Spectra of Argon, Oxygen, and Nitrogen Mixtures*

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The green bands which are associated with the 5577 A oxygen line for oxygen and argon mixtures have been obtained with an ozonizer discharge tube. Nitrogen was found to greatly enhance the intensity of the green if the discharge tube was maintained at the temperature of liquid air. Spectrograms with a plate factor of 1.9 A/mm partially resolve the rotational structure of the overlapping vibrational bands. A 20 cm^{-1} difference appears between several bands. It is assumed that this spectrum results from loosely bound molecular states which may be represented by $A(^1S_0)O(^1S_0)$ and $A(^1S_0)O(^1D_2)$. There are no bands associated with the 2972 A line. The 5577 A line and associated bands have been observed in a dc arc through 3 atmospheres of commercial argon.

A green glow is found to dominate the spectrum of an oxygen and nitrogen mixture if the discharge is maintained at −192°C. This spectrum consists of the 5577 A line, a continuum, and a few diffuse bands.

I. INTRODUCTION

THE 2972 A ($^1S_0-^3P_1$), 5577 A ($^1S_0-^1D_2$), 6300 A ($^1D_2-^3P_2$), and 6363 A ($^1D_2-^3P_1$) lines of oxygen all involve a transition from a metastable level. McLennan[1] first identified the 5577 A line when he used a rare gas to help isolate the metastable oxygen atoms from the walls of the discharge tube. For xenon and oxygen mixtures, bands which are in the neighborhood of the 5577 A line have been reported by Kenty and co-workers,[2] and by Herman.[3,4] Also, Herman has found bands near the 2972 A line for $Xe+O_2$ mixtures. Vegard,[5] Jenkins,[6] and Herman[7] have reported bands which are closely associated with the 5577 A line for a mixture of argon and oxygen. An asymmetric broadening of this oxygen green line in a discharge through nitrogen which contains traces of oxygen has been reported by Kaplan.[8] With one exception,[9] the laboratory produced oxygen red lines have been very weak. Sayers and Emeleus[10] reported that in their experiments a red continuum at 6400 A always accompanied the appearance of the weak 6300 A and 6363 A lines.

The purpose of this research has been to investigate the continua or bands which are associated with the 2972, 5577, 6300, and 6363 A forbidden lines of oxygen whenever the oxygen is excited in the presence of argon.

II. EXPERIMENTAL PROCEDURE

Reagent-grade argon, nitrogen, and oxygen were obtained in break-seal flasks from Air Reduction Company. In some of the experiments, the oxygen was produced by electrolytic means and purified by passing it over hot copper wire, P_2O_5, and then through a liquid nitrogen trap.

Three different types of discharge tubes were utilized. The first source contained internal aluminum electrodes and was 50 cm long with an inside diameter of 6.6 cm. A discharge could be maintained in this tube for pressures up to 6 cm of Hg. The second source was designed so that a dc arc could be maintained between two tungsten electrodes in a rare gas with pressures as high as 6 atmospheres. An ozonizer type discharge tube was used to excite gases up to one atmosphere of pressure. In this third source the gases were excited in the 3-mm spacing between cylindrical external electrodes. Frequencies of 400 cps, 900 cps, and 4 Mc/sec were used for the excitation. For the 4-Mc/sec excitation, an external inductance was chosen to obtain resonance with the 30 $\mu\mu f$ capacity of the ozonizer.

The spectra were obtained with a Hilger constant deviation spectrograph, a large Littrow prism mount with a plate factor of 13 A/mm at 5600 A, and a

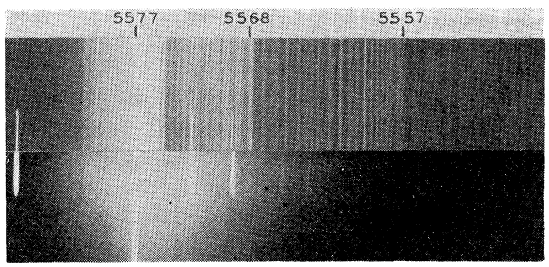

FIG. 1. (a) Green spectrum of A, O_2, and N_2 mixture at −195°C. (b) Green spectrum of O_2 and N_2 mixture at −195°C.

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Littrow mounted plane grating which gave a plate factor of 1.9 A/mm.

III. EXPERMENTAL RESULTS

Our experiments with the large-diameter discharge tube, using argon with a 14% oxygen content, produced the forbidden green and red oxygen lines for total pressures between 3 and 12 mm of Hg. The two red lines were very weak and on low-dispersion spectrograms a continuum was observed to begin at 6400 A. Higher dispersion spectrograms revealed that this continuum, which was first reported by Sayers and Emeleus,[10] is actually the triplet system of CO.

The spectra of an arc between tungsten electrodes, surrounded with argon containing traces of oxygen, were obtained for argon pressures up to 6 atmospheres. Commercial tank argon was used for the experiment and the hydrogen was removed by pumping the gas over hot CuO and P_2O_5. The arc emitted the characteristic argon spectrum if the upper electrode was kept

TABLE I. Band heads near the 5577 A line for $A+O_2+N_2$ mixtures.

λ(A)	ν(cm⁻¹)	Intensities
5576.43	17927.7	*vs*
75.59	930.3	*vs*
71.65	943.1	*s*
61.73	975.1	*w*
56.62	993.5	*ms*
47.28	021.9	*w*
44.4	031	*vw*
41.6	040	*vw*
34.8	062	*ew*
28.6	083	*ew*

directly above the lower one. With an electrode spacing of 3 to 4 mm, a current of 0.25 ampere, a total pressure of 3 atmospheres, and if the upper electrode was displaced slightly from the vertical, a beautiful green flame would appear and extend as much as $2\frac{1}{2}$ in. along the upper electrode. The green flame could be produced with pressures up to 5 atmospheres, but slightly higher currents were needed to maintain the arc and the flame was reduced in height. In all of the experiments, the green flame was the most intense for the lowest current at which the arc could be maintained. Spectrograms of the flame show a strong 5577 A oxygen line with a close-lying continuum. The oxygen producing this line was present as an impurity in the commercial argon. The 6300 A and 6363 A oxygen lines were not observed with the above discharge tube.

When the ozonizer discharge tube was used, the oxygen red lines were not observed, but certain experimental conditions produced a very intense green line and accompanying band structure. When the tube was filled with one atmosphere of argon containing 7 parts per million of oxygen, a weak green band system was obtained. 900 or 400 cps excitation was found to be more effective than 60 cps excitation. A great enhancement of these same bands was produced when a small quantity of nitrogen was added to the mixture and the discharge tube maintained at the temperature of liquid nitrogen. A print of this spectrum is shown in Fig. 1(a) and the prominent band heads are listed in Table I. More than 130 rotational lines have been measured but the overlapping bands have prevented definite rotational assignments.

TABLE II. Diffuse bands near the 5577 A line for N_2+O_2 mixtures.

λ(A)	Intensities	λ(A)	Intensities
5584.63	*ew*	5574.30[a]	
84.11	*ew*	72.87	*w*
82.87	*w*	72.30	*ew*
82.23	*w*	70.08	*edge*
81.28	*w*	69.27	*ew*
80.62	*w*	68.37	*ew*
79.05[a]		67.61	*ew*
77.34	*vs*[b]		

[a] A uniform continuum appears between these two values.
[b] $O(^1S_0 \rightarrow {}^1D_2)$.

In addition to the above green bands, the spectrum of the A, O_2, and N_2 mixture contains the 2972 A oxygen line with no associated bands. Other band systems in the spectra have been identified as NO γ, NO β, second positive N_2, Goldstein-Kaplan N_2, and a very weak first positive N_2. Two new NO β bands were found and assigned as 2845.6 A (3,9) and 2984.9 A (3,10). When the discharge tube, which gave the green bands with 900 cps excitation, was excited at -195°C with a frequency of 4 Mc/sec, the green line and associated bands were completely absent and the first positive N_2 bands were prominent.

Other gas mixtures were tried, with the 900 cps excitation, in an effort to produce the above green bands. A mixture of helium, nitrogen, and oxygen failed to produce any green radiation. A tube filled with oxygen, nitrogen, and argon at the partial pressures of 0.6, 7.2, and 72 cm of Hg, respectively, failed to glow green initially. However, after operating the discharge for 30 minutes, with the tube maintained at -195°C, the discharge glow slowly changed to a brilliant green with the same spectral characteristics as the $A+O_2$ spectrum. Also, an intense green spectrum which consists of the 5577 A line, a continuum, and a few faint bands was obtained with an oxygen (0.05 cm of Hg) and nitrogen (28 cm of Hg) mixture if the tube was maintained at -195°C. The spectrum of this discharge differs from the one found for $A+O_2$ as may be seen in Fig. 1(b). The center of symmetry of the continuum is shifted about 3 cm^{-1} toward the violet relative to the atomic line. The diffuse bands which are superimposed on the continuum are given in Table II.

IV. DISCUSSION

(A) A, O_2, and N_2 Mixtures

The green bands which result from a mixture of oxygen and argon are associated with the 5577 A oxygen line and have been assigned by Herman[7] and Vegard[5] to AO* molecules. The resolving of the rotational lines, by the present research, provides further support for the combination of oxygen in the metastable states, $^1S_0$ and $^1D_2$, with argon to form an excited molecule. Within the discharge we would expect that the collision rate of metastable oxygen atoms with neutral argon will be much greater than the collision rate with argon in any excited state; then it is assumed that the molecular states are formed from the atomic states as follows: $A(^1S_0)O(^1S_0)$ and $A(^1S_0)O(^1D_2)$. The appearance of the 2972 A line with no associated band structure indicates that the $A(^1S_0)O(^3P)$ molecular state is unstable or that the molecular transition $A(^1S_0)O(^1S_0) \rightarrow A(^1S_0)O(^3P)$ is forbidden. The absence of bands in the red region which would represent a $A(^1S_0)O(^1D_2) \rightarrow A(^1S_0)O(^3P)$ transition led Herman[11] to assume Hund's case *a* coupling which would forbid such transitions; yet, in the spectrum of the XeO molecule where the binding energy is greater, bands are observed which appear to be associated with the 2972 A line[4] and a red continuum has been observed around 8000 A.[12] These molecular transitions are not expected for case *a* coupling but they are allowed for case *c* coupling. Preliminary studies of the green XeO bands indicate that the coupling may be case *d*,[12] but the evidence is not conclusive at the present.

Vibrational assignments for the band heads reported in the results section have not been found. The tentative assignments made by Herman[7] cannot be fitted to the present data. In the XeO spectrum the 0,0 band is found at 5062 A and the 0,5 band is the most intense. Using the XeO spectrum as a guide, we would expect that the potential minimum of the $A(^1S_0)O(^1S_0)$ state is shifted toward larger internuclear distance relative to the $A(^1S_0)O(^1D_2)$ minimum. Under such circumstances, it is possible that the 0,0 band of the AO molecules is not observed due to the Franck-Condon principle. The frequency difference of 20 cm^{-1} which is observed between several bands appears to be a vibrational frequency of the ground state.

The overlapping of vibrational bands and the apparent breaking-off of rotational series have prevented an analysis of the rotational structure. It is possible that the rotational lines of the band at 5556.6 A may be assigned if further resolution of the band head is obtained.

It is tempting to explain the increase in intensity of the green bands, when nitrogen is added, as resulting from the presence of active nitrogen. However, the experiments of Noxon[13] on the afterglow of nitrogen at atmospheric pressure have shown that the presence of active nitrogen is not necessary to explain the 5577 A afterglow which results from traces of oxygen. Molecular oxygen is known to accept energy from the $O(^1S_0)$ atom, and we assume that the increase in intensity of the green radiation results from a decrease in the amount of molecular oxygen present. In fact, the experimental conditions favor the production of $O(^1S_0)$ from the dissociation of NO. The discharge spectrum shows the presence of N_2 and NO within the discharge. Any other oxides of nitrogen which were formed were frozen on the cell walls by the liquid air. At room temperature the cell contained a red-brown gas which shows that NO_2 was one of the products of the discharge.

(B) N_2+O_2 Mixtures

Our investigation of the spectrum of the N_2+O_2 mixture at $-195°C$ was undertaken primarily to show that the green bands which appeared were different from the bands which were observed for $A+O_2$. The diffuse bands and continuum which accompany the 5577 A line in the spectra of a N_2+O_2 mixture provide another example of collision induced emission. Very similar broadening of the 2537 A Hg line has been reported by Oldenberg,[14] Kuhn,[15] and Preston.[16] Ch'en and Takeo[17] have reported absorption bands near the principal series lines of the alkali metals for various pressures of a rare gas, and they summarize related experimental data in their review article.

The diffuse bands which are listed in Table II may arise from a loosely bound N_2+O^* molecular state which could result from a two-body collision. The violet shift of the continuum shows that the Van der Waals forces between $O(^1D_2)$ and N_2 are greater than between $O(^1S_0)$ and N_2. This is in agreement with similar data for xenon and oxygen where the $O(^1D_2)Xe(^1S_0)$ state is more tightly bound than the $O(^1S_0)Xe(^1S_0)$ state.

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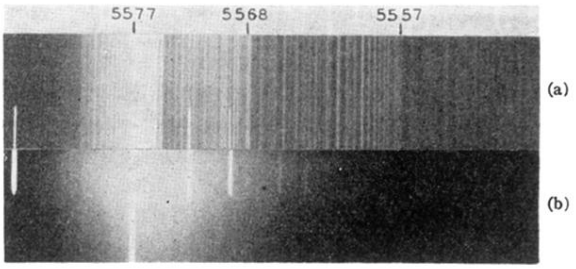

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(b) Green spectrum of O_2 and N_2 mixture at $-195°C$.