LASER AND FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE G⁴ Φ - X⁴ Φ SYSTEM OF TITANIUM MONOFLUORIDE.

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The emission spectrum of the $G^4\Phi - X^4\Phi$ transition of TiF has been observed in the 13500 - 16000 cm⁻¹ region using a Fourier transform spectrometer (FTS), as well as by laser excitation spectroscopy. In the FTS experiments, the bands were excited in a carbon tube furnace by the reaction of titanium metal vapor with CF₄ at a temperature of about 2300 °C. In the laser experiments, the TiF molecules were produced by laser vaporization of a Ti rod followed by reaction with SF₆ using a pulsed supersonic jet source. Three groups of bands with high wavenumber sub-band heads at 14388 cm⁻¹, 15033 cm⁻¹, and 15576 cm⁻¹ have been assigned as 0-1, 0-0, and 1-0 vibrational bands of the $G^4\Phi - X^4\Phi$ transition, respectively. Each vibrational band consists of four sub-bands assigned as ${}^{4}\Phi_{3/2}$ - ${}^{4}\Phi_{3/2}$, ${}^{4}\Phi_{5/2} - {}^{4}\Phi_{5/2}$, ${}^{4}\Phi_{7/2} - {}^{4}\Phi_{7/2}$, and ${}^{4}\Phi_{9/2} - {}^{4}\Phi_{9/2}$. A rotational analysis has been performed and molecular constants for the ground and excited states have been extracted using the combined FTS and laser excitation measurements. The assignment of a ${}^{4}\Phi$ state as the lower state is consistent with recent theoretical predictions and with expectations based on the spectrum of TiH. The similarity between the electronic states of TiF, TiH, and Ti⁺ will be discussed.