Observation of second-order Stark effects in silane, SiH₄

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The Stark effect on rovibrational transitions of the tetrahedral molecule silane has been studied by laser Stark spectroscopy, i.e., by applying dc fields of up to 65 kV/cm and monitoring the absorption of fixed frequency ir laser lines. The coincidences observed occur between the ν₁ fundamental of SiH₄ and N₂O laser lines. Using the inverse Lamb dip technique single M components of three high J transitions could be resolved, and two of these have been identified by rf–ir double resonance. In both cases the Stark shift is due to the second-order Stark mixing of A₁ with A₂ rotational levels. The analysis of the Stark effects is consistent with the ground state centrifugal distortion moment θ₂ = 3.34 × 10⁻¹⁰ D measured previously by Kagann, Ozier, and Gerry. Experiments to measure the frequency offset Δν = ν₃₂ − ν₃₁ of the molecular absorption lines from the nearest laser line have also been performed, using the beat between two N₂O lasers. Direct evidence of the second-order Stark shift has been obtained by observing Stark Lamb dips with a continuously tuned laser.

I. INTRODUCTION

Tetrahedral molecules attract increasing interest in the field of rotational spectroscopy, since the very small dipole moment generated in the ground vibrational state by centrifugal distortion has been studied by refined spectroscopic techniques (see Ref. 1 for a review of this field). A vibration-induced dipole moment is also present in the first excited state of infrared-active fundamentals, but this effect has been the subject of fewer experiments.

Ozier was able to measure the centrifugal distortion-induced dipole moment of CH₄ (denoted θ₂ by Watson) by observing the Stark effect on a molecular beam magnetic resonance spectrum. This work provided the first experimental confirmation of the theory of the centrifugal distortion-induced dipole moment. Subsequently, Kagann, Ozier, and Gerry measured θ₂ for SiH₄ by observing the Stark effect on a pure rotation Q branch transition in a high-sensitivity microwave spectrometer, while Kreiner, Orr, Andersen, and Oka investigated θ₂ for GeH₄ using three different laser techniques.

For all three molecules θ₂ is of the order 10⁻⁶ D. These small dipole moments give rise to Stark shifts which are correspondingly small. Attention has therefore centered on the levels whose rovibrational symmetry in T₄ is E because these levels have a first-order Stark effect. Watson has in fact shown that the E levels of T₄ molecules are the only rovibrational levels of any nonpolar molecule to exhibit a first-order Stark effect. Although Uehara has reported an indication of a second-order effect for the excited state of CH₄, it has generally been thought that the splitting of the M components of the second-order Stark shifts in the ground state levels with symmetry A₁, A₂, F₁, or F₂ in T₄ would be too small to be observed in most experiments.

This paper is concerned with the interpretation of the laser Stark spectrum of SiH₄. In the extensive infrared vibration–rotation spectrum of SiH₄ in the 10 μm region, due to the Coriolis-coupled ν₁ and ν₄ bands, there are several near coincidences with N₂O and CO₂ laser lines. Two silane lines which are near coincident with N₂O laser lines show strong resolvable laser Stark spectra; in each case the Stark shift is caused by the second-order Stark effect on an A₁ or an A₂ rovibrational level.

II. STARK LAMB DIP SPECTROSCOPY

A. Experimental method

The technique, which has now been applied to many molecules (see Ref. 9), consists of tuning the molecular absorption line into coincidence with a fixed-frequency laser line by the application of a dc electric field. In favorable circumstances several M components can be swept across the laser line.

A schematic diagram of the apparatus is shown in Fig. 1. Further details are given elsewhere. The laser consists of a 2.5 m gain cell, with a concave mirror mounted on a piezo crystal at one end and a plane grating blazed at 10 μm at the other. The laser was stabilized to the center of the gain profile; the laser frequency varied by up to ± 2 MHz in different experiments. The direction of polarization could be changed through 90° by using a mirror combination.

The Stark electrodes consist of two polished steel plates, 40 cm long and separated by 1 mm quartz spacers. dc voltage of up to 6000 V was applied to one plate. A ramp voltage of opposite sign, modulated at 2 kHz by

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up to 400 V peak to peak, was connected to the other electrode.

In order to observe Lamb dips the beam is reflected at the end of the Stark cell. Slight tilting of the mirror prevents the reflected beam from disturbing the laser. The frequency resolution is about 1 MHz, mainly limited by laser instabilities.

The absorption signal is monitored by a Pb–Sn–Te detector and fed into a phase-sensitive detector. Detection was used because of its superior signal-to-noise ratio. As a result the second derivative of the line shape was observed.

B. Frequency offset measurements

In the conventional laser Stark experiment the spectrum gives the pattern of $M$ components in the form of absorption plotted against electric field strength. The frequency scale of this pattern is not obtained and it must be established in separate experiments.

We carried out frequency measurements on the component of highest $M$ for the two laser Stark spectra discussed below. Two N$_2$O lasers oscillating on the same line were used. One was locked to its center frequency, serving as a fixed-frequency local oscillator (reference laser), while the other was used to observe the laser Stark spectrum of SiH$_4$ (signal laser). The signal laser was set to different frequencies within its gain profile by tuning the cavity length. The frequency offset between signal and reference lasers was measured by directing out-coupled beams from both lasers to a second detector and monitoring the beat on a spectrum analyzer: the total tuning range was about ±22 MHz from the reference laser. A similar experiment with CO$_2$ lasers has been described for GeH$_4$. 13

By measuring the electric field needed to bring the component of highest $M$ into resonance for each setting of the signal laser, we obtain the Stark effect of this component in the form of frequency shift as a function of electric field strength.

C. Continuous laser scanning

In an alternative experiment, the frequency of the laser was scanned over the Stark split lines by applying a sawtooth voltage to the piezoelectric crystal on which the end mirror is mounted. The maximum range of scanning was limited to 67 MHz determined by the longitudinal mode separation for the 225 cm laser cavity. The linearity of the scanning and the deviation from it were known from the previous experiment, thus enabling us to measure the laser frequency approximately. By using this method for the $R(18)$ transition, we could obtain the splitting pattern as a function of laser frequency. The electric field of the laser was parallel to that of the Stark field leading to observation of $\Delta M=0$ transitions.

D. Results

Laser Stark spectra were observed with three N$_2$O laser lines, $P(25)$, $R(16)$, and $R(24)$. The spectrum associated with $P(25)$ was weak and has not been investigated in detail. Preliminary reports of the spectra associated with $R(16)$ and $R(24)$ have been given earlier. 1,12,13

Figure 2 shows a sequence of $M$ components obtained with the N$_2$O $R(16)$ line. In Fig. 2(a) the laser polarization is parallel to the electric field, giving rise to $\Delta M = 0$ transitions, while in Fig. 2(b) the laser polarization is perpendicular to the electric field, giving rise to $\Delta M = \pm 1$ transitions. The two traces are very similar. Repeated measurements of both types of transition indicated that within the accuracy of the laser stability they occur at the same electric field strengths. The same is true of the spectrum obtained with the N$_2$O $R(24)$ line. This led us to the conclusion that the Stark splitting in the upper state is extremely small, and that the Stark effect arises almost entirely from the ground state. Averaged measurements for the $\Delta M = 0$ transitions of both spectra are given in Table I. The plate spacing needed for the calculation of electric field was
determined sufficiently accurately by measuring the quartz spacers.

The small lines visible in Fig. 2 between the Lamb dips of the $M$ components are believed to be the collision-induced center dips.\textsuperscript{15}

The results of the frequency offset measurements are shown graphically in Fig. 3. It is clear that in both cases the Stark effect is approximately linear with applied electric field over the frequency range studied.

Figure 4 indicates the Stark pattern observed by a

| TABLE I. Observed and calculated resonance fields in the laser Stark spectrum of SiH$_4$.\textsuperscript{a} |
|-----------------|-----------------|-----------------|-----------------|
| $\nu_4$ R(16) laser line | $\nu_4$ R(24) laser line |
| $|M| \quad \epsilon_{\text{calc}}$(kV cm$^{-1}$) | $|M| \quad \epsilon_{\text{calc}}$(kV cm$^{-1}$) |
| 16 | 30.15 | 30.19 | 21 | 34.60 | 34.64 |
| 17 | 31.98 | 31.96 | 20 | 35.36 | 35.37 |
| 18 | 33.76 | 33.76 | 19 | 35.28 | 35.28 |
| 15 | 36.19 | 36.22 | 16 | 40.42 | 40.41 |
| 14 | 38.81 | 38.81 | 17 | 42.74 | 42.79 |
| 13 | 41.42 | 41.40 | 16 | 45.45 | 45.46 |
| 12 | 45.23 | 45.26 | 15 | 48.49 | 48.49 |
| 10 | 49.16 | 49.40 | 14 | 51.11 | 51.95 |
| 16 | 54.05 | 54.34 | 13 | 56.25 | 55.95 |
| 9 | 66.23 | 66.27 | 12 | 60.71 | 60.62 |

Assumed parameters\textsuperscript{a}

\[ \beta^2 = 3.34 \times 10^{-4} \text{ D} \quad \frac{C(U, e)}{\text{D}} = 17.005 \quad \frac{\text{MHz}}{\text{kV cm}} = 20.285 \]

Derived parameter\textsuperscript{b}

\[ \nu_4 - \nu_5 = 25.4 \pm 1 \text{ MHz} \quad \nu_5 = -66.5 \pm 1 \text{ MHz} \]

\textsuperscript{a}$\nu_4$ is obtained from the second-order Stark calculations described in Sec. III. C of text. The upper state Stark effect is assumed to be negligible.

\textsuperscript{b}$\nu_5$ is the zero-field splitting between the $A_1$ and $A_2$ levels.

\textsuperscript{c}$\nu_4 - \nu_5$ is the difference between the molecular transition frequency and the laser frequency. The sign is derived from the frequency offset experiments shown in Fig. 2.
They assigned the spectrum up to \( J' = 12 \) and achieved a partial fit of the transitions using Susskind's Hamiltonian. Later this work was extended to include a recording of the \( \nu_2 \) band, and by considering the Coriolis-coupled \( \nu_2 \) and \( \nu_3 \) bands together a good fit of the spectrum has been obtained up to \( J' = 20 \). Thus it is now possible to use the infrared spectrum with confidence as an aid to assignment of the laser Stark spectra. Throughout we use the notation of the infrared study, for the ground state energy levels this is the notation used by most of the recent papers.

The pattern of \( M \) components as a function of electric field strength shows that the lower state \( J \) values of the two \( \text{SiH}_4 \) infrared transitions involved are 18 and 21, respectively, as assigned in Table I. [It should be emphasized that the product \( \epsilon m \), where \( \epsilon \) is the resonance electric field strength, is expected to be a constant whether the Stark shift is first or second order. This is a consequence of the form of the Stark matrix element connecting different rovibrational levels,

\[
H_{\text{Stark}} = C(J, \kappa) \epsilon^2 m \epsilon,
\]

where \( C(J, \kappa) \) is the Stark coefficient of Dorney and Watson. If each \( M \) component in turn must be shifted by the same constant amount to bring it into coincidence with the laser line, it is clear the \( H_{\text{Stark}} \) must have the same value at resonance for all \( M \) values, regardless of whether it is a diagonal matrix element as in the first-order case or an off-diagonal matrix element as in the second-order case. The effect of Stark matrix elements between different \( J \) levels which do not have such simple \( M \) dependence is negligible in the present case.]

It was recognized at an early stage that the only transitions with these \( J \) values in this region of the infrared, 952.518 cm\(^{-1}\) for the \( \text{N}_2 \text{O} \ R(16) \) line and 958.603 cm\(^{-1}\) for the \( \text{N}_2 \text{O} \ R(24) \) line, are the strongly allowed \( R \) transitions of the \( \text{SiH}_4 \nu_4 \) band.

The first assignment suggested for the \( \text{N}_2 \text{O} \ R(16) \) coincidence was \( \nu_4 \ R' (18), E^{(3)} - E^{(3)} \) of \( \text{SiH}_4 \), but a double-resonance search for the connected ground-state transition \( J=18, E^{(3)} - E^{(3)} \) was unsuccessful. Further-more, the detailed infrared analysis showed that none of the \( E - E \) components of \( R' (18) \) lies near the laser line. Instead, the infrared analysis suggested that the transitions most likely to coincide with the laser line are the three lines \( \nu_4 \ R'(18), A_2^{(2)} - A_2^{(1)}, F_2^{(0)} - F_2^{(0)} \) and \( F_2^{(0)} - F_2^{(0)} \). These were calculated at 952.534 cm\(^{-1}\), 952.571 cm\(^{-1}\), and 952.615 cm\(^{-1}\), respectively, and were observed as a single unresolved peak at 952.530 cm\(^{-1}\) [blended also with two strong \( R' (17) \) lines]. These possibilities could not be distinguished without further experiments.

In order to assign the \( \text{N}_2 \text{O} \ R(24) \) coincidence the theoretical prediction from the infrared constants was extended to \( J' = 22 \), enabling the \( \nu_4 \ R'(20) \) and \( R'(21) \) transitions of \( \text{SiH}_4 \) to be calculated. The prediction was successful in that virtually all the strong infrared lines in the region 956 cm\(^{-1}\) to 967 cm\(^{-1}\) which were previously unassigned could be attributed to \( R'(20) \) and \( R'(21) \) transitions, the predictions falling mainly within about 0.05-0.08 cm\(^{-1}\) from the observed lines. The \( R'(21) \) transition closest to the laser line appeared to be \( \nu_4 \ R'(21), A_2^{(2)} - A_3^{(3)} \) of \( \text{SiH}_4 \), calculated at 958.552 cm\(^{-1}\) and observed at 958.596 cm\(^{-1}\).

B. Confirmation by rf-ir double resonance

The rf-ir double resonance technique consists in placing a coaxial waveguide absorption cell inside the laser cavity. If a high-power rf pump is applied to a rotational transition sharing a common level with an infrared transition within the Doppler profile of the laser, the laser acts as a monitor for the change in population density in the pumped level. Therefore, by sweeping the radio frequency, rotational transitions can be found by recording the laser output. We also obtained an indication of the Stark effect on the double resonance signals by applying a dc electric field to the coaxial cell, although the effect cannot be interpreted quantitatively because of inhomogeneity in the field.

For \( \text{SiH}_4 \) the energy level splittings in the ground vibrational state are known with considerable precision from the microwave work of Ozier, Lees, and Gerry. Their paper tabulates these splittings up to \( J=20 \), with
was observed for GeH₄. Instead we observe that the signal broadens and moves to higher frequency, which is consistent with the second-order Stark effect (see Fig. 5).

Connected with the N₂O R(24) laser line we observed a double resonance signal at 859.01 ± 0.1 MHz. This is roughly one-tenth the intensity of the 993 MHz line. The 859 MHz line is assigned as the ground-state interval J = 21, A₁ (2) — A₁ (0), for which we calculate 859.09 MHz from the constants of Ozier et al. This confirms the assignment of the infrared transition suggested from the high-resolution infrared spectrum. The energy level scheme is shown in Fig. 5(b).

C. Stark effect calculations

Quantitative calculations of the Stark effect on the ground-state levels J = 18, A₁ (2) and J = 21, A₁ (2) were carried out. In each case the Stark coefficient C(J, k) for mixing of the A₁ level with the nearby A₁ (2) level of the same J was computed by the method of Dorney and Watson, using the appropriate eigenvector elements of a diagonalization of the ground-state rotational Hamiltonian in a (Jhₐm) basis of symmetric rotor functions referred to one of the Sₐ axes of the molecule. We found that for the J = 18 A₁ — A₁ pair |C(J, k)| = 17.605, while for the J = 21 A₁ — A₁ pair |C(J, k)| = 20.285. Dorney and Watson noted that for the closely spaced bunches of levels at the upper limit of the energy manifolds, the C(J, k) approach the value of J with increasing J.

The Stark effects were then calculated by solving the 2x2 Stark matrices as a function of M and e. The 993 MHz line was calculated with 0.5 W rf power and 30 ms time constant, whereas for the two double resonances near 10 GHz an rf power greater than 10 W was required. We therefore assign the infrared transition as ν₄ R′(18), A₁ (2) — A₁ (0) of SiH₄, and we attribute the laser Stark spectrum as arising from the second-order Stark mixing of the ground-state levels J = 18, A₁ (2), and A₁ (0). The energy level scheme is shown in Fig. 5(a). The weak double resonance lines observed around 10 GHz are probably due to accidental near coincidences with other infrared transitions; the 10.293.78 MHz line identified as J = 18, F₂ (2) — F₁ (0) might possibly be associated with ν₄ R′(18), F₂ (2) — F₁ (1) or 28SiH₄ in 4.7% natural abundance.

The Stark effect on the 993 MHz double resonance line is shown in Fig. 6. For a first-order Stark effect a symmetrical splitting of the line would be expected, as uncertainties of less than 0.1 MHz even at the highest J values. It follows that definite assignments can be made from double resonances which involve these ground state splittings. The splittings in the ν₄ = 1 and ν₄ = 1 states are, however, known with much less accuracy, perhaps to ±100 MHz at best.

Connected to the N₂O R(16) laser line an extremely strong rf field was detected at 993.02 ± 0.1 MHz. This is identified as the ground-state interval J = 18, A₁ (2) — A₁ (0), which may be compared with 993.062 MHz calculated from the microwave work. Although two much weaker double resonances associated with this laser line were detected earlier, one of which was identified by Ozier et al. as the ground-state interval J = 18, F₂ (2) — F₁ (3), we believe that the 993 MHz transition must be associated with the coincidence which gives rise to the laser Stark spectrum because of its intensity. For example, the 993 MHz line could be detected with 0.5 W rf power and 30 ms time constant, whereas for the two double resonances near 10 GHz an rf power greater than 10 W was required. We therefore assign the infrared transition as ν₄ R′(18), A₁ (2) — A₁ (0) of SiH₄, and we attribute the laser Stark spectrum as arising from the second-order Stark mixing of the ground-state levels J = 18, A₁ (2), and A₁ (0). The energy level scheme is shown in Fig. 5(a). The weak double resonance lines observed around 10 GHz are probably due to accidental near coincidences with other infrared transitions; the 10.293.78 MHz line identified as J = 18, F₂ (2) — F₁ (0) might possibly be associated with ν₄ R′(18), F₂ (2) — F₁ (1) or 28SiH₄ in 4.7% natural abundance.

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periment described earlier, confirms the presence of a second-order Stark effect.

We also report here several additional double resonances connected with laser lines other than \( \text{N}_2 \text{O} R(16) \) and \( R(24) \). None of these near coincidences shows a laser Stark spectrum but it is convenient to summarize all the double resonance observations (including also those given earlier by Kreiner and Oka\textsuperscript{[25]} in this paper. In most cases the assignment of both the rf transition and the infrared transition can be made by comparison with the published results.\textsuperscript{[16,22]} This information is given in Table II.

V. DISCUSSION

Since the second-order Stark effect in a nonpolar molecule is an unusual phenomenon, we have set out the evidence for our interpretation of the laser Stark spectrum in some detail. Examination of the energy level pattern for the ground vibrational state of tetrahedral molecules\textsuperscript{[20,22]} shows that close \( A_1-A_2 \) pairs of energy levels which might have relatively fast second-order Stark effects are uncommon. They occur only at the top of the energy manifolds for every third \( J=12,15,18,21,\ldots \) which always begin with the sequence \( A_1-F_1-F_2-A_2 \) or \( A_2-F_3-F_1-A_1 \). It is remarkable that in the few laser coincidences investigated for SiH\textsubscript{4}, two laser lines have been found to strike a member of these \( A_1-A_2 \) pairs. Close \( F_1-F_3 \) pairs of energy levels are, however, much more common, and these may well provide candidates for the future observation of second-order Stark effects in tetrahedral molecules.

One of the most interesting points about our observations is that the experimental results can be explained satisfactorily on the basis of the Stark effect on the ground state alone. This is demonstrated by Fig. 2, although a small Stark effect of the upper state is presumably present but not detected with the present experimental resolution: a small upper state Stark effect could also improve the agreement of the calculated curve with the frequency offset measurements shown in Fig. 3. Nevertheless, any Stark shift in the upper state.

FIG. 6. Recordings of the ground-state rf transitions \( J = 18 \text{ or } 21 \) at 993.02 MHz and \( J = 21 \text{ or } 24 \) at 859.01 MHz. The traces of the 993 MHz line show the effect of a dc electric field of 1154 V/cm (mean value) applied to the waveguide cell. The broadening of the line and its shift to higher frequency are the behavior expected for a second-order Stark effect (see text and Fig. 5).
must be roughly an order of magnitude smaller than in the ground state.

Two factors are involved in calculating the upper state Stark effect, the separation of the $A_1-A_2$ energy level pair and the size of the Stark matrix element connecting them. The energy level separations in the upper state are certainly somewhat larger than in the ground state, but not by an order of magnitude. For the upper state of the SiH$_4$ $\nu_3 R'(21)$ line, for example, the separation between $J'=22, R=21$, $A_2^{21}$, and $A_1^{21}$ is calculated to be $\sim 1500$ MHz. The multiplet in the infrared spectrum suggests that the prediction is underestimate splitting, and that it may be $\sim 3000$ to $3500$ MHz. These figures compare with the $A_1-A_2$ ground-state splitting of 859 MHz. It is difficult to avoid the conclusion that even though the upper state splitting is somewhat larger, the effective dipole moment in the upper state must be smaller than that in the ground state.

This conclusion is at first sight surprising. For GeH$_4$ the effective dipole moment operator in the upper state was found to be smaller by a factor of 9 than that in the lower state, and it appeared that the vibration-induced dipole moment must be cancelling the centrifugal distortion-induced dipole moment. There, however, the upper state belongs to the $\nu_4$ band, which is vibrationally forbidden in the infrared and acquires its intensity only by Coriolis mixing with $\nu_4$: thus a small value of the vibration-induced dipole moment seemed reasonable. In the case of SiH$_4$ the upper states of both infrared transitions belong to the infrared allowed $\nu_4$ band, which would be expected to have a much larger vibration-induced dipole moment. Perhaps the explanation lies in the fact that the vibration-induced dipole moment in the $\nu_4=1$ state contains two terms, one containing $\theta_{p44}/\theta_{q44}$ and the other $\theta_{p44}(\theta_{p44}/\theta_{q44})/\lambda_{44} + \theta_{p44}(\theta_{p44}/\theta_{q44})/\lambda_{44}$ and it is of course possible for the resultant dipole moment to be small if there is accidentally a large degree of cancellation between these terms. There are so many unknowns in the expressions that we have not attempted to calculate the vibration-induced dipole moment at present.

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