

LASER SPECTROSCOPY ON THE  $\text{MgH } A^2\Pi - X^2\Sigma^+$  BAND SYSTEM

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The  $A^2\Pi - X^2\Sigma^+$  electronic transition of MgH has been studied by the laser excitation spectroscopy. Some new transitions have been observed for the first time. Rotational parameters of the X and A state have been derived and compared with other experimental values.

## INTRODUCTION

Diatomic hydrides are of considerable interest in spectroscopy and molecular dynamics. The MgH molecule, among those of astrophysical importance,<sup>1,2</sup> has been a subject of spectroscopic and kinetic studies.<sup>3-19</sup>

The ground electronic state of MgH and its lowest two excited electronic states have been determined to be  $X^2\Sigma^+$ ,  $A^2\Pi$  and  $B'^2\Sigma^+$ , respectively.<sup>1-8</sup> Rotational perturbations have been observed in the A-X band system.<sup>1,4</sup> Balfour and Cartwright<sup>4,5</sup> have shown that the A state is perturbed by the B' state, which is only weakly bound at large internuclear distances. Note that the RKR potential of the B' state is not consistent with the known molecular constants.<sup>3,5</sup> The highest vibrational levels observed for these three electronic states are  $v = 9, 3$  and  $9$ , respectively. The dissociation energy of MgH has been estimated to be 1.27 eV experimentally<sup>7</sup> and 1.25 eV theoretically.<sup>11</sup> Its long-range coefficients remain to be determined although related theoretical values have already been calculated.<sup>12,13</sup> It appears that more spectroscopic studies on this molecule are desirable.

MgH may be produced either (a) by a dc discharge between magnesium electrodes in a hydrogen/helium atmosphere<sup>7,8</sup> or (b) by a laser-induced chemical reaction of a (Mg + H<sub>2</sub>/D<sub>2</sub>) mixture or some (Mg + alkane) mixtures.<sup>14-16</sup> The laser-induced reaction not only provides a relatively greater concentration of MgH for spectral

studies, but also allows one to investigate some fundamental physical and chemical processes, such as state-specific reaction dynamics,<sup>15-19</sup> energy transfer,<sup>14</sup> relaxation mechanism and chemical kinetics.<sup>18,19</sup>

In this report we present our spectroscopic study on the  $A^2\Pi - X^2\Sigma^+$  band system, as a portion of our long-term research project on alkaline-earth hydrides.

## EXPERIMENTAL

The experimental setup is shown in Figure 1. One frequency-doubled beam and another frequency-tripled beam, both generated from a 10 Hz Nd:YAG laser (Quanta Ray DCR2A) using an angle-tuned KD\*P crystal, were separately and simultaneously used to pump two different dye lasers (PDL2). The former beam was used to pump a dye mixture, Rhodamine 590/610 with ratio 4/1, which covers the spectral range 550-580 nm. The output dye laser beam was then frequency-doubled and tuned to the 285.2 nm line to excite reactive magnesium  $\text{Mg}(3p^1P)$  atoms which subsequently react with hydrogen molecules H<sub>2</sub> to form MgH.<sup>18</sup> The tripled beam was used to pump the laser dye Coumarin 500, which covers the spectral range 492-521 nm. The output dye laser beam was used to excite the MgH A-X band system. Typically the dye laser power was about 0.2 mJ/pulse.

A five-armed stainless-steel crossed heat-pipe oven was used to generate magnesium vapor. This oven allows one both to observe the excitation spectra perpendicular to the laser beam, and to monitor the oven temperature with a directly inserted stainless-steel encased thermocouple through the vertical arm. In this work, the oven was charged with magnesium metal (99% purity) in the center, and was operated about 750 K with 0.5-10 torr H<sub>2</sub>, which functioned as both a reaction partner and a buffer gas.

Two experimental modes, one excitation and the other laser-induced fluorescence (LIF), were used. The LIF mode was used only to confirm the spectral assignments. For the excitation spectrum, the interference excitation technique,<sup>20</sup> which in this experiment covered only a smaller spectral bandpass (9 nm) than the conventional broad bandpass (100 nm), was used. In this mode the probe laser

was tuned through some selected wavelength range while the monochromator was fixed at a particular observation wavelength. In the LIF mode, the laser was fixed at some particular wavelength while the monochromator was scanned through some spectral range. In both modes, the excited spectra were collected with a two-lens optical system and focused onto the slit of a double monochromator (SPEX 1680) equipped with two 1200-lines/mm echelle gratings. The spectral output was detected with a photomultiplier tube (EMI 9658) from which the signal was fed into a boxcar-integrator system (EG&G PAR 4400 system). The output was stored on diskettes for later processing.

## RESULTS AND DISCUSSION

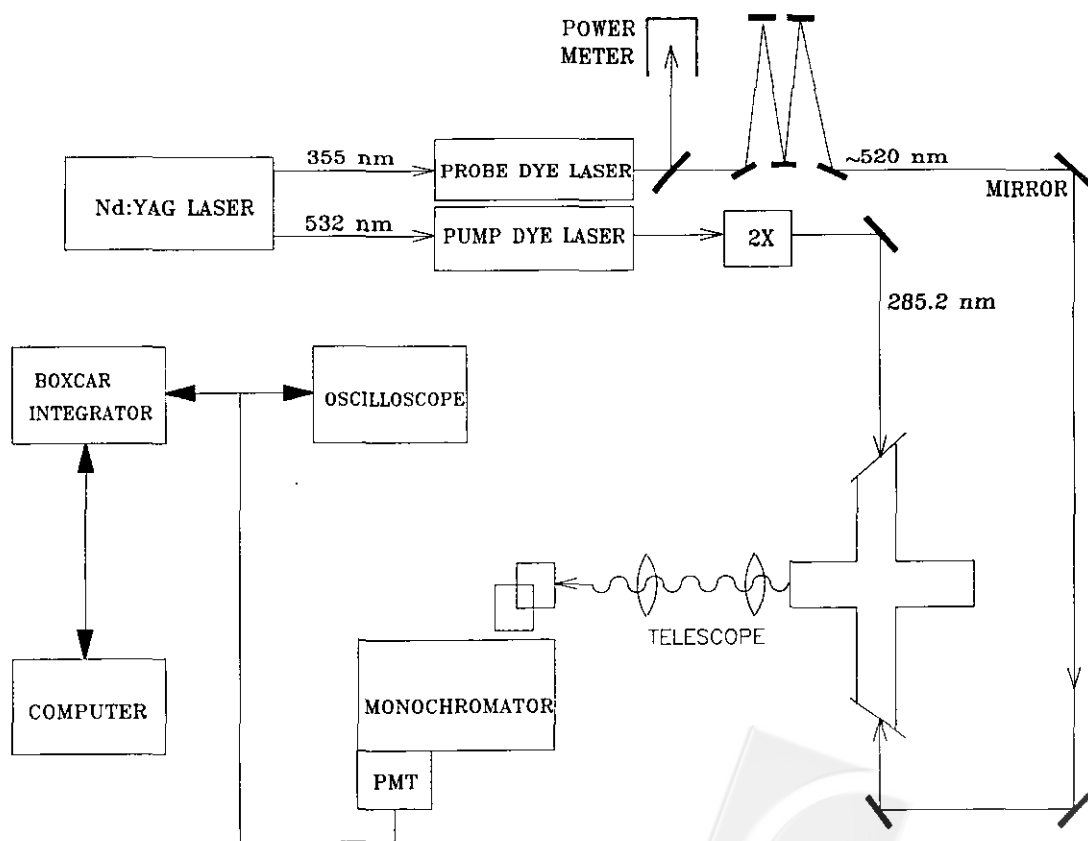


Fig. 1. Experimental setup.

### Theoretical treatment

The electronic transition involved in this work is the  $A^2\Pi - X^2\Sigma^+$  transition of MgH. The ground electronic state  $X^2\Sigma^+$  belongs to Hund's case(b) and its defined quantum numbers are  $N$  for rotational angular momentum,  $S$  for spin angular momentum, and  $J$  for total angular momentum<sup>21</sup> apart from nuclear spin. The upper  $A^2\Pi$  state has been shown also to belong to Hund's case(b)<sup>21</sup> and similar quantum numbers are defined.

The rotational term values of the  $X^2\Sigma^+$  state may be given by<sup>21</sup>

$$F_1(N) = BvN(N+1) - Dv(N(N+1))^2 + 0.5\gamma N, \quad (1)$$

$$F_2(N) = BvN(N+1) - Dv(N(N+1))^2 - 0.5\gamma(N+1), \quad (2)$$

where  $F_1(N)$  refers to the components with  $J = N + 0.5$  and  $F_2(N)$  refers to those with  $J = N - 0.5$ ,  $N$  and  $\gamma$  are the rotational quantum number and the spin splitting constant, respectively.

The rotational term values of the Hund's case(b)  $A^2\Pi$  state may be given by<sup>21</sup>

$$F_1(N) = Bv[N(N+1) - \Lambda^2 + \frac{Y(4-Y)}{8(N+1)}\Lambda^2 + \dots] - Dv(N+0.5)^4 + 0.5\gamma N, \quad (3)$$

$$F_2(N) = Bv[N(N+1) - \Lambda^2 - \frac{Y(4-Y)}{8(N+1)}\Lambda^2 + \dots] - Dv(N+0.5)^4 - 0.5\gamma N, \quad (4)$$

where

$$Bv = B_e - (v+0.5)\alpha_e + (v+0.5)^2\gamma_e, \quad (5)$$

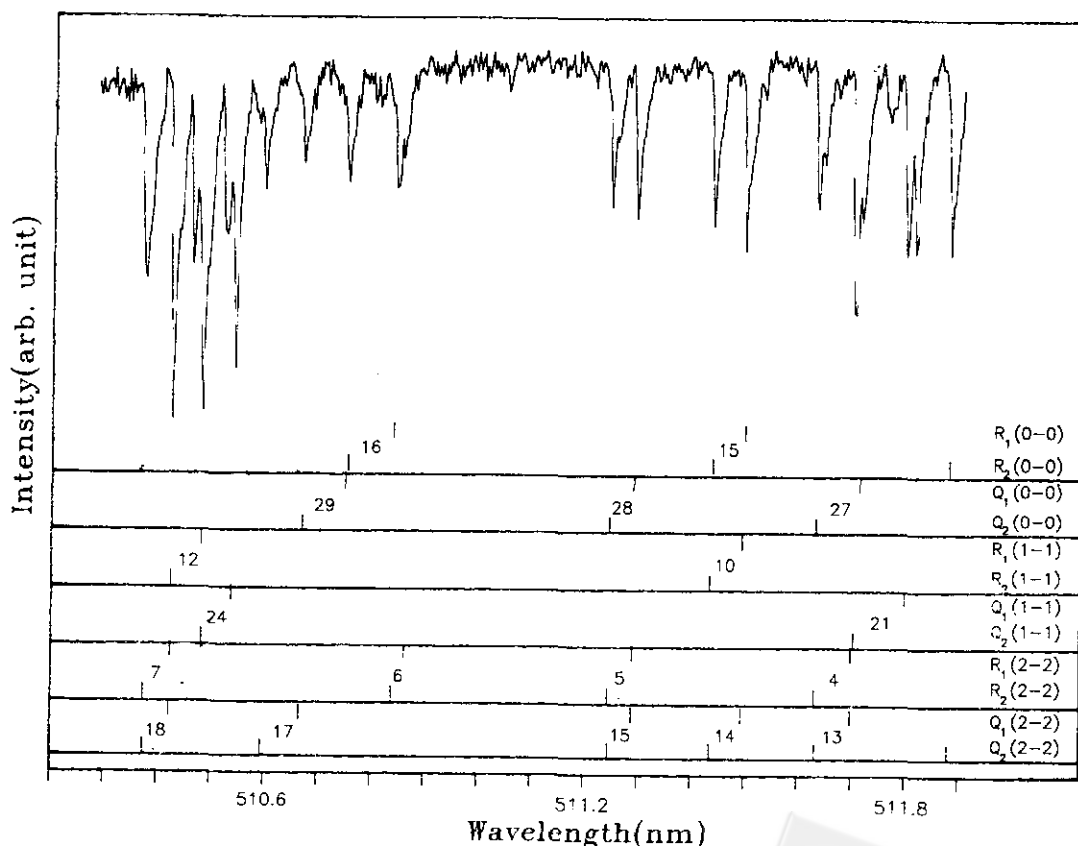


Fig 2. A portion of the excitation spectrum of the  $A^2\Pi - X^2\Sigma^+$  electronic transition. The observation bandpass is set at  $(530 \pm 4.5)$  nm. The oven is operated at  $\sim 760$  K and the hydrogen pressure is  $\sim 5$  torr. The top trace is the excitation spectrum. Spectral assignments are given in the lower part:  $R_1(0,0)$  represents the  $R_1$  branch and the  $(v'=0, v''=0)$  band, the number represent the rotational quantum number  $N$ .

$$Dv = D_e + (v + 0.5)\beta_e + (v + 0.5)^2\delta_e, \quad (6)$$

$Y = A'/Bv$ ,  $A'$  is the spin-orbit coupling constant,  $\Lambda = 1$  for the  $\Pi$  state, and the  $\Lambda$ -doubling constant is not included.

The selection rules for the  $A^2\Pi(v',J') - X^2\Sigma^+(v'',J'')$  transition are as follows<sup>21,22</sup>

$$\Delta J = J' - J'' = 0; e \leftrightarrow f \quad (7)$$

$$\Delta J = J' - J'' = -1, +1; e \leftrightarrow e \text{ and } f \leftrightarrow f \quad (8)$$

$$\Delta N = N' - N'' = -1, 0, +1 \quad (9)$$

$$\Delta v = v' - v'' = \text{any}, \quad (10)$$

where  $e$  and  $f$  are the parities of the rotational energy levels.<sup>22</sup> Therefore three main doublet branches ( $R_1, R_2$ ), ( $Q_1, Q_2$ ) and ( $P_1, P_2$ ), corresponding to the three  $\Delta N = \Delta J$  values  $+1, 0$ , and  $-1$ , respectively, are expected to be observed. Note that there are also four satellite branches, for which  $\Delta N \neq \Delta J$ , whose intensities would decrease rather rapidly with increasing  $N$ .<sup>21</sup>

### Excitation spectrum

The excitation spectrum of the A-X band system were scanned in the spectral region 492-521 nm. The monochromator was selected at three different observation wavelength bandpasses:  $(521.5 \pm 4.5)$ ,  $(530 \pm 4.5)$  and  $(557 \pm 4.5)$  nm, which simultaneously covered the  $(v' = 0, v'' = 1)$ ,  $(1, 2)$  and  $(2, 3)$  transition bands. A portion of the excitation spectrum of the A-X band system is reproduced in Figure 2, in which spectral assignments are also included. For calibration, the observed bandhead of the  $P_1$  branch of the A-X (0,0) band has been calibrated according to the more accurate values reported by Balfour and

Cartwright<sup>6</sup> using the spectrographic method. The known transition frequencies<sup>6</sup> of the (0,0) band have been used as references for observed lines. This method is more efficient than that through the optogalvanic signals from the currently available Ne-filled Mg hollow cathode lamp which covers only a few lines. The overall uncertainty is estimated to be  $\sim 1 \text{ cm}^{-1}$ . Several hundred ro-vibrational lines<sup>23</sup> in the spectral range 492-521 nm have been unambiguously assigned to the (0,0), (1,1) and (2,2) bands by comparing with those known lines reported by Balfour and Cartwright.<sup>6</sup> Among them some transition lines, particularly those with higher rotational quantum numbers, have been observed for the first time and presented in Appendix I.

### Rotational parameters

The rotational parameters of the X state and the A state have been calculated using the second combination relations,  $\Delta_2 F''(N)$  and  $\Delta_2 F'(N)$ .<sup>21</sup> The derived rotational parameters of these two states are close to, especially for  $B_e$  and  $D_e$ , previously reported values,<sup>6,10</sup> shown in Table 1.

### CONCLUSION

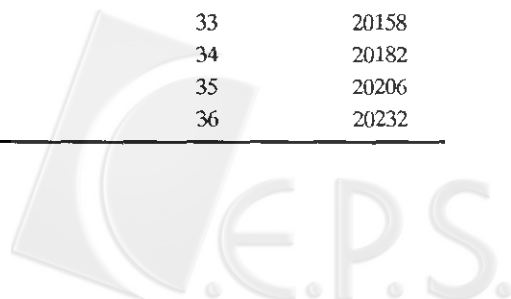
It is demonstrated that MgH, produced in a laser-induced chemical reaction, can be spectroscopically studied using a laser excitation method. The  $A^2\Pi - X^2\Sigma^+$  band system has been studied. Some new transition lines have been observed for the first time. The derived rotational parameters are close to those known values. This study

Table 1. Comparison between the derived rotational parameters with known values. The units of all quantities are  $\text{cm}^{-1}$ . The uncertainty of the derived values is estimated to be  $\pm 10\%$ .

	$X^2\Sigma^+$			$A^2\Pi$	
	This work	Ref. 6	Ref. 10	This work	Ref. 6
$B_e$	6.0	5.8257	5.824801	6.2	6.1913
$\alpha_e$	0.34	0.1859	0.175002	0.36	0.1931
$\gamma_e$	0.075	0.0039	-0.0031626	0.079	0.0005
$D_e \times 10^4$	3.3	3.44	3.55421	3.3	3.60
$\beta_e \times 10^6$	0.77	0.14	-2.91	10.	6.1

Appendix I. New transitions of the MgH  $A^2\Pi - X^2\Sigma^+$  band system. N is the rotational quantum number of the  $X^2\Sigma^+$  state and  $\nu$  is the transition frequency (in  $\text{cm}^{-1}$ ) with an uncertainty  $\pm 1 \text{ cm}^{-1}$

$(v',v'')$	Branch	N	$\nu$				
						32	20070
						33	20080
						34	20126
						35	20153
						36	20181
						37	20218
(0,0)	P <sub>1</sub>	34	19322			38	20246
		39	19404			39	20276
	P <sub>2</sub>	34	19324	(2,2)	Q <sub>1</sub>	30	19781
		39	19405			31	19795
	Q <sub>1</sub>	49	20063			32	19813
	R <sub>1</sub>	39	20196		Q <sub>2</sub>	30	19784
		42	20298			31	19798
(1,1)	P <sub>1</sub>	25	19327			32	19815
		27	19343			20	19841
		31	19386		R <sub>1</sub>	21	19864
		32	19398			23	19912
		33	19410			24	19936
	P <sub>2</sub>	29	19364			25	19961
		31	19387			26	19985
		32	19400			27	20013
	Q <sub>1</sub>	41	19932			28	20041
		42	19957			29	20065
		43	19985			30	20090
		44	20013			31	20111
		45	20043			32	20134
		46	20077			33	20157
	Q <sub>2</sub>	41	19934			34	20180
		42	19960			35	20205
		43	19987			36	20230
		44	20015			21	19865
		45	20045		R <sub>2</sub>	22	19890
		46	20080			23	19914
	R <sub>1</sub>	29	19987			24	19938
		30	20013			25	19962
		31	20041			26	19987
		32	20069			27	20014
		33	20096			28	20042
		34	20124			29	20067
		35	20151			30	20093
		36	20179			31	20114
		37	20216			32	20136
		38	20244			33	20158
		39	20273			34	20182
	R <sub>2</sub>	29	19988			35	20206
		30	20015			36	20232
		31	20043				



indicates that with a laser having a narrower linewidth such as an excimer-pumped dye laser or a ring dye laser, the rotational perturbation phenomena of the  $A^2\Pi$  state and the questionable molecular constants<sup>3,5</sup> of the  $B^2\Sigma^+$  state may be further studied.

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## Key Word Index-

MgH; Electronic Transition; Rotational Constants.

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