

Determination of  $D_0^0(\text{AlO})$  from Crossed-Beam Chemiluminescence of  $\text{Al} + \text{O}_3$ 

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In a molecular beam apparatus, a thermal beam of aluminum atoms ( $\approx 1700^\circ\text{K}$ ) intersects an uncollimated thermal beam of ozone molecules ( $300^\circ\text{K}$ ) and the resulting visible chemiluminescence is recorded with a 1 m scanning monochromator. The chemiluminescence spectrum consists of (1) the  $\text{AlO } B \ ^2\Sigma^+ - X \ ^2\Sigma^+$  blue-green system for which we have assigned bands to the strongly structured features in the region 4200–4900 Å, and (2) more intense weakly structured features in the region 4500–8500 Å, which appear to be emission from a polyatomic aluminum oxide on which there seems to be superimposed the  $\text{AlO } B \ ^2\Sigma^+ - A \ ^2\Pi$  band system. From the chemiluminescent spectrum a minimum value of  $5.13 \pm 0.05$  eV is deduced for the dissociation energy of the ground state of aluminum oxide. By accepting the upper limit of 5.20 eV deduced by MacDonald and Innes from Tyte's shock tube absorption data, we recommend the value  $D_0^0(\text{AlO}) = 5.15 \pm 0.5$  eV.

## INTRODUCTION

In principle, chemiluminescence should be an excellent method to establish bounds on the dissociation limits of molecules because no detailed analysis of the spectrum is required.<sup>1</sup> In practice, however, chemiluminescence studies often suffer from the occurrence of multiple secondary reactions that obscure the luminescence produced by a given reaction. In order to apply chemiluminescence studies to the determination of molecular dissociation energies, we have developed means for carrying out chemiluminescent reactions under single-collision conditions.<sup>2</sup> A molecular beam apparatus, called LABSTAR, has been constructed in which metal atoms from a differentially pumped source chamber traverse a scattering chamber where they intersect a poorly defined beam of reactant molecules. The short wavelength limit of the light from the chemiluminescent reaction provides a lower bound to the heat of formation of the reaction products. Still more stringent lower bounds can be derived from an analysis of the chemiluminescent spectrum in which ( $v'$ ,  $v''$ ) band assignments are made. Previously, this method has been applied to the chemiluminescent reaction of barium atoms with  $\text{NO}_2$  molecules from which a minimum value for the ground state dissociation energy of  $\text{BaO}$  has been deduced.<sup>3</sup> We report here a determination of the ground state dissociation energy of aluminum monoxide based on an analysis of the chemiluminescence resulting from the reaction of aluminum atoms with ozone molecules.

## EXPERIMENTAL

The beam apparatus, LABSTAR, has been described previously.<sup>2,3</sup> Aluminum filings (99% purity) are placed inside a molybdenum crucible that fits inside a resistance-heated cylindrical graphite heating element. The aluminum atom beam flux is monitored using a Granville-Phillips film thickness monitor. In order to obtain a flux of aluminum atoms corresponding to  $1.5 \times 10^{15}$  atoms/cm<sup>2</sup>·sec, the graphite heating element is operated at temperatures on the order of  $1700^\circ\text{K}$ .

Ozone for a number of experimental runs is generated with a Welsbach ozonizer. The freshly prepared ozone is frozen in a silica gel trap where it is kept at the temperature of dry ice. Before using the ozone, the silica gel trap is pumped on to remove  $\text{O}_2$  generated by the decomposition of ozone. The ozone is then leaked into the scattering chamber through a micrometer needle valve.

The chemiluminescence is detected with a 1 m Interactive Technology Czerny-Turner spectrometer operated in first order with a Bausch and Lomb 1200 groove/mm grating blazed at 5000 Å. A Centronic S-20 photomultiplier inside a cooled housing ( $\approx 250^\circ\text{K}$ ) is attached to the exit slits of the spectrometer. The photomultiplier signal is detected by a Keithley 417 fast picoammeter whose output signal (fully damped) drives a Leeds and Northrup strip chart recorder. The latter provides a tracing of the spectrum.

## APPEARANCE OF CHEMILUMINESCENT SPECTRUM

Figure 1 shows a rapid scan (500 Å/min) of the chemiluminescence accompanying the reaction of aluminum atoms with ozone. The chemiluminescent spectrum extends from about 4000 to 8500 Å and is dominated by the presence of a broad emission feature in the red that appears weakly structured under low resolution. The onset of this emission continuum occurs at about 4500 Å. Towards the blue, between 4000 and 4900 Å, are easily recognized bands of the well known  $\text{AlO } B \ ^2\Sigma^+ - X \ ^2\Sigma^+$  blue-green system.

Figure 2 shows a slower scan (50 Å/min) of the  $\text{AlO } B - X$  system between 4200 Å and 4900 Å and Fig. 3 shows a more resolved scan of the region extending from 4650 to 4725 Å. In the spectral region from 4200 to 4900 Å the overlap with the dominant continuum is small. We have identified transitions from  $0 \leq v' \leq 18$  of the  $B$  state to  $0 \leq v'' \leq 16$  of the  $X$  state. It is clear from an examination of Fig. 2 that, when account is taken of the Franck-Condon factors,<sup>4</sup> the higher vibrational levels of the  $B$  state are preferentially populated

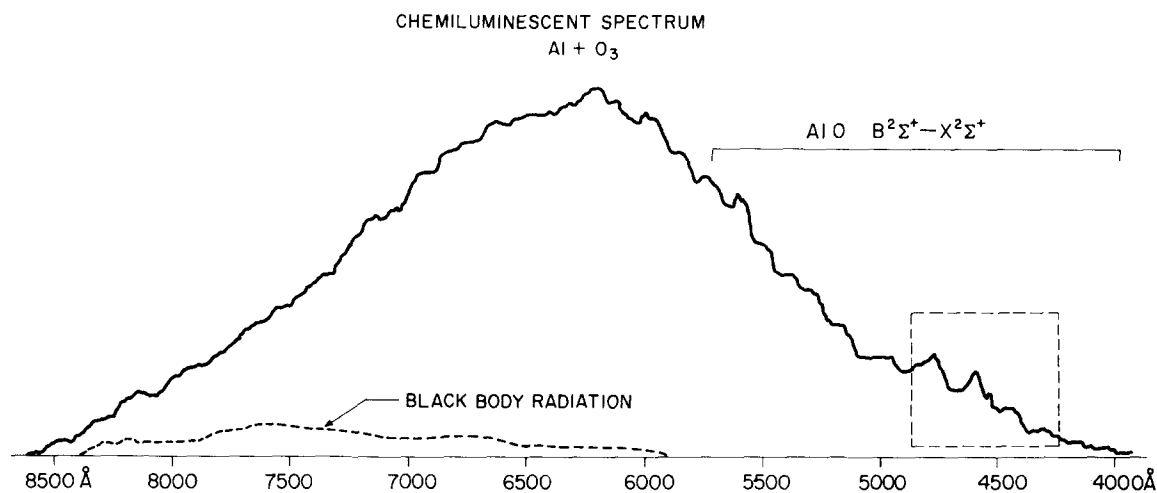


Fig. 1. Chemiluminescent spectrum for the reaction of Al+O<sub>3</sub>. Blackbody radiation from the oven is indicated by dotted lines in the figure. The portion of the spectrum enclosed by the dashed lines is shown at higher resolution in Fig. 2.

in the reaction  $\text{Al} + \text{O}_3 \rightarrow \text{AlO}(B^2\Sigma^+) + \text{O}_2$ . The inverted population of the *B* state resulting from this chemical reaction may have important implications in future chemical laser technology. Table I lists several new bandhead measurements resulting from this study. Previously,<sup>4</sup> Deslandres tables of band heads for the AlO *B-X* system were limited to  $v'' \leq 12$  and  $v' \leq 16$ .

The emission continuum for the Al+O<sub>3</sub> reaction,

which appears to be whitish yellow when viewed by eye, is thought to result primarily from a polyatomic emitter. The most likely choice is believed to be AlO<sub>2</sub>. We speculate that this emitter may be the same as that seen in releases of trimethyl aluminum in the upper atmosphere.<sup>5</sup>

A further feature of this emission continuum is the presence of weak but reproducible bumplike structure

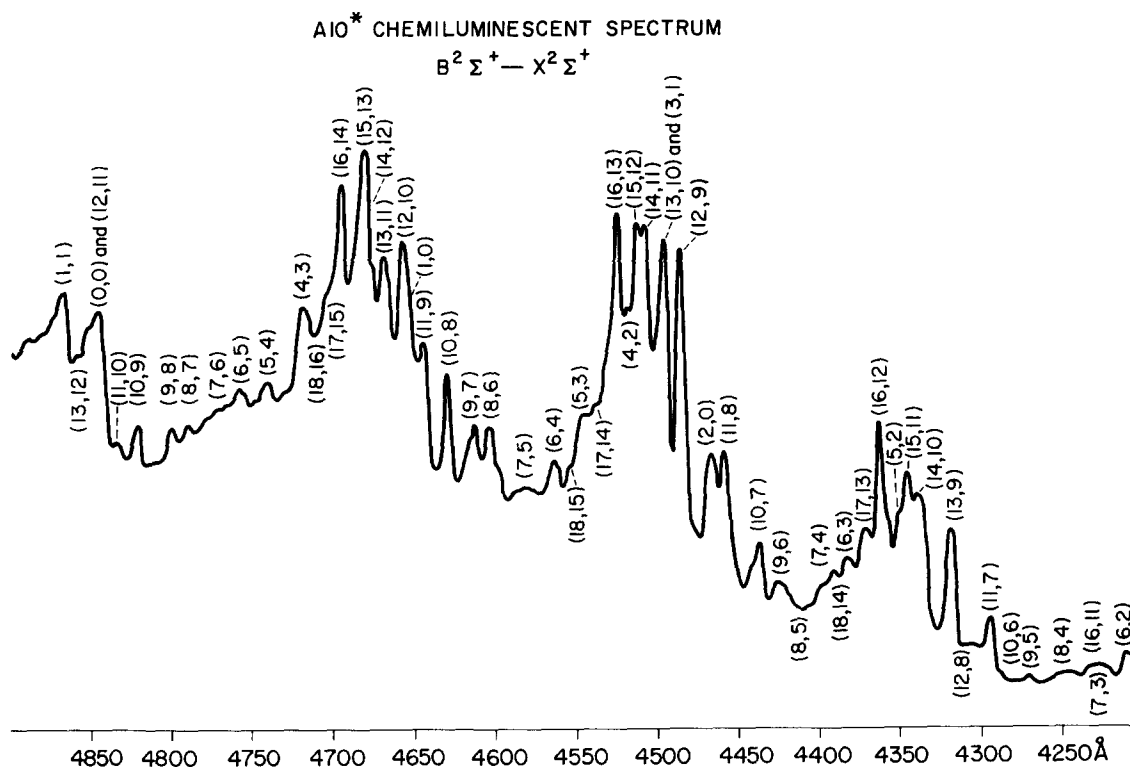
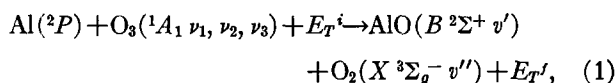


Fig. 2. AlO *B*<sup>2</sup>Σ<sup>+</sup>-*X*<sup>2</sup>Σ<sup>+</sup> chemiluminescent emission from the reaction Al+O<sub>3</sub>. The bandheads are designated by (v', v''). The position of new bandheads is given in Table I.

that spans the entire length of the continuum. Using the spectroscopic data of Tyte and Nicholls<sup>4</sup> for the  $B$  state ( $\nu_{00}=20635.2\text{ cm}^{-1}$ ;  $\omega_e=870.05\text{ cm}^{-1}$ ;  $\omega_e x_e=4.15\text{ cm}^{-1}$ ) and of McDonald and Innes<sup>6</sup> for the  $A$  state [ $\nu_{00}(^2\Pi_{3/2})=5219.4\text{ cm}^{-1}$ ;  $\nu_{00}(^2\Pi_{1/2})=5348.5\text{ cm}^{-1}$ ;  $\omega_e=728.5\text{ cm}^{-1}$ ;  $\omega_e x_e=4.15\text{ cm}^{-1}$ ], we calculated approximate band head positions for the  $B-A$  system and compared them to the observed structural features. The calculated values were found to agree closely with the bumplike structure, but the weakness of these features makes their identification tentative. It would appear that we see transitions from the preferentially populated high vibrational levels of the  $B$  state to comparable vibrational levels ( $v\leq 16$ ) of the  $A$  state. Because of the strong underlying continuum and the poor signal-to-noise of the bumplike features we could not determine a quantitative value of the branching ratio. However, we estimate that the  $\text{AlO } B-A$  system is approximately an order of magnitude less intense than the  $\text{AlO } B-X$  system.

### CALCULATION OF A LOWER BOUND TO $D_0^0(\text{AlO})$

Consider the gas-phase reaction



where aluminum atoms and ozone molecules in their ground states collide with relative initial translational

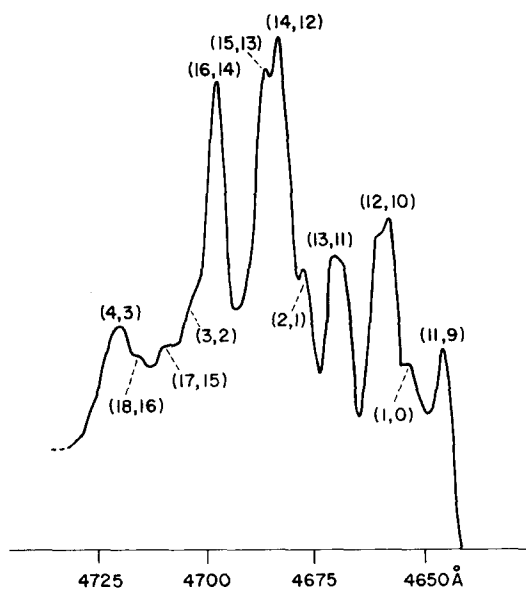
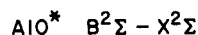


Fig. 3. Higher resolution scan of the  $\text{Al}+\text{O}_3$  chemiluminescence emission extending from 4650 to 4725 Å.

TABLE I. New bandheads observed in the  $\text{AlO } B^2\Sigma^+-X^2\Sigma^+$  band system.

Bandhead	$\lambda(\text{Å})$
(17, 13)	4373 Å
(17, 14)	(4534 Å) <sup>a</sup>
(17, 15)	4706 Å
(18, 14)	(4384 Å) <sup>a</sup>
(18, 15)	(4545 Å) <sup>a</sup>
(18, 16)	(4716 Å) <sup>a</sup>
(13, 9)	4325 Å
(14, 12)	4674 Å
(15, 13)	(4684 Å) <sup>a</sup>
(16, 13)	4523 Å
(16, 14)	4694 Å

<sup>a</sup> Overlapped by other band(s).

energy  $E_T^i$  to form excited-state  $\text{AlO}$  molecules and ground state  $\text{O}_2$  molecules with relative final translational energy  $E_T^f$ . In the above reaction, the energy liberated in the formation of the strong  $\text{Al-O}$  bond of aluminum monoxide is considerably in excess of the energy required to rupture the weak  $\text{O-O}_2$  bond of ozone. This reaction exoergicity may appear as internal excitation of the  $\text{AlO}$  molecules, as internal excitation of the  $\text{O}_2$  molecules, and as relative final translational energy of the products.

Conservation of energy requires that all forms of energy on the righthand side of Eq. (1) exactly balance all forms of energy on the lefthand side of Eq. (1). Let us choose  $\text{Al}(^2P) + \text{O}(^3P) + \text{O}_2(X^3\Sigma_g^- v''=0)$  to be the reference energy.<sup>7</sup> Then we may write

$$-D_0^0(\text{O-O}_2) + E_{\text{int}}(\text{O}_3) + E_T^i = -D_0^0(\text{AlO}) + E_{\text{int}}(\text{AlO}) + E_{\text{int}}(\text{O}_2) + E_T^f, \quad (2)$$

where  $E_{\text{int}}(\text{O}_3)$ ,  $E_{\text{int}}(\text{AlO})$ , and  $E_{\text{int}}(\text{O}_2)$  are the internal energies (electronic, vibrational, rotational) of  $\text{O}_3$ ,  $\text{AlO}$ , and  $\text{O}_2$ , respectively, measured with respect to the lowest energy level of each species. The energy sum  $E_{\text{int}}(\text{O}_2) + E_T^f$  is unknown and cannot be obtained from the chemiluminescent spectrum. Thus we obtain the inequality

$$D_0^0(\text{AlO}) \geq E_{\text{int}}(\text{AlO}) + D_0^0(\text{O-O}_2) - [E_{\text{int}}(\text{O}_3) + E_T^i]. \quad (3)$$

The value of  $E_{\text{int}}(\text{AlO})$  may be obtained from the chemiluminescent spectrum shown in Fig. 2 by identifying the highest vibrational level of the  $\text{AlO } B$  state populated in the reaction of  $\text{Al}+\text{O}_3$ . With the assignment of the (18, 15) band at  $21996\text{ cm}^{-1}$  (4545 Å), [note that the (18, 16) and (18, 14) bands have also been observed], we have

$$\begin{aligned} E_{\text{int}}(\text{AlO}) &= E(\text{AlO } B^2\Sigma^+ v') - E(\text{AlO } X^2\Sigma^+ v''=0) \\ &= 21996\text{ cm}^{-1} + G''(15) - G''(0) \\ &= 34947 \pm 50\text{ cm}^{-1} \quad (4.33\text{ eV}), \end{aligned} \quad (4)$$

where the energy difference  $G''(15) - G''(0)$  between the  $v''=15$  and  $v''=0$  vibrational levels of the ground state is obtained from extrapolation of the  $G''(v)$  data listed by Tyte and Nicholls.<sup>4</sup> It should be noted that we have already accounted for a large part of the rotational excitation of the AlO product molecules formed in the  $v'=18$  level of the  $B$  state by combining the band head measurement for (18, 15) with the band origin data for  $G''(15) - G''(0)$ . The error in  $E_{\text{int}}(\text{AlO})$  embraces the spread of values obtained in a similar manner from the (18, 16) and the (18, 14) bands.

The internal excitation of the ozone molecules  $E_{\text{int}}(\text{O}_3)$  is calculated to be  $\frac{3}{2}RT = 0.025$  eV where  $T = 300^\circ\text{K}$ . This estimate takes account of the rotational energy of the ozone molecules but ignores the possible excitation of the  $\nu_2$  bending mode. Since the frequency of the latter is  $705\text{ cm}^{-1}$ , the population of the  $\nu_2=1$  level is only 3% of the  $\nu_2=0$  level, and hence the contribution of  $\text{O}_3$  molecules in the  $\nu_2=1$  level to the population of the highest  $v'$  level of the AlO  $B$  state is negligible for these studies. The calculation of  $E_T^i$  is more difficult. The reaction rate  $k$  is given by

$$\int_0^\infty u f(u) Q(u) du,$$

where  $u$  is the relative velocity,  $f(u)$  is the relative velocity distribution of the reactants, and  $Q(u)$  is their velocity-dependent cross section.<sup>8</sup> We have no knowledge of the dependence of the reactive cross section on relative velocity. Accordingly, we have crudely estimated  $E_T^i$  as  $\frac{3}{2}RT_{\text{Al}} + \frac{3}{2}RT_{\text{O}_3} = 0.23 \pm 0.03$  eV, where  $T_{\text{Al}}$  and  $T_{\text{O}_3}$  are the temperatures of the aluminum and ozone beams. Thus, we take the value of the thermal energy of the reactants to be  $E_{\text{int}}(\text{O}_3) + E_T^i = 0.26 \pm 0.03$  eV. We believe this value of  $E_T^i + E_{\text{int}}(\text{O}_3)$  is, if anything, an overestimate of this quantity so that the inequality shown in Eq. (3) is preserved. The uncertainty in  $E_T^i + E_{\text{int}}(\text{O}_3)$  reflects the spread in thermal energies that might contribute to the excitation of the highest  $v'$  level of the AlO  $B$  state in the reaction.

The value of  $D_0^0(\text{O}-\text{O}_2)$  is not known spectroscopically but may be obtained from a thermodynamic cycle based on the recommended<sup>9</sup> standard heat of formation of ozone  $\Delta H_{f\text{O}_3}^\circ = -34.74$  kcal/mole ( $\frac{3}{2}\text{O}_2 \rightarrow \text{O}_3$ ) at  $0^\circ\text{K}$  and the standard heat of atomization of oxygen  $\Delta H_{f\text{O}}^\circ = 58.983$  kcal/mole ( $\frac{1}{2}\text{O}_2 \rightarrow \text{O}$ ) at  $0^\circ\text{K}$ . We find

$$\begin{aligned} D_0^0(\text{O}-\text{O}_2) &= 24.24 \pm 0.4 \text{ kcal/mole} \\ &= 1.05 \pm 0.02 \text{ eV,} \end{aligned} \quad (5)$$

where the uncertainty in  $D_0^0(\text{O}-\text{O}_2)$  reflects the uncertainty in the calorimetric determinations<sup>10</sup> of the standard heat of formation of ozone.

Substitution of numerical values for  $E_{\text{int}}(\text{AlO})$ ,  $E_{\text{int}}(\text{O}_3) + E_T^i$ , and  $D_0^0(\text{O}-\text{O}_2)$  in Eq. (3) yields a lower bound of

$$D_0^0(\text{AlO}) \geq 5.13 \pm 0.05 \text{ eV} \quad (6)$$

to the ground state dissociation energy of aluminum monoxide.

Referring to Fig. 2, we note that the reaction  $\text{Al} + \text{O}_3 \rightarrow \text{AlO}(B^2\Sigma^+) + \text{O}_2$  results in a monitored product distribution for AlO extending over the first eighteen vibrational energy levels of the  $B^2\Sigma^+$  state, i.e., there is a distribution over the accessible internal modes of the products as well as in the relative translational energy of the products. Equality in Eq. (6) assumes (1) that the internal energy of  $\text{O}_2$  and the relative translational energy of the products can be neglected, and (2) that  $E_{\text{int}}(\text{AlO})$  corresponds to the identification of the highest energetically accessible internal quantum state of AlO populated in the  $\text{Al} + \text{O}_3$  reaction.

## DISCUSSION

The ground state dissociation energy of AlO has been a subject of some controversy. The earliest determinations were spectroscopic in nature, based on linear Birge-Sponer extrapolations of bandhead data primarily obtained from the AlO  $B^2\Sigma^+ - X^2\Sigma^+$  blue-green band system. In this manner, Lessheim and Samuel<sup>11</sup> (1933) report a value of  $D_e(\text{AlO}) = 4.15$  eV using Mecke's<sup>12</sup> vibrational analysis of the AlO blue-green bands while Roy<sup>13</sup> (1939) reports a value of  $D_e(\text{AlO}) = 4.03$  eV based on his own extension and refinement of Mecke's analysis. Later, Bekart, and Declerck<sup>14</sup> (1960) reported a value of  $D_0^0(\text{AlO}) = 5.04$  using the previously mentioned spectroscopic analysis of Mecke, but this must be a typographical error. Direct substitution into the Morse relation  $D_e = \omega_e^2 / 4\omega_e x_e$  yields the values  $D_e = 4.17$  eV from Mecke's bandhead formula and  $D_e = 4.16$  eV from Roy's bandhead formula. In any case, a linear Birge-Sponer extrapolation cannot be considered a reliable means of estimating  $D_0^0(\text{AlO})$  because (1) the vibrational data is too limited, (2) higher-order anharmonicity corrections have not been included, and (3) Birge-Sponer extrapolations are suspect for molecules with ionic bonding.<sup>15</sup>

By contrast, the determination of  $D_0^0(\text{AlO})$  by flame spectrophotometry has led to much larger values. Thus Gurvich and Viets<sup>16</sup> (1958) report a value of  $D_0^0 = 5.95 \pm 0.17$  eV while Newman and Page<sup>17</sup> (1970) find  $D_0^0 = 6.30 \pm 0.26$  eV. However, objections can be raised to both these studies because of interference of other combustion species e.g.,  $\text{Al}_2\text{O}$ ,  $\text{AlO}_2$ ,  $\text{Al}_2\text{O}_2$ , and  $\text{Al}_2\text{O}_3$ , and because of the possible departure from equilibrium in the flame.

There has been only one mass spectrometric determination of  $D_0^0(\text{AlO})$ . Drowart, De Maria, Burns, and Inghram<sup>18</sup> (1960) studied the evaporation of alumina under nearly neutral conditions in tungsten and molybdenum Knudsen cells. They determined a value of  $D_0^0(\text{AlO}) = 5.00 \pm 0.21$  eV, which is intermediate between those values derived from spectroscopic extrapolations and from flame studies. However, it is known that mass spectrometric results require care in interpretation for oxides, especially refractory ones,

where complex oxides of the sample and the cell walls may be formed.

In an attempt to make a direct spectroscopic measurement of the dissociation energy, Tyte<sup>19</sup> (1967) used a shock tube to study the absorption spectrum of AlO in the region extending from 2000 to 3000 Å. He found an absorption continuum whose long wavelength limit (onset) occurs at  $2729 \pm 5$  Å. Tyte interpreted this to be a transition from the  $v''=0$  level of the ground state to a repulsive or very weakly bound upper state of AlO. With the assumption that the ground and upper states dissociate to the same atomic products, Tyte deduced an upper limit for the AlO dissociation energy of  $4.54 \pm 0.01$  eV. In 1968 Gaydon<sup>15</sup> reviewed this unsatisfactory situation and recommended the value  $D_0^0(\text{AlO}) = 4.6 \pm 0.1$  eV, which is obviously weighted strongly by Tyte's determination.

However, in 1969, McDonald and Innes<sup>6</sup> cast new light on these discrepant measurements of  $D_0^0(\text{AlO})$ . These authors carried out a rotational analysis of two emission bands found near 2500 and 2800 Å. They deduced that the observed spectra correspond to emission from two highly excited states of AlO to a common lower  $^2\Pi$  state lying only  $5300 \text{ cm}^{-1}$  (0.66 eV) above the AlO ground state. Based upon the fact that Tyte found both the 2500 and 2800 Å systems in absorption, McDonald and Innes hypothesized that Tyte's absorption continuum corresponds to transitions from the low-lying  $A^2\Pi$  state. Assuming that both upper and ground states dissociate to the same separated atom limit a value of 5.20 eV ( $4.54 + 0.66$  eV) was determined for the AlO ground state dissociation energy, in good agreement with the mass spectrometric values. This value of  $D_0^0(\text{AlO})$  is also an upper limit since dissociation of the excited states to products other than the ground state atoms would only lead to the determination of a lower dissociation energy.

We accept McDonald and Innes' reinterpretation of Tyte's absorption data. With their upper limit of 5.20 eV and our lower limit of  $5.13 \pm 0.05$  eV we believe it is reasonable to estimate  $D_0^0(\text{AlO}) = 5.15 \pm 0.05$  eV.

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