

# The vibration–rotation emission spectrum of MgH<sub>2</sub>

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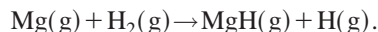
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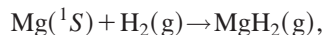
The gaseous MgH<sub>2</sub> molecule has been discovered in an electrical discharge inside a high temperature furnace. The vibration–rotation emission spectrum of <sup>24</sup>MgH<sub>2</sub> was recorded with a Fourier transform spectrometer and the antisymmetric stretching mode ( $\nu_3$ ) was detected near 1589 cm<sup>-1</sup>. In addition, three hot bands involving  $\nu_2$  and  $\nu_3$  were found and rotationally analyzed. The MgH<sub>2</sub> molecule has a linear structure with an  $R_0$  Mg–H bond distance of 1.703 327(3) Å. © 2003 American Institute of Physics. [DOI: 10.1063/1.1609973]

## INTRODUCTION

The reaction of magnesium vapor with hydrogen has been studied many times in the last two decades.<sup>1–6</sup> It is known that Mg atoms in the  $3s3p$  excited electronic states ( $^3P$  and  $^1P$ ) can activate the H–H bond,<sup>5</sup> and the MgH<sub>2</sub> molecule is assumed to be a reaction intermediate in the production of MgH in the following reaction:



This reaction has been studied extensively by pump–probe laser experiments<sup>4–6</sup> as well as by far wing laser scattering.<sup>2,3</sup> Breckenridge has recently reviewed the experimental and theoretical status of the reactivity of Mg, Zn, Cd, and Hg with H–H, Si–H, and C–H bonds.<sup>5</sup> The reaction of ground state  $^1S$  magnesium with H<sub>2</sub> is inhibited by a large barrier to insertion. The ground state reaction,



is calculated to be endoergic by 5 kcal/mol<sup>7</sup> or 3 kcal/mol<sup>8</sup> depending on the level of theory used. In fact, Ahlrichs *et al.*<sup>8</sup> state that “... we conclude that MgH<sub>2</sub> is *not* bound with respect to Mg+H<sub>2</sub> and hence not likely to be a stable species.” We report here on the discovery of free gaseous MgH<sub>2</sub>.

As MgH<sub>2</sub> is a relatively small molecule, it has been studied several times by *ab initio* methods.<sup>7–11</sup> For example, Tschumper and Schaefer calculated the molecular geometry and the harmonic vibrational frequencies of MgH<sub>2</sub> using high level *ab initio* methods with large basis sets.<sup>11</sup> In spite of this interest in MgH<sub>2</sub>, the molecule remains unknown except for the detection of its infrared spectrum in argon,<sup>12</sup> krypton, and xenon matrices<sup>13</sup> at 10–12 K.

Solid MgH<sub>2</sub> is well known.<sup>14</sup> Molecular hydrogen is easily released by heating the solid MgH<sub>2</sub> to 85 °C.<sup>14</sup> This heating results in decomposition to the elements, not the produc-

tion of gaseous MgH<sub>2</sub>. MgH<sub>2</sub> and related materials have been proposed for hydrogen storage because of their low cost and large hydrogen-storage capacity.<sup>15,16</sup>

Recently we reported on our detection of gaseous BeH<sub>2</sub>,<sup>17,18</sup> and we now present results on MgH<sub>2</sub>. The only known gaseous metal dihydrides are BeH<sub>2</sub>,<sup>17,18</sup> MgH<sub>2</sub>, and FeH<sub>2</sub>.<sup>19</sup>

## EXPERIMENTAL DETAILS

The high resolution vibration–rotation emission spectrum of MgH<sub>2</sub> was recorded with a Fourier transform spectrometer. The MgH<sub>2</sub> molecule was generated in an emission source that combines an electrical discharge with a high temperature furnace. The central part of an alumina tube (5 cm × 120 cm) was heated to 650 °C by a CM Rapid Temp furnace. The ends of the tube were cooled by water and sealed with CaF<sub>2</sub> windows. About 20 g of powdered magnesium metal was placed in the center of the tube, and a slow flow of argon (1.6 Torr) and hydrogen (0.9 Torr) was passed through the cell. A dc discharge (3 kV, 333 mA) was struck between two stainless steel tube electrodes inside the cool ends of the alumina tube. The emitted light from the source was focused with a CaF<sub>2</sub> lens to the entrance aperture of a Bruker IFS 120 HR Fourier transform spectrometer. The spectrum was recorded using a CaF<sub>2</sub> beamsplitter and a liquid nitrogen-cooled HgCdTe (MCT) detector at an instrumental resolution of 0.01 cm<sup>-1</sup>. The spectral region was limited to 1200–2200 cm<sup>-1</sup> by the CaF<sub>2</sub> beamsplitter and a 2200 cm<sup>-1</sup> long-wave pass filter. Approximately 550 scans were added during 8 h of integration. The recorded spectrum contained atomic and molecular emission lines, as well as absorption lines from atmospheric water vapor.

## RESULTS AND ANALYSIS

The strongest emission lines in the spectrum are from the  $v = 1 \rightarrow 0$  fundamental band of MgH, for which the band head is at 1578.8 cm<sup>-1</sup>. In addition, a series of weaker lines

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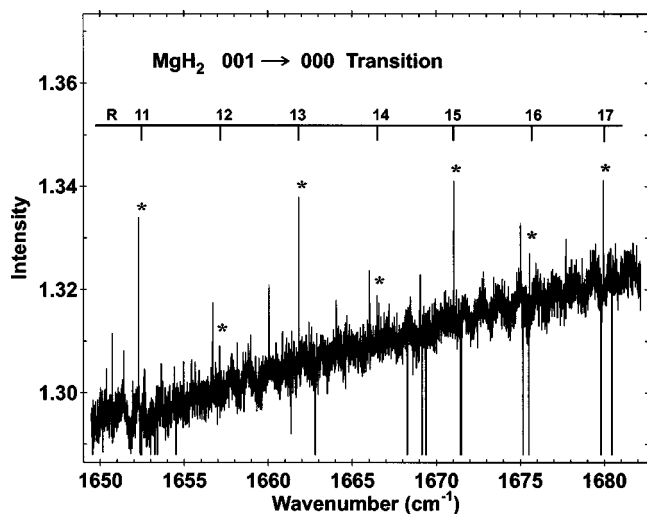


FIG. 1. An expanded view of the *R* branch of the 001→000 band of  $^{24}\text{MgH}_2$ . The  $\text{MgH}_2$  lines are marked with asterisks and display a 3:1 intensity alternation. The absorption lines are from atmospheric water vapor.

with alternating 3:1 intensities were observed to higher wave numbers (Fig. 1), which are due to the antisymmetric stretching fundamental band of  $^{24}\text{MgH}_2$ .

The program WSPECTRA written by Carleer (Université Libre de Bruxelles) was used to determine the line positions. The spectrum was calibrated using impurity CO lines, and the absolute accuracy of the measured lines is better than  $0.001\text{ cm}^{-1}$ . A color Loomis-Wood program was used as an aid for the assignment of the observed bands.

The lines of Table I are assigned to the  $\nu_3$  ( $\sigma_u$ ) antisymmetric stretching mode of the linear  $\text{MgH}_2$  molecule for the following reasons:

- (1) For the linear  $\text{MgH}_2$  molecule with  $D_{\infty h}$  symmetry, the adjacent rotational lines have a 3:1 intensity ratio due to the *ortho-para* nuclear spin statistical weights  $(I+1)/I$  associated with the  $I=\frac{1}{2}$  hydrogen nuclei,<sup>20</sup> which is consistent with our observation.
- (2) There are three measurements of the band origin of the  $\nu_3$  mode of  $\text{MgH}_2$  in argon, krypton, and xenon matrices that predict the band origin at 1571.9, 1558, and 1569  $\text{cm}^{-1}$ , respectively.<sup>12,13</sup> The band origin of 1588.672  $\text{cm}^{-1}$  observed in our spectrum matches these measurements if matrix shifts are taken into account.
- (3) A high level *ab initio* calculation<sup>11</sup> predicted the Mg–H equilibrium distance ( $R_e$ ) at 1.7108 Å. The observed value of  $R_0$  in our experiment is 1.703 327(3) Å, which is in good agreement with the theoretical prediction.

In addition to the  $\nu_3$  fundamental band, 001–000  $\Sigma_u^+ - \Sigma_g^+$ , three hot bands of  $\text{MgH}_2$  were also assigned and rotationally analyzed:

$$011-010 \quad \Pi_g - \Pi_u, \quad 002-001 \quad \Sigma_g^+ - \Sigma_u^+,$$

$$02^2 1(f) - 02^2 0(f) \quad \Delta_u - \Delta_g.$$

The absolute rotational assignment of the 001–000,  $\Sigma_u^+ - \Sigma_g^+$ , fundamental band was made based on the “missing line” at the band origin and the 3:1 intensity alternation.

TABLE I. The line positions of the 001→000,  $\Sigma_u^+ - \Sigma_g^+$ , band of  $^{24}\text{MgH}_2$  (in  $\text{cm}^{-1}$ ).

Assignment	Line position	Assignment	Line position
R(29)	1726.1501(−43) <sup>a</sup>	P(1)	1582.9065(0)
R(27)	1719.3386(5)	P(2)	1577.0738(−7)
R(25)	1712.1626(4)	P(3)	1571.1767(2)
R(23)	1704.6319(5)	P(4)	1565.2155(20)
R(22)	1700.7389(43)	P(5)	1559.1867(4)
R(21)	1696.7513(4)	P(6)	1553.0933(−29)
R(20)	1692.6794(−17)	P(7)	1546.9445(8)
R(19)	1688.5263(4)	P(8)	1540.7292(−9)
R(18)	1684.2864(6)	P(9)	1534.4569(5)
R(17)	1679.9607(−11)	P(10)	1528.1244(11)
R(16)	1675.5565(20)	P(11)	1521.7316(−3)
R(15)	1671.0645(−2)	P(12)	1515.2838(5)
R(14)	1666.4919(−14)	P(14)	1502.2176(−4)
R(13)	1661.8409(1)	P(15)	1495.6029(−4)
R(12)	1657.1066(−15)	P(16)	1488.9360(7)
R(11)	1652.2959(−1)	P(17)	1482.2138(−11)
R(9)	1642.4374(3)	P(18)	1475.4443(13)
R(8)	1637.3909(−10)	P(19)	1468.6206(−1)
R(7)	1632.2703(−6)	P(20)	1461.7492(2)
R(6)	1627.0746(0)	P(21)	1454.8288(2)
R(5)	1621.8047(6)	P(22)	1447.8610(1)
R(4)	1616.4613(12)	P(23)	1440.8472(7)
R(3)	1611.0441(4)	P(25)	1426.6819(0)
R(2)	1605.5584(26)	P(27)	1412.3408(−18)
R(1)	1599.9963(−8)	P(31)	1383.1706(6)
		P(33)	1368.3525(8)

<sup>a</sup>Observed minus calculated values computed with the constants of Table II (in units of  $10^{-4}\text{ cm}^{-1}$ ).

The next strongest band had a large *l*-type doubling, and was assigned to the first bending mode hot band, 011–010,  $\Pi_g - \Pi_u$  transition. In this transition, the absolute rotational assignment was made based on the fact that *e* and *f* parity levels have the same band origins. We used the energy level expression:

$$E(v_1, v_2, v_3, J) = G(v_1, v_2, v_3) + F(J), \quad (1)$$

with

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 \pm \frac{1}{2}[qJ(J+1) + q_D J^2(J+1)^2] \quad (2)$$

in our least-squares fitting program. The constants of Table II were determined for  $^{24}\text{MgH}_2$  using Eq. (2), in which  $q = q_D = 0$  for  $\Sigma$  states, and the plus (minus) sign refers to *e* (*f*) parity for  $\Pi$  states. The observed line positions and the outputs of the least-squares fits for all the bands have been placed in Electronic Physics Auxiliary Publication Service (EPAPS).<sup>21</sup> By fitting the 001–000 and 011–010 bands, we determined two vibration–rotation interaction constants,  $\alpha_2$  and  $\alpha_3$ , using<sup>20</sup>

$$B_{v_1, v_2, v_3} = B_e - \alpha_1(v_1 + \frac{1}{2}) - \alpha_2(v_2 + 1) - \alpha_3(v_3 + \frac{1}{2}). \quad (3)$$

For the other hot bands, 002–001 and 021–020, fewer lines were observed and the absolute rotational assignments were more difficult. The  $B_{v_1 v_2 v_3}$  values of these vibrational levels were predicted from  $B_{000}$  and  $\alpha$  values. Different absolute

TABLE II. Spectroscopic constants of <sup>24</sup>MgH<sub>2</sub> in cm<sup>-1</sup> (all uncertainties are 1σ).

Level	$G_v - \text{ZPE}$	$B$	$10^5 D$	$10^{10} H$	$10^2 q$	$10^6 q_D$
000 $\Sigma_g^+$	0.0	2.882 607(11)	3.9178(25)	6.49(17)		
001 $\Sigma_u^+$	1588.671 57(24)	2.848 667(11)	3.8919(28)	6.53(21)		
002 $\Sigma_g^+$	3165.420 02(52)	2.815 078(13)	3.8664(39)	6.57(35)		
010 <sup>a</sup> $\Pi_u$	$a$	2.891 557(15)	4.0865(47)	7.20(45)	-5.0460(19)	3.239(29)
011 $\Pi_g$	$a + 1582.695 60(26)$	2.857 499(15)	4.0581(50)	6.84(52)	-4.9976(20)	3.212(33)
02 <sup>2</sup> 0( $f$ ) $\Delta_g$	$b$	2.900 037(21)	4.1711(28)			
02 <sup>2</sup> 1( $f$ ) $\Delta_u$	$b + 1576.706 89(63)$	2.865 913(21)	4.1515(31)			

<sup>a</sup>The estimated value of  $a$  ( $\nu_2$ ) is 437 cm<sup>-1</sup>, and the value of  $b$  is approximately 2 times  $\nu_2$  (see the text).

rotational assignments were attempted for these two bands, and in each band only one rotational assignment resulted in  $B_{v_1 v_2 v_3}$  values close to the predicted ones. The 001–000 and 002–001 bands were fitted together, and that also confirmed our assignment.

We observed a large splitting between  $e$  and  $f$  levels of the 02<sup>2</sup>0 ( $\Delta_g$ ) and the 02<sup>2</sup>1 ( $\Delta_u$ ) vibrational levels, which is due to the  $l$ -type resonance with the 02<sup>0</sup>0 ( $\Sigma_g^+$ ) and the 02<sup>0</sup>1 ( $\Sigma_u^+$ ) levels, respectively.<sup>22–25</sup> Since all the  $\Sigma^+$  rotational levels have  $e$  parity, they interact only with the  $\Delta$  state  $e$  levels, and therefore the  $\Delta$  ( $f$ ) energy levels are unaffected. In our previous work on BeH<sub>2</sub>, we performed a more complete analysis of the  $l$ -type resonance by using a Hamiltonian matrix that included the appropriate interaction matrix elements.<sup>18</sup> However, the number of observed lines for MgH<sub>2</sub> was smaller and the data were not sufficient to determine the desired constants. Only the  $f$  parity of the  $\Delta$  states, 02<sup>2</sup>1 ( $f$ )–02<sup>2</sup>0 ( $f$ ) band, was fitted using a simple  $\Sigma$  state energy expression, and the constants are presented in Table II.

## DISCUSSION

The vibrational energy  $G(v_1, v_2, v_3)$  in Eq. (1) can be written as<sup>20</sup>

$$G(v_1, v_2, v_3) = \omega_1(v_1 + \frac{1}{2}) + \omega_2(v_2 + 1) + \omega_3(v_3 + \frac{1}{2}) + x_{11}(v_1 + \frac{1}{2})^2 + x_{22}(v_2 + 1)^2 + x_{33}(v_3 + \frac{1}{2})^2 + x_{12}(v_1 + \frac{1}{2})(v_2 + 1) + x_{13}(v_1 + \frac{1}{2})(v_3 + \frac{1}{2}) + x_{23}(v_2 + 1)(v_3 + \frac{1}{2}) + g_{22}l_2^2. \quad (4)$$

The vibrational energies in Table II are presented as the difference between  $G(v_1, v_2, v_3)$  and the zero point energy

(ZPE),  $G(0,0,0)$ . We estimated the value of  $\{G(0,1,0) - G(0,0,0)\}$  in Table II ( $\nu_2$ ) using<sup>24,25</sup>

$$q_{010} = -\frac{2B_e^2}{\omega_2} \left( 1 + \frac{4\omega_2^2}{\omega_3 - \omega_2} \right). \quad (5)$$

Equation (5) is for equilibrium constants, which are not available, so we employed  $B_0$ ,  $\nu_2$ , and  $\nu_3$  instead of  $B_e$ ,  $\omega_2$ , and  $\omega_3$ , respectively. Equation (5) results in a value of 437 cm<sup>-1</sup> for  $\nu_2$  which is close to the matrix isolation value of 439.8 cm<sup>-1</sup>.<sup>12</sup> The Mg–H bond distance ( $R_0$ ) was calculated from  $B_0$  to be 1.703 327(3) Å, in agreement with the *ab initio* value of 1.7108 Å.<sup>11</sup> We were also able to determine  $x_{23}$  and  $x_{33}$  in Eq. (4) using the 001–000, 011–010, and 002–001 band origins (Table III).

Although BeH<sub>2</sub>, MgH<sub>2</sub>, and the dihydrides of group 12 elements (ZnH<sub>2</sub>, CdH<sub>2</sub>, and HgH<sub>2</sub>) are linear,<sup>26</sup> the heavier dihydrides of the group 2 elements (CaH<sub>2</sub>, SrH<sub>2</sub>, and BaH<sub>2</sub>) may be bent.<sup>27</sup> A very recent *ab initio* calculation has predicted the H–M–H bond angles of CaH<sub>2</sub>, SrH<sub>2</sub>, and BaH<sub>2</sub> to be 180°, 136°, and 123°, respectively.<sup>9</sup> There are other *ab initio* calculations predicting different bond angles for these molecules.<sup>28,29</sup> In fact, Xiao *et al.* recorded the infrared spectrum of CaH<sub>2</sub> in krypton and xenon matrices at 12 K, and they assigned a very weak vibrational band to the symmetric stretching mode of CaH<sub>2</sub> assuming that it is bent.<sup>30</sup>

We have performed experiments similar to our BeH<sub>2</sub> and MgH<sub>2</sub> work trying to record the vibration–rotation emission spectra of group 2 and 12 dihydrides in the gas phase to determine their structures. So far we have found gaseous ZnH<sub>2</sub> with a linear structure.<sup>31</sup> We also recorded the infrared emission spectra of CaH, SrH, and BaH with high signal-to-noise ratios, but we did not see any sign of CaH<sub>2</sub>, SrH<sub>2</sub>, or BaH<sub>2</sub>.

In summary, we observed the gaseous MgH<sub>2</sub> molecule for the first time. The antisymmetric stretching mode ( $\nu_3$ ) and a few hot bands were rotationally analyzed. The predicted linear structure of MgH<sub>2</sub> with  $D_{\infty h}$  symmetry was confirmed and the  $R_0$  Mg–H bond distance was determined.

## ACKNOWLEDGMENT

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TABLE III. Molecular constants of <sup>24</sup>MgH<sub>2</sub> in cm<sup>-1</sup>.

$R_0$ (Å)	1.703 326 7(31)
$B_0$	2.882 607(11)
$\alpha_2$	-0.008 950(18)
$\alpha_3$	0.033 940(15)
$q_{010}$	-0.050 460(19)
$\nu_2$ ( $\pi_u$ )	437 <sup>a</sup>
$\nu_3$ ( $\sigma_u$ )	1588.671 57(24)
$x_{23}$	-5.975 97(35)
$x_{33}$	-5.961 56(35)

<sup>a</sup>Calculated from the  $q_{010}$  value and Eq. (5).

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