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A LASER-INDUCED FLUORESCENCE TECHNIQUE TO MONITOR H_2S

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by

F. B. Wampler, Project Leader

University of California, Los Alamos National Laboratory
P. O. Box 1663
Los Alamos NM 87545

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I. INTRODUCTION

The objective of this research project is to develop a means for detecting H_2S at the 0.1-ppm level via laser-induced fluorescence (LIF). Because the upper electronic states of H_2S are repulsive, it is necessary to use a two-laser pump-probe technique. The first laser (ArF, 193 nm) photodissociates H_2S into HS and H. Subsequently, a probe dye laser is used to pump the HS ground-state radicals to their $A^2\Sigma^+$ state from which the radicals then fluoresce. This fluorescence signal can be related back to the H_2S concentration prior to dissociation and thus affords a real-time diagnostic for the species of interest.

II. EXPERIMENTAL

The main photodissociation source is a modified Tachisto rare-gas halide excimer laser (ArF, 193 nm). This laser is typically operated at 3 Hz with an output energy of 15 mJ (25-ns FWHM). A Quanta-Ray YAG-laser pumped-dye laser, operating in the 320-325-nm region, is presently employed as the probe laser. This laser beam spatially overlaps the beam from the dissociative ArF laser and is temporally delayed to fire at selected delay times, typically 1-50 μs, to provide the optimum fluorescence emission signal. The detection system, which is situated perpendicular to the laser beams, is composed of signal-collection optics, band-pass filters, a 1/4-m monochromator (or band-pass filter), and a RCA C31034 photomultiplier tube. The fluorescence signal is then processed with the use of boxcar averagers and a chart recorder for spectral scanning. Transient digitizers and a minicomputer are used for temporal studies and signal-averaging experiments.

Two different photolysis furnaces are employed for the experiments, one for the experiments at 150°F and the other for the 1200°F work. Both furnaces are from the best designs available, and the oven employed for the 150°F work was developed at Los Alamos by our research team for optical studies.[1] The high-temperature furnace is a modification of the design reported by Felder, et al.[2] All gas pressures are monitored with MKS Baratron heads.

III. RESULTS

The fluorescence signal has been scrutinized via both excitation and emission studies in some earlier work by our research team. Refer to Figs. 1, 2, and 3. The HS band system of interest in these studies is the $A^2\Sigma^+ - X^2\Pi$. We can readily distinguish between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. These figures (depicting rotational lines) illustrate the spectral resolution capability that our investigations have afforded and we can spectrally identify HS fluorescence in a simple and unambigious manner.

The intensity of fluorescence (I_f) from the HS($A^2\Sigma^+$) state is proportional to the ground-state population of HS, and the HS population is proportional to the H_2S precursor concentration. The details of these functional relationships will not be presented here (they are given in the proposal). However, one major point that must be considered is the extent to which the I_f signal is attenuated under the operating conditions of a coal gasifier. The intensity of the HS($A^2\Sigma - X^2\Pi$) fluorescence is reduced by the presence of collisional partners that can quench the fluorescene. However, the extent to which the fluorescence is quenched depends upon the ratio between the quenching rate and the first-order decay of the $A^2\Sigma$ state. The shorter the radiative lifetime, the less effect quenching will have. The reported value in the literature for this value is 550 ns.[3] The value that we have determined is ≦10 ns. Our temporal resolution is limited to 10 ns. This is an exceedingly important finding because it will diminish the effect of quenching on the desired signal. The lifetime may be short enough to eliminate any significant quenching effects under the conditions of a gasifier. We are confident we are correct in evaluating the lifetime. The previously reported work did not use very sophisticated experimental apparatus and they appear to have been monitoring emission from another species. We have made our temporal measurements after unequivocally identifying the HS $(A^2\Sigma)$ state via LIF excitation spectra.

The excited electronic state of HS under investigation is predissociative, and we have studied the effect of varying the degree of rotational excitation upon the lifetime. We cannot distinguish any change in our preliminary experiments for HS, but for DS the lifetime changes from 190 ns at the lowest J values to 120 ns at $J = 7\frac{1}{2}$. Both the HS and DS lifetimes appear to be in qualitative agreement with what one would anticipate from integrated absorption data. However, we are investigating this further.

Preliminary quenching experiments at room temperature have been performed using O_2, Ar, and CO_2. At pressure up to 100 torr, we cannot detect any change in the $HS(A^2\Sigma^+)$ lifetime. These experiments will be extended to much higher pressures and temperatures. Experiments are under way to estimate the lifetime of the $HS(A^2\Sigma^+)$ state (our temporal resolution provides only an upper limit, i.e., ≦10 ns) via noting the relative changes in I_f at very high pressures (if detectable), assuming that the quenching proceeds with a gas kinetic rate constant ($\approx 10^{11}$ ℓ/mol-s), and solving for the first-order competitive rate constant (inverse of the desired lifetime value).

This work to date is very encouraging because the major concern at the onset of the research was quenching, and now it appears this will be much less than previously anticipated. Everything we have found supports the conclusion that the program has an excellent chance of success. Because of the significant finding of the short lifetime, we have solicited and obtained support, at our expense, from our Theoretical Chemistry Group at the Los Alamos National Laboratory to perform the necessary theoretical calculations on the $A^2\Sigma^+$ state of HS to provide further insight into this area.

References

1. R. N. Shelton, W. W. Rice, F. B. Wampler, and J. J. Tiee, "Temperature-Controlled Cell for Laser-Induced Fluorescence and Absorption Studies," Rev. Sci. Instrum., in press (1981).
2. W. Felder, A Fontijn, H. N. Voltrauer, and D. R. Voorhees, Rev. Sci. Instrum. 51, 195 (1980).
3. K. H. Becker and D. Hanks, J. Photochem. 1, 177 (1973).

Figure Captions

1. Fluorescence excitation spectrum of the ${}^2\Pi_{3/2} - {}^2\Sigma^+$ transition of the HS radicals with a delay time of (a) 1 μs and (b) 50μs between the two lasers.

2. Fluorescence excitation spectrum of the ${}^2\Pi_{1/2} - {}^2\Sigma^+$ transition of the HS radicals with a delay time of 1 μs between the two lasers.

3. Emission spectrum of the HS radicals when excited by the dye laser tuned to the $R_1 + {}^RQ_{21}$ band head of the (0,0) ${}^2\Pi_{3/2} - {}^2\Sigma^+$ transition.

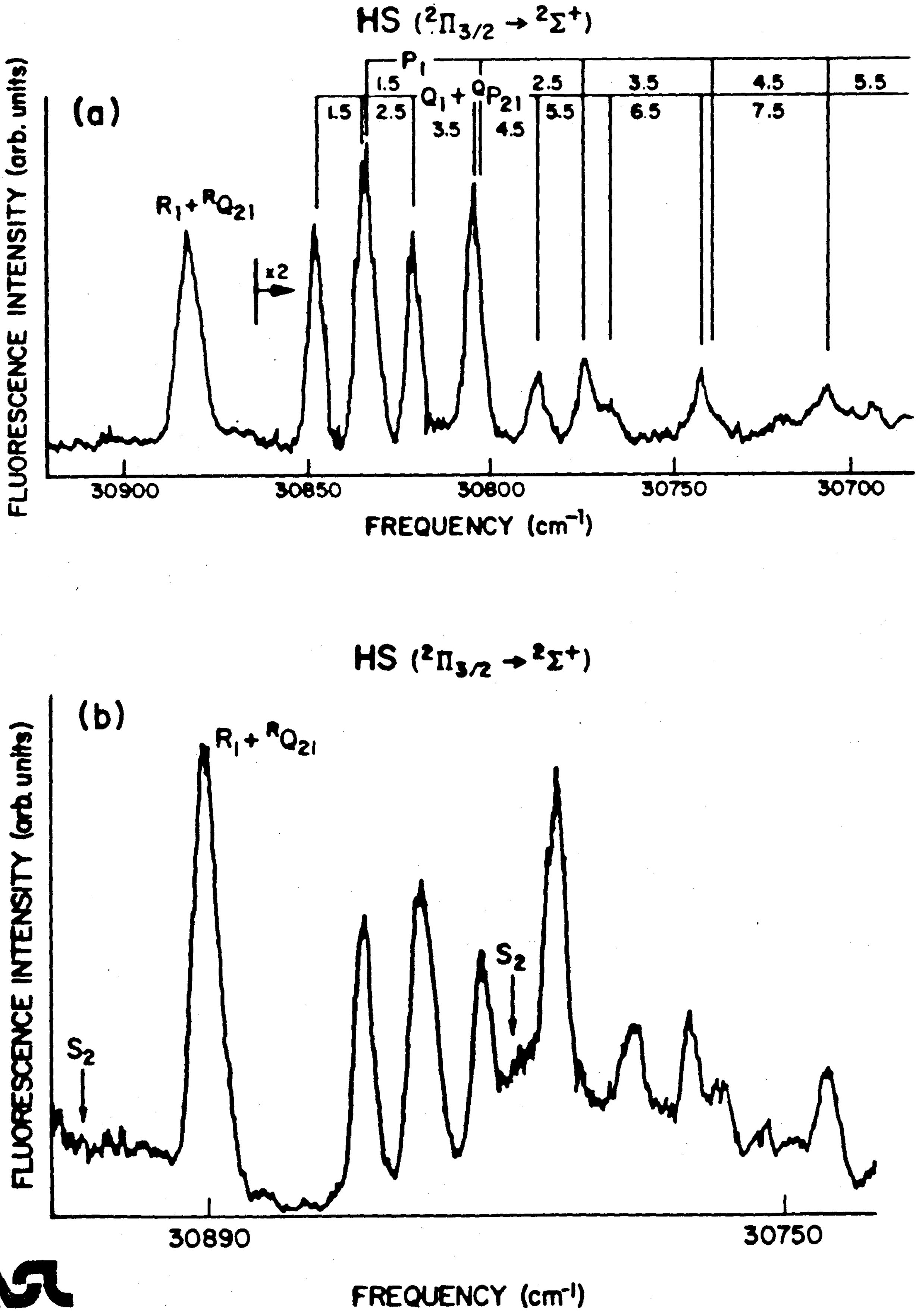
HS ($^2\Pi_{3/2} \rightarrow {}^2\Sigma^+$)
(a)
FLUORESCENCE INTENSITY (arb. units)
P_1
1.5
2.5
3.5
4.5
5.5
$Q_1 + {}^QP_{21}$
1.5
2.5
3.5
4.5
5.5
6.5
7.5
$R_1 + {}^RQ_{21}$
x2
30900
30850
30800
30750
30700
FREQUENCY (cm^{-1})
HS ($^2\Pi_{3/2} \rightarrow {}^2\Sigma^+$)
(b)
FLUORESCENCE INTENSITY (arb. units)
$R_1 + {}^RQ_{21}$
S_2
S_2
30890
30750
FREQUENCY (cm^{-1})

Figure 1

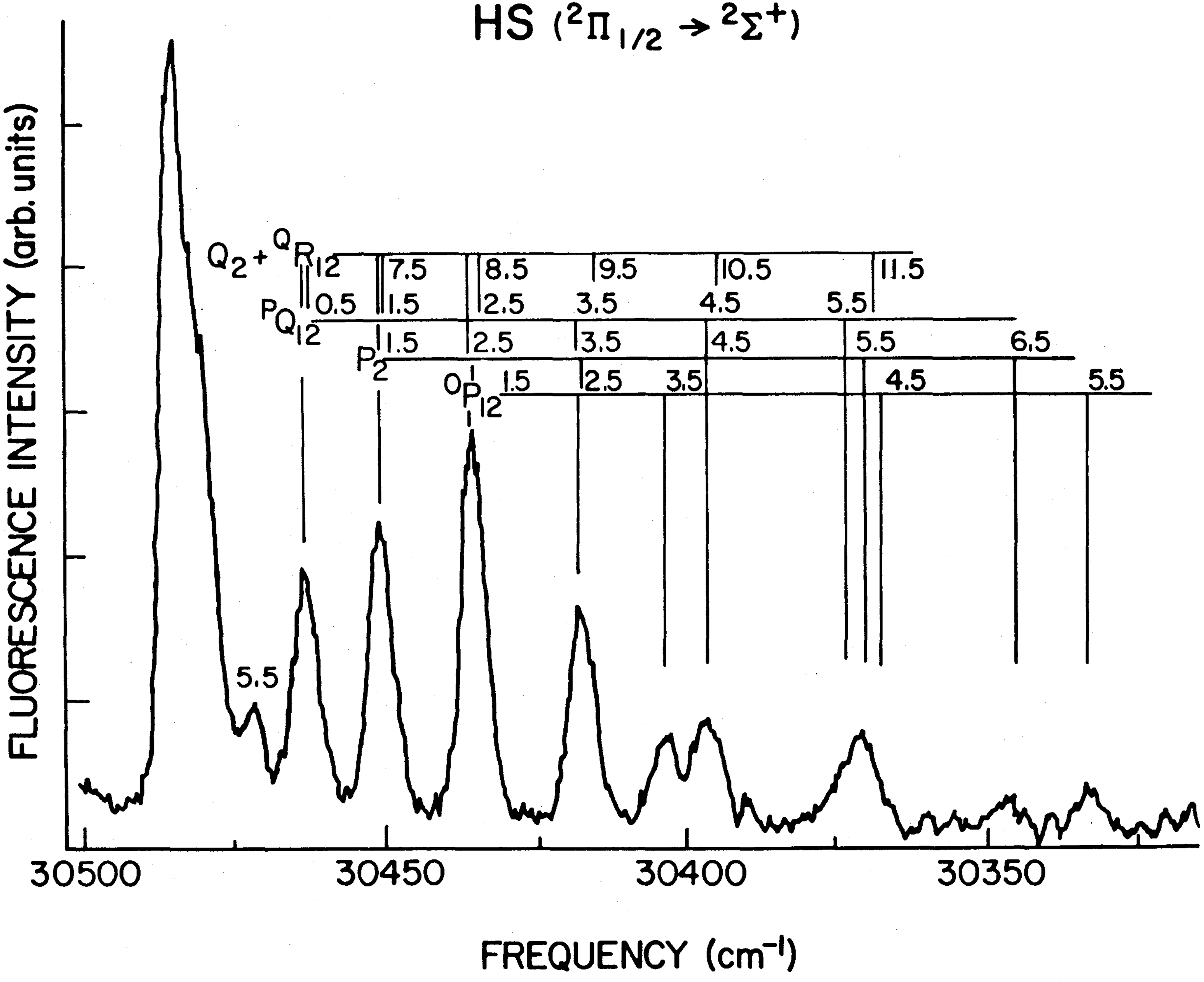

Figure 2

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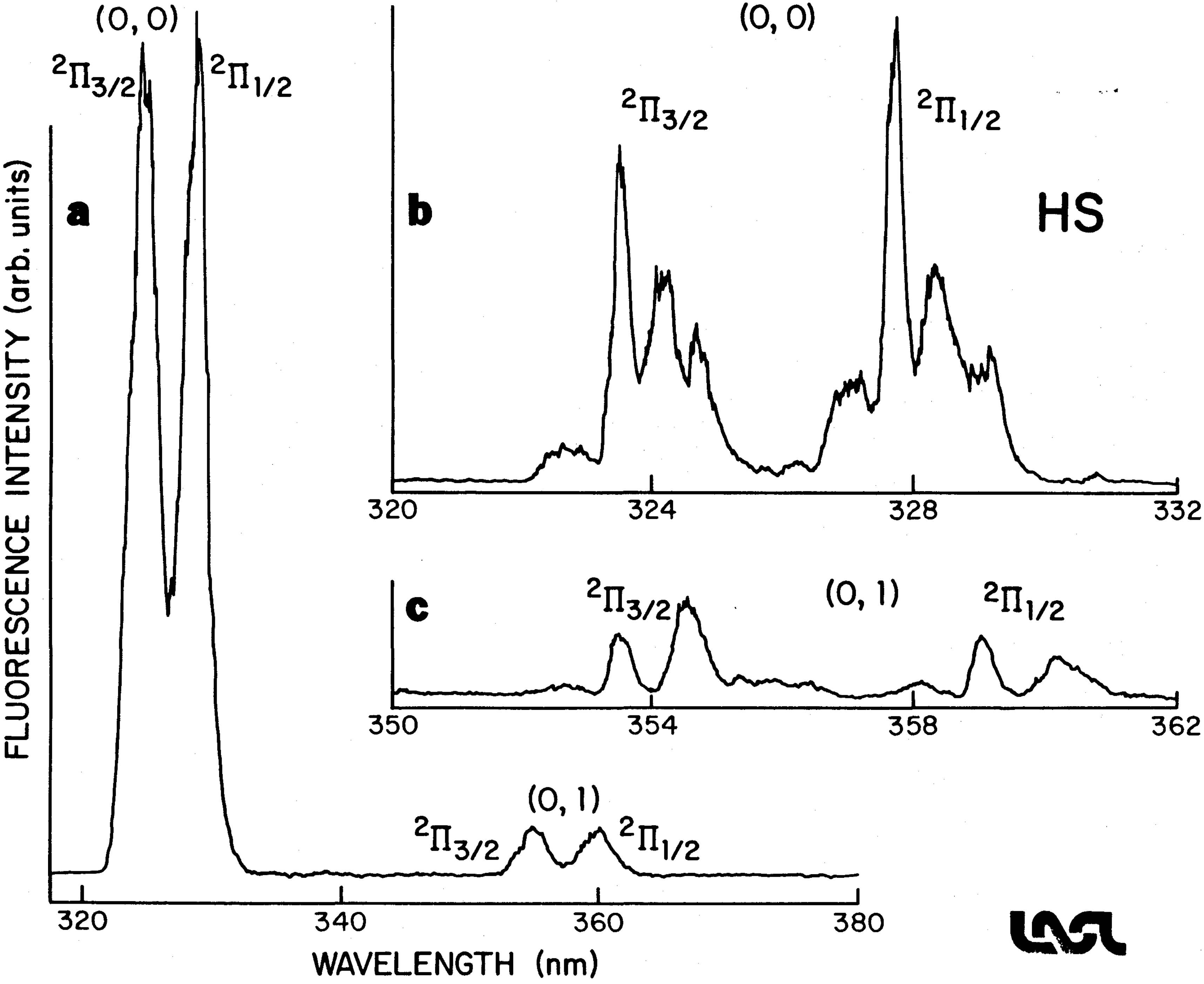

Figure 3

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