THE SPECTRUM OF MAGNESIUM HYDRIDE

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ABSTRACT

Emission spectra of the $A^2\Pi-X^2\Sigma^+$ system of MgH have been studied at high resolution and with high signal-to-noise ratio through the use of a Fourier transform spectrometer. On the basis of a rotational analysis of these data, frequencies are predicted for the lowest pure rotational transitions with an accuracy approaching ± 30 MHz. Frequencies of the (1, 0) vibration-rotation lines are calculated to an accuracy of ± 0.002 cm^{-1}. The excitation and observability of MgH in interstellar clouds are discussed.

Subject headings: interstellar: molecules — molecular processes — laboratory spectra

I. INTRODUCTION

Magnesium hydride is an astrophysically important molecule. Lines of the $A^2\Pi-X^2\Sigma^+$ transition appear prominently in the absorption spectra of the Sun (Sotirovski 1972) and of late-type stars generally (Boesgaard 1968). The strengths of MgH lines are sensitive to luminosity in cool stars. Very recently, Bell, Edvardsson, and Gustaffson (1985) have shown that MgH line strengths can be used in conjunction with a magnesium abundance determined from Mg I lines to estimate the surface gravity of Arcturus. The strongest lines of the $A-X$ system of MgH near 5000 Å suffer blending with other features in the spectra of cool stars. In stars later than mid-K, there may be some advantage to studying MgH by means of its vibration-rotation transitions in the infrared, for which high precision spectroscopic data have been lacking until now.

In the laboratory, MgH has been studied for many years beginning with Watson and Rudnick in 1926. More recently Balfour and coworkers have thoroughly reexamined the MgH and MgD spectra. Balfour and Cartwright (1975*a*, *b*; 1976*a*, *b*) found a new electronic state ($B'^2\Sigma^+$) that is responsible for extensive perturbations in the $A^2\Pi$ state. The $B'-X$ transition could be followed to dissociation (Balfour and Lindgren 1978) providing a $D_0 = 1.27(3)$ eV for the $X^2\Sigma^+$ state, in excellent agreement with the best theoretical estimate of 1.25 eV for the dissociation limit (Meyer and Rosmus 1975). Huber and Herzberg (1979) have a nearly complete set of laboratory references to work prior to 1977.

It is possible that MgH will be of some interest in the interstellar medium. It has been suggested that metal atoms such as Na, Mg, Ca, and Fe and their first ions play an important role in the overall ionization balance of an interstellar molecular cloud (Oppenheimer and Dalgarno 1974). Under conditions of low fractional ionization, the neutral metal atoms can remove molecular ions by charge transfer and the resulting metal ions, which are generally unreactive, can account for much of the total ionization. The importance of this effect depends upon the extent to which the metals have been removed from the gas phase by being bound up in solid particles and the extent to which the gas phase metals are present in molecular form (presumably simple hydrides and oxides). It has also been suggested (e.g., by Plambeck and Erickson 1982 in connection with NaH) that the presence of metal hydrides could be taken as an indication of active grain surface chemistry.

With these considerations in mind and in view of the increasing efforts in astronomical spectroscopy at wavelengths between 1 μm and 1 mm, we have predicted the frequencies of the lowest pure rotational transitions and the fundamental vibration-rotation lines of MgH. This work demonstrates that high-resolution optical emission spectroscopy can provide rotational energy level splittings that are probably accurate to ± 30 MHz in molecules like MgH. The direct observation of MgH in the submillimeter and infrared spectral regions would provide the most precise rotational and vibration-rotation line positions. Such measurements are possible with existing techniques but are by no means routine. On the other hand, the results presented here show that relatively routine Fourier transform emission spectroscopy coupled with careful data analysis can provide measurements that approach the results of submillimeter and infrared spectroscopy in precision.

Metal hydrides like MgH and NaH have large rotation constants and large permanent dipole moments; consequently, the transition probabilities of their lowest rotational transitions are large compared with collisional excitation rates in all but the densest interstellar clouds. The conditions required for detectable interstellar lines are made more severe by the fact that most dense, warm clouds are themselves sources of local continuum emission near 1 mm wavelength. This increases the total background emission against which the lines must be detected. We discuss the excitation of interstellar MgH lines and consider briefly how interstellar magnesium in other forms might be detected.

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II. SPECTROSCOPY OF MgH

a) The Experiment

Magnesium hydride was produced in a standard hollow cathode discharge operated at 250 mA current. Argon gas at 0.83 torr pressure with about 15 mtorr of added hydrogen flowed through the magnesium cathode. The emission spectrum was recorded with the Fourier transform spectrometer at the McMath Solar Telescope of the National Solar Observatory on Kitt Peak. The unapodized resolution was 0.026 cm^{-1}, and seven scans were co-added in a one-hour run. The signal-to-noise ratio for strong lines of the (0, 0) band of the $A^2\Pi-X^2\Sigma^+$ transition was greater than 1000. Data were also obtained for the (0, 1) band but with a maximum signal-to-noise ratio of about 50. The $A-X$ transition is quite diagonal so off-diagonal Frank-Condon factors are small

TABLE 1A

VACUUM FREQUENCIES[a] OF THE LINES OF THE (0, 0) BAND OF $A^2\Pi-X^2\Sigma^+$ TRANSITION OF ^{24}MgH

J''	P_2[b]	Q_2	R_2	P_{12}
1.5	...	...	19319.7061 (13)	...
2.5	19249.7521 (-4)	19285.3020 (-29)	19333.4784 (25)	...
3.5	19239.5475 (-15)	19287.6274 (-21)	19348.1306 (26)	...
4.5	19230.5137 (13)	19290.8633 (-14)	19363.5614 (20)	19178.1109 (1)
5.5	19222.4356 (27)	19294.9171 (-4)	19379.7169 (15)	19158.5930 (8)
6.5	19215.2280 (22)	19299.7423 (26)	19396.5618 (4)	19139.7677 (-7)
7.7	19208.8545 (13)	19305.3144 (22)	...	19121.6947 (-34)
8.5	19203.2966 (-9)	19311.6121 (7)	19432.2262 (-22)	19104.4158 (-34)

J''	P_1	Q_1	R_1	Q_{12}
0.5	...	19273.2736 (42)	19287.3657 (-13)	...
1.5	...	19275.9302 (11)	19301.1999 (7)	...
2.5	19252.9318 (-27)	19278.3075 (3)	19315.3159 (-4)	...
3.5	19243.8581 (6)	19280.9804 (-15)	19329.9233 (-9)	...
4.5	19235.1097 (20)	19284.1637 (-48)	19345.1027 (-13)	...
5.5	19226.9068 (-12)	19287.9533 (-35)	19360.8876 (-11)	...
6.5	19219.3561 (0)	19292.3884 (3)	19377.2898 (-11)	...
7.5	19212.5038 (15)	19297.4842 (-10)	19394.3125 (-2)	19206.5993 (-9)
8.5	19206.3771 (12)	19303.2579 (10)	19411.9517 (7)	19201.2480 (13)
9.5	19200.9968 (8)	19309.7092 (2)	19430.2017 (28)	...

[a] In cm^{-1}.

[b] Numbers in parentheses give the observed minus calculated line positions in units of 10^{-4} cm^{-1}.

TABLE 1B

VACUUM FREQUENCIES[a] FOR THE LINES OF THE (0, 1) BAND OF THE $A^2\Pi-X^2\Sigma^+$ TRANSITION OF ^{24}MgH

J''	P_2	Q_2	R_2
0.5	...	...	17875.4250 (-4)
1.5	...	17853.2141 (-23)	17888.8113 (-19)
2.5	17819.9535 (57)	17855.4992 (-10)	17903.6754 (42)
3.5	17811.1923 (-15)	17859.2739 (-4)	17919.7738 (10)
4.5	17803.9708 (12)	17864.3227 (8)	17937.0160 (-5)
5.5	17798.0662 (6)	17870.5507 (5)	17955.3494 (14)
6.5	17793.3982 (10)	17877.9145 (10)	17974.7330 (1)
7.5	17789.9267 (-3)	17886.3862 (1)	17995.1423 (-42)
8.5	17787.6351 (-28)	17895.9535 (17)	18016.5642 (-46)

J''	P_1	Q_1	R_1
0.5	...	17841.2997 (76)	17855.3895 (-2)
1.5	...	17844.3158 (11)	17869.5843 (-4)
2.5	17822.0442 (-12)	17847.4188 (7)	17884.4259 (-13)
3.5	17814.0549 (-14)	17851.1815 (8)	17900.1221 (-9)
4.5	17806.7551 (-19)	17855.8181 (3)	17916.7525 (-7)
5.5	17800.3703 (-3)	17861.4195 (0)	17934.3500 (-13)
6.5	17794.9909 (-42)	17868.0275 (-3)	17952.9295 (-5)
7.5	17790.6817 (6)	17875.6641 (0)	17972.4913 (-3)
8.5	17787.4578 (-4)	17884.3398 (6)	17993.0333 (0)
9.5	17785.3471 (14)	17894.0607 (19)	18014.5510 (2)

NOTE.—Additional weak satellites observed: $P_{12}(4.5)$ 17751.5806 (126), $P_{12}(3.5)$ 17769.8739 (117), $P_{12}(1.5)$ 17808.0142 (29), $Q_{12}(2.5)$ 17814.1496 (44), $Q_{12}(0.5)$ 17830.1703 (-86), $R_{21}(0.5)$ 17886.4971 (0), $R_{21}(1.5)$ 17910.9387 (-10).

[a] In cm^{-1}.

($q_{0-0} = 0.94$, $q_{0-1} = 0.053$; Dwivedi and Lin 1978). The line width for unblended lines was observed to be 0.075 cm^{-1}. Absolute wavelength calibration was provided by Norlen's measurements of the argon emission spectrum (Norlen 1973). Our MgH measurements (Table 1) should have an absolute accuracy of 0.001 cm^{-1}.

b) Analysis

The interferograms were transformed by standard methods, and a rotational analysis was performed on the resulting spectrum. Rotational energy level splittings can be determined very precisely from high-resolution optical emission spectra if the signal-to-noise ratio (S/N) is high enough so that line center positions can be measured to a small fraction, $(S/N)^{-1}$, of a line width. Ideally the lines should be isolated (i.e., unblended) and their profiles should be symmetric about their centers. It should be emphasized that MgH presents a particularly pathological test case for such measurements. First, three isotopic species of magnesium are present in significant amounts (^{24}Mg: 78.7%; ^{25}Mg: 10.1%; and ^{26}Mg: 11.2%) so that blended lines are common in the A–X system, especially in the (0, 0) band for which the isotope shifts are very small. Second, there are numerous unresolved satellite lines, some of which are comparable in intensity to lines of the main branches for the low values of rotational quantum number of greatest interest in the present study. Finally, the hydrogen hyperfine structure is fairly large and can produce slight asymmetries in the line profiles.

Line positions were derived from the spectrum with the aid of DECOMP, a data reduction program developed at Kitt Peak. Overlapped lines were fitted by least squares with Voigt lineshape functions to extract the "true" line positions. The severe blending in the MgH spectrum made this step crucial. The observed line positions of the A–X (0, 0) and (0, 1) bands of ^{24}MgH are listed in Table 1 for lower state rotational quanta $N'' < 10$. The lines were assigned using the previous work of Balfour and Cartwright (1976a, b) and Balfour (1970a, b) as a guide. Note that several low-N lines previously attributed to the Q_2 and P_2 branches by Balfour and Cartwright (1976a, b) must be misassignments since the energy levels involved do not exist. See Herzberg (1950: § V, 3) for an energy level diagram of a $^2\Pi$–$^2\Sigma$ transition and a description of the spectroscopic notation. A rotational analysis was performed on the line positions of Table 1 by means of a direct, simultaneous, nonlinear least-squares fit of both the (0, 0) and (0, 1) bands. The Hamiltonian matrices were set up in a Hund's case (a) basis set and diagonalized to provide the energy eigenvalues. The $^2\Pi$ and $^2\Sigma$ matrix elements of Zare et al. (1973) were used (see, e.g., Kotlar et al. 1980 for an explicit tabulation of the matrix elements). The resulting molecular constants are displayed in Table 2. The simultaneous fitting of the (0, 0) and (0, 1) bands tends to reduce correlations among parameters and provides more precise predictions of the infrared fundamental vibration-rotation transitions than would result from independent fits.

Contrary to the usual spectroscopic practice only low N lines ($N'' < 10$) were included in our fit. We are not trying to account for all observed lines of MgH but to predict the pure rotational and vibration-rotation transitions as accurately as possible. Unfortunately the $A^2\Pi$ state is perturbed (near $J = 33.5$ for $v = 0$) by the $B'^2\Sigma^+$ state (Balfour and Cartwright 1976a; Balfour and Lindgren 1978). Although this perturbation appears to be local, in fact it affects the entire $A^2\Pi$ $v = 0$ state to some extent and has large effects on the lambda doubling. As a result, the quality of the fit deteriorates as higher rotational levels are added. Additional centrifugal distortion matrix elements cannot cope with these levels since the Hamiltonian (Zare et al. 1973) is inadequate if there is a nearby $^2\Sigma$ state. In spite of our efforts, small systematic residuals remain (see Table 1), owing to the perturbing effects of the nearby $B'^2\Sigma^+$ state and to imperfect separation of blended lines.

The measurements discussed here represent a significant improvement over previous work (Balfour and coworkers). For example, earlier optical spectroscopy at lower resolution could not establish the value of the ground-state spin-splitting constant, γ_0, to better than one significant figure. The present results yield $\gamma_0 = 0.02640 \pm 0.00013$ cm^{-1}, somewhat larger than the ab initio theoretical value $\gamma_0 = 0.019$ cm^{-1} (Cooper 1982) and slightly larger than a value $\gamma_0 = -2B_0 \Delta g = 0.023$ cm^{-1} that can be estimated from electron spin resonance (ESR) measurements of g-factors in matrix-isolated MgH (Knight and Weltner 1970, 1971). Our determination of γ_0 rests on the observation of several weak satellite branches. The fit also provides values (Table 2) for the Λ-doubling parameters $p_0 = 0.0258$ cm^{-1} and $q_0 = 0.00178$ cm^{-1}. The signs and magnitudes of these parameters are consistent with a distant

TABLE 2
DERIVED MOLECULAR CONSTANTS FOR ^{24}MgH[a]

State	Constant	This Work[b]	Previous Work	Ref.
$X^2\Sigma^+$ $v = 0$......	T_0	0.0	0.0	
	B_0	5.736463(53)	5.7328	1
	D_0	$3.5242(49) \times 10^{-4}$	3.44×10^{-4}	1
	γ_0	0.02640(13)	0.019	2
$X^2\Sigma^+$ $v = 1$......	T_1	1431.9773(10)	1431.984	1
	B_1	5.555266(57)	5.5532	1
	D_1	$3.5426(55) \times 10^{-4}$	3.45×10^{-4}	1
	γ_1	0.02541(14)		
$A^2\Pi$ $v = 0$.......	T_0	19284.6508(7)		
	B_0	6.093133(47)	6.0943	1
	D_0	$3.6876(37) \times 10^{-4}$	3.62×10^{-4}	1
	A_0	35.0072(13)	35.3	3
	q_0	0.001788(11)		
	p_0	0.02583(13)		

[a] In cm^{-1}.
[b] One standard deviation in the last digits is quoted in parentheses.
REFERENCES.—(1) Balfour and Cartwright 1976b; (2) Cooper 1982; (3) Balfour 1970b.

TABLE 3

TERM VALUES FOR ^{24}MgH[a]

J	Kronig Parity[b]	$X^2\Sigma^+$ $v = 0$	$X^2\Sigma^+$ $v = 1$	$A^2\Pi_{1/2}$ $v = 0$	$A^2\Pi_{3/2}$ $v = 0$
0.5......	e	0.0	1431.9773	19273.2400	...
0.5......	f	11.4451	1443.0610	19273.2694	...
1.5......	e	11.4847	1443.0991	19287.3670	19318.4744
1.5......	f	34.3665	1465.2581	19287.4138	19318.4865
2.5......	e	34.4325	1465.3216	19312.6839	19354.0389
2.5......	f	68.7340	1498.5387	19312.7397	19354.0713
3.5......	e	68.8264	1498.6276	19349.7488	19402.1518
3.5......	f	114.5223	1542.8774	19349.8083	19402.2099
4.5......	e	114.6411	1542.9918	19398.7507	19462.5622
4.5......	f	171.6975	1598.2403	19398.8096	19462.6503
5.5......	e	171.8427	1598.3800	19459.7451	19535.1349
5.5......	f	240.2174	1664.5847	19459.7995	19535.2569
6.5......	e	240.3890	1664.7498	19532.7314	19619.7732
6.5......	f	320.0312	1741.8596	19532.7777	19619.9328
7.5......	e	320.2291	1742.0502	19617.6798	19716.3918
7.5......	f	411.0796	1830.0056	19617.7143	19716.5927
8.5......	e	411.3040	1830.2216	19714.5419	19824.9065
8.5......	f	513.2951	1928.9547	19714.5609	19825.1522
9.5......	e	513.5459	1929.1960	19823.2550	19945.2294

[a] In cm^{-1}.
[b] Brown *et al.* 1975.

interaction between the $A^2\Pi$ and $X^2\Sigma^+$ states. Since $p_0(A^2\Pi) \approx \gamma_0(X^2\Sigma^+)$, these two states form a unique perturber pair at low N (Zare *et al.* 1973). At higher N the interaction with the $B'^2\Sigma^+$ state becomes important.

The computed term values of the $X^2\Sigma^+$ $v = 0$ and $v = 1$ and $A^2\Pi$ $v = 0$ levels are provided in Table 3. These term values can be used to generate all of the satellite branches of the A–X (0, 0) and (0, 1) bands or to predict the vibration-rotation spectrum of ^{24}MgH. The infrared fundamental is a $^2\Sigma$–$^2\Sigma$ transition and thus has a very weak Q branch and doubled P and R branches. The predicted spectrum is given in Table 4 and should be accurate to ± 0.002 cm^{-1}.

In order to predict the rotational spectrum of MgH, it is also necessary to account for the relatively large proton hyperfine structure. Hyperfine structure constants can be taken over directly from ESR measurements of MgH trapped in a solid argon matrix (Knight and Weltner 1971). Differences between hyperfine constants for matrix-isolated MgH and for gas-phase MgH are expected to be no larger than the uncertainties in the rotational and spin splittings derived here. Knight and Weltner derived $A_{\rm dip} = 0.9 \pm 0.2$ MHz and $A_{\rm iso} = 296 \pm 1$ MHz for the dipolar and isotropic contributions to the hyperfine interaction in MgH on the H nucleus. The energy of each spin-hyperfine component of each rotational level can be written

$$E(N, J, F) = [B_0 - D_0 N(N + 1)]N(N + 1) + E(J, F),$$

where the expressions for the relative spin and hyperfine energies, $E(J, F)$ are taken from equations (12) of Carrington, Milverton, and Sarre (1978) for a $^2\Sigma^+$ state:

$$E(J = N + 1/2, F = N + 1) = \gamma_0 N/2 + b_F/4 - tN/(4N + 6),$$

$$E(J = N \pm 1/2, F = N) = 0.25\{-\gamma_0 - b_F + t \pm [\gamma_0^2(2N + 1)^2 + 4b_F^2 - 4\gamma_0 b_F + 4b_F t - 2\gamma_0 t + t^2]^{1/2}\},$$

$$E(J = N - 1/2, F = N - 1) = -\gamma_0(N + 1)/2 + b_F/4 - t(N + 1)/(4N - 2).$$

In these expressions, the Fermi contact parameter $b_F = A_{\rm iso} = 296$ MHz; $t = A_{\rm dip} = 0.9$ MHz; and N, J, and F are, respectively, the quantum numbers of rotational angular momentum, angular momentum including electron spin but excluding nuclear spin, and

TABLE 4

PREDICTED LINE POSITIONS FOR THE FUNDAMENTAL (1, 0) VIBRATION-ROTATION BAND OF ^{24}MgH[a]

N	$P_1(N)$	$P_2(N)$	$R_1(N)$	$R_2(N)$
0.........	...	...	1443.099	...
1.........	1420.493	...	1453.837	1453.813
2.........	1408.667	1408.695	1464.195	1464.172
3.........	1396.495	1396.524	1474.165	1474.143
4.........	1383.987	1384.016	1483.739	1483.718
5.........	1371.149	1371.180	1492.907	1492.887
6.........	1357.991	1358.023	1501.661	1501.642
7.........	1344.521	1344.554	1509.993	1509.974
8.........	1330.746	1330.780	1517.892	1517.875
9.........	1316.676	1316.711	1525.351	1525.335

[a] In cm^{-1}.

TABLE 5
PREDICTED ROTATIONAL SPECTRUM OF ^{24}MgH

N'	J'	F'	N''	J''	F''	v	A
1......	3/2	2	0	1/2	1	344,303. MHz	2.61 (−4) s^{-1}
1......	3/2	1	0	1/2	1	344,124.	8.67 (−5)
1......	3/2	1	0	1/2	0	344,420.	1.74 (−4)
1......	1/2	0	0	1/2	1	343,115.	2.58 (−4)
1......	1/2	1	0	1/2	1	343,000.	1.72 (−4)
1......	1/2	1	0	1/2	0	343,296.	8.61 (−5)
2......	5/2	3	1	3/2	2	687,957.	3.74 (−3)
2......	5/2	2	1	3/2	2	687,790.	3.74 (−4)
2......	5/2	2	1	3/2	1	687,969.	3.37 (−3)
2......	3/2	1	1	3/2	2	685,978.	1.03 (−4)
2......	3/2	1	1	3/2	1	686,157.	5.16 (−4)
2......	3/2	1	1	1/2	1	687,281.	1.04 (−3)
2......	3/2	1	1	1/2	0	687,166.	2.07 (−3)
2......	3/2	2	1	3/2	2	685,849.	5.56 (−4)
2......	3/2	2	1	3/2	1	686,028.	6.19 (−5)
2......	3/2	2	1	1/2	1	687,152.	3.11 (−3)

angular momentum including nuclear spin. In terms of the traditional Frosch and Foley (1952) parameters $b_F = b + c/3$ and $t = c/3$.

In Table 5 we list the predicted line frequencies for all spin and hyperfine components of the $N = 1–0$ and $N = 2–1$ transitions. It is worth noting that the $N = 1–0$ transition of MgH lies within a rather good atmospheric window not far from the frequencies of the CO $J = 3–2$ and CS $J = 7–6$ transitions. The corresponding spontaneous transition probabilities, $A(N', J', F'; N'', J'', F'')$ are also presented in Table 5, and are based upon the *ab initio* theoretical value of the ground-state permanent dipole moment, $\mu = −1.283$ debye, computed by Meyer and Rosmus (1975). The relative intensities of the spin-hyperfine components will be proportional to $(2F' + 1)A(N', J', F'; N'', J'', F'')$ when the lines are optically thin and the upper levels are populated according to their statistical weights.

The rotational constants for ^{24}MgH (Table 2) are $B_0 = 171974.8 \pm 1.6$ MHz, $D_0 = 10.565 \pm 0.015$ MHz, and $\gamma_0 = 791.5 \pm 3.9$ MHz. The uncertainties correspond to the formal (1 σ) errors in the least-squares fit to the optical emission line data. However, systematic errors will be much larger. We estimate that the overall uncertainties in the predicted frequencies of Table 5 are of the order of ± 30 MHz. In the $N = 1–0$ lines, this corresponds to a Doppler velocity shift of ± 26 km s^{-1}. The estimated accuracy of these predictions is thus good enough to permit an efficient astronomical search for MgH. It is also worth noting that the distinctive pattern of spin and hyperfine components can be used as a definitive test of the identification with MgH of any astronomical lines that might appear near the predicted frequencies.

As mentioned above, the practical limit on the accuracy of the derived rotational splittings in MgH is set not by purely instrumental constraints, but rather by the difficulty of fitting asymmetric profiles that are due to isotopic blends and unresolved satellite lines and hyperfine structure. In more favorable cases of simple molecules with isolated lines, we expect that similar optical emission spectroscopy can provide rotational frequencies accurate to ± 2 MHz or better.

III. ASTRONOMICAL CONSIDERATIONS

The observability of an interstellar molecule depends upon its abundance and degree of excitation. There are two different methods by which MgH might be observed in molecular clouds: by pure rotational lines in emission at submillimeter wavelengths and by lines of the $A–X$ electronic transition in absorption in the visible spectra of background stars. We consider various factors that affect the detectability of interstellar MgH by these two methods.

For a rotational transition, the intensity depends not only on the abundance of the molecule but also on the local density, temperature, and radiation field that govern whether the transition can be excited perceptibly above the adjacent background continuum emission. In the case of a molecule like MgH with rotational transitions at submillimeter wavelengths and large transition probabilities, the populations of the lowest rotational levels will be coupled strongly to the thermal bath of the ambient radiation field unless the density is high enough to couple the molecule to the thermal bath of the gas by collisions.

We illustrate these points by considering a two-level MgH molecule having a single $N = 1–0$ rotational line at 343,840 MHz with a mean transition probability $A_{10} = 2.6 \times 10^{-4}$ s^{-1}. If we assume a cross section for collisional de-excitation $N = 1–0$ by H$_2$ of $\sigma = 5 \times 10^{-16}$ cm^2, then the corresponding rate coefficients are

$$C_{10} = 1.8 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ s}^{-1}$$

and

$$C_{01} = 5.3 \times 10^{-12} T^{1/2} \exp(-16.50/T) \text{ cm}^3 \text{ s}^{-1},$$

for de-excitation and excitation, respectively. Even in a warm, dense region like the core of the Orion molecular cloud, OMC-1, MgH will not be easily excited. Based upon the published flux measurements for OMC-1 at wavelengths between 0.4 and 1.0 mm (Westbrook *et al.* 1976; Keene, Hildebrand, and Whitcomb 1982), we estimate a peak continuum intensity of $I_v = 5.1 \times 10^{-14}$ ergs s^{-1} cm^{-2} Hz^{-1} sr^{-1} at the frequency of the $N = 1–0$ transition. This implies an internal brightness temperature within the cloud of approximately $T_b = 5.2$ K, including the contribution of the 2.7 K cosmic background radiation. At the observed kinetic tem-

perature of $T = 75$ K, the rate of collisional excitation, $n(H_2)C_{01} = 3.7 \times 10^{-11} n(H_2)$ s^{-1}, exceeds the rate of absorption in this radiation field,

$$I_\nu B_{01} = 3A_{10}/[\exp(h\nu/kT_b) - 1] = 3.5 \times 10^{-5}\ \text{s}^{-1}$$

only at densities $n(H_2) > 10^6$ cm^{-3}, where B_{01} is the Einstein B coefficient for absorption. Even though the mean density in OMC-1 approaches this value, the abundance of MgH must be large enough to produce a line that can be seen against a total continuum brightness temperature of $T_c = 6.5$ K at 344 GHz. In a cloud like OMC-1 where $T = 75$ K and $n(H_2) = 10^6$ cm^{-3}, a column density $N(MgH) = 1.5 \times 10^{12} \Delta V$ cm^{-2} will be required to produce a 344 GHz line with a peak brightness temperature in excess of background of $T_L = 0.5$ K, where ΔV is the full width at half-maximum of the line in velocity units of km s^{-1}.

For comparison, in a cold cloud at $T = 15$ K where the density is $n(H_2) = 5 \times 10^5$ cm^{-3} and the only continuum radiation at 344 GHz is due to the 2.7 K cosmic background, a column density $N(MgH) = 3.9 \times 10^{12} \Delta V$ cm^{-2} is required to produce a $T_L = 0.5$ K line. Densities much less than $n(H_2) = 4 \times 10^5$ cm^{-3} will be inadequate to excite the line above the background, regardless of how much MgH is present. In short, only in the densest parts of molecular clouds will detectable emission lines of MgH be expected. Hot clouds like OMC-1 are not necessarily more favorable than cold clouds for excitation of MgH lines, because they will usually provide more intense continuum emission at the transition frequencies. The above examples suggest that for total H_2 column densities of the order of 10^{22} to 10^{23} cm^{-2}, relative abundances as low as MgH/$H_2 = 10^{-10}$ may be detectable in the densest interstellar clouds by means of the 344 GHz emission lines.

It is worth noting that the effect of the strong coupling of molecular level populations to the local submillimeter radiation field inside a molecular cloud applies to all molecules with large rotational constants and spontaneous transition probabilities. Plambeck and Erickson (1982) have discussed their search for the $J = 1-0$ transition of interstellar NaH at 289.864 GHz under the assumption that the only background radiation is the 2.7 K cosmic background. As we have seen, the brightness temperature of internal radiation at this frequency is significantly larger in a hot cloud like OMC-1. Thus the NaH column density limit, $N(NaH) < 5.9 \times 10^{12}$ cm^{-2}, derived by Plambeck and Erickson for Orion A (OMC-1) is too low, a value of the order of 10^{14} cm^{-2} being more appropriate.

Now that it is feasible to do sensitive, optical absorption line studies of genuine molecular clouds (see, e.g., Hobbs, Black, and van Dishoeck 1983; Lutz and Crutcher 1983; Crutcher 1985), searches for the visible lines of MgH will be of value. The strongest interstellar absorption lines of MgH will be those arising in the $v = 0$, $N = 0$ ground state. The wavelengths in standard air and the relative oscillator strengths of the lines of interest in the $A-X$ (0, 0) band are listed in Table 6. The $A-X$ (0, 0) band has a fairly large oscillator strength, $f_{00} = 0.161$, (Kirby, Saxon, and Liu 1979). The experimental band oscillator strength computed from the measured $A-X$ lifetime (Nedelec and Dufayard, 1978) agrees with the theoretical value to within experimental error. If we assume that all of the molecules are in the $N = 0$, $J = \frac{1}{2}$ ground state in a cloud of modest density, and consider a minimum measurable equivalent width of 3 mÅ in the (0, 0) $R_1(\frac{1}{2})$ line at 5183.3 Å, then a column density as low as $N(MgH) = 2 \times 10^{11}$ cm^{-2} is potentially observable. It is worth pointing out that neutral atomic Mg is also observable by ground-based optical techniques through its $3s3p\ ^3P_1 - 3s^2\ ^1S_0$ intercombination line at 4571.104 Å. The oscillator strength of this line is $f = 2.11 \times 10^{-6}$ (Laughlin and Victor 1979). At the level of 3 mÅ equivalent width, a column density $N(Mg) = 7.7 \times 10^{15}$ cm^{-2} is detectable. The MgO molecule also has a strong band system in the visible. The transition moment function derived by Diffenderfer, Yarkony, and Dagdigian (1983) for the $B^1\Sigma^+ - X^1\Sigma^+$ system of MgO implies a value of the (0, 0) band oscillator strength of $f_{00} = 0.153$. If the ground-state rotational levels are populated according to an excitation temperature $T_{ex} = 2.7$ K in a low density cloud, then the $B-X$ (0, 0) $R(1)$ line at 4997.124 Å will have an equivalent width of 3 mÅ for a total column density $N(MgO) = 3 \times 10^{11}$ cm^{-2}. In a cloud of total column density 10^{22} cm^{-2}, we see that MgH, Mg, and MgO are detectable by optical absorption line techniques at the levels of 2×10^{-11}, 7.7×10^{-7}, and 3×10^{-11}, respectively, in terms of abundance relative to that of hydrogen, and of 5×10^{-7}, 0.02, and 7.5×10^{-7}, respectively, in terms of the solar magnesium abundance (Mg/H $= 4 \times 10^{-5}$; Lambert and Luck 1978).

The microwave frequencies of the lowest rotational transitions of MgO have also been measured recently in the laboratory by Steimle, Azuma, and Carrick (1984).

It is difficult to predict the abundances of magnesium-bearing molecules in interstellar clouds because the processes by which they might form are poorly understood. Leung, Herbst, and Huebner (1984) have suggested that MgH may form in the gas phase by
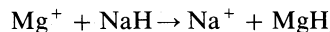
$$Mg^+ + NaH \rightarrow Na^+ + MgH$$

TABLE 6

POTENTIAL INTERSTELLAR ABSORPTION LINES OF ^{24}MgH
IN THE $A-X$ (0, 0) BAND

Line	$\tilde{\nu}_{vac}$ (cm^{-1})	λ_{air} (Å)	f/f_{00}	Notes
$^SR_{21}(\frac{1}{2})$	19318.4744	5174.9509	0.260	1
$R_1(\frac{1}{2})$	19287.3657	5183.2977	0.407	
$Q_{f1}(\frac{1}{2})$	19273.2736	5187.0876	0.333	2

NOTES.—The band oscillator strength is $f_{00} = 0.161$ (Kirby *et al.* 1979). (1) The frequency of the $^SR_{21}$ line is computed from the energy levels tabulated in Table 3; those of the other lines are the measured values. (2) The designation of a first line Q_{f1} and the determination of its relative strength follow the suggestion of Schadee (1975).

and by a sequence of ion-molecule reactions initiated by

$$Mg^+ + H_2 \rightarrow MgH_2^+ + h\nu .$$
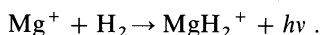
Their chemical models predict fractional abundances MgH/H_2 in the range 10^{-13} to 10^{-11} if heavy elements are severely depleted from the gas phase (i.e., by factors of 100 relative to solar abundances) and in the range 10^{-10} to 10^{-9} if the heavy element abundances are characteristic of those given in the older literature for the ζ Oph diffuse cloud (Morton 1975). The most recent study of interstellar magnesium (Murray *et al.* 1984), however, suggests that the gas phase abundance of magnesium in diffuse clouds is rather higher than indicated by the earlier work, viz., 40% of the solar abundance, on average. It is also possible that magnesium-bearing molecules form on the surfaces of interstellar grains and are then injected back into the gas phase. In any event, observational information about the abundances of various forms of magnesium in interstellar clouds is needed. The atomic forms of magnesium may play a significant role in the overall ionization balance of a molecular cloud. Searches for MgH and MgO can be used to constrain the chemistry of metals and to estimate the contribution of grain surface reactions to gas phase abundances.

There exist upper limits on interstellar lines in the *A–X* (0, 0) band toward two stars. Herbig (1968) found no MgH lines with equivalent widths greater than 3 mÅ toward ζ Oph, and Crutcher (1985) set limits of 8 mÅ on the MgH lines toward HD 29647.

IV. CONCLUSIONS

The $A^2\Pi–X^2\Sigma^+$ (0, 0) and (0, 1) transitions of MgH have been analyzed at high resolution using a Fourier transform spectrometer. The derived spectroscopic constants and vibrational and rotational energy levels of the $X^2\Sigma^+$ state are considerably more accurate than any previously available. Frequencies of the lowest $N = 2–1$ and $N = 1–0$ pure rotational lines are predicted with an estimated precision of ± 30 MHz. Positions of the (1, 0) vibration-rotation lines are predicted with an uncertainty of ± 0.002 cm^{-1}. Interstellar MgH should be detectable at a relative abundance level of $MgH/H_2 = 2 \times 10^{-11}$ by means of its visible absorption lines and at a level $MgH/H_2 = 10^{-10}$ by means of its 344 GHz emission lines. In the former case, observations will be restricted to lines of sight where suitable background stars are present, while in the latter case, observations will be productive only in the densest interstellar regions where the MgH lines can be excited into emission above the background continuum.

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Note added in proof.—We have recently learned that 12 pure rotational transitions ranging $N = 2–1$ to $N = 6–5$ have been observed directly by far-infrared absorption spectroscopy by L. R. Zink, K. R. Leopold, K. M. Evenson, and D. A. Jennings at the National Bureau of Standards in Boulder, Colorado. Their results agree with ours within our claimed accuracy.

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