced dipole moment does not exist for the pure $\nu_2$ state from symmetry, the Coriolis mixing between the $\nu_2$ and $\nu_4$ states will cause a small vibration-induced dipole moment in the $\nu_2$ state of $GeH_4$.

## IV. STARK LAMB-DIP SPECTROSCOPY

### A. Method

Doppler-free laser Stark spectroscopy can also be performed by using the technique of inverse Lamb dips.[25,26] Such a technique was first applied to $NH_2D$,[27] and since then to many other molecules: $NH_3$,[28,29] $CH_3F$,[29,30] $SiH_4$,[1,31] $H_2CO$,[29,32] NO,[33] HDCO,[34] and HNO.[35]

The $CO_2$-laser radiation is passed through a Stark cell, reflected by a mirror so that the molecules experience radiation fields traveling in opposite directions, and detected. A dc electric field up to 70 kV/cm is applied to the Stark plates. More details of the apparatus are given in Ref. 30.

Although equally Doppler-free, the Stark Lamb-dip method has two difficulties in measuring the small dipole moment of $GeH_4$ which do not exist in the infrared double-resonance method described in the previous section:

(1) The observed Stark shift is a combination of level shifts from both ground and excited states. We attempted to separate these two shifts by using two optical configurations of the laser electric field $E_L$ and the dc electric field $\epsilon$: $E_L \parallel \epsilon$ gives $\Delta m = 0$ transitions and $E_L \perp \epsilon$ gives $\Delta m = \pm 1$ transitions. Unfortunately, since the Stark shift in the excited state is much smaller than that in the ground state, the difference between them was within the experimental uncertainty. Therefore the two shifts could not be separated from this ex-

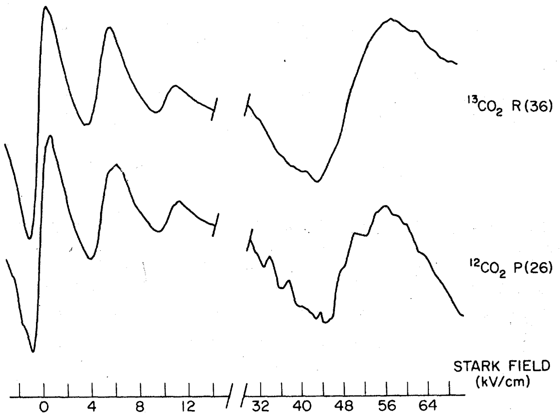

FIG. 4. Infrared-infrared double-resonance signals using modulation sidebands with $\nu = 0.5300$ MHz. The signals at the lower dc electric field correspond to double resonance in the ground vibrational state, while the signals at the higher dc field correspond to double resonance in the excited vibrational state. The lower trace is taken using the $^{12}CO_2$ $P(26)$ laser line while the upper trace is taken using the $^{13}CO_2$ $R(36)$ laser line. The pressure of the gas is ~ 3 mTorr and the time constant of detection is 3 sec.

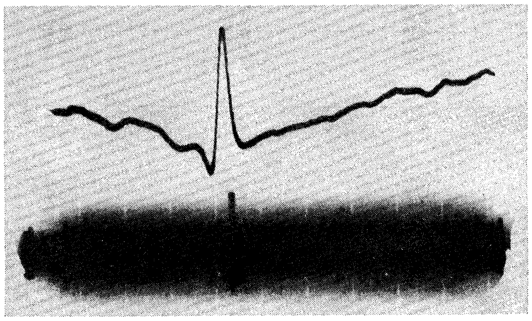

FIG. 5. An example of oscilloscope traces of the field-free $GeH_4$ Lamb dip and the beat marker of two laser lines, one used to monitor the dip and the other stabilized at the center. This was used to determine the difference between the center of the $CO_2$ gain profile and that of the molecular absorption. The pressure of the sample is ~ 3 mTorr and the time constant of detection is 1 sec.

periment alone.

(2) In the absence of an externally applied frequency standard (such as the rf modulation frequency in the infrared double-resonance method), it was necessary to measure the frequency difference between the center of the $GeH_4$ transition and that of the $CO_2$ laser. To do this, we used two $CO_2$ lasers, one swept around the center of the $GeH_4$ Lamb dip and the other tuned to the center of the laser-gain profile, and monitored their beat signal by means of a PbSnTe infrared detector and an all-wave receiver. Figure 5 shows an example of the $GeH_4$ Lamb dip and the frequency marker due to the beat. The frequency difference was measured to be

$$\nu(\mathrm{GeH_4}) - \nu(^{12}\mathrm{CO_2}\ P(26)) = -23.0\ \mathrm{MHz}$$

and

$$\nu(\mathrm{GeH_4}) - \nu(^{13}\mathrm{CO_2}\ R(36)) = 3.0\ \mathrm{MHz}.$$

The accuracy (±2 MHz) of the centering of the $CO_2$ laser line to the gain profile limited the accuracy of Stark shift measured by this method. This would be improved if better frequency stabilization of the laser were made by the method of Freed and Javan.[36]

### B. Results

An example of the Stark Lamb-dip pattern of $GeH_4$ is shown in Fig. 6. The first three dips, corresponding to $m = 11$, 10, and 9, were observed for the $E_L \parallel \epsilon$ configuration. The symmetric shape of the Lamb dips arises from use of the $2f$ detection mode of the phase-sensitive detector. Weak collision-induced center dips[29] should also be noted.

An average of four measurements gave the following resonance fields:

$$\epsilon = 41.86\ \mathrm{kV/cm} \quad \text{for } m = 11,$$

$$\epsilon = 46.81\ \mathrm{kV/cm} \quad \text{for } m = 10,$$

and

$$\epsilon = 50.89\ \mathrm{kV/cm} \quad \text{for } m = 9.$$

The error in the resonance field $\epsilon$ is ~ ±10%, arising from the ±2 MHz uncertainty in the laser frequency. These values give

$$(C\theta)_{\mathrm{eff}} + 2.882\theta_z^{xy} = (9.89 \pm 1) \times 10^{-5}\ \mathrm{D}.$$

The only information which this formula gives beyond what has already been obtained by the method of infrared-infrared double resonance is that $(C\theta)_{\mathrm{eff}}$ for the excited state is probably positive, that is, opposite in sign to that for the ground state.

## V. DISCUSSION

In summary, three methods of laser spectroscopy have been applied to the measurement of very small Stark shifts due to the distortion-induced dipole moment of $GeH_4$. These methods should also be useful for observing small Stark effects such as those due to the polarizability anisotropy of nondipolar molecules, to vibration-induced dipole moments, or to small dipole moments arising from partial deuteration of otherwise nonpolar hydrides.

Each of the methods has its strength and its weakness. The infrared-rf double-resonance method gives very clear rotational assignments and accurate values of the dipole moment, but its applicability is limited because it requires a pair of

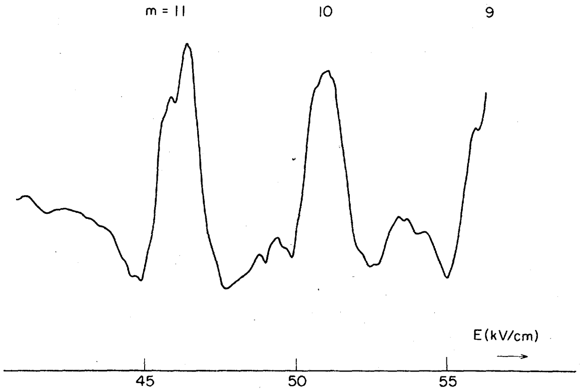

FIG. 6. An example of laser Stark Lamb-dip of $GeH_4$ observed by using the $P(26)$ $CO_2$ line. The pressure of the gas is ~ 10 mTorr and the time constant of detection is 3 sec.

levels split by an interval which lies in the rf (or microwave) region. The infrared-infrared double-resonance method gives the most accurate value of the dipole moment and clear separation of the contributions from ground and excited states. This latter point is particularly useful for studying "anomalous" Stark effects such as those in tetrahedral molecules in which there is a large difference between dipole moments in the ground and excited states. However, this method is not particularly useful for making rotational assignments, since individual Stark components are not resolved for first-order Stark effects. The laser Stark Lamb-dip method is the easiest to apply and to use in making rotational assignments. However, the accuracy is limited by the facts that the Stark shifts in the upper and lower states are not separated and that the frequency stability of the laser is very critical for accurate measurement of small Stark shifts.

The observed value of $\theta_z^{xy} = (3.33 \pm 0.05) \times 10^{-5}$ D is in excellent agreement with the value ($3.4 \times 10^{-5}$ D) determined by Ozier and Rosenberg[37] from the intensity of the far-infrared spectrum. The dipole moment is considerably higher than the value[2] for $CH_4$ ($2.41 \times 10^{-5}$ D) but is close to the value[7] for $SiH_4$ ($3.34 \times 10^{-5}$ D). It has been already noticed that $SiH_4$ and $GeH_4$ are similar to each other and different from $CH_4$ in structure (the rotational constants $B_0$ are 5.245 cm$^{-1}$,[38] 2.8574 cm$^{-1}$,[39] and 2.696 cm$^{-1}$,[37] respectively, for $CH_4$, $SiH_4$, and $GeH_4$) and in mechanical properties (the quartic tensor distortion constant $D_t = 132.94$ kHz,[40] 74.75 kHz,[41] and 67.77 kHz[12]). The present result confirms this trend also with regard to electric properties.

The most unexpected, and therefore the most interesting, result of this work is that the effective dipole moment in the excited vibrational state is so small. We observed a similar effect in the laser Lamb-dip spectrum of $SiH_4$.[31,1] Whether the subtraction of the rotation-induced dipole moment and the vibration-induced dipole moment in such examples occurs in general remains to be studied experimentally and theoretically.

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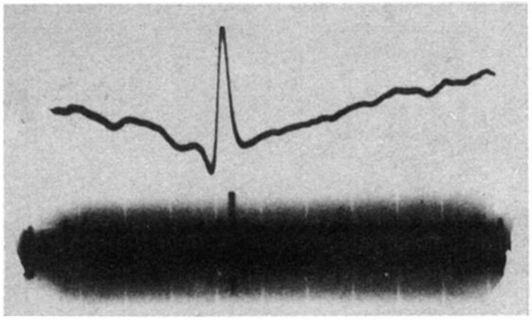

FIG. 5. An example of oscilloscope traces of the field-free $GeH_4$ Lamb dip and the beat marker of two laser lines, one used to monitor the dip and the other stabilized at the center. This was used to determine the difference between the center of the $CO_2$ gain profile and that of the molecular absorption. The pressure of the sample is ~ 3 mTorr and the time constant of detection is 1 sec.