COLOR CENTER LASER SPECTROSCOPY OF FREE RADICALS

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An electrical discharge through argon over a coating of polyacetylene has been found to provide an abundant source of free radicals. Using a computer controlled color center laser, magnetic rotation spectroscopy combined with differential detection[1] and a multipass cell was used to obtain high-resolution infrared absorption spectra for both a deuterated and non-deuterated coating.

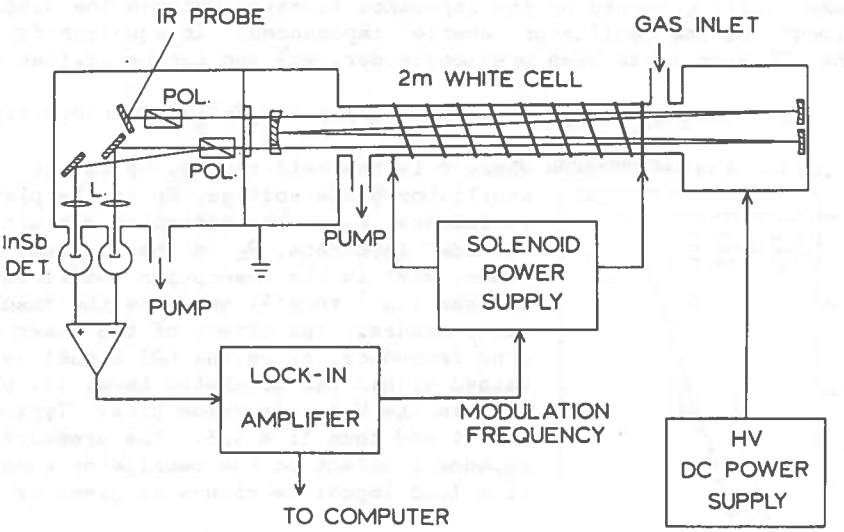

Fig. 1. Experimental apparatus. POL = polarizer, Ge = germanium flat, L=lens.

In previous work, the $A^2\Pi \leftarrow X^2\Sigma^+$ transition of C_2H was observed and assigned[2] and the first observation in absorption of the Ballik-Ramsey $b^3\Sigma_g^- \leftarrow a^3\Pi_u$ system of C_2 was made in this discharge system[3]. Recently the discharge was inadvertently operated with small atmospheric impurities arising from the opening of an undetected sample cell leak. This resulted in the appearance of new bands exhibiting remarkable signal-to-noise. These were found to be due to metastable states of CO and N_2 and were successfully assigned to the $a'^3\Sigma \leftarrow a^3\Pi$ (v=0←2) system in CO[4] and the Wu-Benesch $B^3\Pi_g \leftarrow W^3\Delta_u$ (v=4←2, 5←3, 6←4) system in N_2[5].

chopping frequency above 400 Hz. The pressure dependence of the LOG signals in RF discharges of C_2H_4, D_2O and NO_2 is shown plotted in Figure 2. The LOG pressure dependence is seen to be linear over most of the pressure range where the discharge could be sustained except at low pressures (.1 - .2 torr) in C_2H_4 and D_2O discharges, and also in a NO_2 discharge at pressures greater than 1.5 torr.

The observed LOG signal behavior was modeled under the following conditions: 1) The electrical behavior of the RF discharge is well described by a positive column DC discharge. 2) The discharge impedance increases linearly with pressure over the $\simeq$ 1 torr range over which the discharge can be maintained. 3) The LOG signals are essentially due to volume heating of the gas discharge. The net temperature rise due to laser absorption in the gas was calculated for a simple two-level system. 4) The Colpitts circuit response is essentially governed by the impedance mismatch between the discharge "load" and the oscillator "source" impedances. An equation for the LOG signal has been previously derived[5] and can be written as

$$V_s = (1/4\pi r^2)(VpRp/R_s)[(1-\exp(-1/f\tau))/(C_0 f+C_1)]h(b,p)P_o\alpha(\nu)p \quad (1)$$

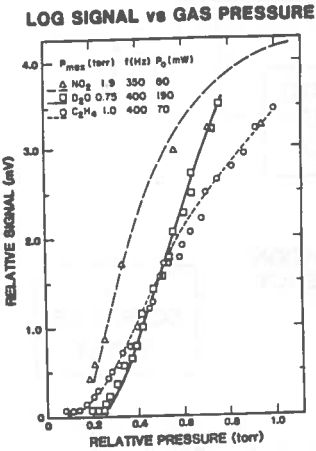

Fig. 2

where r is the cell radius, Vp is the oscillator plate voltage, Rp is the plate resistance, R_s is the effective circuit "source" impedance, P_o is the incident laser power, $\alpha(\nu)$ is the absorption coefficient of the gas (cm^{-1} $torr^{-1}$) and p is the discharge gas pressure. The effect of the laser chopping frequency, f, on the LOG signal is contained within the bracketed term, [], where $\tau(p)$ is the V-T relaxation time. Typically, $f\tau \leq 1$ and thus [] $\propto 1/f$. The pressure dependent effect on the oscillator response to a load impedance change is given by

$$h(b,p) = b(bp-1)/(bp+1)^3 \quad (2)$$

where $bp = R_L/R_S$ is the ratio of the load and source impedances. Using estimated discharge parameters, it has been shown that[5] h(b,p) is constant to within ±5% over a $\simeq$ .5 torr pressure range of the discharge, which is consistent with the generally linear pressure dependence of the LOG signals. The fitted curves in Fig. 2 show, however, that the nonlinear pressure effects can be well accounted for using (1) which was scaled by a constant to fit each data set.

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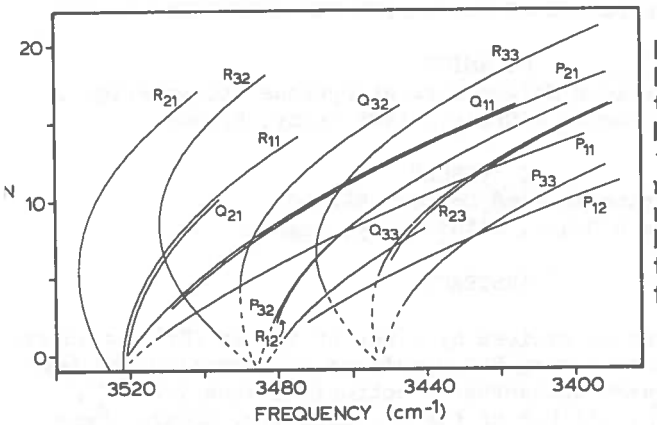

Fig. 2. Partial Fortrat diagram of the $a'^3\Sigma \leftarrow a^3\Pi$ v=0←2 band of CO. The index N is the rotational quantum number K" for large N but the correlation breaks down for N<2.

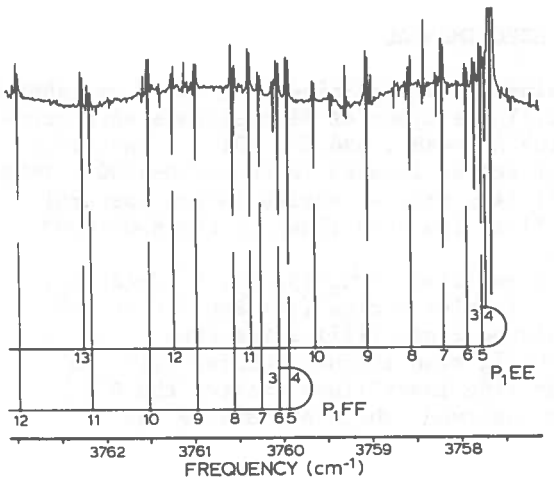

Fig. 3. $B^3\Pi_g \leftarrow W^3\Delta_u$ v=5←3 band of N_2.

Two bands of the spectrum of C_2D have been tentatively identified in the deuterated polyacetylene discharge and their analysis is now in progress. One appears to be a hot band involving the (0,1,0) state.

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