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Leo Brewer and Richard F. Porter

January 12, 1954

Berkeley, California

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ABSTRACT

The ultraviolet band system, produced in emission from magnesium oxide vapor in thermal equilibrium with the solid oxide, is shown to originate from a gaseous monomer of MgO .

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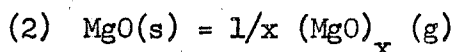
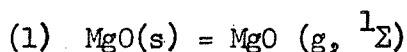
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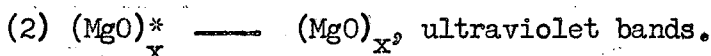
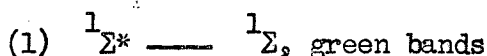
As shown previously,¹ it is possible to distinguish a monomer from a polymer by comparison of intensities of the ultraviolet and green bands produced in emission from MgO vapor in equilibrium with solid MgO at varying thermodynamic activity.

The equilibria to be considered are:



where $(\text{MgO})_x$ represents the unknown "ultraviolet" specie.

The transitions are:



The relationship between intensities was shown to be:

$$\left\{ \frac{I_{{}^1\Sigma}(\text{activity 1})}{I_{{}^1\Sigma}(\text{activity 2})} \right\}_T^x = \left\{ \frac{I_{(\text{MgO})_x}(\text{activity 1})}{I_{(\text{MgO})_x}(\text{activity 2})} \right\}_T$$

Where $I_{{}^1\Sigma}$ is the intensity of the green bands and $I_{(\text{MgO})_x}$ is the intensity of ultraviolet bands.

Experimental

Solid MgO was heated in the King furnace as described earlier.¹ The graphite heating element was lined with tantalum and tungsten respectively and the MgO was in contact with the tungsten only. When the furnace had reached the desired temperature, light emitted from the vapor was focused onto the slit of a three meter concave grating and reflected from the grating directly to the slit of LP28 photomultiplier tube. The device for recording intensities was that described by Phillips.² Several intensity tracings were made at one temperature for both systems. These measurements are shown in Table 1.

Table 1

	T°K	I_{12}	$I_{(MgO)_x}$
		(unit solid activity)	(unit solid activity)
	2605	12.4	28.6
	2600	13.5	25.8
	2600	12.3	23.4
Average	2600	13.0 ± 1	26.0 ± 3

The furnace temperature was then increased to 2750°K at which temperature the solid MgO reacts rapidly with the tungsten lining. The furnace was then lowered to approximately its original temperature and several tracings of both systems were made. The results of these measurements are shown in Table 2.

Table 2

T°K	$I_{\frac{1}{2}}$	$I_{(MgO)}^x$
	(reduced solid activity)	(reduced solid activity)
2595	3.5	11.3
2595	4.75	8.25
2595	4.0	7.8
Average	4.1 ± .5	9.1 ± 2

In the initial runs solid MgO existed in the furnace and hence the intensities shown in Table 1 pertain to the solid at unit activity. Tungsten reacting with the solid eventually removes the MgO phase and produces a second phase at reduced MgO activity. This reduction in activity causes the reduction of intensity shown in Table 2.

For both systems integrated intensities were measured. The reported values are proportional to the areas inclosed by the bands and extrapolated background, and all intensities are adjusted to the same amplification gain. For the ultraviolet system the region between $\lambda 3700$ and $\lambda 3830$ was used, and the 0,0 sequence at $\lambda 5007$ was treated for the green system.

Conclusions and Discussion

The comparison of the two sets of data is shown in Table 3. The values of Table 2 are compared with the average value of each set in Table 1. The values of each set of data in Table 3 at the most deviate 20% from the average values. Within this experimental uncertainty the two sets of values are equal, hence we must conclude $x = 1$ and a monomer of MgO is involved in the ultraviolet transition.

$\left\{ \begin{array}{l} \frac{I_{\Sigma}(\text{unit solid activity})}{I_{\Sigma}(\text{reduced solid activity})} \end{array} \right\}$		$\left\{ \begin{array}{l} \frac{I_{(\text{MgO})x}(\text{unit solid activity})}{I_{(\text{MgO})x}(\text{reduced solid activity})} \end{array} \right\}$	
T = 2595 -2600		T = 2595 -2600	
.27 .36 .31		.43 .32 .30	
Average .32 ± .06		.35 ± .08	

If the molecule were a dimer, that is, if $x = 2$, the ultraviolet bands should decrease as $(.32)^2$ or to approximately one tenth of their original value. If this were the case, the ultraviolet intensities would be off by a factor of three which is far from the limits of uncertainty.

If the gaseous molecules were not in equilibrium within the furnace we would expect an anomalous trend in the two sets of figures. Equilibrium is fairly certain since all runs were made under .2 atms of argon to cut down diffusion of the vapor out the ends of the tube. In case a dimer had been formed in the gas phase, the total pressure of MgO vapor would still be high enough to insure a sufficient number of collisions between vapor species themselves.

It was also possible to reduce the MgO activity by heating MgO and ZrO_2 mixtures. A mixture of 20 mole percent MgO was heated to 2600°K, and tracings of both systems were made. The two systems appeared with comparable intensity, and both were decreased to approximately one-fifth the intensity observed with pure MgO at the same temperature. Accurate integrated intensities could not be compared, however, since chlorine impurities in the ZrO_2 produce MgCl(g) which has many strong bands in the same ultraviolet region as MgO.

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REFERENCES

1. Porter, Richard F., University of California Radiation Laboratory
Unclassified Report UCRL-2416 (December, 1953).
2. Phillips, J. G., ONR Contract No. Nonr....160(00) (1953).