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Quarterly Status Report #1

"Investigation of New Systems for Potential Laser Action"

Grant NGR 22-011-025

Period Covered: 1 December 1968 through 28 February 1969

Date Submitted: 4 April 1969

Sponsored by the

National Aeronautics and Space Administration

Electronics Research Center

submitted for the staff by

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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 spectrum of HgI in the near infrared and vacuum ultraviolet regions excited by a microwave discharge, of the fluorescence spectra of HgI_2 and its fragments in the visible and near infrared and of the electronic absorption spectra of the mercury halides.

A. Microwave Excitation Experiments on HgI_2

Since most practical lasers have been those excited by electron impact, we have examined the emission when HgI_2 is subjected to a microwave discharge. Most of the effort has been devoted to the region from 2000 A to 1600 A using a one meter vacuum ultraviolet monochromator equipped with a photoelectric detection system. A 50 micron slit width was used, resulting in a measured instrumental band width of 1.0 Å. Numerous molecular bands and atomic lines were found. As expected, the atomic lines could all be identified with well known lines of iodine or mercury.

The intensity of the molecular bands is a strong function of the pressure in the discharge tube. In all cases the molecular bands showed a distinct degradation of rotational band heads to the red and appeared to be arranged in simple vibrational progressions. In the 2170-2110 A region, these bands agree in position with the most prominent bands in the H system of HgI reported by Ramasastry and Rao.[1] Since the bands below 2110 A have the same general appearance as those between 2170 and 2110 A (i.e. sharp and degraded to the red), they are probably HgI bands.

Unfortunately, molecular iodine[2,3,4] is reported to have many emission bands in this region and mercury[3,4] has a few. Blank experiments were carried out in which I_2 and Hg were separately subjected to microwave discharges under experimental conditions as close as possible to those used for HgI_2. No molecular bands were found at the same places from Hg and I_2 as from HgI_2. However, the extreme sensitivity of the bands to experimental conditions prevent these blank experiments from being entirely conclusive. The I_2 bands are reported[2,3,4] to be degraded to the blue instead of the red, which makes it seem very unlikely that I_2 can be responsible for the bands we observe.

During the next quarterly period, we plan to examine the spectra produced by microwave discharges through vapors of ZnI_2, CdI_2 and PbI_2 and related MX_2 metal halides. The reason for examining these compounds in the 1600-2000 A region is two-fold. First, the spectra of ZnI, CdI and PbI have not been reported in this region. Since they are so closely related to HgI, their spectra should aid in the interpretation of the spectrum of HgI. Secondly, if the same bands should be obtained from any of these compounds as we have obtained from HgI_2, then we will know that the spectrum we have been observing is not that of HgI but some common product such as I_2 or Hg_2. On the other hand, failure to find the same bands can be taken as pretty conclusive proof of the correctness of our identification of the spectrum as due to HgI since a wide variety of experimental conditions will have been employed in examining the spectra from the MX_2 compounds.

A preliminary survey of the emission spectrum from a microwave discharge through HgI_2 in the near infrared region from 1-2.7 microns was made using a Block Engineering Model 200S Interferometer Spectrometer equipped with a PbS detector. Numerous emission lines were found in this region, but because of the low resolution of this instrument (40 cm^{-1} maximum) it was difficult to distinguish atomic lines from molecular bands. Furthermore, the PbS detector prevented examination of the 3.2 micron region where the $^2\Pi_{3/2} \rightarrow {}^2\Pi_{1/2}$ transition of HgI is expected to occur. The Block instrument was used because it was being employed for the HgI_2 fluorescence experiments which will be discussed below, but it is not well suited for the microwave spectra. Next quarter, the near infrared spectrum will be examined using a grating instrument equipped with a detector sensitive to beyond 3.2 microns.

B. Gas Phase Fluorescence Spectra From HgI_2

Terenin and his group[5] had reported that either

$$HgI_2 \xrightarrow{h\nu} HgI^* + I$$

$$\text{or} \quad HgI_2 \xrightarrow{h\nu} HgI + I^*$$

can occur, with high energy radiation favoring the former process. Here I* was presumed to be the $^2P_{\frac{1}{2}}$ state of the iodine atom although there was no direct experimental evidence for this. The assignment was made solely by analogy with diatomic metal halides. If the $^2P_{\frac{1}{2}}$ state of the iodine atom is indeed produced as postulated by Terenin, then there should be no problem in achieving laser action at 1.315 microns due to the inversion of population between the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ states of dissociated atomic iodine, as in the case of CF_3I.

During this quarter we first checked the result of Terenin that illumination of HgI_2 in its 2660 A absorption band produces no fluroescence from HgI in the visible region. The fluorescence apparatus described in Progress Report #2 was used with the modification that the Jarrell-Ash 8200 scanning monochromator was replaced by a small Bausch and Lomb monochromator. We found no visible fluorescence in agreement with Terenin's results.

We next looked at the 1.3 micron region using a PbS cell hooked to a lock-in amplifier as our detection system. No fluorescence could be detected in the initial experiments. While efforts were underway to optimize the sensitivity of the apparatus, a Block Engineering Model 200S Interferometer

Spectrometer became available for use. Since this is an extremely sensitive instrument, we immediately substituted it as the analyzing unit. No iodine atom emission was obtained. However, these initial experiments were quite crude. Minor improvements in the arrangement of the apparatus using the Interferometer to better advantage should result in an increase in sensitivity of several orders of magnitude. During the next quarter, after these changes are made, the sensitivity of the whole apparatus will be calibrated. In addition, excitation of HgI_2 in its shorter wavelength bands will be tried and the near infrared emission spectra examined.

C. Gas Phase Absorption Spectra of HgI_2 and $HgBr_2$

Spectral studies of the metal halides were undertaken to aid in understanding their electronic structure and hence indirectly in evaluating their laser potential. The vacuum ultraviolet absorption spectrum of HgI_2 was reported in Progress Report #4, and that of $HgBr_2$ in Progress Report #5. The data obtained at that time were in the form of strip chart records of I_o and I as a function of the counter reading of the monochromator.

Since that time, the relative light intensities I_o and I have been read from the recorder charts at intervals of 0.2 - 0.3 Å using a digital curve reader and placed on punched cards. The absorption coefficient k, in cm^{-1}, was then calculated at each wavelength from the usual expression

$$k = \frac{1}{\ell} \frac{760}{P} \frac{T}{273} \ln \frac{I_o}{I}$$

Appropriate corrections were made in the calculation of k for the small scattered light level (less than 5%). Wavelengths were determined by fitting the locations of known emission lines to a straight line using the method of least squares. Wavelengths were converted into wavenumbers and the absorption coefficient k *versus* wavenumber was plotted automatically.

These computer plots of the HgI_2 and $HgBr_2$ spectra became available during this quarterly period and have been subjected to a preliminary analysis. Table I lists the oscillator strengths, f, and the positions of the band maxima for mercuric iodide and mercuric bromide. The oscillator strengths are only approximate because the mercuric halide pressures were assumed to be the equilibrium vapor pressure and it was difficult to be sure that the temperature measured was at the coldest region of the cell. The diffuse vibrational structure on the 2080 Å band and the comparatively sharp structure on the 1800 Å band of HgI_2 and the 1830 Å band of $HgBr_2$ had been observed previously by Wieland.[6] Wehrli[7] has made a careful study of the structure on the 2080 Å band of HgI_2, the 1830 Å band of $HgBr_2$, and the 1690 Å band of $HgCl_2$. He has made an essentially complete vibrational analysis of all three bands. His band maxima and vibrational assignments for the 2080 Å band of HgI_2 and the 1830 Å band of $HgBr_2$ are shown in Tables II and III. Our results agree with those of Wehrli within the experimental error of locating the maxima of diffuse bands and our lower resolution.

TABLE I. Oscillator Strengths and Positions of Mercuric Halide Band Maxima

HgI_2

Band (Å)	ν_{max} (cm^{-1})	k_{max} (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	f	Vibrational Structure	Electronic Assignment
2660	37,600	64	5,900	0.01	None	
2240	44,590	160	2,500	0.02	Very Diffuse	
2080	48,026	80	800	0.003	Diffuse	Σ_u^+
1920	51,927	90	1,300	0.005	None	
1800	55,600	7,000	400	0.02	Comparatively Sharp	Σ_u^+ (?)
1740	57,520	20,000	3,400	0.3	Probably None	

$HgBr_2$

Band (Å)	ν_{max} (cm^{-1})	k_{max} (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	f	Vibrational Structure	Electronic Assignment
2260	44,000	210	3,000	0.03	None	
1990	50,312	550	3,500	0.08	Possibly Very Diffuse	
1830	54,500	400	550	0.01	Comparatively Sharp	Σ_u^+
1750	57,028	68	400	0.001	Diffuse	Σ_u^+ (?)

TABLE II. Vibrational Maxima on HgI_2 Bands

2240 Å Band

ν (cm^{-1})	Δν (cm^{-1})		ν (cm^{-1})	Δν (cm^{-1})
41,860	220		43,460	80
42,180	220		43,540	80
42,400	150	}220	43,620	80
42,550	70		43,700	80
42,620	130	}220	43,780	80
42,750	90		43,860	80
42,840	120	}220	43,940	80
42,960	100		44,020	80
43,060	80		44,100	80
43,140	80		44,180	80
43,220	80		44,260	80
43,300	80		44,340	80
43,380			44,420	

2080 Å Band[a]

ν	Quantum Number		ν	Quantum Number	
(cm^{-1})	v'_s v'_δ v'_{as}	v''_s v''_δ v''_{as}	(cm^{-1})	v'_s v'_δ v'_{as}	v''_s v''_δ v''_{as}
47,414	000	300	47,921	020	000
47,529	000	210	48,006	100	000
47,572	000	200	48,045	120	000
47,615	020	200	48,133	200	000
47,672	000 200	110 300	48,161	300	020
47,733	000	100	48,224	300	010
47,793	000	020	48,266	300	000
47,882	000	000	48,378	400	000

(a) Taken from M. Wehrli, Helv. Phys. Acta, 11, 339 (1938).

TABLE II. Vibrational Maxima on HgI_2 Bands (continued)

1800-1740 Å Bands

ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
55,220	160	56,140	140
55,380	160	56,280	140
55,540	140	56,430	150
55,680	100	56,570	140
55,780	220	56,700	130
56,000		56,840	140

TABLE III. Vibrational Maxima on $HgBr_2$ Bands

1830 Å Band[a]

ν	Quantum Number		ν	Quantum Number	
(cm^{-1})	$v'_s\ v'_\delta\ v'_{as}$	$v''_s\ v''_\delta\ v''_{as}$	(cm^{-1})	$v'_s\ v'_\delta\ v'_{as}$	$v''_s\ v''_\delta\ v''_{as}$
53,711	000	310	54,416	000	000
53,769	000	300	54,466	020	000
53,865	000 040	220 300	54,603	100	000
53,905	100	310	54,630	130	110
53,937	200	400	54,681	200	020
53,972	000	200	54,714	210	020
54,010	010	200	54,792	200	000
54,089	000	120	54,837	220	000
54,159	100	200	54,933	400	100
54,192	000	100	54,978	300	000
54,236	020	100	55,005	330	010
54,315	000	020	55,151	400	000

(a) Taken from M. Wehrli, Helv. Phys. Acta, 11, 339 (1938).

1750 Å Band

ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
~56,250	~130	56,930	
56,380	120	57,080	150, 160
56,500	100	57,240	160
56,600	100	57,400	150
56,700	120	57,550	160
56,820	110	57,710	

Wieland[6] reported structure on the 1800 Å band of HgI_2, which we also obtain (see Table II). Interestingly enough, Wehrli did not study this band, and no vibrational assignments have been made for it. Wieland[6] found a very weak band at 1750 Å in the spectrum of $HgBr_2$, but attributed it to impurities. Our spectra of $HgBr_2$ show a band at 1750 Å which has diffuse vibrational structure on it (see Table III). Although it may not be obvious from Tables II and III, mercuric iodide's 1800 Å band and mercuric bromide's 1750 Å band both look very similar to the 1830 Å band of $HgBr_2$. No detailed analysis of these two bands has yet been attempted, but the same pattern found by Wehrli for the 1830 Å band of $HgBr_2$ does seem to fit them as well.

On the basis of Wehrli's vibrational analysis, Sponer and Teller[8] have assigned the 1690 Å, 1830 Å, and 2080 Å absorption bands of $HgCl_2$, $HgBr_2$, and HgI_2 to $\Sigma_u^+ \leftarrow \Sigma_g^+$ transitions. If our preliminary vibrational assignments are correct, then the 1800 Å band of HgI_2 and the 1750 Å band of $HgBr_2$ can also be assigned to $\Sigma_u^+ \leftarrow \Sigma_g^+$ transitions. Such transitions are allowed in linear molecules, and it is somewhat surprising to find oscillator strengths as small as 0.003 for the 2080 Å band of HgI_2 and 0.001 for the 1750 Å band of $HgBr_2$. Even the oscillator strengths of 0.02 for the 1800 Å band of HgI_2 and 0.01 for the 1830 Å band of $HgBr_2$ are small for allowed transitions.

The very diffuse vibrational structure on the 2240 Å band of HgI_2 has not previously been reported in the literature. As Table II shows, this structure seems to consist mostly of a progression in 80 cm^{-1}. Since the ground state frequencies of HgI_2 are reported to be 156 cm^{-1} for the symmetric stretch, 33 cm^{-1} for the bending mode and 235 cm^{-1} for the asymmetric stretch,[7,8] an 80 cm^{-1} vibration in an upper state is hard to understand. Any attempt to make a vibrational assignment must await a careful study of the effect of temperature on the intensities of these bands.

References

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