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NOTES

Measurement of the Radiative Lifetime of the $v = 0$ Level of the $B^3\Pi_1$ State of TiO

The dynamics of the excited electronic states of titanium monoxide has been the subject of numerous studies, mainly because of its astrophysical importance (*1*). For this reason, laboratory measurements of lifetimes of electronic excited states are especially interesting. This has been carried out by several authors for the $C^3\Delta$ state (*2–4*), the $c^1\Phi$ state (*5*), and the $E^3\Pi$ state (*6*). Using the same method we have been able to measure the lifetime of a fourth state, the $B^3\Pi$ state, which is the upper state of the γ'-system (*7*). The method used was the so-called pulse decay method as described below.

The excitation light source was a pulsed nitrogen laser-pumped tunable dye laser (Molectron UV 300, DL 400) which delivered light pulses of 5 nsec duration, 10–40 kW of peak power, 0.01 nm linewidth (fwhm), and 15 Hz repetition rate. Rhodamine 610 dye was used to cover the 600–620 nm wavelength range.

The laser light was vertically focused into the fluorescence cell, which was a Broida-type oven (*8*). Atomic titanium vapor was produced by vaporizing the metal in a carbon crucible heated to 2300 K using a resistive tungsten wire basket heater. The metal vapor was entrained in a flow of argon into the interaction chamber in which it reacted with oxygen. The fluorescence cell pressure was measured with a membrane-type gauge: it varied from 0.1 to 50 Torr.

The fluorescence decay signals were detected with a Hamamatsu RS 928 photomultiplier tube through a SOPRA F 1150 monochromator used as a narrow band filter. The slit width was typically 300 μm. A second RS 928 photomultiplier detected directly the whole emitted fluorescence light through a cut-off interference filter used to block the scattered laser light. Both signals were fed into a two-channel PAR 162 boxcar averager, supplied with Tektronix S2 sampling heads, running in the "A/B" mode to prevent fluorescence intensity fluctuations. The averaged signal ratio was recovered by scanning boxcar apertures of 2 nsec duration over the decay curve. It was digitized and stored in the memory of a computer.

The laser was tuned to 615.79 nm and the monochromator was set at 618.65 nm on the R line of a fluorescence triplet which was assigned as the $R(22)$, $Q(23)$, $P(24)$ triplet of the 0, 0 band of the γ'-system ($B^3\Pi_1 \rightarrow X^3\Delta_2$) of TiO (Table I). The observed 99.5 cm^{-1} separation between the two fluorescence triplets indicates that the laser excitation populated the $J' = 23$ upper rotational level of the 0, 0 $B^3\Pi_1 \leftarrow X^3\Delta_1$ satellite band studied by J. G. Phillips (*9*).

A decay curve and the dye laser pulse that produced it are shown in Fig. 1. Since the lifetime of the level was not much longer than the laser pulse duration, it was necessary to numerically deconvolve the lifetime from the observed decay.

TABLE I

TiO Observed Laser Fluorescence Lines

Wavelength (nm)	Wavenumber (cm^{-1})			Assignment
	This work	Reference [19]		
614.87	16 259.1	16 259.060	R(22)	0,0 $B^3\Pi_1 \leftarrow X^3\Delta_1$
615.79*	16 234.8	16 234.799	Q(23)	
616.71	16 210.5		P(24)	
618.65	16 159.6		R(22)	0,0 $B^3\Pi_1 \rightarrow X^3\Delta_2$
619.61	16 135.3		Q(23)	
620.52	16 111.0		P(24)	

* laser line

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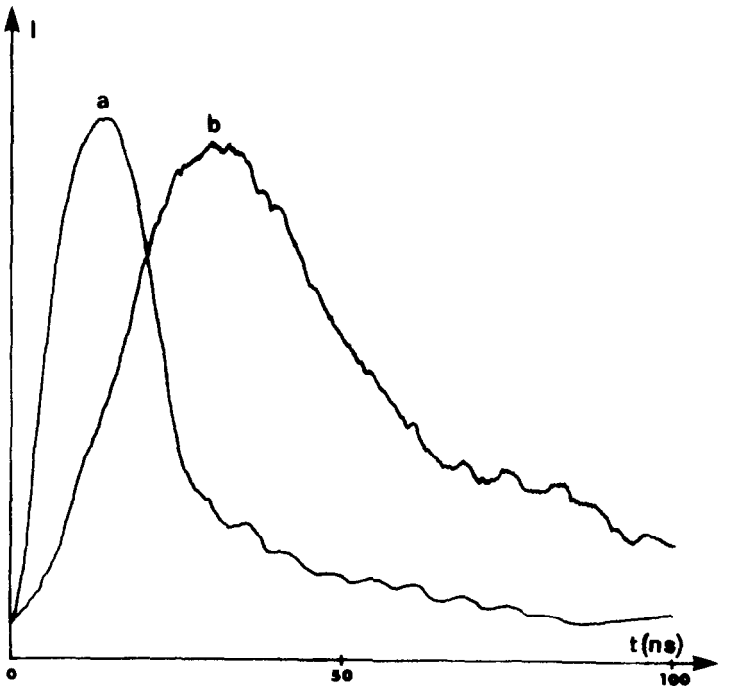

FIG. 1. TiO decay curve and laser pulse: (a) laser pulse, (b) fluorescence decay of the $v = 0$ $B^3\Pi_1$ state. Both curves were recorded with a 2-nsec wide gate and a 100-nsec aperture delay range.

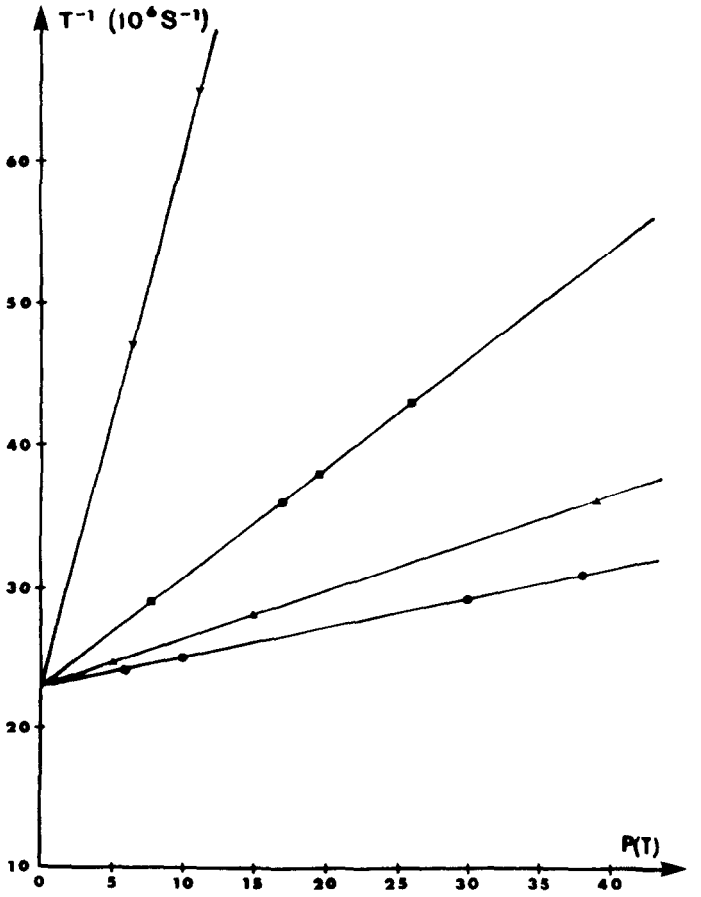

FIG. 2. Stern–Volmer plots of inverse of measured lifetime vs argon pressure for the 0, 0 $B^3\Pi_1 \rightarrow X^3\Delta_2$ transition of TiO.

The measured lifetime depends on the collision rate between the excited TiO molecules and other gases in the interaction chamber according to the equation

$$\tau^{-1} = \tau_0^{-1} + Cp, \tag{1}$$

where τ is the measured lifetime, τ_0 is the radiative lifetime, p is the pressure of the oven, and C is the collisional deactivation constant. Traces of oxygen were introduced into the cell and decay curves recorded at different O_2 pressures. Four plots of τ^{-1} versus argon pressure are shown in Fig. 2. The intercept of these plots gives the radiative lifetime of the $v = 0$ $B^3\Pi_1$ state of TiO: it was found to be 44 ± 2 nsec.

Another value of the radiative lifetime of the $B^3\Pi_1$ state of TiO can be derived from previous absorption coefficients measurements (*7*) assuming a single-channel deexcitation. This indirect method yields a radiative lifetime of 43 nsec, a value very close to ours though less reliable because of a large uncertainty (about 30% compared to 5% here). However, this very good agreement between values measured by two different methods allows us to conclude that deexcitation of the $B^3\Pi_1$ state to the $X^3\Delta$ ground state occurs without any cascade via intermediate states and/or without any noticeable radiationless processes other than inelastic collisions.

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