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NOTE

Observation of Ground State Rotational Transitions in Silicon Tetrafluoride

The centrifugal distortion-induced Q-branch rotational spectra in the ground vibronic state of tetrahedral molecules have been of considerable interest because of the possibility of deriving tensor centrifugal distortion constants and of measuring rotation-induced dipole moments. So far only hydrides (or deuterides) have been studied (*1*) because their small moments of inertia cause fairly large values of Watson's distortion moment θ_z^{xy} (*2*) thus making the rotational transitions stronger. For heavier species such as SiF_4 (*3*), CF_4 (*4*), and OsO_4 (*5*), the tensor distortion constants have been determined by combining high-precision infrared measurements with radiofrequency-infrared transitions in the *excited* state. In this paper we report our direct double resonance measurement of the ground state rotational transitions of SiF_4. Rotation-induced transitions in the heavy symmetric top molecule BF_3 have recently been reported (*6*).

We have performed infrared-radiofrequency double resonance and sub-Doppler infrared spectroscopy of the ν_3 fundamental band of SiF_4 using microwave modulation sidebands of CO_2 laser lines. Infrared radiation ν_i from a CO_2 laser and microwave radiation ν_m (12–18 GHz), generated by a synthesizer sweeper and amplified to 20 W, are mixed in a CdTe modulator to generate modulation sidebands $\nu_i \pm \nu_m$ with the power of ~1 mW and with high spectral purity ($\Delta\nu \leqslant 50$ kHz) (*7*). Frequency modulation at 9.8 kHz with a modulation depth of 150 kHz and a phase sensitive detection at $2f$ was used for the infrared spectroscopic

TABLE I

Observed Lamb Dip Frequencies and Rf Resonance in SiF_4

IR Transition	Laser Line $\pm \nu_m$/MHZ	rf resonance (MHz) in the ν_3 state	rf resonance (MHz) in the ground state
R(39) F_2^9	9P(32)+15 992.496(22)*		
F_1^9	+15 981.313(18)	7.957(5)	3.216(6)
P(33) F_1^7	9P(40)-15 686.340(17)		
F_2^6	-15 543.560(9)	120.307(29)	22.510(7)
R(29) F_1^7	9P(32)-15 544.037(13)		
F_2^6	-15 499.902(15)	37.345(5)	6.789(5)
R(12) $A_1 2$	9P(34)-14 473.430(21)		
A_2^1	-14 406.665(12)	64.886(6)	1.899(8)

* Error is one standard deviation.

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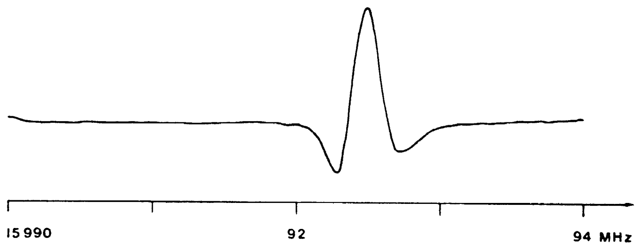

FIG. 1. Saturation dip of the transition $R(39)F_2^9$ in the ν_3 fundamental of SiF_4. The upper sideband of the CO_2 9P(32) laser line was used. Modulation: FM at 9.8 kHz, time constant 1.25 sec. Sample pressure 30 mTorr.

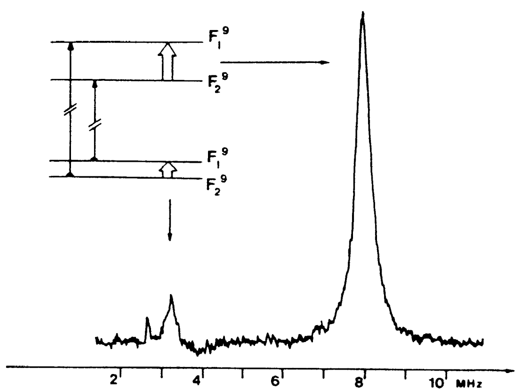

FIG. 2. Level scheme and DR recordings of the excited state transition $J = 40$, $R = 39F_1^9 - F_2^9$ at 7.957(5) MHz and the ground state transition $J = 39F_1^9 - F_2^9$ at 3.216(6) MHz. The narrow feature at 2.6 MHz corresponds to one-third of the excited state transition. A 9.8-kHz amplitude modulation of the radiofrequency and 400-msec time constant were applied. Upper sideband (+15 991 MHz) of the 9P(32) CO_2 laser line was used as pump frequency.

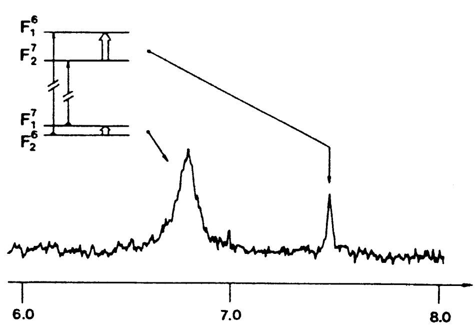

FIG. 3. Ground state rotational transition $J = 29F_1^7 - F_2^6$ at 6.789(5) MHz. RF power of 10 W and a time constant of 400 msec were used. The narrow feature at 7.47 MHz corresponds to one-fifth of the excited state transition which was observed at 37.345(5) MHz. Lower sideband (−15 519 MHz) of the 9P(32) CO_2 laser line.

measurements. Figure 1 shows a sub-Doppler spectral line for the $R(39)\ F_2^0$ transition of SiF_4. The observation and assignment of the transition are based on the extensive diode laser spectroscopy by McDowell *et al.* (*8*).

The same absorption cell was used for both the double resonance and the sub-Doppler spectroscopy. The cell was made from a 7-ft brass tube (1″ × 1″) and equipped with an insulated metal septum which can be used as a coaxial transmission line for the radiofrequency radiation. For the double resonance experiments, rf power between 1 and 10 W (amplitude modulated at 9.8 kHz) was fed into the septum. The rf frequency was limited to 85 MHz because of the available equipment. Examples of the double resonance signals are shown in Figs. 2 and 3. The excited state radiofrequency transitions are strong and often observed by harmonics of the rf radiation. The ground state transitions are much weaker and observed only for high-J transitions.

The observed Lamb dip frequencies and the rf resonances are listed in Table I. From the radiofrequency resonance frequencies the tensor centrifugal distortion constant D_t for the ground state has been determined to be

$$D_t = 147.55\,(10)\,\text{Hz}.$$

This value can be compared with the value $D_t = 142 \pm 5$ Hz obtained by Takami and Kuze (*3*) from the diode laser spectroscopy and excited states double resonance.

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