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SPECTRAL ANALYSIS OF PYROTECHNIC HCL EMISSIONS.(U)  
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SPECTRAL ANALYSIS OF PYROTECHNIC HCL EMISSIONS

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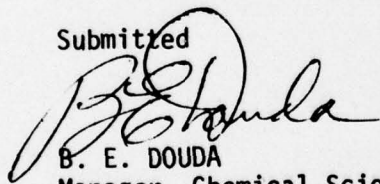
30 September 1977

INTERIM REPORT for Period June 1975 to November 1976

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Prepared for  
COMMANDER  
NAVAL AIR SYSTEMS COMMAND  
WASHINGTON, DC 20361

Submitted

A handwritten signature in cursive script, appearing to read "B. E. Douda". The signature is written in dark ink and is positioned to the right of the word "Submitted".

B. E. DOUDA  
Manager, Chemical Sciences Branch  
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REPORT DOCUMENTATION PAGE

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) In HCl-producing pyrotechnic flames, the effective flame temperature experimentally determined from HCl infrared spectral analysis (1-0 vibration-rotation emission band) was approximately 1780 K, compared with 1900-1950 K derived theoretically. For another, more fuel rich composition, approximately 1620 K was experimentally derived, compared with 1800-2250 K theoretically, assuming 0-10% air admixture, and remaining near 2250 K for higher percentages.		

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left is for the left half of the spectrum, and is 50% of the intensity scale on the right hand side. That is, the local intensity maximum near 2.8  $\mu\text{m}$  is actually only 50% as high as the maximum near 4.4  $\mu\text{m}$ .

Details of the 3.2-4.2  $\mu\text{m}$  region of Figure 4 are shown in Figure 5.

The spectrum in this region consists of HCl rotation-vibration lines underlain by a graybody-like continuum and, near 3.2  $\mu\text{m}$ , water vapor absorptions and emissions. The HCl emission lines are grouped into the P branch lines from 3.5 to 4.1  $\mu\text{m}$ , and R branch lines, less well resolved, from 3.2 to near 3.4  $\mu\text{m}$ . Spectroscopic notation is shown on the figure, indicating P branch lines from the 1-0 and 2-1 bands.

Spectra from separate flares of the same type are very similar, showing good reproducibility from flare to flare. The main difference between IR-9 and IR-12 spectra is that there is a larger underlying continuum in the latter group.

#### DATA ANALYSIS AND DISCUSSION

In order to learn more about the basic thermodynamic and kinetic processes occurring in the flame, the HCl peaks were analyzed to determine the rotational temperature using the following equation:<sup>2</sup>

$$I_{em} = \frac{C_{em} \nu^4}{Q_r} (J'+J''+1) e^{-B'J'(J'+1)hc/kT}$$

where  $I_{em}$  is the emission intensity,  $\nu$  is the frequency (in wavenumbers) of a particular line,  $J'$  is the quantum number for the rotational levels in the upper vibrational state of the transition,  $J''$  is the quantum number for the rotational levels in the lower vibrational state of the transition,  $B'$  is the rotational constant for the upper vibrational state,  $T$  is the absolute temperature, and  $h$ ,  $c$ , and  $k$  are constants.  $C_{em}$  and  $Q_r$  can be considered constant for a particular vibrational transition.

A plot of

<sup>2</sup> G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules (D. Van Nostrand Co., Inc., Princeton, NJ, 1950), p. 205.

$$\ln \frac{I_{em}}{(J'+J''+1)v^4} \text{ vs } J'(J'+1)$$

enables T to be obtained from

$$- \frac{B'hc}{kT}$$

the slope.

Since rotation-translation relaxation times are so short, it is expected that rotational temperatures would closely approach the translational temperature.

It was decided to use the P-branch data, rather than the R-branch, because of better resolution, less underlying continuum, and no interference from water vapor absorption/emission.

This technique has been applied to HCl flames in the past.<sup>3-7</sup> Figure 6 shows an example of a plot which is based on a spectrum of the emission from composition IR-12. This is for the P-Branch of the 1-0 transition. All such plots for either IR-9 or IR-12 had the same general shape, with a steep section near the left, leading to a small "knee", then to a linear portion. This is similar to the shape of the

<sup>3</sup> H. P. Broida, "Temperature of Flames", NBS Report No. 4418, National Bureau of Standards, Gaithersburg, MD. Available Defense Documentation Center, Cameron Station, Alexandria, VA 22314, DDC-AD080550.

<sup>4</sup> E. E. Bell, P. B. Burnside, and F. P. Dickey, "Spectral Radiance of Some Flames and Their Temperature Determination", J. Opt. Soc. Am. 50, 1286 (December 1960).

<sup>5</sup> F. D. Findlay and J. C. Polanyi, "The Hydrogen-Chlorine System in the MM Pressure Range. I. Energy Distribution Among Vibrationally Excited States", Canadian Journal of Chemistry 42, 2176 (1964).

<sup>6</sup> J. K. Cashion and J. C. Polanyi, "Infrared Chemiluminescence. I. Infrared Emission from Hydrogen Chloride Formed in the Systems Atomic Hydrogen Plus Chlorine, Atomic Hydrogen Plus Hydrogen Chloride, Atomic Hydrogen Plus Deuterium Chloride, and Atomic Deuterium Plus Hydrogen Chloride", Proc. Roy. Soc. A258, 529 (1960).

<sup>7</sup> J. T. Latimore, et. al., "H<sub>2</sub>-Cl<sub>2</sub> Chemical Laser Program. Part 1--CHEMLUM Code for Spectroscopic Data Analysis", RK-CR-74-9, U.S. Army Missile Command, Redstone Arsenal, AL (January 1974). Available DDC--AD780178.

graph shown in reference 3. This shape remained the same whether peak heights or peak areas were used. A limited number of points from the P-Branch of the 2-1 transition were analyzed, but, due to the small peak size, scatter was present in the results between two flares of the same type.

Table 2 summarizes the results of the rotational analyses. Here, it can be seen that temperature from flares of identical composition are within 50K of each other, when examining the 1-0 data. These values experimentally derived are in agreement with those obtained experimentally in reference 4 for HCl flames.

In order to compare our experimental results with computer predictions of adiabatic temperature, a NASA thermodynamic program was used. This program can predict temperatures and species resulting from the combustion of reactants under given conditions. By inputting the reactants (their relative amounts and heats of formation) and varying the amounts of air, the information derived in Table 3 is obtained. The temperatures and mole fractions so derived assume no radiation loss, which is certainly not the actual case. Nevertheless, those temperatures are within 200 K for IR-9 (compare with 1-0 results in Table 2). For IR-12 the computer predictions are from 200 to 600 K higher depending on the amount of air mixed in. Admittedly, it is difficult to decide which is the most reasonable percentage of air to be added.

Obviously, simple experiments and calculations like those described above cannot adequately serve to define the complex flame system under investigation. This flame is not expected to be homogeneous in either species type or concentration, or in temperature, as one progresses across or up the plume. Certainly there are non-equilibrium conditions. Furthermore, spectral resolution was insufficient to resolve any self-absorption that may have been present in the 1-0 bands, and the spectrometer field of view did not encompass the entire plume. However, given these handicaps it is interesting that there is gross correlation between theory and experiment at least for composition IR-9. One possible explanation for the larger discrepancy between theory and experiment for IR-12 is the following:

Composition IR-12 is more fuel-rich than IR-9 and therefore the effect of adding differing amounts of air should be more pronounced in raising the temperature. This is seen in Table 3, where the adiabatic temperature for IR-12 is lower than IR-9 at 0% air, but generally is higher than IR-9 after air is admitted. Above 10% air, the IR-12

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<sup>8</sup> S. Gordon and B. J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations", NASA SP-273, Lewis Research Center (1971). Available NTIS--N7137775.

adiabatic temperature is relatively constant. The spectrometer field of view, small compared to the plume size, is located relatively close to the burning surface, presumably in a region where air admixture is still low. The discrepancy between experiment and theory for IR-12, therefore, depends on how much air is assumed to enter the plume at the field of view position. If it is assumed that less than 10% air is added, the difference between theory and experiment for IR-12 is 200 K, as good as that for IR-9. Above 10%, the difference rapidly rises to about 600 K and remains there.

A further correlation between theory and experiment was attempted using the radiant source model developed by Dr. Goldman at Denver Research Institute. The goal here was to duplicate the experimental spectrum using temperature, HCl concentration, and spectral resolution as inputs into Goldman's model. However, there was only fair agreement since the radiant source model conditions were not optimized to match the experimental conditions. Therefore, the results are not shown here. More work needs to be done to establish correlation and to generate the correct HCl spectrum from Goldman's model.

- 
- <sup>9</sup> A. Goldman, et. al., "Distribution of Water Vapor in the Stratosphere as Determined from Balloon Measurements of Atmospheric Emission Spectra in the 24-29  $\mu\text{m}$  Region", Applied Optics 12, 1045 (1973).
- <sup>10</sup> A. Goldman, et. al., "Solar Absorption in the CO Fundamental Region", Astrophysical Journal 182, 581 (1973).
- <sup>11</sup> A. Goldman, et. al., "Infrared Spectral Radiance of Hot HF and DF in The  $\Delta\nu = 1$  Bands Region as Seen Through an Atmospheric Path", J. Quant. Spectrosc. Radiat. Transfer 14, 299 (1974).
- <sup>12</sup> A. Goldman and S. C. Schmidt, "Infrared Spectral Line Parameters and Absorptance Calculations of NO at Atmospheric and Elevated Temperatures for the  $\Delta\nu = 1$  Bands Region", J. Quant. Spectrosc. Radiat. Transfer 15, 127 (1975).
- <sup>13</sup> R. N. Stocker and A. Goldman, "Infrared Spectral Line Parameters of HBr and DBr at Elevated Temperatures", J. Quant. Spectrosc. Radiat. Transfer 16, 335 (1976).

## CONCLUSIONS

It is possible to obtain gross correlation between rotational temperatures derived from infrared vibration rotation spectra of pyrotechnically produced HCl emission, and theoretically calculated temperatures. In fuel-rich compositions, the amount of assumed air admixture can greatly change the theoretical results.

**Table 1. Flare Compositions (Wt. Percent)  
to Produce HCl Emission**

<u>Ingredients</u>	<u>Formulas</u>	
	<u>IR-9</u>	<u>IR-12</u>
Hydrazine Bisborane	30	27
Hexachloroethane	40	36
Ammonium Perchlorate	20	17
Boron	--	10
Sylgard 182 *	10	10

---

\*This is used as a binder to hold the composition together. It is a product of Dow Corning Corporation, Midland, Michigan.

Table 2. Experimentally Determined Rotational Temperatures

<u>Flare</u>	Temperature, K	
	<u>P Branch 1-0 Transition</u>	<u>P Branch** 2-1 Transition</u>
IR-9 #1*	1799	--
IR-9 #2	1755	1553
IR-12 #1	1637	1910
IR-12 #2	1600	1536

---

\*The rotations #1 and #2 refer to different flares with the same formula.

\*\*2-1 data not as reliable as 1-0 data due to smaller intensities.

Table 3. Predicted Species and Plume Temperatures\*

IR-9

<u>Air**</u>	<u>Temp., K (Adiabatic)</u>	<u>HCl***</u>	<u>CO<sub>2</sub>***</u>	<u>H<sub>2</sub>O***</u>
0	1877	.195	.00002	.00035
10	1919	.189	.00004	.00079
20	1932	.177	.00006	.0011
30	1935	.164	.00008	.0014
40	1941	.148	.00008	.0015
50	1955	.131	.00008	.0015
60	2074	.117	.0011	.020
70	2277	.094	.0077	.092

IR-12

<u>Air**</u>	<u>Temp., K (Adiabatic)</u>	<u>HCl</u>	<u>CO<sub>2</sub></u>	<u>H<sub>2</sub>O</u>
0	1807	.120	--	.00003
10	2252	.140	--	.00007
20	2247	.142	.00001	.00023
30	2207	.134	.00002	.0004
40	2167	.122	.00003	.0006
50	2125	.109	.00004	.0008
60	2080	.094	.00005	.0009
70	2196	.082	.00055	.010

\*These were obtained from the NASA thermodynamic computer program (reference 9)

\*\*Expressed as percentage of total reactants

\*\*\*Expressed as mole fraction

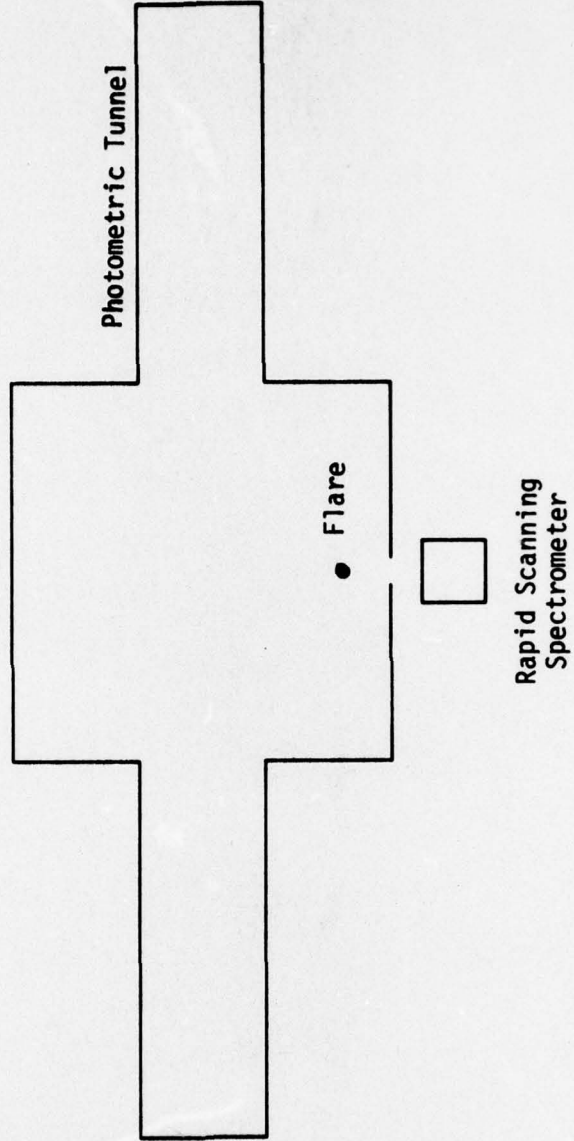


Figure 1. Typical Arrangement for Obtaining Flare Spectra. The flare is burned in the center of the NAVPNSUPPCEN Crane photometric tunnel. The spectrometer views the radiation through a porthole.

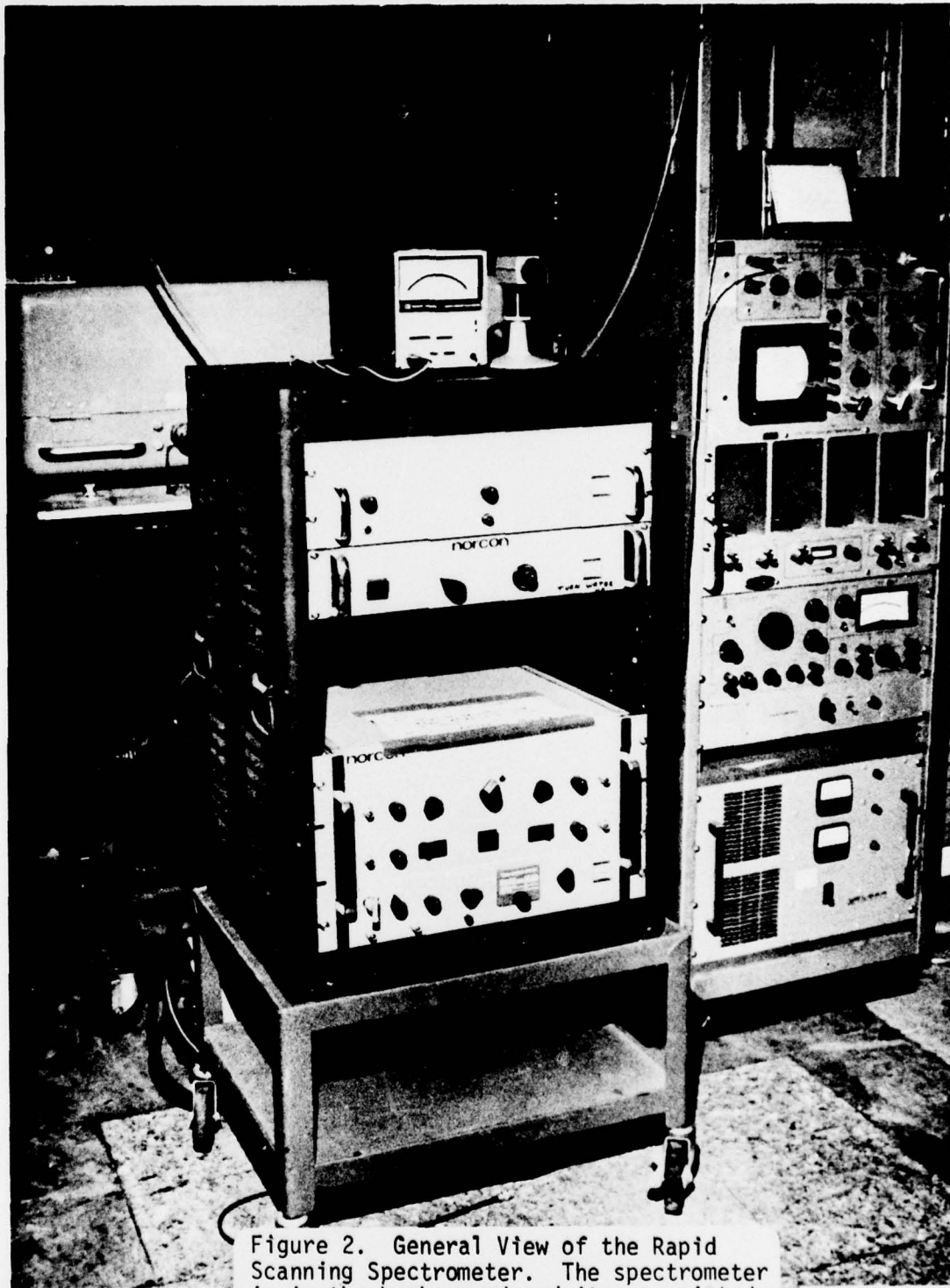


Figure 2. General View of the Rapid Scanning Spectrometer. The spectrometer is in the background and its associated electronics are enclosed in the electronics rack in the left foreground.

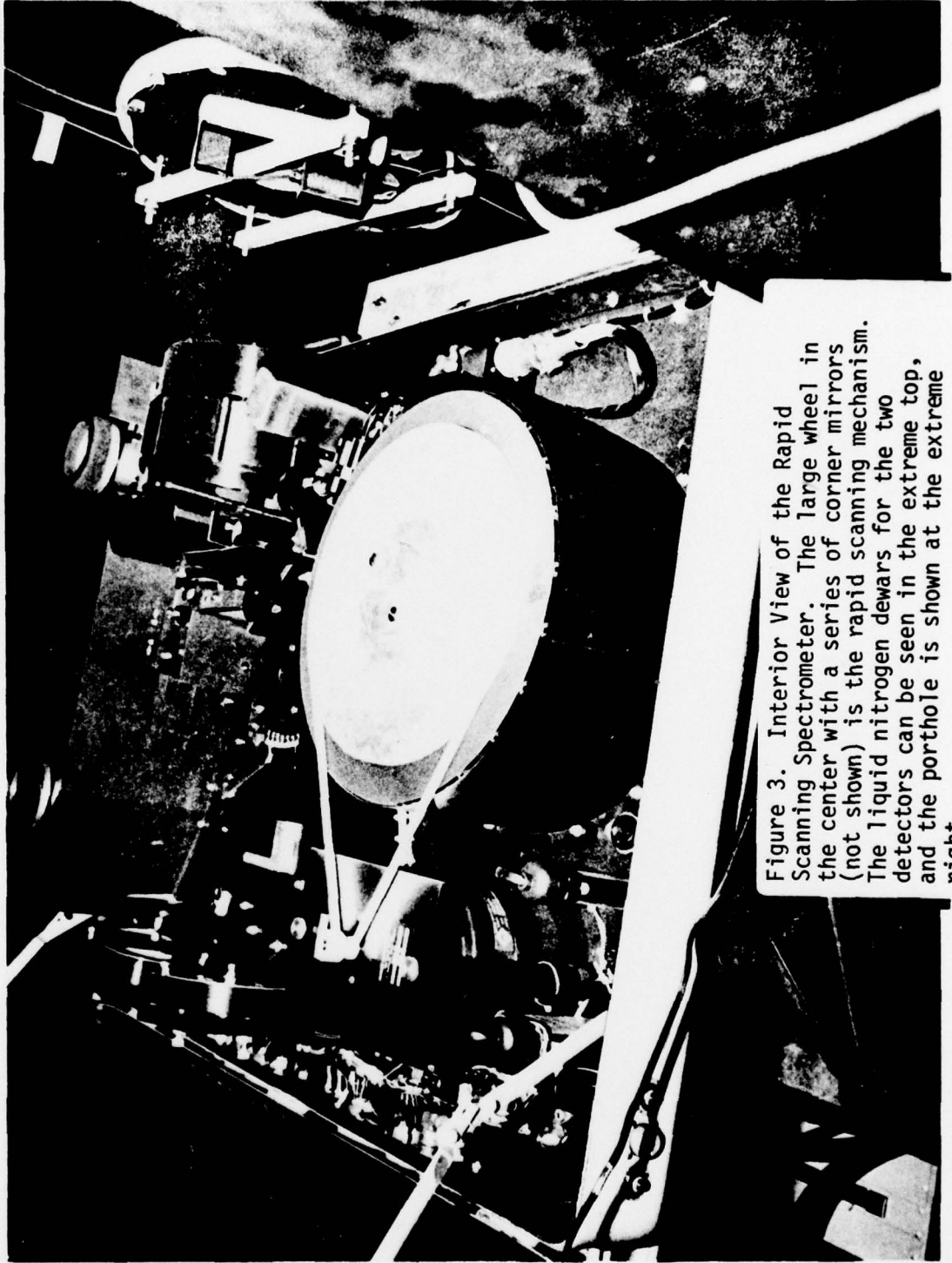


Figure 3. Interior View of the Rapid Scanning Spectrometer. The large wheel in the center with a series of corner mirrors (not shown) is the rapid scanning mechanism. The liquid nitrogen dewars for the two detectors can be seen in the extreme top, and the porthole is shown at the extreme right.

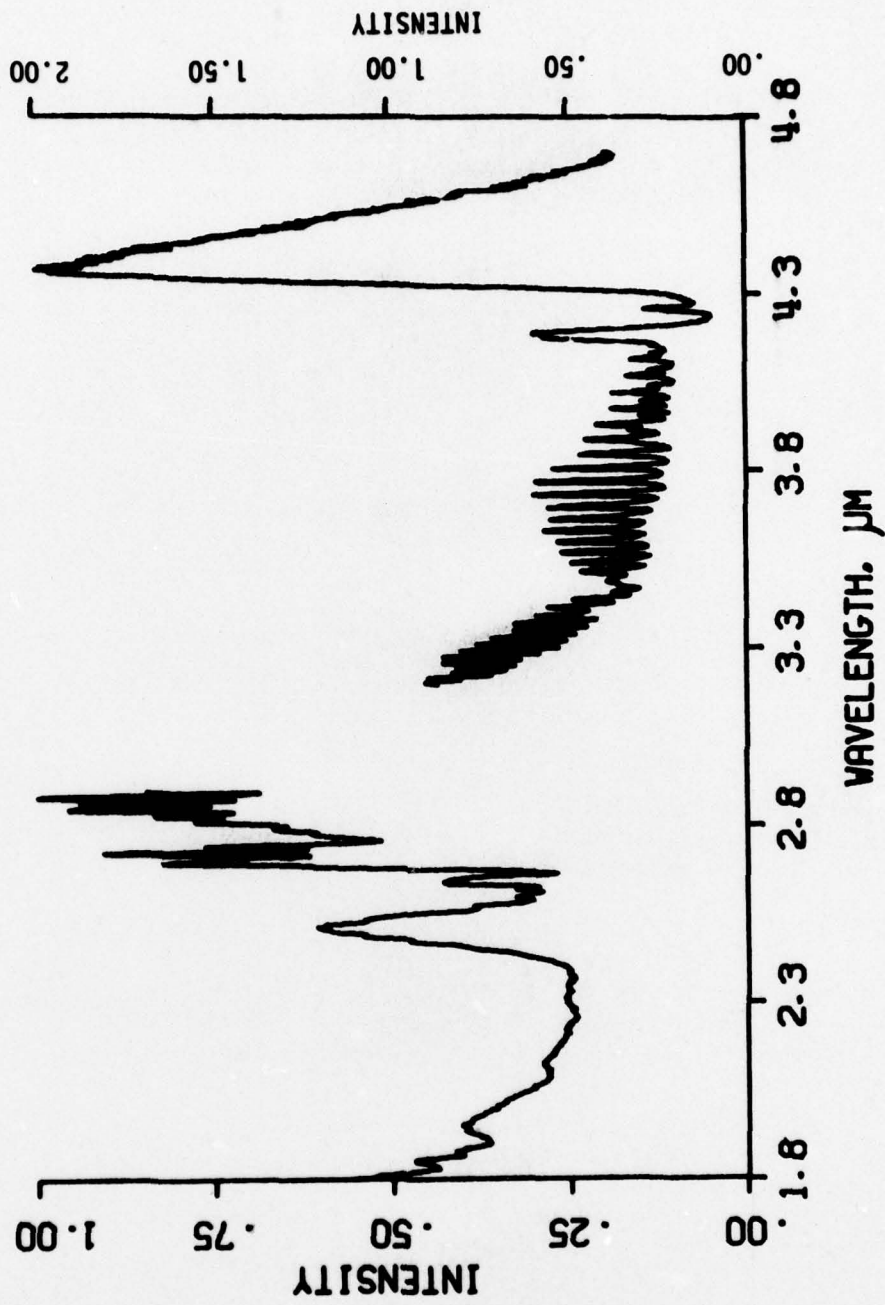


Figure 4. Relative Intensity Spectrum of Emissions From Pyrotechnic Composition IR-9. The left intensity scale is for the left half of the spectrum, and correspondingly for the right half.

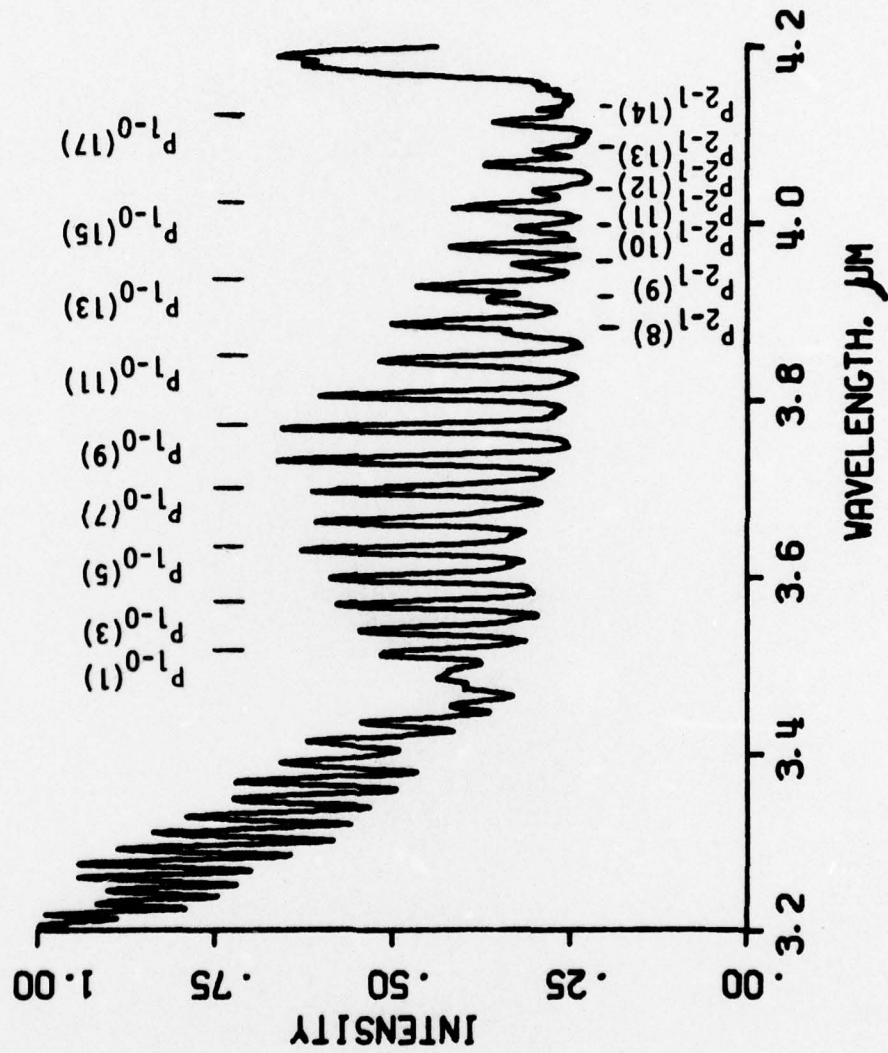


Figure 5. HCl Emission. This is an expanded portion of figure 4. Spectroscopic notation for the spectral lines is included.

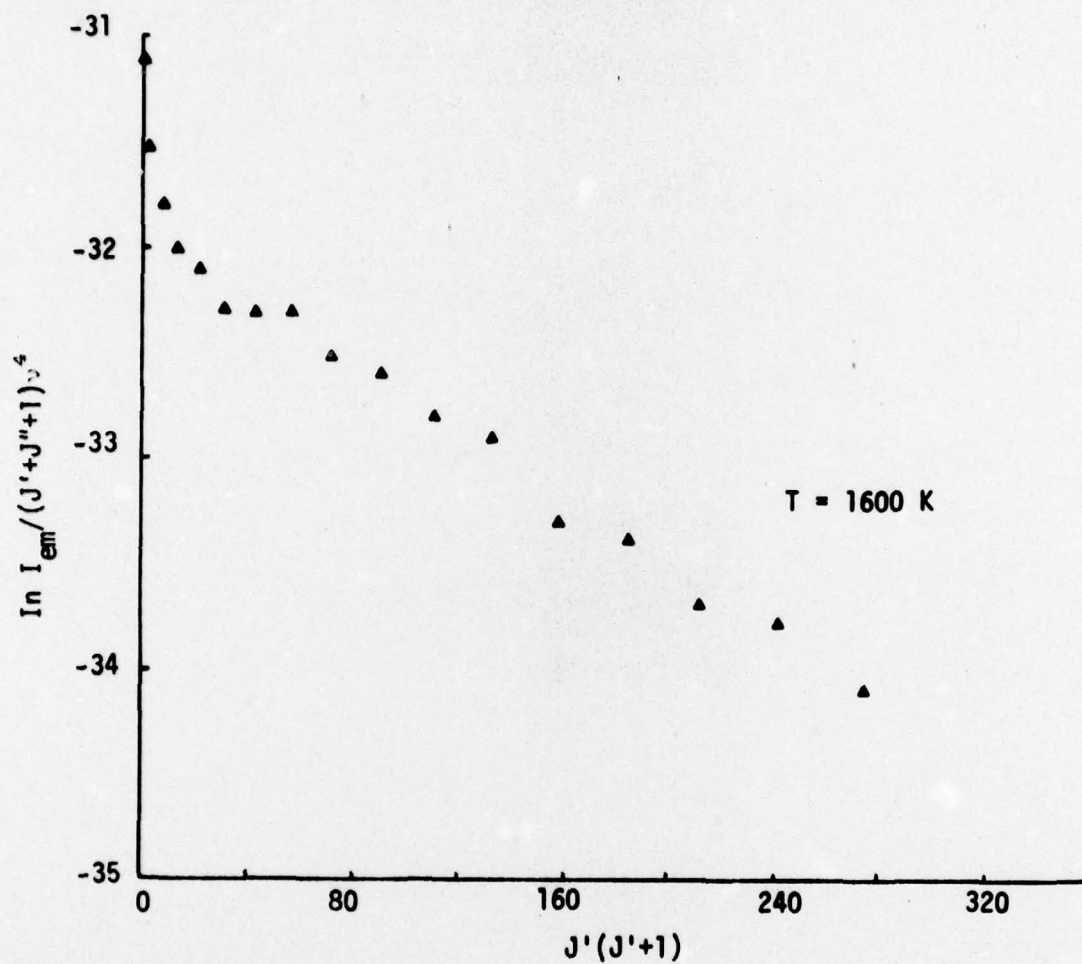


Figure 6. IR-12 #2. Plot of 1-0 P Branch Intensities. Temperature is determined from slope. See text and reference 2 for details of notation and method.

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