PHYSICAL REVIEW A VOLUME 14, NUMBER 3 SEPTEMBER 1976

Measurement of the radiative lifetime of the $A\,^2\Sigma(v'=0)$ state of SiF

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(Received 5 April 1976)

We report a measurement of the $A\,^2\Sigma(v'=0)$ radiative lifetime in silicon monofluoride. In this experiment, SiF radicals were produced by the microwave discharge of SiF_4. The ground-state SiF molecules were then excited to the $A\,^2\Sigma(v'=0)$ state by a dye-laser pulse. The resultant fluorescence was recorded and its decay rate measured. The measured lifetime was 0.23 ± 0.02 μsec and was independent of SiF_4 pressure in the range 0.05 to 1.0 Torr.

I. INTRODUCTION

There has been long-standing interest in the spectroscopy of the diatomic molecule SiF. Since the first observations[1] in 1911 numerous experimental papers[2-12] reporting new band systems and spectroscopic constants have appeared. Recently, several theoretical investigations have reported calculations of spectroscopic constants, ionization potentials, Franck-Condon factors, and dipole and quadrupole moments.[13-19] SiF has been observed in stellar atmospheres[20] and may be a constituent of the solar atmosphere,[19] so it is of astrophysical interest. Recent experiments have also shown that SiF is an attractive candidate as an electronic-transition chemical laser.[21]

To our knowledge, there have been no reported values (experimental or theoretical) for the radiative lifetimes of any of the excited electronic states in SiF. There has been a report of the determination of the transition moment for the $A\,^2\Sigma \rightarrow X\,^2\Pi$ system done by SiF absorption.[22] However, this was not a direct measurement, in that theoretically calculated Franck-Condon factors and Honl-London factors had to be used to obtain the transition moment from the absorption data. Reliable transition probabilities are important for determining abundances of SiF in stellar atmospheres and for calculating potential optical gain for laser applications. Measured transition probilities also serve as sensitive tests of theoretical wave functions. We report here a direct measurement of the radiative lifetime of the $A\,^2\Sigma(v'=0)$ state of SiF done by laser-induced fluorescence.

II. EXPERIMENT

The technique of time resolved fluorescence spectroscopy provides a clean, direct method for measuring radiative lifetimes. A pulsed dye laser was chosen as the excitation source because of its short, spectrally narrow, and tunable output pulses. A problem in working with SiF is that it is not chemically stable, the stable fluorine-silicon compound being SiF_4. SiF radicals were produced by flowing SiF_4 gas through a continuous microwave discharge which was run in a sidearm of the fluorescence cell. The relevant energy levels of SiF are shown in Fig. 1. The ground-state SiF molecules produced absorbed the resonant dye-laser radiation and were excited to the $A\,^2\Sigma$ state. The resultant fluorescence was detected with a fast photomultiplier. By pulsing the dye laser at ~20 Hz, the photomultiplier output could be signal averaged using a boxcar integrator, and the average of many pulses was displayed on a strip-chart recorder. Illustrated in Fig. 1 is the 162-cm^{-1} spin-orbit separation of the $X\,^2\Pi_{3/2}$ and $X\,^2\Pi_{1/2}$ components of the ground state. We utilized this splitting by pumping the $A^2\Sigma \leftarrow X^2\Pi_{1/2}$ system at ~4368 Å and observing fluorescence from the $A\,^2\Sigma \rightarrow X^2\Pi_{3/2}$ system at ~4400 Å. In this way we were able to better isolate the detection system from the scattered laser light by using narrow-bandpass filters.

III. APPARATUS

A block diagram of the experiment is shown in Fig. 2. The AVCO C-950 pulsed nitrogen laser

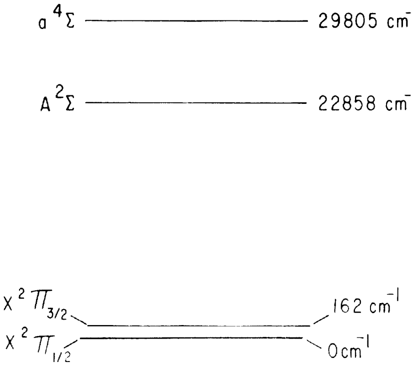

FIG. 1. Lower-lying electronic energy levels of SiF. The potential chemical laser transition is between the $a^4\Sigma$ and $A\,^2\Sigma$ states.

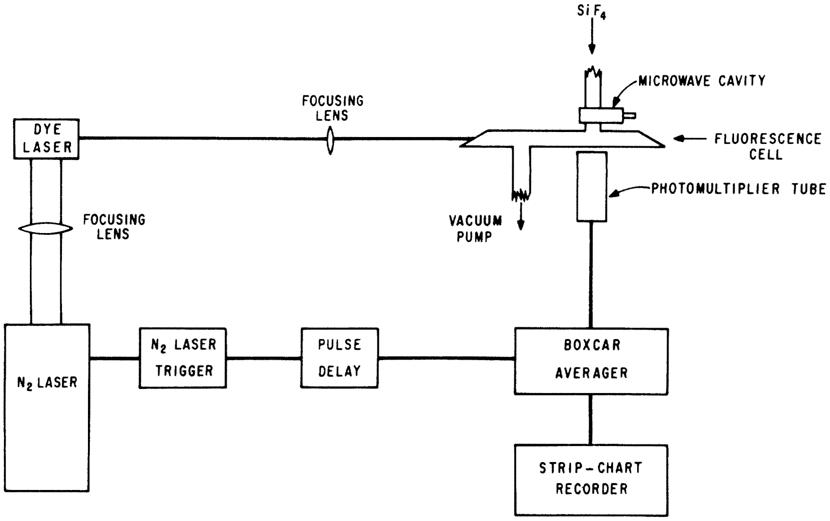

FIG. 2. Block diagram of apparatus.

produced short (~10 nsec) pulses which were focused onto the rectangular quartz cell containing Coumarin-120 dye solution (1.3×10^{-3} mole in MeOH). The irradiated dye solution lased, and by using a diffraction grating as the back reflector, ~10-nsec, 1-Å-wide output pulses were obtained. The dye-laser output was run through an optical train and into an adjacent room to shield the detection system from rf produced by the nitrogen laser. The beam was then focused inside the Brewster-windowed quartz fluorescence cell. The cell contained two sidearms through which SiF_4 entered and exited. The entrance sidearm was enclosed by a microwave cavity used to produce SiF radicals. An RCA-8575 photomultiplier tube was used to monitor the resultant fluorescence. A He-Cd laser filter was placed between the sample cell and the photomultiplier to reduce the amount of scattered laser light entering the photomultiplier. The photomultiplier output was connected to the input of a PAR 163/162 boxcar averager which was triggered by a 12-V pulse generated in the nitrogen laser. The boxcar averager slowly, at a predetermined rate, scanned the repetitive waveform of the photomultiplier and displayed the average of many pulses on a strip-chart recorder; the minimum time resolution of the detection system was a few nanoseconds. A recording of the boxcar output of scattered laser light is shown in Fig. 3. This shows the rise and fall times to be a few nanoseconds, demonstrating both the shortness of the laser pulse and the fast response of the detection system. The time base of the boxcar averager and strip-chart recorder system was monitored on a model 5233L HP counter and was found to be accurate to within 1 part in 500.

IV. MEASUREMENTS

A. Procedure

Before making measurements, the sample cell was evacuated to 1×10^{-6} Torr and held there for 1 h. After this, the measurements proceeded as follows: The dye laser was tuned to approximately

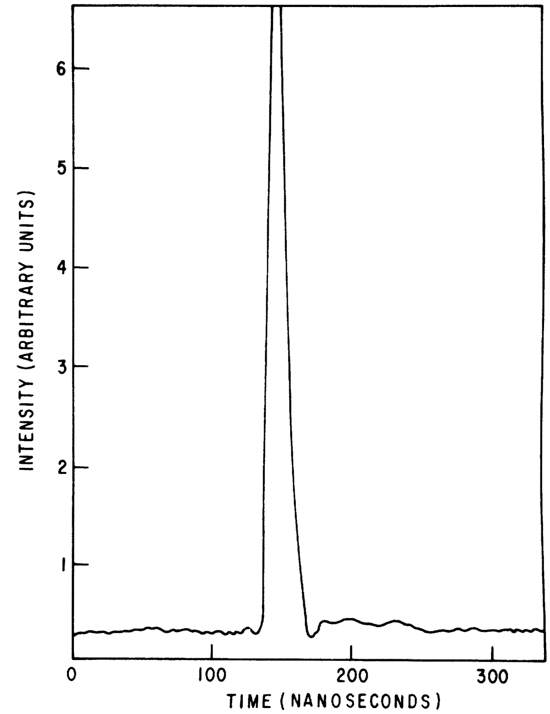

FIG. 3. Boxcar output when laser was operating at ~4340 Å. This peak is due to scattered laser light.

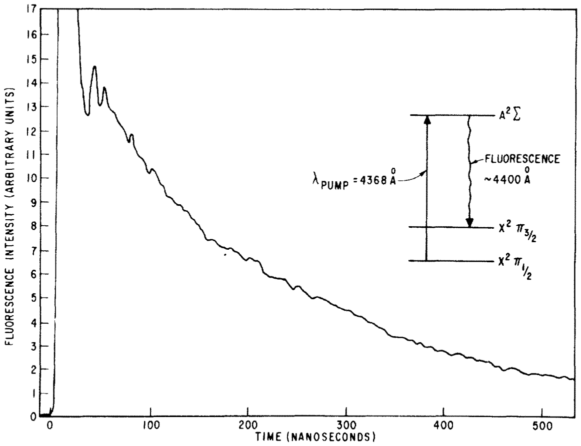

FIG. 4. Boxcar output when laser was operating at 4368 Å. The scattered laser light is clearly visible as the large off-scale spike. The laser-induced fluorescence is seen as the long, relatively slowly decaying tail. The pumping scheme is shown as an inset.

4368 Å. A low-density (~10^{15} molecules/cm^3) stream of SiF_4 was discharged in the microwave cavity and passed into the sample cell. The boxcar was then scanned well past the laser peak, ~150 nsec and held at that point. By focusing the laser and optimizing the fluorescent signal seen by the multiplier, the boxcar output was maximized. The laser wavelength was then fine tuned to further optimize the fluorescent signal. The microwave power and SiF_4 pressure were then recorded, and the boxcar was reset and allowed to scan the signal. A single scan lasted several minutes. Since the repetition rate of the dye laser was ~20 Hz, this meant that the recorded output was the average of several thousand shots. A run consisted of a single scan. A strip-chart recording of a typical run is shown in Fig. 4. A semilog plot of the data of Fig. 4 is plotted in Fig. 5. The origin of the time axis was chosen as 100 nsec to insure that any convolution effects of the laser pulse were minimal. The plot is clearly a single exponential, and the time needed to reach the $1/e$ point is 220 nsec.

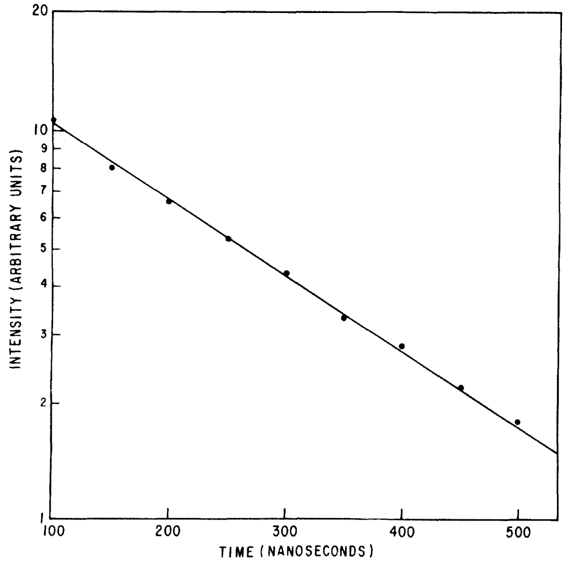

FIG. 5. Semilog plot of fluorescence intensity vs time; data points were taken from Fig. 4. The lifetime for this run was determined to be 220 nsec.

B. Systematic errors

There were several possible sources of systematic errors present in this experiment. One major concern was the possible saturation of the photomultiplier tube, which would seriously affect its time response. As a check for this, runs were made using several different neutral-density filters in front of the photomultiplier tube. Also, the multiplier was run at several voltages. By turning up the laser power we were able to saturate the multiplier tube and obtain lifetimes as long as 300 nsec. By reducing the amount of light incident on the multiplier such that a further reduction left the decay time unchanged, we felt confident that we were below the saturation limit. Care was taken to keep all runs below this level.

A second source of error was encountered in the inherent instabilities of the microwave discharge. Since the number density of the ground-state SiF molecules, hence the fluorescence intensity, was proportional to the microwave power coupled into the SiF_4 gas, fluctuations in the cavity were observed as bumps in the strip-chart recordings of the fluorescence. Also, zero drift in the boxcar and recorder accounted for run-to-run variations in the slope of the semilog plots which were used

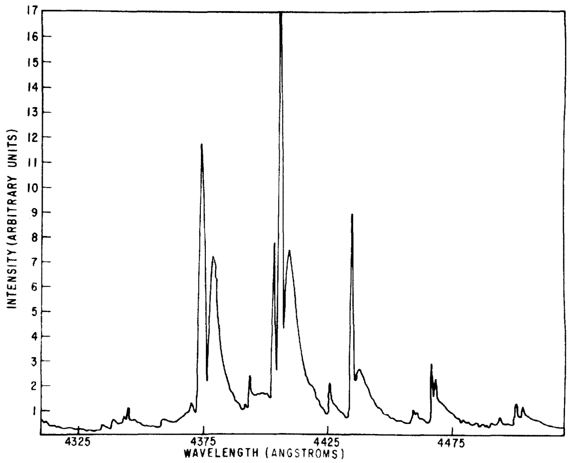

FIG. 6. Spectrum of microwave discharge of SiF_4. This emission is due to the SiF $A^2\Sigma \rightarrow X^2\Pi$ system.

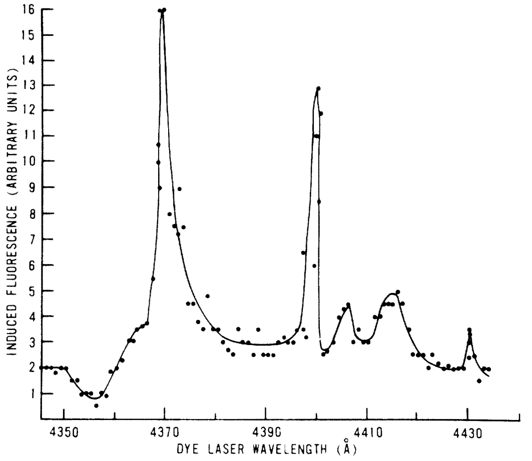

FIG. 7. Plot of the fluorescence intensity as a function of the dye-laser wavelength.

to determine the lifetimes.

An obvious question which had to be answered concerned the source of the fluorescence. As an initial test, a spectrum of the SiF_4 discharge was recorded and is shown in Fig. 6. This spectrum is entirely due to $A\,^2\Sigma \rightarrow X\,^2\Pi$ SiF emission. This led us to believe that SiF ($X\,^2\Pi$) ground-state molecules were present. As a further and more conclusive test, the fluorescence intensity was monitored as a function of the dye-laser excitation wavelength. The boxcar was set ~150 nsec beyond the start of the laser pulse, so that only fluorescence was observed. The resultant dependence of the fluorescence intensity on the excitation wavelength is shown in Fig. 7. Distinct peaks in the fluorescence are seen at ~4368 and 4400 Å. These correspond to the 0, 0 bandheads of the SiF($A\,^2\Sigma \leftarrow X\,^2\Pi$) system. A smaller peak is observed at ~4430 Å, which corresponds to the 1, 1 bandhead of SiF($A\,^2\Sigma \leftarrow X\,^2\Pi$). This laser-induced spectrum is conclusive evidence that the fluorescing species is indeed $A\,^2\Sigma$ SiF.

In any experiment designed to measure radiative lifetimes by fluorescent decay one must be concerned with quenching of the excited state by collisions with other species. To check this, the SiF_4 pressure was varied over more than an order of magnitude, from 0.05 to 1.0 Torr. Within our estimated error, there was no dependence of the observed lifetime on the SiF_4 pressure. This is summarized in Fig. 8.

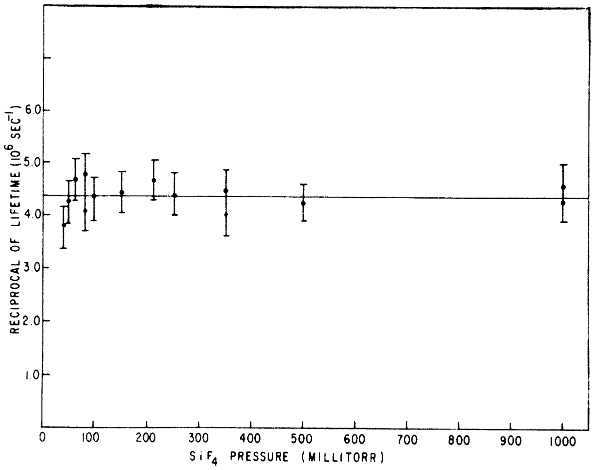

FIG. 8. Plot of $1/\tau$ vs pressure of SiF_4. The solid line represents the average value of $1/\tau$ for all runs regardless of SiF_4 pressure.

Care was taken to avoid radiation entrapment by keeping the number density of SiF radicals low. The absence of a dependence of the observed lifetime on SiF_4 density would seem to confirm that radiation trapping was not a serious problem. As an additional check, the position of the laser beam in the fluorescence tube was varied. Since the diameter of the beam was only about 1 mm, this meant that the fluorescing source was a thin line. By varying the position of this line we could vary the path length of ground-state SiF molecules that the fluorescent radiation had to cross before reaching the photomultiplier. Variations of factors of 20 produced no systematic change in the observed lifetime. Had radiation trapping been present large effects should have been observed.

V. RESULTS

The average of all of the runs was 0.23 μsec. The variation from run to run appeared to be statistical. We quote as our result

$$\tau(A\,^2\Sigma(v'=0)) = 0.23 \pm 0.02\ \mu\text{sec}\,,$$

where the error represents one standard deviation. This is the same magnitude as our estimate of the systematic error on each run.

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