

LASER-INDUCED FLUORESCENCE STUDIES OF CS $A^1\Pi(v = 0)$

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Perturbations in the optical spectrum of CS arise through interaction of the $A^1\Pi$ with several neighbouring triplet states as in CO. In CS however, the larger spin-orbit interaction and density of vibronic levels leads to more pronounced effects. Analysis of the absorption spectrum shows that for $A^1\Pi(v=0)$ the major interaction is with the $a'^3\Sigma^+(v=10)$ state [1,2] reaching maximum at $J' = 14$ and 20 for Q branch excitation and $J' = 16$ in the P and R branches. In the absence of other effects the radiative lifetime will vary with rotational level reflecting the extent of mixing with the $a'^3\Sigma^+$ state. Only limited lifetime data exists for CS with large discrepancies between the Hanlé effect [3] and phase shift [4] measurements and no quenching rates have been measured. We have used a frequency doubled dye laser to measure lifetimes and quenching rates of several rotational levels in the $A^1\Pi(v=0)$ state throughout the region of the perturbation.

CS molecules were generated in crossed sprays by the reaction $O + CS_2 \rightarrow CS + SO$ at low pressure ($\sim 5 \times 10^{-3}$ Torr) in a stainless steel vacuum chamber evacuated by a 6" oil diffusion pump. The frequency doubled output from a nitrogen-pumped dye laser (Molelectron UV300/DL200) passed through the reaction zone where fluorescence was excited by pumping the $A^1\Pi(0) \rightarrow X^1\Sigma^+(0)$ transition using Coumarin 152A dye and an angle tuned KPB frequency doubling crystal. Fluorescence was detected perpendicular to the laser beam by a photomultiplier tube and the signal either averaged by a boxcar integrator and output onto a chart recorder as a laser-excitation spectrum, or displayed single shot on a fast storage scope (Tektronix 466) for lifetime measurements.

A typical laser-excitation spectrum of the CS $A^1\Pi-X^1\Sigma^+(0-0)$ band is shown in Fig. (1). The observed spectrum was assigned by computing a fluorescence spectrum using the term energies for $A^1\Pi(v=0)$ from [5] and convoluting over the laser bandwidth. Since, over most of the spectrum, the laser bandwidth resulted in simultaneous excitation of at least 2 rotational levels of the $A^1\Pi$ state, the lifetimes reported in Table 1 are averages over a few levels. The transitions populating these levels are tabulated together with our estimate of the most highly populated J' level, the percent $A^1\Pi$ character in the J' level and, for several levels, the variation of lifetime with various added quenching gases.

The lifetimes in Table 1 clearly show the effect of the perturbation. For Q-branch excitation τ increases from 180 nsec for the relatively unperturbed low J' levels to a maximum of 220 nsec at $J' = 14$. Similarly in the R branch τ increases from 170 to 199 nsec as J' decreases towards the highly perturbed $J' = 16$. The data was combined to give an unperturbed lifetime for $A^1\Pi(v=0)$ of $\tau = 171 \pm 10$ nsec, in good agreement with the Hanlé effect measurement of 174 ± 14 nsec.

The measured lifetime, together with the values of r-centroids, Franck-Condon factors and variation of transition moment with r-centroid from [6] enable us to compute an absolute value of the transition moment, R_e of

$$R_e(\bar{r}_{\infty}) = 0.32 \pm 0.09 \text{ a.u.}$$

a variation of transition moment with r-centroid of

$$R_e(\bar{r}_{v'v''}) = 0.85 (1 - 0.38 \bar{r}_{v'v''}) \text{ a.u.}$$

and an absorption oscillator strength

$$f_{\infty} = 1.0 \pm 0.1 \times 10^{-2}$$

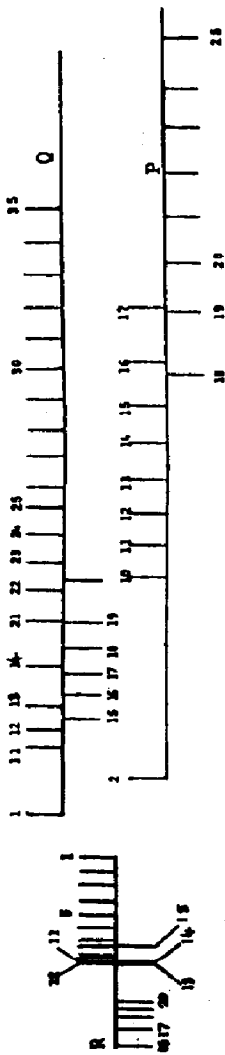


Fig. 1

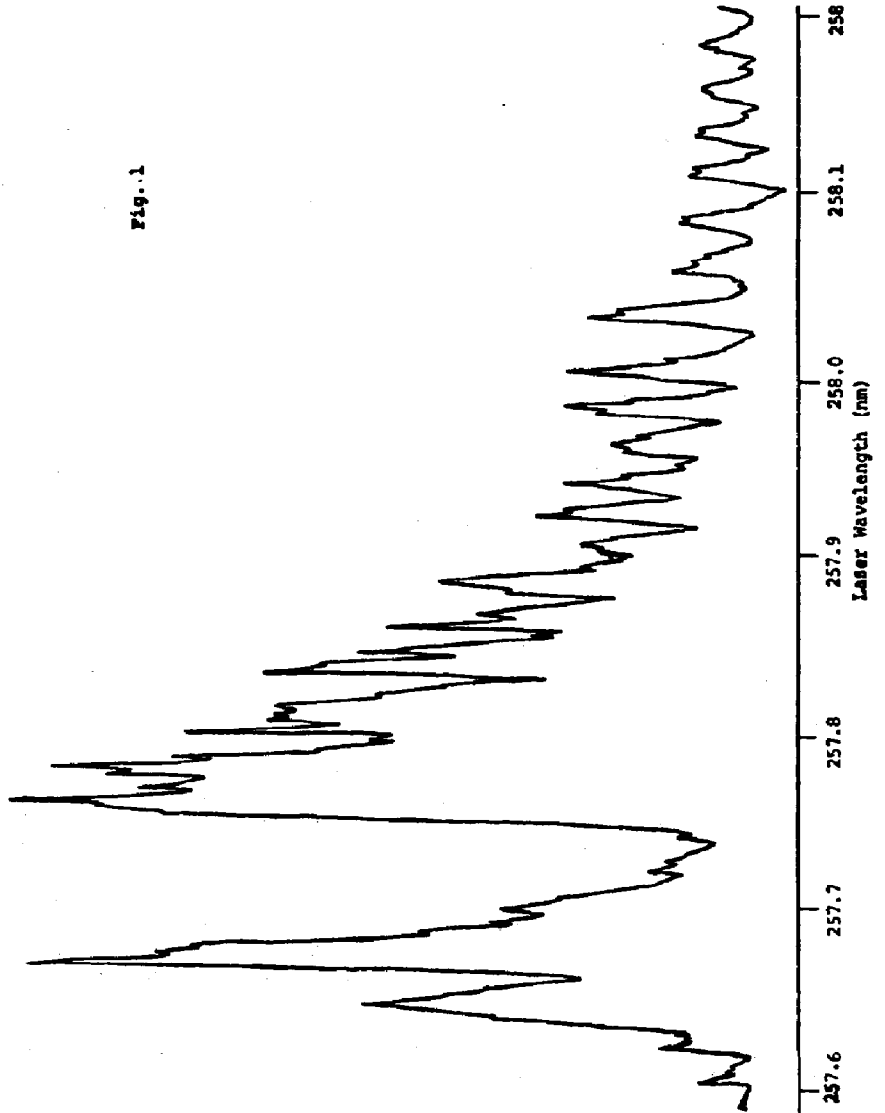


Table 1

J'	Overlapping Lines	τ (ns)	$\pm\sigma$	%A ¹ Π	K (10 ⁶) Torr s ⁻¹	
					O ₂	CO
1	Q(1,2)	185	6	94	6.5±0.6	12.8±2.0
3	Q(1,2,3)	181	8	94		
6	Q(4,5,6)	189	10	94		
8	Q(7,8)	196	6	93		
9	Q(9,10)	206	14	93		
10	Q(10)	216	19	92		
14	Q(14,17)	226	13	49	6.0±0.7	10.3±1
15	Q(12,15)	206	7	76		
9,16	R(8,15)	199	17	93,61		
13,14	R(12,13)	199	4	90,86	8.4±0.6	
19	R(17,18,19)	185	3	81		
20	R(18,19,20)	174	5	92		
22	R(19,20,21,22,23)	163	6	95		
24	R(22,23,24)	173	10	96		

Table 1 contains rate constants for quenching of fluorescence for several J' levels with O₂ and CO which show no difference between perturbed and unperturbed levels. This was confirmed by scanning laser excitation spectra of the A-X(O-O) band at successively higher pressures of added O₂, CO and CS₂. Up to pressures of 1 Torr there was no significant difference between the spectra, demonstrating that the perturbation does not accelerate the quenching rate in collision with these molecular species. In the case of atomic oxygen however, a pronounced selective quenching process rapidly reduces the fluorescence yield of the perturbed levels compared to the unperturbed levels. Computer simulation of the quenching process indicates a quenching cross section for the perturbed levels which is between one and two orders of magnitude greater than that for the unperturbed levels.

A possible removal mechanism is chemical reaction in the excited state. The increased efficiency of this process over that involving CS A¹Π may result from the electron configuration of the CS a³Σ⁺ state (σ²π³π*) where a bonding 2π electron is promoted to a 3π* orbital. The molecule also contains 10 quanta of vibrational energy and a dipole moment of 1.70 (D) [2]. This can be compared to the pure A¹Π state where a slightly anti-bonding 7σ electron is promoted to the 3π* orbital and the dipole moment is only 0.63 (D) [2]. The CS a³Σ⁺ (v=10) molecule therefore presents a large, loosely bound, vibrationally excited target compared to the A¹Π state, which may account for the enhanced quenching rates of the mixed levels.

References

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