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The millimeter-wave spectrum of the MgOH radical ($X\,^2\Sigma^+$)

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The pure rotational spectrum of the ground electronic state ($X\,^2\Sigma^+$) of the MgOH radical has been observed using millimeter/sub-millimeter direct absorption spectroscopy, as well as that of MgOD, and the less abundant magnesium isotopically-substituted species ^{25}MgOH and ^{26}MgOH. The free radicals were created in a Broida-type oven by the reaction of metal vapor with hydrogen peroxide. The spin–rotation splitting was readily observed in these data; however, the hyperfine structure was only resolved for ^{25}MgOH. The rotational and spin–rotation constants of the radicals have been determined from a non-linear least-squares fit using a $^2\Sigma$ Hamiltonian. The ^{25}Mg hyperfine constants are also estimated.

1. Introduction

Studies of small metal-containing molecules are of interest because of their likely presence in flames and in high-temperature reactions involving catalysis and corrosion processes [1]. Also, they may be found in the upper atmosphere [2], and in the interstellar medium, either in the circumstellar envelopes of late-type stars or in dense molecular clouds [3]. Certain metals such as magnesium and iron have rather large cosmic abundances, and whether they exist in molecular form in interstellar gas is an important question for astrochemistry.

Many small metal-containing species have been observed optically via their electronic transitions [4,5], but relatively few have been studied at high resolution by measuring their pure rotational spectra. Among the exceptions are several diatomic oxides, hydrides, and sulfides, including MgO [6], MgS and CaS [7], AlO [8], and MgH [9]. In addition, the pure rotational spectra of several alkali metal monohydroxides have been observed, such as CsOH and RbOH [10,11]. The metal hydroxides are of particular interest, because their structures may be linear, bent, or "quasi-linear". Evidence of quasi-linearity was observed in RbOH, for example, through anomalous behavior of its excited vibrational modes [11]. The degree of non-linearity in the metal monohydroxides is thought to indicate the degree in which the metal–OH bond is covalent as opposed to ionic [12]. The more covalent the bond, the more an H_2O bent-type structure is likely to occur; for an ionic bond, the species should be linear.

Clearly it would be of interest to study more metal monohydroxide molecules to examine their linearity and nature of the metal–OH bond. An obvious choice are the alkaline earth monohydroxides. Optical spectra of several of these species have been observed, including SrOH [13], BaOH [14], CaOH [15,16], and MgOH [12]. These species are free radicals and exhibit $^2\Sigma^+$ ground states. Interestingly, the optical data suggest that the first three radicals are strictly linear; MgOH however, appears to show some quasi-linear behavior, in that it has a quartic bending potential [12]. Theoretical calculations also indicate the probable existence of a quartic potential for this radical [17].

With the goal of examining the nature of the M–OH bond, we have begun a systematic high-resolution study of the pure rotational spectra of alkaline-earth hydroxides using millimeter/sub-millimeter direct absorption spectroscopy. We have successfully measured the mm/sub-mm spectrum of both CaOH

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[3] and SrOH [18] in their ground vibrational state, as well as in their (0, 1, 0), (0, 2, 0), and (1, 0, 0) vibrational modes [19]. These two species appear to be quite linear, as optical studies suggest. In this paper, we present our measurements of the mm/sub-mm spectrum of MgOH, including the magnesium 25 and 26 isotopically substituted species, as well as that of MgOD. We have determined rotational, spin-rotation, and hyperfine constants for the (0, 0, 0) vibrational mode of these species. In the ground vibrational state, the molecule does appear to be very nearly linear. We have also observed several transitions of MgOH originating in the (0, 1, 0), (0, 2, 0), and (1, 0, 0) vibrational modes. These measurements will appear in a later paper [19].

2. Experimental

The mm/sub-mm direct absorption spectrometer was similar to that used in our other experiments [3,18], and is described in detail elsewhere [20]. Briefly, the instrument consists of a source of coherent, tunable mm/sub-mm radiation, a gas cell, and a detector. The sources of radiation are Gunn oscillators, operating in the range 65–115 GHz (J.E. Carlstrom Co.). To obtain higher frequencies up to 390 GHz, frequency multipliers (Millitech Corporation) are used. The Gunn oscillators are phase-locked to frequency-stabilize them by mixing their output with a harmonic of a frequency synthesizer (Fluke 6082A) operating near 2 GHz. The radiation from the Gunn source is quasi-optically injected into the cell by a scalar feedhorn and several machined teflon lenses. The cell is a double-pass system 0.5 m in length, with both ends sealed by teflon lenses. At one end is a rooftop reflector, which folds the beam onto itself after one pass through the cell, and rotates the beam polarization by 90°. The beam passes through the cell a second time and is reflected into the detector by a wire grid. A Broida-type oven is incorporated into the cell, which is evacuated by a Roots-blower-type pump (Edwards EH500/E2M40). The detector is a helium-cooled InSb bolometer (Cochise Instruments), whose output is fed into a lock-in amplifier (EG&G PAR 5301). Phase-sensitive detection is accomplished by FM modulation of the Gunn oscillator at a rate of ≈25 kHz; signals are detected at $2f$ by the lock-in-amplifier.

Spectra are taken by changing the frequency of the 2 GHz synthesizer, which in turn scans the Gunn oscillator frequency through the phase-lock loop. A typical time for a scan covering a range of 100 MHz is ≈6 min. Linewidths of spectra measured vary from about 200 to 700 kHz for the frequency range of 89–385 GHz. The larger linewidth at the higher frequencies is due primarily to modulation broadening.

MgOH was produced by the reaction of metal vapor and hydrogen peroxide (≈75% concentration in water). The reaction of magnesium vapor and H_2O_2 was the method used to produce MgOH in the measurement of its optical spectrum [12]. The vapor was generated in a Broida-type oven by resistively heating a metal sample in an alumina crucible contained in a tungsten basket. The metal vapor was entrained in ≈20–30 mTorr argon carrier gas and then reacted with H_2O_2 vapor of up to 50 mTorr in pressure. The total pressure in the reaction mixture was typically 70–80 mTorr. No chemiluminesence was observed when the H_2O_2 was reacted with the metal, in contrast to CaOH [3]. This is expected since the electronic transitions of MgOH are located in the ultraviolet region [21].

The magnesium 25 and 26 isotopically substituted species of MgOH were observed in their natural abundances (^{24}Mg: 78.70%; ^{25}Mg: 10.13%; ^{26}Mg: 11.17%). However, MgOD was produced by the reaction of metal vapor and deuterated hydrogen peroxide. D_2O_2 was made by the exchange of D_2O and H_2O_2.

3. Results

The observed rotational transitions of MgOH and ^{26}MgOH are given in tables 1 and 2. As the tables illustrate, ten rotational transitions of MgOH were measured in the frequency range 89–385 GHz, and six were recorded for the 26 isotope. The spin–rotation splitting was readily observed in all of these data, as shown in fig. 1. Hyperfine structure, arising from the interaction of the proton spin and unpaired electron spin, was not seen in either species, except in $N=2\rightarrow3$ transition of the main isotope line at 89 GHz. In this transition the lines were ≈100 kHz broader than what was reproducibly observed in

Table 1
Observed transition frequencies of ^{24}MgOH: X $^2\Sigma^+$ ($v=0$)

$N\to N'$	$J\to J'$	$F\to F'$	ν_{obs} (MHz)	$\nu_{obs}-\nu_{calc}$ (MHz)	$N\to N'$	$J\to J'$	$F\to F'$	ν_{obs} (MHz)	$\nu_{obs}-\nu_{calc}$ (MHz)
2→3	3/2→5/2	1→2	88913.315[a]	−0.005	8→9	15/2→17/2	7→8	266710.039	0.007
		2→3	88913.215[a]	−0.103			8→9		0.015
	5/2→7/2	2→3	88951.128[a]	−0.083		17/2→19/2	8→9	266747.652	0.027
		3→4	88951.028[a]	−0.058			9→10		0.038
4→5	7/2→9/2	3→4	148193.213	−0.015	9→10	17/2→19/2	8→9	296326.642	0.001
		4→5		0.004			9→10		0.008
	9/2→11/2	4→5	148230.880	−0.010		19/2→21/2	9→10	296364.264	0.035
		5→6		0.030			10→11		0.044
5→6	9/2→11/2	4→5	177828.755	0.026	10→11	19/2→21/2	9→10	325936.944	−0.012
		5→6		0.041			10→11		−0.006
	11/2→13/2	5→6	177866.334	−0.025		21/2→23/2	10→11	325974.531	−0.009
		6→7		0.002			11→12		−0.001
6→7	11/2→13/2	5→6	207460.423	−0.025	11→12	21/2→23/2	10→11	355540.349	0.002
		6→7		−0.012			11→12		0.006
	13/2→15/2	6→7	207498.046	−0.014		23/2→25/2	11→12	355577.911	−0.018
		7→8		0.006			12→13		−0.012
7→8	13/2→15/2	6→7	237087.750	−0.008	12→13	23/2→25/2	11→12	385136.187	<0.001
		7→8		0.002			12→13		0.004
	15/2→17/2	7→8	237125.358	<0.001		25/2→27/2	12→13	385173.745	−0.021
		8→9		0.014			13→14		−0.016

[a] Determined from deconvolution of blended line profiles.

Table 2
Observed transition frequencies of ^{26}MgOH: X $^2\Sigma^+$ ($v=0$)

$N\to N'$	$J\to J'$	$F\to F'$	ν_{obs} (MHz)	$\nu_{obs}-\nu_{calc}$ (MHz)	$N\to N'$	$J\to J'$	$F\to F'$	ν_{obs} (MHz)	$\nu_{obs}-\nu_{calc}$ (MHz)
7→8	13/2→15/2	6→7 7→8	229709.481	−0.020	10→11	19/2→21/2	9→10 10→11	315795.605	0.029
	15/2→17/2	7→8 8→9	229745.993	0.060		21/2→23/2	10→11 11→12	315832.014	0.005
8→9	15/2→17/2	7→8 8→9	258410.366	−0.014	11→12	21/2→23/2	10→11 11→12	344478.734	0.025
	17/2→19/2	8→9 9→10	258446.815	0.002		23/2→25/2	11→12 12→13	344515.113	−0.029
9→10	17/2→19/2	8→9 9→10	287105.878	−0.058	12→13	23/2→25/2	11→12 12→13	373154.786	0.042
	19/2→21/2	9→10 10→11	287142.369	<0.001		25/2→27/2	12→13 13→14	373191.138	−0.038

other lines under identical conditions. The hyperfine splitting, however, could not be resolved. The frequencies of the individual hyperfine lines for the $N=2\to3$ transition were determined from a deconvolution of the broadened line profiles assuming a symmetrical split about the center of ±50 kHz.

Table 3 lists the data obtained for ^{25}MgOH. For this species, only one rotational transition, the $N=12\to13$, was detected. This is because magnesium 25 has a nuclear spin of 5/2; such a large spin results in hyperfine interactions, even at high N. Hence, the weaker lines of the less abundant isotope are further reduced in intensity as they are split by hyperfine structure. Ten individual hyperfine com-

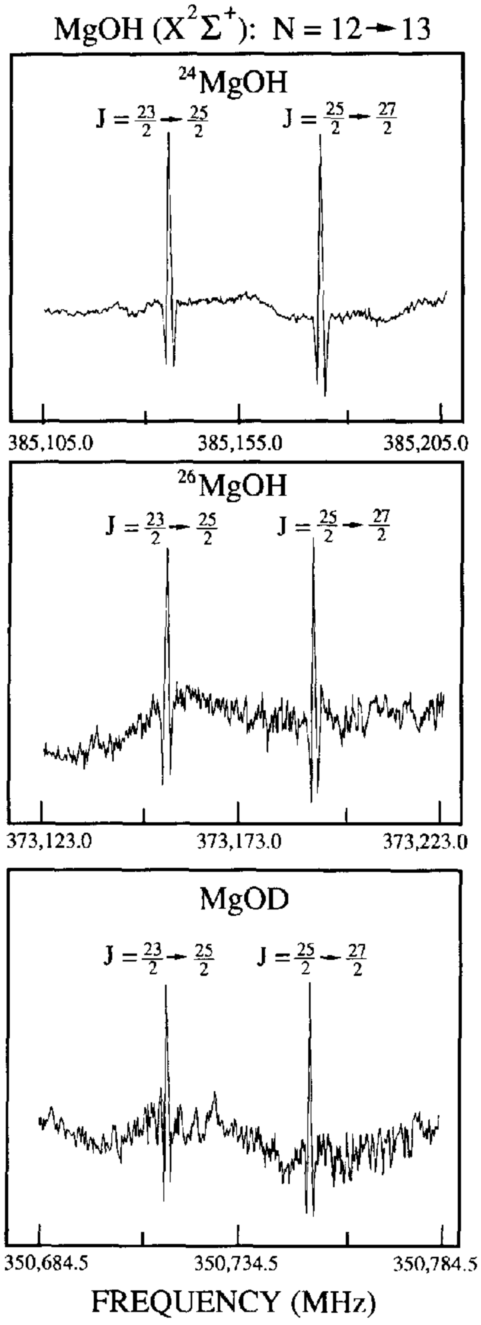

Fig. 1. Spectra of the $N=12\rightarrow13$ rotational transitions of MgOH, ^{26}MgOH, and MgOD observed in this work near 350–385 GHz. The spectra appear in emission because of the modulation scheme employed. Spin–rotation splitting is clearly resolved in these data, although no hyperfine interactions are apparent. These spectra represent averages of 2–4 six-minute scans, 100 MHz wide in frequency.

ponents were detected for the $N=12\rightarrow13$ transition, as shown in fig. 2. This is the first laboratory observation of ^{25}MgOH, as well as ^{26}MgOH, in the gas phase.

Table 4 lists the five rotational transitions observed for MgOD. Again, the splitting arising from spin–rotation interactions is readily apparent in these data. In fact, the spin–rotation splitting decreases slightly with increasing N, suggesting the presence of centrifugal distortion in the spin–rotation coupling. Hyperfine structure, however, was not observed. Deuterium, as opposed to hydrogen, has a spin of 1 versus 1/2 so electric quadrupole interactions might have been present. Such structure was not apparent in the data; line widths for MgOD were comparable to those measured for MgOH at similar frequencies.

Fig. 1 also displays a sample spectrum of MgOD, as well as MgOH and ^{26}MgOH. The spectra are plotted on the same frequency scale such that the variation in spin–rotation splitting can be seen. The average spin–rotation splitting for MgOH is 37.57 MHz, for MgOD $\gamma=37.50$ MHz and for ^{26}MgOH it is 36.43 MHz. The spin–rotation constant thus scales approximately as $\mu^{-1/2}$, where μ is the reduced mass, if the OH group on the molecules is considered as a unit.

Table 5 lists the rotational constants B_0 and D_0, and spin–rotation constant γ for MgOH, MgOD, and the magnesium 26 and 25 species. Estimates of the Frosh and Foley b and c hyperfine constants are also given for the proton nucleus of the main magnesium isotope, where some hyperfine interactions were observed. For MgOD, a centrifugal distortion correction to γ, γ_D, is also determined. Estimates of the b hyperfine constant and quadrupole coupling constant eqQ are given for ^{25}MgOH for the magnesium nucleus, as well. All constants were determined from a non-linear least-squares fit to the data, using a $^2\Sigma$ Hamiltonian. The centrifugal distortion correction to γ is incorporated into the Hamiltonian as

$$H_{sr}=[\gamma-\gamma_D N(N+1)]\boldsymbol{N}\cdot\boldsymbol{S}\,. \qquad (1)$$

As tables 1, 2 and 4 illustrate, these constants reproduce the measured rotational transitions to an accuracy of $\nu_{obs}-\nu_{calc}\lesssim44$ kHz for MgOH (except for the $N=2\rightarrow3$ data), $\nu_{obs}-\nu_{calc}\lesssim60$ kHz for ^{26}MgOH, and $\nu_{obs}-\nu_{calc}\lesssim29$ kHz for MgOD.

For ^{25}MgOH, only one rotational transition was

Table 3
Observed transition frequencies of ^{25}MgOH: X $^2\Sigma^+$ ($v=0$)

$N \rightarrow N'$	$J \rightarrow J'$	$F \rightarrow F'$	ν_{obs} (MHz)	$\nu_{obs}-\nu_{calc}$ (MHz)
12→13	23/2→25/2	9→10	378896.155	−0.004
		10→11	378899.136	−0.076
		11→12	378902.481	−0.039
		12→13	378906.384	−0.062
		13→14	378911.456 [a]	0.159
		14→15		0.095
	25/2→27/2	13→14	378918.132 [a]	−0.086
		14→15		−0.044
		12→13	378922.990	0.051
		11→12	378926.793	0.042
		10→11	378930.135	0.005
		15→16	378933.240	−0.016

[a] Blended lines.

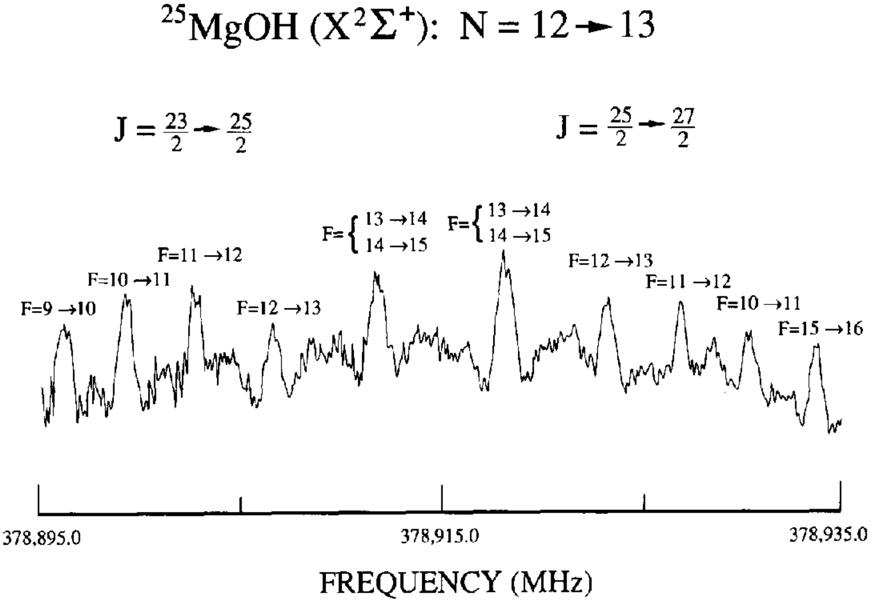

Fig. 2. Spectrum of the $N=12\rightarrow13$ transition of ^{25}MgOH near 378 GHz measured in this work. In these data, hyperfine structure, resulting primarily from the interaction of the 5/2 spin of the ^{25}Mg nucleus, is clearly resolved. This spectrum is an average of about 6 three-minute scans, 40 MHz wide in frequency.

observed. Hence, the centrifugal distortion constant D_0 was fixed to derive the other constants. The quadrupole coupling constant was also kept as a free parameter because a better fit was obtained using it. Hyperfine constant c was fixed at zero in this case. Estimates of the hyperfine constants are given for the ^{25}Mg nucleus only, and not for the proton. Since the contribution of the proton spin is likely to be small, this splitting was assumed to be negligible in fitting the data. The constants determined for ^{25}MgOH reproduce the measured frequencies to an accuracy of $\nu_{obs}-\nu_{calc} \lesssim 160$ kHz. The lesser accuracy partly arises from the blending of several of the hyperfine components.

Also shown in table 5 are the rotational constants of MgOH and MgOD derived from the optical work

Table 4
Observed transition frequencies of ^{24}MgOD: X $^2\Sigma^+$ ($v=0$)

$N \to N'$	$J \to J'$	$F \to F'$	ν_{obs} (MHz)	$\nu_{obs} - \nu_{calc}$ (MHz)	$N \to N'$	$J \to J'$	$F \to F'$	ν_{obs} (MHz)	$\nu_{obs} - \nu_{calc}$ (MHz)
9→10	17/2→19/2	8→9 9→10	269835.285	−0.023	12→13	23/2→25/2	11→12 12→13	350716.284	0.019
	19/2→21/2	9→10 10→11	269872.309	0.029		25/2→27/2	12→13 13→14	350752.844	−0.027
10→11	19/2→21/2	9→10 10→11	296801.354	0.019	13→14	25/2→27/2	12→13 13→14	377664.140	−0.020
	21/2→23/2	10→11 11→12	296838.183	−0.012		27/2→29/2	13→14 14→15	377700.653	0.029
11→12	21/2→23/2	10→11 11→12	323761.827	0.005					
	23/2→25/2	11→12 12→13	323798.542	−0.019					

Table 5
Molecular constants for MgOH and MgOD [a]

Constant		Millimeter-wave (MHz)	Optical (MHz) [b]	ESR (MHz) [c]
^{24}MgOH	B_0	14822.5161(22)	14918(9)	
	D_0	0.0262225(92)	0.033(6)	
	γ	37.567(36)		
	b	9.3(3.9) [d]		|10.1(3)|
	c	−4.8(2.8) [d]		|4.7(4)|
^{26}MgOH	B_0	14361.1373(37)		
	D_0	0.024648(14)		
	γ	36.433(4)		
	b	–		
	c	–		
^{25}MgOH [e]	B_0	14581.7987(27)		
	D_0	0.024130 [e]		
	γ	37.01(22)		
	b	−304.4(4.6)		|300.7(3)|
	c	0.0 [e]		|12.0(4)|
	eqQ	−41(17)		
^{24}MgOD	B_0	13496.8901(30)	13470(21)	
	D_0	0.021004(10)	0.018(18)	
	γ	37.50(14)		
	γ_D	0.00176(31)		
	b	–		
	c	–		

[a] Errors quoted are 3σ statistical uncertainties and apply to the last quoted digits.

[b] Ref. [12].

[c] Ref. [22]: Constants derived from ^{25}MgOH; constants listed as absolute values because signs were not determined.

[d] Based primarily on the $N=2\to3$ transition (see text).

[e] Based on the $N=12\to13$ transition only; D_0 and c are held fixed (see text).

of Ni [12]. As the table illustrates, the new millimeter-wave constants vary significantly from the values of B_0 and D_0 estimated from the optical data.

Table 5 additionally lists the hyperfine constants determined from ESR/matrix studies of ^{25}MgOH done by Brom and Weltner [22]. The *b* hyperfine constant derived from the one transition of ^{25}MgOH observed in this work is in good agreement with that found from the matrix studies (-304 MHz versus -301 MHz). The proton hyperfine constants, estimated from the ^{24}MgOH data, are in reasonable agreement with those measured from the ESR studies of ^{25}MgOH.

Errors quoted in table 5 are 3σ and purely statistical, arising from the goodness of the fit to the data. These errors do not include other sources of uncertainties, which include the frequency stability of the 2 GHz synthesizer, as well as the ability to determine the center of any given spectral line. The frequencies were determined from a Gaussian fit to the line profiles in almost all cases. Considering these other sources of error, a conservative estimate of all measured MgOH frequencies is ± 60 kHz for the main isotope, and ± 75 kHz for MgOD and ^{26}MgOH. An uncertainty of ± 150 kHz is assigned to the ^{25}MgOH transitions.

Table 6 lists the r_0 bond lengths derived for the O–H and Mg–O bonds from the millimeter-wave data, neglecting zero-point vibrations. The bond lengths were calculated comparing both ^{24}MgOH/^{26}MgOH and ^{24}MgOH/MgOD. As expected, the bond distances derived from these two sets of isotopes are not the same because the O–H and O–D bond lengths are known to be different [12]. They also differ slightly from the r_0 bond lengths determined from optical data (see table 6); the optical values were estimated using MgOH and MgOD only.

Also given in table 6 are the r_s bond lengths derived from a partial substitution structure. Since the oxygen atom was not substituted in this work, a complete structure could not be calculated and hence the r_s values are only approximate. As the table illustrates, the r_s and r_0 values do not vary much for the Mg–O bond. For the O–H bond, on the other hand, the r_s length of 0.825 Å differs considerably from $r_0 = 0.943$ Å determined from ^{24}MgOH and ^{26}MgOH. The r_s value also seems rather small for an O–H bond length, which is 0.97 Å for the OH radical [12]. This may indicate large amplitude bending of the H atom with respect to the Mg–O axis.

Theoretical values for bond lengths from several different sources [17,23,24] are given in table 6 as well for comparison. These were calculated assuming the molecule to be linear. There is reasonable agreement between the millimeter-wave and theoretical values, especially for Mg–O bond lengths. On the other hand, for the O–H bond length, the theoretical estimates agree well only with the r_0 value derived from ^{24}MgOH/^{26}MgOH. The r_s O–H length is noticeably smaller than the theoretical values.

4. Discussion

As table 5 illustrates, the millimeter-wave rotational constants refine those determined from optical data considerably. On the other hand, the estimates of the hyperfine constants for both the proton spin on MgOH, and the 25 magnesium spin on the isotopically substituted species, are in reasonably

Table 6
Bond lengths for MgOH (in Å)

Millimeter-wave				Optical [d]		Theoretical	
r_0(MgO)	r_0(OH)	r_s(MgO) [c]	r_s(OH) [c]	r_0(MgO)	r_0(OH)	r(MgO)	r(OH)
1.785 [a] 1.722 [b]	0.822 [a] 0.943 [b]	1.780	0.825	1.770	0.912	1.768 [e] 1.780 [f] 1.773 [g]	0.931 [e] 0.948 [f] 0.941 [g]

[a] Determined from ^{24}MgOH/^{24}MgOD. [b] Determined from ^{24}MgOH/^{26}MgOH.
[c] Calculated from a partial substitution structure using ^{24}MgOH, ^{26}MgOH, and MgOD.
[d] Ref. [12]. [e] Ref. [24]. [f] Ref. [17]. [g] Ref. [23].

good agreement with those determined from matrix studies, particular for the Mg nucleus. The fact that the constants for the magnesium nucleus are much larger than those arising from the proton spin is additional evidence that the unpaired electron is located close to the metal atom. This supports the notion of ionic bonding in the molecule where the lone electron resides on the metal in a Mg^+OH^- structure. The hyperfine constants of MgOH do appear to be somewhat larger than those of CaOH, however [3]. This also suggests that the bonding in MgOH is slightly more covalent than that of CaOH. The fact that MgOH does appear to exhibit some quasi-linear behavior supports the larger character of covalent bonding in this species.

A $^2\Sigma$ Hamiltonian does appear to fit the data for MgOH fairly well. This suggests that the species is linear or very nearly linear in its ground vibrational state. However, the r_s O–H bond length of MgOH appears to be unusually short, perhaps indicating the presence of large-amplitude bending. Some suggestions of quasi-linearity are also apparent in the rotational spectra of the excited vibrational modes of the radical. These will be discussed in a later paper, as mentioned [19].

Determination of the frequencies of the rotational transitions of MgOH will now allow for a definitive search for this species in the interstellar medium. Small molecules containing magnesium are of particular interest, because of the element's large cosmic abundance.

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