The antisymmetric stretching fundamental band of free MgD$_2$[1]

Alireza Shayesteh, Dominique R.T. Appadoo, Iouli Gordon, and Peter F. Bernath

Abstract: The gaseous MgD$_2$ molecule has been synthesized for the first time in an electrical discharge inside a high-temperature furnace. The high-resolution infrared emission spectrum of MgD$_2$ was recorded with a Fourier transform spectrometer, and the antisymmetric stretching mode (ν_3) was detected near 1176.5 cm^{-1}. The ν_3 band was rotationally analyzed, and the r_0 Mg—D bond distance was determined to be 1.700 874(8) Å.

Key words: gaseous MgD$_2$, vibration–rotation emission spectrum, Mg-D bond distance.

Résumé : Faisant appel à une décharge électrique dans une fournaise à haute température, on a synthétisé pour la première fois une molécule de MgD$_2$ gazeuse. On en a enregistré le spectre d'émission infrarouge à haute résolution à l'aide d'un spectrophotomètre à transformée de Fourier et on a détecté le mode d'élongation antisymétrique (ν_3) près de 1176,5 cm^{-1}. On a analysé la bande ν_3 d'un point de vue rotationnel et on a déterminé que la longueur r_0 de la liaison Mg—D est égale à 1,700 874(8) Å.

Mots clés : MgD$_2$ gazeux, spectre d'émission vibration-rotation, longueur de la liaison Mg-D.

[Traduit par la Rédaction]

Introduction

We recently published a paper on the discovery of MgH$_2$ in the gas phase and the analysis of its vibration–rotation emission spectrum (1). The MgH$_2$ molecule is a favorite target for ab initio methods (2–6) because it is a closed-shell system with only a few electrons. The previous studies on the reaction of the magnesium atom with molecular hydrogen and the properties of solid MgH$_2$ were discussed in our earlier paper (1). Although the ground-state reaction

$$\text{Mg } (^1\text{S}) \text{ (g)} + \text{H}_2 \text{ (g)} \rightarrow \text{MgH}_2 \text{ (g)}$$
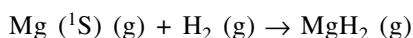
was predicted to be slightly endoergic (2, 3), we were able to produce gaseous MgH$_2$ in our furnace-discharge emission source.

The previous experimental work on MgD$_2$ is limited to matrix isolation experiments. McCaffrey et al. (7) recorded the infrared spectra of MgH$_2$, MgHD, and MgD$_2$ in krypton and xenon matrices at 12 K. They found the antisymmetric stretching frequency (ν_3) of MgD$_2$ at 1153 and 1144 cm^{-1} in krypton and xenon matrices, respectively, while the bending modes (ν_2) were observed at 309 and 300 cm^{-1}. Tague and Andrews (8) recorded the infrared spectra of MgH$_2$ and MgD$_2$ in an argon matrix at 10 K, and they detected the antisymmetric stretching mode of MgD$_2$ at 1163.2 cm^{-1}.

We have produced gaseous MgD$_2$ in a discharge source, and the analysis of its vibration–rotation emission spectrum is reported in this paper.

Experiment and results

The high-resolution vibration–rotation spectrum of MgD$_2$ was recorded with a Bruker IFS 120 HR Fourier transform spectrometer. An emission source that combines a high-temperature furnace with an electrical discharge was used to generate gaseous MgD$_2$. Except for some minor changes, the same experimental setup was used as described in the earlier paper on MgH$_2$ (1). About 50 g of magnesium (cut from a rod) was placed in the central part of an alumina tube and was heated to 600 °C to produce approximately 1 torr of magnesium vapor (1 torr = 133.322 Pa). Although we used a mixture of argon and hydrogen in our MgH$_2$ experiment (1), it was found later that pure hydrogen yields a stronger signal. About 1 torr of pure deuterium flowed slowly through the cell. The tube was sealed with BaF$_2$ windows, and a BaF$_2$ lens was used to focus the emission from the tube onto the entrance aperture of the spectrometer. A KBr beamsplitter was used, and the spectrum was recorded with a liquid-nitrogen-cooled HgCdTe (MCT) detector at an instrumental resolution of 0.01 cm^{-1}. The detector response, the BaF$_2$ lens, and a 1700 cm^{-1} longwave pass filter limited the spectral region to 800–1700 cm^{-1}. In order to improve the

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[1] This article is part of a Special Issue dedicated to the memory of Professor Gerhard Herzberg.
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Fig. 1. An expanded view of the spectrum showing the relative intensities of MgD_2 lines, compared to the lines from MgD.
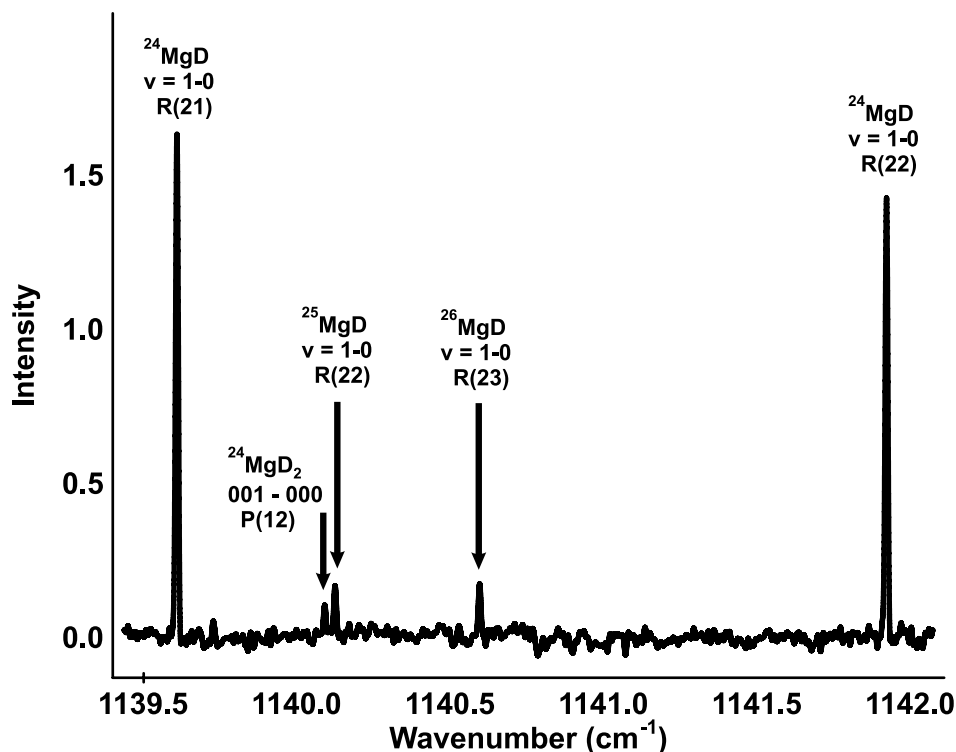
signal-to-noise ratio, about 1200 scans were co-added during 18 h of integration.

The spectrum contained blackbody emission from the hot tube, plus atomic and molecular emission lines, and absorption lines from atmospheric water vapor. The strongest emission lines in the spectrum are from the ^{24}MgD $v = 1 \rightarrow 0$ band and from atomic lines. Four hot bands of ^{24}MgD ($v = 2 \rightarrow 1$ to $v = 5 \rightarrow 4$) were also found and rotationally analyzed (9). The natural abundances of the magnesium isotopes ^{24}Mg,^{25}Mg, and ^{26}Mg are 79:10:11, and for the minor isotopomers, ^{25}MgD and ^{26}MgD, only the $v = 1 \rightarrow 0$ to $v = 4 \rightarrow 3$ bands were detected. In addition to these bands, a series of very weak lines, which was assigned to the v_3 antisymmetric stretching fundamental band of ^{24}MgD$_2$, was observed to higher wavenumbers. An expanded view of the spectrum showing the relative intensities of the MgD and MgD$_2$ lines is given in Fig. 1. The signal-to-noise ratio for the MgD$_2$ lines was much smaller than that for the MgH$_2$ lines (1) for several reasons:

- The intrinsic band strength for v_3 of MgD$_2$ was calculated by Tague and Andrews (8) to be about 2 times smaller than that of MgH$_2$.
- The Einstein *A* coefficient for spontaneous emission is proportional to $\tilde{v}^3$. The band origin of MgH$_2$ is at 1588.7 cm^{-1}, while the band origin of MgD$_2$ is at 1176.5 cm^{-1}. This difference makes the Einstein *A* coefficient of MgD$_2$ about 2.5 times smaller than that of MgH$_2$.
- For technical reasons, the quality of spectra generally decreases at lower wavenumbers. In this case, for example, the 1700 cm^{-1} longwave pass filter that was used for MgD$_2$ is made of germanium, and it has a transmittance of ~50% in the 1200 cm^{-1} spectral region. The 2200 cm^{-1}

longwave pass filter used for MgH$_2$ is made of CaF$_2$, and it has a transmittance of ~90% in the 1600 cm^{-1} spectral region.

Analysis and discussion

The line positions were determined using the program WSpectra written by M. Carleer (Université Libre de Bruxelles). The spectrum was calibrated using several atomic lines common to both the MgH$_2$ and MgD$_2$ spectra, while the MgH$_2$ spectrum was calibrated using impurity CO lines. The absolute accuracy of calibrated MgD$_2$ lines is better than 0.002 cm^{-1}. The assignment of the bands was facilitated by the use of a color Loomis–Wood program.

The antisymmetric stretching vibrational mode of MgD$_2$ (linear) has σ_u symmetry, and the observed vibration–rotation band (001 $\rightarrow$ 000) is a Σ_u^+–Σ_g^+ transition having only P and R branches. A list of line positions and assignments is presented in Table 1. For the MgD$_2$ molecule with $D_{\infty h}$ symmetry, the adjacent rotational lines have a 2:1 intensity ratio (($I + 1$)/I) due to the ortho–para nuclear spin statistical weights associated with the $I = 1$ deuterium nuclei. In this particular band (Σ_u^+–Σ_g^+), the lines with even J'' should be twice as intense as odd-J'' lines, because deuterium nuclei are bosons. The signal-to-noise ratio for MgD$_2$ lines was small and the 2:1 intensity ratio was not clearly observed, but the even-J'' lines were stronger than the odd-J'' lines. A few lines near the band origin were missing (i.e., too weak to be observed), and this made the absolute rotational numbering difficult. The absolute rotational assignment was made based on three criteria:

Table 1. The line positions of the $001 \rightarrow 000$, $\Sigma_u^+ - \Sigma_g^+$, band of $^{24}MgD_2$.

Assignment	Line position (cm^{-1})	Assignment	Line position (cm^{-1})
P(34)	1064.7581(−16)	R(4)	1190.5640(3)
P(32)	1072.0120(6)	R(6)	1195.9973(24)
P(31)	1075.6099(3)	R(7)	1198.6693(9)
P(30)	1079.1882(−7)	R(8)	1201.3190(57)
P(28)	1086.2911(10)	R(10)	1206.5151(−19)
P(27)	1089.8115(1)	R(11)	1209.0786(34)
P(26)	1093.3130(3)	R(12)	1211.6035(−7)
P(25)	1096.7928(−11)	R(14)	1216.5708(−25)
P(24)	1100.2550(4)	R(15)	1219.0145(15)
P(22)	1107.1143(7)	R(16)	1221.4244(17)
P(20)	1113.8870(−5)	R(18)	1226.1510(4)
P(18)	1120.5743(−1)	R(20)	1230.7547(−8)
P(16)	1127.1724(3)	R(23)	1237.4242(−48)
P(15)	1130.4315(−54)	R(24)	1239.5880(−22)
P(14)	1133.6775(−11)	R(25)	1241.7188(−7)
P(13)	1136.8975(5)	R(29)	1249.9150(11)
P(12)	1140.0935(17)	R(30)	1251.8824(16)
P(10)	1146.4112(14)	R(32)	1255.7142(−12)
P(9)	1149.5300(−24)		
P(8)	1152.6289(−16)		
P(7)	1155.7024(−15)		
P(6)	1158.7515(−6)		
P(5)	1161.7764(12)		

Note: The numbers in parentheses (in units of 10^{-4} cm^{-1}) are the observed minus calculated line positions computed with the constants of Table 2.

- The rotational lines with even J'' should be stronger than odd-J'' lines.
- The r_0 value of MgD$_2$, which is determined from B_0, should be close to the r_0 value of MgH$_2$.
- The band origin should be relatively close to the matrix isolation values (7, 8) when small matrix shifts are taken into account.

Three different rotational numberings were attempted, and only one rotational assignment (Table 1) satisfies all of the conditions listed above.

The rotational lines were fitted to the customary energy level expression:

$$[1] \qquad E(v_1, v_2, v_3, J) = G(v_1, v_2, v_3) + BJ(J + 1)$$
$$- DJ^2(J + 1)^2$$

using our least-squares fitting program, and the constants of Table 2 were determined. We determined the Mg—D bond distance (r_0) for $v = 0$ to be 1.700 874(8) Å (1 Å = 0.1 nm), using the atomic mass of 2.014 101 779 amu (10) for deuterium.

In our earlier paper on MgH$_2$ (1), we found the r_0 Mg—H bond distance to be 1.703 327(3) Å. The average Mg—D bond distance is expected to be slightly smaller than the Mg—H bond distance at the zero-point level because the potential energy surface is anharmonic. The vibrational frequencies of MgD$_2$ are smaller than those of MgH$_2$, so the MgD$_2$ zero-point level lies deeper in the anharmonic potential surface.

The ν_3 band origins of MgH$_2$ and MgD$_2$ observed or calculated in different studies are compared in Table 3. The

Table 2. Spectroscopic constants (in cm^{-1}) of $^{24}MgD_2$.

v_1 v_2 v_3	G_v	B_v	$10^6 D_v$
000	0.0	1.446 575(14)	9.5872(92)
001	1176.502 82(51)	1.433 237(14)	9.5221(94)

Note: All uncertainties are 1σ.

argon matrix shift (8) for MgH$_2$ is −16.8 cm^{-1}, which is −1.06% in relation to the gas-phase band origin. Similarly, the shift for MgD$_2$ is −13.3 cm^{-1} or −1.13% in relation to the observed ν_3 band origin. The relative shifts for the MgH$_2$ and MgD$_2$ band origins in krypton and xenon matrices (7) are also very similar. This consistency in the relative matrix shifts for MgH$_2$ and MgD$_2$ supports our absolute rotational assignment.

Summary

The gaseous MgD$_2$ molecule was produced for the first time and was identified via its infrared emission spectrum. The antisymmetric stretching fundamental band $001 \rightarrow 000$ was observed and rotationally analyzed to yield spectroscopic constants. MgD$_2$ has a linear structure with an r_0 Mg—D bond distance of 1.700 874(8) Å.

Acknowledgement

Table 3. A comparison of the antisymmetric stretching frequencies (in cm^{-1}) of MgH$_2$ and MgD$_2$ observed in the gas phase and in matrices.

Molecule	Gas phase	Ar matrix	Kr matrix	Xe matrix	Ab initio
MgH$_2$	1588.6716(2)[a]	1571.9[b]	1558[c]	1544[c]	1628.2[d]
					1641.3[b]
MgD$_2$	1176.5028(5)[e]	1163.2[b]	1153[c]	1144[c]	1205.1[b]

[a]Reference 1.
[b]Reference 8.
[c]Reference 7.
[d]Reference 6.
[e]This work.

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