NORTHEASTERN UNIVERSITY
Department of Chemistry
Photochemistry and Spectroscopy Laboratory
Boston, Massachusetts 02115

Quarterly Report #3

"Investigation of New Systems for Potential Laser Action"

Grant NGR 22-011-025

Period Covered: 1 June 1969 through September 30, 1969

Date Submitted: November 12, 1969

Sponsored by the
National Aeronautics and Space Administration
Electronics Research Center
Mr. Sejfi Protopapa

Submitted for the staff by

John L. Roebber

I. Purpose of This Research

The purpose of this research is to find new chemical systems which can exhibit laser action. Metal compounds which can undergo photodissociation have been selected as the most promising candidates for laser applications. The project involves the spectroscopic study of selected metal derivatives, the characterization of any chemical changes which occur on their photolysis, and the performance of cavity experiments for the detection of laser action.

II. Research Activities Undertaken and Planned

During this quarterly period, we have been engaged in studies of the emission spectra produced in the vacuum ultraviolet region when metal halide vapors are excited by microwave or radio-frequency discharges. In addition, the absorption spectra of the mercury halides have been obtained in the 1600-1050A region.

A. Microwave and Radio-frequency Excitation Experiments on Metal Halides

Using the modified microwave apparatus described in Quarterly Report #2, we have obtained emission spectra from products produced when HgI_2 is excited in a large excess of helium gas. Our efforts to obtain emission spectra using around 300 watts of R.F. power have also been successful during this quarterly period. The double shielding around the R.F. Source eliminated the enormous pickup problems we had previously experienced. These experiments have shown that the bands in the 1600-1800A region listed in Table I of Quarterly Report #2 and shown in Figure 1 of Quarterly Report #2 are due to an impurity in the mercury halides. The same bands were observed in the helium carrier gas spectrum before the addition of any mercury halide, but they disappeared when the helium was purified by passage through a liquid nitrogen cooled trap filled with molecular sieve. These bands are undoubtedly due to traces of nitrogen or oxygen which were not completely removed from the powdered mercuric halide compounds by our degassing procedure.

However, the bands which appear in the 1800-2100 A region of the spectrum of the microwave or R.F. discharge products of HgI_2 (with or without the presence of about 0.5mm Hg pressure of helium) which were listed in Table II and shown in Figure 2 of Quarterly Report #2 are not due to the nitrogen or oxygen impurity. The most regularly spaced of these bands are listed in Table I and shown in Figure 1. These bands are not obtained from a microwave discharge through $HgBr_2$, PbI_2 or I_2. The only common bands between pure HgI_2 and $HgBr_2$ are those due to Hg atoms. Therefore, there is a good chance that these bands in the 1800-2100 A region may be due to HgI.

Caution must be exercised in assigning these bands to HgI, however. Haranath and Rao (J.Mol. Spectr. 2, 428 (1958)) have reported seeing a series of bands extending from 1950-1790 A in emission from I_2 upon excitation by a condensed discharge or a R.F.

discharge. Unfortunately, these authors do not list the wavelengths of these bands and the reproductions of their spectra in their article are too blurred to show them. Experiments with I_2 will have to be carried out very carefully using our R.F. apparatus before we can rule out I_2 as a possible source of these bands. Of course, unknown impurities may also be the cause of these bands rather than HgI.

Unfortunately work on this project has had to be temporarily suspended due to the departure of the post-doctoral fellow, Dr. Philip Russell, who has been conducting them. As soon as Dr. Russell is replaced, these experiments will be resumed.

B. Gas Phase Spectra of Metal Halides

A stainless steel cell equipped with lithium fluoride windows has been designed, built and tested. With it the spectra of HgI_2, $HgBr_2$, and $HgCl_2$ have been run in the 1600-1050Å region. These spectra were obtained on a 1-meter vacuum ultraviolet spectrometer having a measured instrumental bandwidth of about 1.0Å. Since this is a single beam instrument and since the hydrogen many-line emission spectrum was used as the light source, the data have to be reduced by a computer before the absorption spectrum can be obtained. The data reduction is now being done.

Studies in the infrared region using the matrix isolation technique have indicated that the mercuric halides may form an appreciable concentration of dimers in the gas phase.[1] This could complicate the interpretation of the gas phase vacuum-ultraviolet

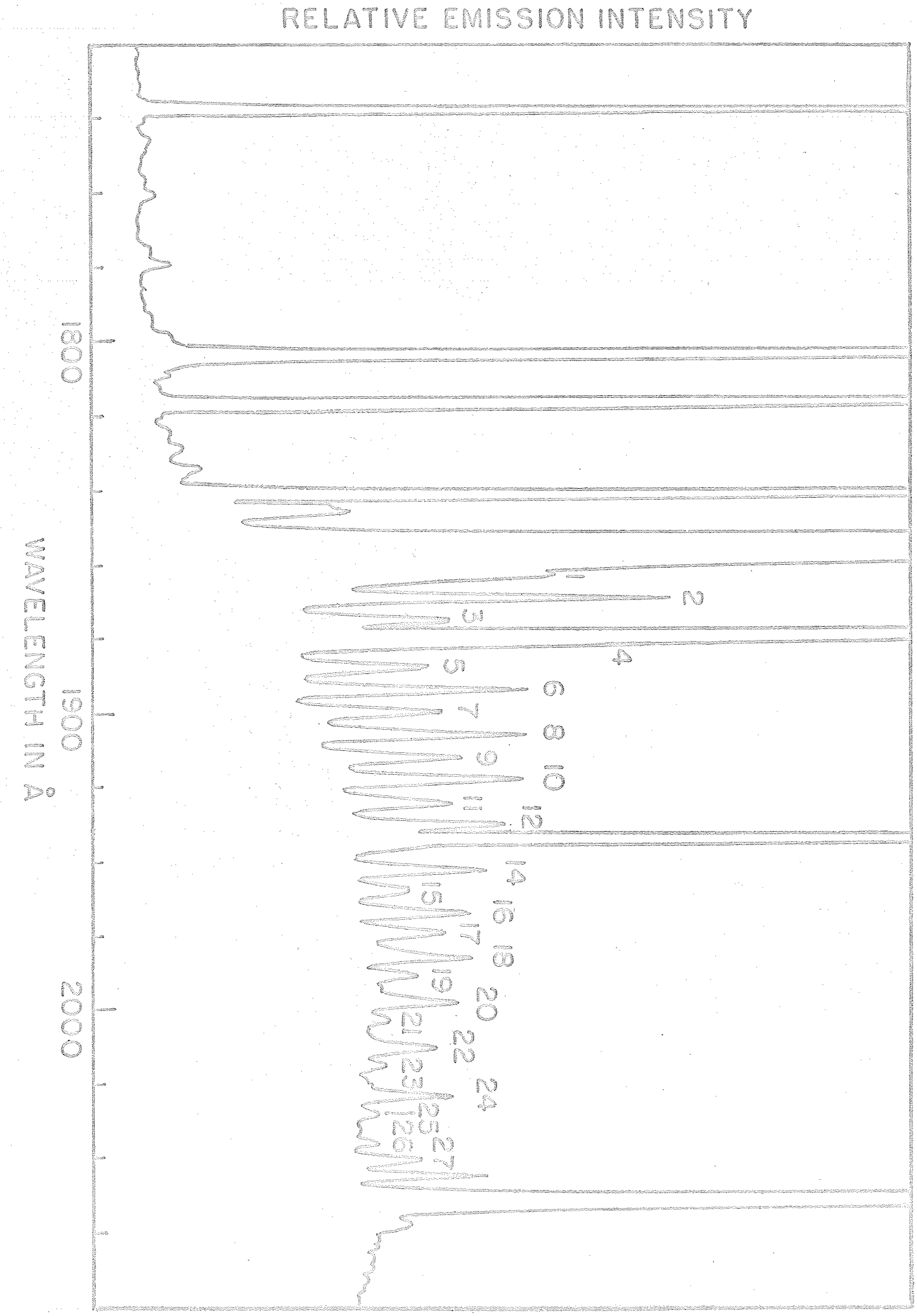
(1) A.Loewenschuss, A.Ron, and O.Schnepp, J.Chem.Phys.50,2502(1969).

spectrum. Therefore, we plan to check the dimerization by means of a mass spectrometer during the next quarter. We also plan to measure the ionization potential of the mercury halides and carry out a semiempirical quantum mechanical calculation to help interpret the spectroscopic data.

Table I. Emission bands from a microwave or radio-frequency discharge through HgI_2

Band Label	Wavelength Å	Wavenumber cm^{-1}	Difference cm^{-1}
1	1856.2	53,873	
2	1863.9	53.650	223
3	1871.5	53,433	217
4	1878.5	53,234	199
5	1886.4	53,010	224
6	1893.8	52,804	206
7	1901.1	52,600	204
8	1909.2	52,379	221
9	1916.8	52,170	209
10	1924.2	51,970	200
11	1933.0	51,732	238
12	1939.4	51,563	169
13	1947.2	51,355	208
14	1952.0	51,231	124
15	1959.3	51,039	192
16	1964.5	50,904	135

Figure 1. The emission spectrum from HgI_2 excited by a radio-frequency discharge in the presence of 0.5cm Hg of He.



RELATIVE EMISSION INTENSITY
WAVELENGTH IN Å
1800
1900
2000
1 2 3 4 5 6 7 8 9 10 11 12 14 15 16 17 18 19 20 21 22 23 24 25 26 27