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Observation of Highly Endoergic Chemiluminescent Reactions on Laser Ablation of Metals. Detection of AlH ($A^1\Pi$), AlN ($A^3\Pi_i$), AlO ($B^2\Sigma^+$) and MgO ($B^1\Sigma^+$) in Al + NH_3, Al + H_2O, and Mg + O_2 Systems

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Occurrence of highly endoergic chemiluminescent reactions was observed using laser ablation of metal targets for Al + NH_3, Al + H_2O and Mg + O_2 systems. Observed chemiluminescent species were AlH ($A^1\Pi$), AlN ($A^3\Pi_i$), AlO ($B^2\Sigma^+$) and MgO ($B^1\Sigma^+$).

Chemiluminescence (CL) studies of metal-containing free radicals have a long history1-5). Early works have, however, been limited to alkaline earth metals because of vapor pressure problems. Mercury is another target, naturally. For example, Hayashi et al.6) detected CL of HgBr ($B^2\Sigma^+$) using metastable Hg ($^3P_{0,2}$).

Recently a technical breakthrough was achieved by the use of laser ablation (or laser vaporization) of metals in combination with the cell or molecular beam of reacting gas. Simard et al. 7) used laser-vaporized Zr atoms in the reaction with carbonyl sulfide (OCS) injected near the metal target. ZrS was observed by laser induced fluorescence (LIF). Ebben et al.8) demonstrated the efficiency of laser evaporation of a solid target followed by adiabatic expansion for the production of cold beams of neutral small free radicals. They detected CuH ($X^1\Sigma$), CH ($X^2\Pi$), SiH ($X^2\Pi$), CuO ($X^2\Pi$) and FeO ($X^5\Delta$) by LIF. Ebben et al.9) also detected SiC using this technique. Costes et al.10) used a pulsed crossed supersonic molecular beam apparatus to study reactions of Al atoms with O_2, CO_2 and SO_2 by LIF. In these works free radicals are formed in their ground states, and detected by LIF. Kasatani et al.11) detected CL of AlO ($B^2\Sigma^+$) species using laser ablation/static gas combination for the Al + O_2 system. Levy12) employed a laser-ablated pulsed beam of Mn atoms to study Mn (a^6S, a^6D_J, etc.) + O_2, NO_2, CO_2 and SO_2 systems. In the present paper, Al + NH_3, Al + H_2O, and Mg + O_2 systems have been studied using laser ablation/static gas combination. CL of AlH ($A^1\Pi$), AlN ($A^3\Pi_i$), AlO ($B^2\Sigma^+$, $C^2\Sigma^+$), and MgO ($B^1\Sigma^+$) has been detected.

The experimental set up is essentially the same as previously reported$^{11)}$. Briefly, an aluminum (Wako) or magnesium (Nakarai) substrate was placed in a octangular pillar-type vacuum chamber (one side 7 cm, 17.4 cm high) evacuated to 1 mTorr (1 Torr = 133.322 Pa) by a rotary pump (200 l/min). Ammonia (Seitetsu, 99.9%), water (bidistilled), or oxygen (Takachiho, 99.95 %) was introduced into the chamber through a 1/4-inch copper pipe and a variable leak valve (Swagelok kel-F). Second harmonic (532 nm) from a Nd^{3+}:YAG laser (Quanta-Ray, DCR-2, 50-100 mJ, 10 Hz) was softly focused on the substrate by a quartz lens (f = 20 cm). The diameter of the laser spot on the Al substrate was ca. 2 mm. CL was collected by a quartz lens (f = 10 cm) onto the entrance slit of a monochromator (Nikon G-250) equipped with a photomultiplier (Hamamatsu R166, 1P28 or R928). The substrate was rotated by a small motor so as to a new surface of the substrate was ablated by each laser shot. The signal from the photomultiplier was fed into a Boxcar integrator (Evans Associates gated integrator module 4130) and stored in a microcomputer via an A/D converter.

(A) Al + H_2O system. Typical observed emission spectrum is shown in Fig. 1. Pressure of H_2O in the vacuum chamber was 1.0 Torr under the flow conditions. Laser power was 83 mJ/pulse. The $\Delta v = v'-v'' = -2, -1, 0, 1, 2$ sequences of AlO $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition were observed, together with the $(v', v'') = (0,0)$ band of $A^1\Pi \rightarrow X^1\Sigma^+$ transition of AlH. A weak feature due to AlO $C^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition was observed in the 300-320 nm range. Expanded spectrum of the Δv=-1 sequence bands of AlO $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition is shown in the upper panel of Fig. 2. Pressure of H_2O was 0.5 Torr. In the lower panel of the same figure, a simulated spectrum is given. In the simulation Franck-Condon factors of Coxon and Naxakis$^{13)}$ are used. It is assumed that rotational temperature (T_R) is 1300 K, and that relative vibrational distribution for v' = 0-7 is 100:75:54:33:19:14:11:5. This vibrational distribution can be fitted reasonably well by a Maxwell-Boltzmann distribution (T_v = 2700 ± 200 K). Similar

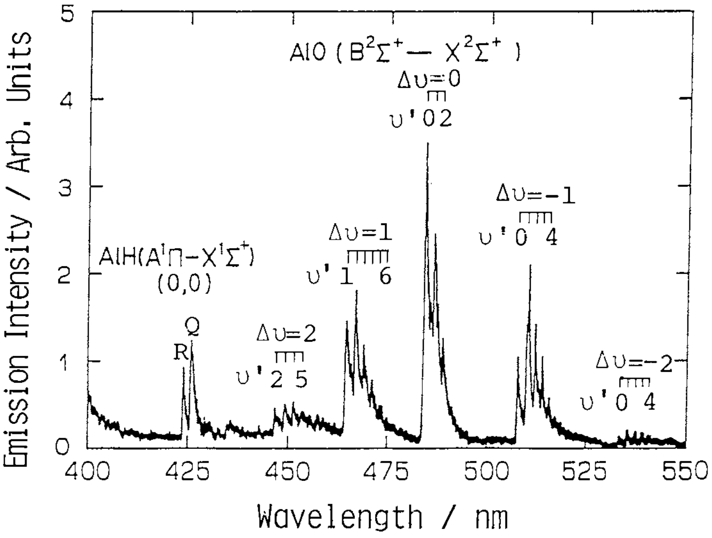

Fig. 1. Chemiluminescence spectrum of Al + H_2O system.

results were obtained for $\Delta v = 1$ sequence bands. Vibrational temperatures are higher than rotational ones.

A quadratic dependence on H_2O pressure was observed for AlO $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ CL intensity, while AlH $A^1\Pi \rightarrow X^1\Sigma^+$ intensity increased linearly with the H_2O pressure.

(B) Al+NH_3 system. Under the conditions of NH_3 flow (0.5-1.0 Torr) and laser power of 82 mJ pulse^{-1}, the following emission bands were observed in addition to emission of Al atoms and Al^+ ions: (a) 420-440 nm bands, assignable$^{14)}$ to (0,0) and (1,1) sequences of $A^1\Pi \rightarrow X^1\Sigma^+$ of AlH, (b) a band near 508 nm, assignable$^{15)}$ to the (0,0) band of $A^3\Pi_i \rightarrow X^3\Pi_i$ of AlN, and (c) the bands in the 335-340 nm range assignable$^{16)}$ to the (0,0), (1,1), (2,2) sequences of $A^3\Pi \rightarrow X^3\Sigma^-$ transition of NH.

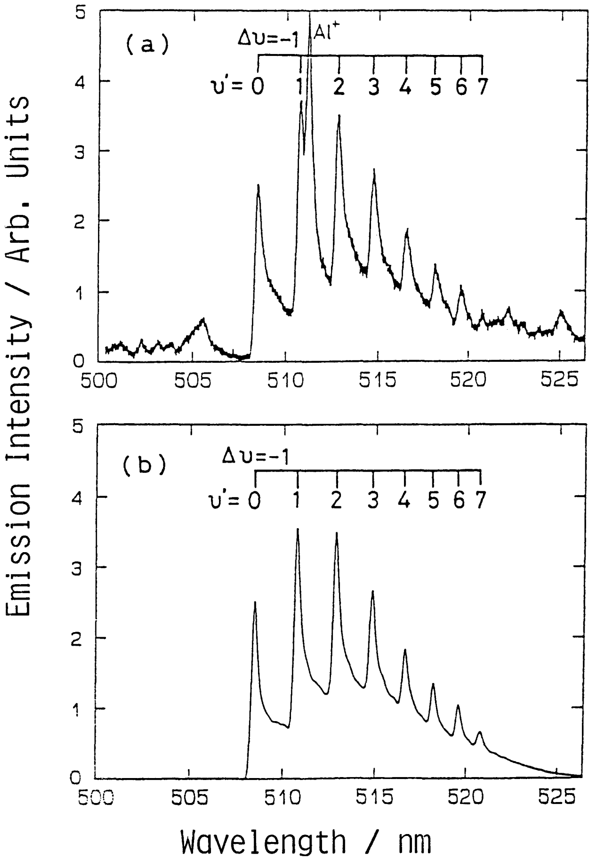

Fig. 2. Δv=-1 sequence bands of AlO B $^2\Sigma^+ \rightarrow X^2\Sigma^+$ system. Observed (a) and simulation (b).

Both of Al + H_2O and Al + NH_3 reactions to give excited AlO and AlN, respectively, are highly endoergic (for example, D(Al-O)$^{17)}$ = 508.5 kJ mol^{-1}, D(H-OH)$^{18)}$ = 499 kJ mol^{-1}, D(O-H) = 427 kJ mol^{-1}, AlO($B^2\Sigma^+$) is 247.5 kJ mol^{-1} above the ground state$^{17)}$). Therefore, highly-energetic Al atoms (those with a large amount of KE and/or excited ones) must be involved in the reaction.

(c) Mg + O_2 system. Under the conditions of O_2 flow (0.1-0.15 Torr) and laser power of 70 mJ pulse^{-1}, Δv=0 sequence ((0,0) to (4,4)) of MgO $B^1\Sigma^+ \rightarrow X^1\Sigma^+$ emission was found in 487-502 nm range. Typical CL spectrum and its simulation are shown in Fig. 3 (a) and (b), respectively. Simulation was made with Franck-Condon factor values given by Dube and Kai.$^{19)}$ T_R= 5000 K and relative vibrational distribution (for v'=0-4) 200:155:125:85:43 reproduce well the observed spectrum. This vibrational distribution corresponds to T_V=4000 K. The rotational temperature is higher than the vibrational one.

The intensity of CL was found to depend quadratically on O_2 pressure (0.05-0.30 Torr). Since MgO is very weakly bonded (340.6 kJ mol^{-1}) the reaction

$$Mg + O_2 \rightarrow MgO(X) + O \qquad (1)$$

is also highly endoergic. Probable mechanism for the production of MgO in the B state is that which Mg^* (Mg atoms with a large amount of KE and/or metastable $Mg(^3P)$ at 261.6 kJ mol^{-1} above the ground state) is involved:

$$Mg^* + O_2 \rightarrow MgO(X) + O \qquad (2)$$

$$Mg + O + O_2 \rightarrow MgO(B) + O_2 \qquad (3)$$

which is consistent with the quadratic dependence of the MgO B → X emission intensity on the O_2 pressure.

In conclusion, several highly endoergic chemiluminescent reactions of metal atoms (Al and Mg) were observed using laser ablation of metal substrates. Origins of the highly energetic metal atoms responsible for these reactions are under study.

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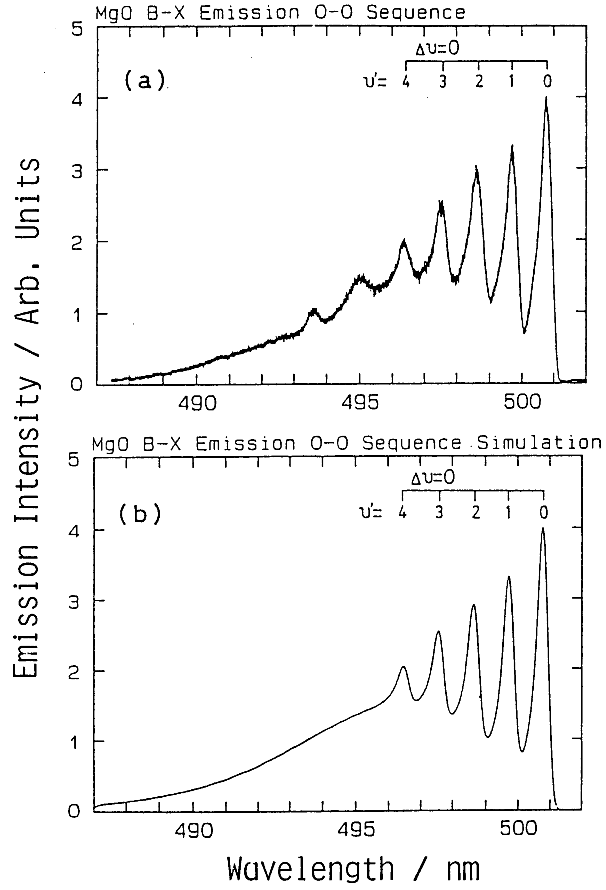

Fig. 3. Δv=0 sequence bands of MgO $B^1\Sigma^+ \rightarrow X^1\Sigma^+$ system. Observed (a) and simulation (b).

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