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# Millimeter-wave spectroscopy of MgF: Structure and bonding in alkaline-earth monofluoride radicals

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The pure rotational spectrum of the MgF radical in its ground electronic state ( $X^2\Sigma^+$ ) has been recorded using millimeter/submillimeter direct absorption techniques. Transitions arising from the  $v=0, 1, 2$ , and 3 vibrational modes of the main magnesium isotopic species,  $^{24}\text{MgF}$ , have been observed. In addition, spectra of the isotopomers  $^{26}\text{MgF}$  and  $^{25}\text{MgF}$  in the natural abundances of magnesium have been detected. Rotational and fine structure constants have been determined for these species, as well as hyperfine parameters for the fluorine nucleus ( $I=1/2$ ). For  $^{25}\text{MgF}$ , the hyperfine structure was also resolved arising from the magnesium nucleus, which has  $I=5/2$ , yielding the  $^{25}\text{Mg}$  hyperfine and quadrupole constants. Comparison of these hyperfine parameters with those of the heavier alkaline-earth monofluorides and the free  $^{25}\text{Mg}^+$  atom suggests that there is an increase in covalent bonding in MgF vs its heavier fluoride counterparts. This behavior is also apparent in the hybridization of the wave function of the unpaired electron in MgF, which appears to consist of almost equal  $s$  and  $p$  character.

## I. INTRODUCTION

Small metal-containing molecules are present in high temperature reactions that occur in flames, catalysis, and corrosion processes.<sup>1</sup> They also exist in the interstellar medium, especially in the circumstellar envelopes of late-type stars,<sup>2,3</sup> and possibly in the upper atmosphere. Understanding the characteristics of individual bonds to metals is thus of chemical interest.

One class of small metal-bearing species where several models of the bonding have been proposed are the alkaline-earth monohalide compounds. These species are considered to be highly ionic, and thus serve as useful candidates for testing semiclassical theories of bonding. Several models have been developed in recent years, including a ligand field theory by Rice *et al.*,<sup>4</sup> and one involving a modified electrostatic Rittner-type approximation put forth by Topping *et al.*<sup>5</sup> Such models have been used to derive physical properties of the alkaline-earth halide species, such as dipole moments and spectroscopic parameters.

In order to test such bonding theories, however, the actual physical parameters of alkaline-earth halide molecules need to be measured with high accuracy. Extensive high resolution spectroscopic data exist for alkaline-earth diatomic chloride species such as  $\text{BaCl}$ ,<sup>6</sup>  $\text{SrCl}$ ,<sup>7</sup>  $\text{CaCl}$ ,<sup>8</sup> and  $\text{MgCl}$ .<sup>9</sup> Several of their fluoride counterparts, which all have  $^2\Sigma$  ground electronic states, have been studied as well. The millimeter-wave spectrum of  $\text{BaF}$  (Refs. 6, 10) has been measured with rotational resolution, resulting in a detailed analysis of its hyperfine structure, including that of the  $^{137}\text{BaF}$  isotopomer, where the metal atom has a nuclear spin. The rotational spectrum of  $\text{SrF}$  and its isotopomers has also been examined extensively both by microwave<sup>7</sup> and molecular beam rf-optical double reso-

nance<sup>11,12</sup> techniques. The hyperfine and fine structure of  $\text{CaF}$  has been well-determined by rf-optical double resonance spectroscopy<sup>13,14</sup> as well, and, more recently, its pure rotational millimeter-wave transitions have been measured.<sup>15</sup>

Very little spectroscopic work, however, has been carried out for the MgF radical. A few optical studies have been done of its electronic spectrum by Barrow and Beale,<sup>16</sup> who determined the rotational constants and equilibrium bond length of the radical to a fair degree of accuracy. In addition, electron spin resonance (ESR) measurements have been carried out of the hyperfine structure of MgF, while frozen in an argon matrix by Knight *et al.*<sup>17</sup> These authors were able to estimate hyperfine constants  $b$  and  $c$  for the fluorine atom in MgF, which has a nuclear spin of  $1/2$ . They found that less than 4% of spin density is on the F atom, supporting the ionic picture of the radical as  $\text{Mg}^+\text{F}^-$ , where the unpaired electron is located almost exclusively on the metal nucleus.

In order to better quantify the bonding and structure in MgF and in alkaline-earth monofluorides in general, we have measured the pure rotational spectrum of magnesium fluoride using millimeter/submillimeter (mm/sub-mm) direct absorption spectroscopy. We have observed rotational transitions of  $^{24}\text{MgF}$  in its  $v=0, 1, 2$ , and 3 vibrational modes, where we have resolved its fine and hyperfine structure. We have also detected the millimeter-wave spectra of the magnesium isotopomers,  $^{26}\text{MgF}$  and  $^{25}\text{MgF}$ , and have measured the hyperfine structure associated with the  $^{25}\text{Mg}$  nucleus, for which  $I=5/2$ . In this paper we present our analysis of the spectra, including determination of the hyperfine structure, and discuss its implications for structure and bonding in metal monofluoride species.

## II. EXPERIMENT

The spectra of MgF, its  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$  isotopomers, as well as the excited vibrational states, were measured using

<sup>a)</sup>NASA Space Grant Fellow.

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direct absorption spectrometer operated in the mm/sub-mm region ( $\sim 65$ –500 GHz). The details of the spectrometer are given elsewhere.<sup>18</sup> Briefly, the instrument consists of a tunable source of mm/sub-mm radiation, a gas cell, and a detector. The tunable sources in this case are phase-locked Gunn oscillators, used in conjunction with Schottky diode multipliers for higher frequency work. The radiation from these devices is quasioptically propagated through the gas cell by scalar feed horns and a series of Teflon lenses. The cell, a double pass system, has a rooftop reflector at one end to reflect the radiation back through the cell after a single pass. The detector is a helium-cooled InSb bolometer. Phase sensitive detection is accomplished by fm modulation of the Gunn oscillators and by use of a lock-in amplifier.

The MgF radical was created by the reaction of metal vapor, produced in a Broida-type oven, with a mixture of  $F_2$  and He gases. The metal vapor was carried into the cell by a flow of argon carrier gas, typically at a pressure of 30 mTorr. The  $F_2$  and He gases were added in approximately a 1:1 ratio, with a total pressure of about 25 mTorr. When adding the  $F_2$ /He mixture to the magnesium vapor, a bright blue-green chemiluminescence was observed.

The full width at half-maximum of the spectra ranged from 200 to 800 kHz over the frequency range 90–400 GHz. For the  $^{25}\text{MgF}$  species, some of the lines measured were a little broader ( $\sim 1.1$  MHz) due to the blending of hyperfine components. Both the 25 and 26 magnesium isotopomers of MgF were observed in their natural abundances ( $^{24}\text{Mg}$ : 78.70%;  $^{25}\text{Mg}$ : 10.13%;  $^{26}\text{Mg}$ : 11.17%).

### III. RESULTS

Eight rotational transitions for  $^{24}\text{MgF}$  in its ground  $v=0$  vibrational mode were measured in this work between 92 and 340 GHz. Each transition consists of four hyperfine components, which were resolved in every measurement. The four components result from electron spin–rotation coupling, as well as magnetic hyperfine interactions arising from the fluorine nuclear spin of  $1/2$ . Four rotational transitions were observed for  $^{24}\text{MgF}$  in its  $v=1$  and 2 excited vibrational modes, as well, and three lines for the  $v=3$  mode, in the frequency range 276–368 GHz. Again, in these spectra, fine and hyperfine structure were resolved. Rotational transitions were additionally measured for the two magnesium isotopomers,  $^{26}\text{MgF}$  and  $^{25}\text{MgF}$ . For the magnesium 26-substituted species, four transitions were observed in the range 239–329 GHz, and again four components are present per transition. In the case of  $^{25}\text{MgF}$ , however, the spectra are far more complex because  $^{25}\text{Mg}$  has a nuclear spin. Thus, the hyperfine structure in this isotopomer arises from both the magnesium and fluorine nuclei. Electric quadrupole interactions are present as well because  $I > 1$  for the  $^{25}\text{Mg}$  nucleus. Thus, the two rotational transitions measured at 334 and 365 GHz each consist of 24 components, some which were individually resolved but many which were blended together. Transition frequencies for all species are given in Anderson, Allen, and Ziurys (1993).<sup>19</sup>

In Figs. 1 and 2, the MgF hyperfine interactions are

clearly shown. Figure 1 shows the  $N=10 \rightarrow 11$  transitions of  $^{24}\text{MgF}$  in its  $v=0$  and  $v=1$  modes near 340.7 and 337.7 GHz, as well as that of  $^{26}\text{MgF}$  in its  $v=0$  state at 329.2 GHz. Four lines are clearly present in each spectrum. The

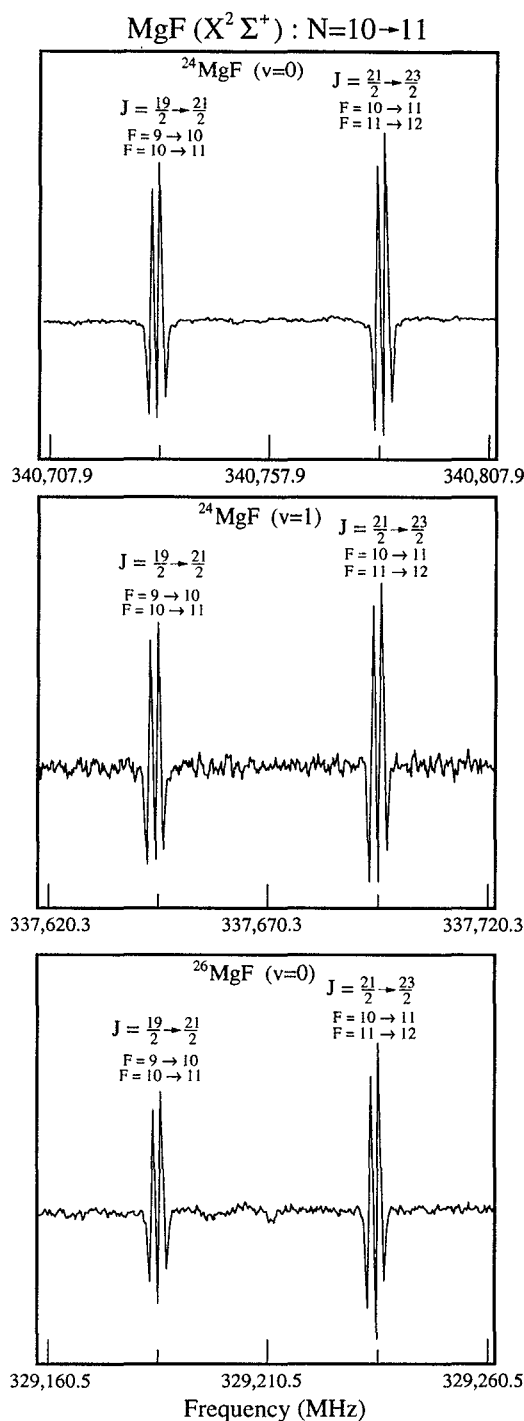


FIG. 1. Spectra of the  $N=10 \rightarrow 11$  rotational transition of  $^{24}\text{MgF}$  and  $^{26}\text{MgF}$  in their ground ( $v=0$ ) vibrational and electronic ( $X^2\Sigma^+$ ) states, as well as the  $v=1$  mode of  $^{24}\text{MgF}$ , observed in this work at 340.7, 329.2, and 337.7 GHz, respectively. Both fine and hyperfine structure are apparent in the data, which arise from the interaction of the unpaired electron spin with the molecular rotation and nuclear spin of the fluorine nucleus. The hyperfine structure observed is barely resolved, and indicates that only a small fraction of the unpaired electron density resides on the  $^{19}\text{F}$  nucleus, which has  $I=1/2$ .

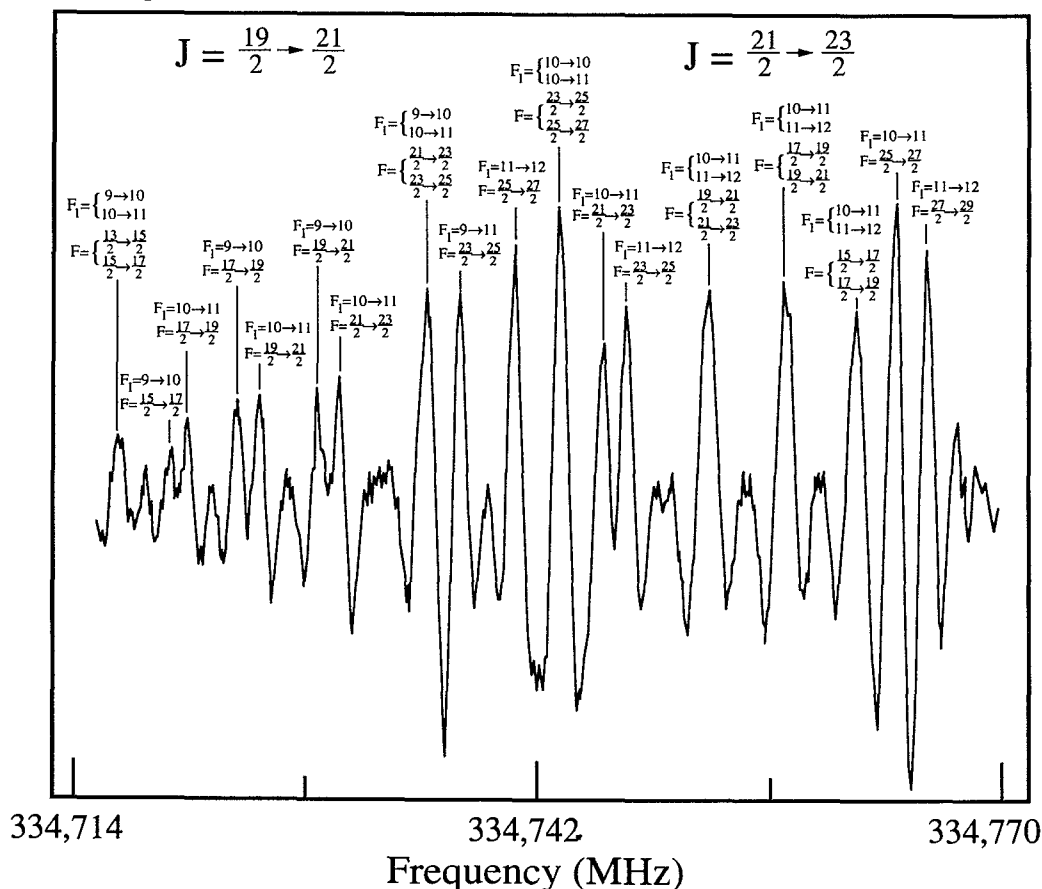
$^{25}\text{MgF} (X^2\Sigma^+): N = 9 \rightarrow 10$ 

FIG. 2. The spectrum of the  $N=9 \rightarrow 10$  rotational transition of  $^{25}\text{MgF}$  in its ground vibrational ( $v=0$ ) and electronic ( $X^2\Sigma^+$ ) states observed in this work near 334.7 GHz. The complicated hyperfine structure arises from the coupling of two nuclear spins: that of the  $^{25}\text{Mg}$  nucleus, which has  $I=5/2$ , and the  $I=1/2$  spin of the  $^{19}\text{F}$  nucleus.

larger splitting results from spin-rotation coupling, with a spin-rotation constant  $\gamma \sim 48\text{--}50$  MHz, and the smaller interactions are due to magnetic hyperfine effects of the fluorine nucleus, which are barely resolved at the high  $N$  values of these lines. Figure 2 shows the spectrum of the  $N=9 \rightarrow 10$  transition of  $^{25}\text{MgF}$  ( $v=0$ ) near 334.7 GHz. In this case the  $^{25}\text{Mg}$  spin has resulted in additional hyperfine interactions which clearly has complicated the spectrum with many more components.

#### IV. DATA ANALYSIS

MgF has a  $^2\Sigma^+$  ground electronic state, and its rotational spectrum can be described by the following effective Hamiltonian:

$$\hat{H}_{\text{rot}}^{\text{eff}} = B\hat{N}^2 - D\hat{N}^4 + \gamma\hat{N}\hat{S} + b\hat{I}\hat{S}_z + c\hat{S}_z\hat{I}_z + c_I\hat{I}\hat{N} + T^2(\Delta\hat{E})T^2(\hat{Q}). \quad (1)$$

This effective Hamiltonian is appropriate for a Hund's case  $b_{\text{BJ}}$  coupling scheme. The energy level pattern of MgF for the higher rotational transitions measured here are those of a nearly pure case  $b_{\text{BJ}}$  molecule because the spin-rotation interactions are larger than those due to hyperfine effects.

The first two terms in the Hamiltonian arise from molecular rotation, while the third describes the electron spin-rotation interactions. The next two terms describe the magnetic hyperfine coupling, expressed in terms of the Frosch and Foley<sup>20</sup>  $b$  and  $c$  constants. The following term represents the nuclear spin-rotation interaction, and the final expression is for electric quadrupole coupling, which had to be considered for  $^{25}\text{MgF}$ .

Using this Hamiltonian, spectroscopic constants for MgF and its isotopomers were determined using a nonlinear least-squares analysis, and are listed in Table I. Because several vibrational modes were observed,  $B_e$ ,  $\alpha_e$ , and  $\gamma_e$  were derived for  $^{24}\text{MgF}$  and appear in the table as well. As the table shows, the rotational constants  $B_0$  and  $D_0$ , spin-rotation constant  $\gamma$ , and  $^{19}\text{F}$  hyperfine parameters  $b$  and  $c$  were independently determined for  $^{24}\text{MgF}$  in its  $v=0$  mode. The data were also fit considering nuclear spin-rotation interaction, but addition of this term only worsened the fit. Hence,  $c_I$  was set to zero. For the excited vibrational states and for  $^{26}\text{Mg}$  isotopomer, a better fit was obtained by fixing  $c$  to the value obtained for the  $v=0$  mode of  $^{24}\text{MgF}$ . The rotational constants derived in this manner are within a few MHz of the past values deter-

TABLE I. Molecular constants for MgF:  $X^2\Sigma^+$ .<sup>a</sup>

	Constant	Millimeter wave (MHz)	Optical <sup>c</sup>	ESR/argon matrix <sup>d</sup>
<sup>24</sup> MgF	$B_e$	15 567.39(14)	15 566	
	$\alpha_e$	141.42(21)	141	
	$\gamma_e$	0.523(96)	...	
<sup>24</sup> MgF ( $\nu=0$ )	$B_0$	15 496.812 5(29)	15 495.25(90)	
	$D_0$	0.032 328(16)	0.032 377(90)	
	$\gamma_0$	50.697(49)		
	$b$	154.7(1.4)		143(3)
	$c$	178.5(3.0)		188(6)
<sup>24</sup> MgF ( $\nu=1$ )	$B_1$	15 356.439(12)	15 354.34(90)	
	$D_1$	0.032 241(55)	0.032 227(90)	
	$\gamma_1$	49.75(14)		
	$\gamma_D$	0.000 9 <sup>b</sup>		
	$b$	154.2(6.3)		
	$c$	178.5 <sup>b</sup>		
<sup>24</sup> MgF ( $\nu=2$ )	$B_2$	15 217.118(13)		
	$D_2$	0.032 149(55)		
	$\gamma_2$	49.03(15)		
	$\gamma_D$	0.001 1 <sup>b</sup>		
	$b$	152.3(6.4)		
	$c$	178.5 <sup>b</sup>		
<sup>24</sup> MgF ( $\nu=3$ )	$B_3$	15 078.840(17)		
	$D_3$	0.032 028(67)		
	$\gamma_3$	48.53(15)		
	$\gamma_D$	0.000 7 <sup>b</sup>		
	$b$	153.7(7.5)		
	$c$	178.5 <sup>b</sup>		
<sup>26</sup> MgF ( $\nu=0$ )	$B_0$	14 971.406(12)		
	$D_0$	0.030 170(62)		
	$\gamma_0$	48.75(14)		
	$\gamma_D$	0.001 <sup>b</sup>		
	$b$	154.9(5.4)		
	$c$	178.5 <sup>b</sup>		
<sup>25</sup> MgF ( $\nu=0$ )	$B_0$	15 223.127(18)		
	$D_0$	0.031 365(30)		
	$\gamma_0$	49.605(43)		
	$b(^{19}\text{F})$	158.37(38)		
	$c(^{19}\text{F})$	189.75(75)		
	$b(^{25}\text{Mg})$	-309.01(26)		
	$c(^{25}\text{Mg})$	14.72(22)		
	eq $Q(^{25}\text{Mg})$	-20.02(50)		

<sup>a</sup>Errors quoted are  $3\sigma$  statistical uncertainties and apply to the last quoted digits.<sup>b</sup>Held fixed (see the text).<sup>c</sup>Reference 16.<sup>d</sup>Reference 17.

mined from the optical studies of Barrow and Beale<sup>16</sup> for the  $\nu=0$  and  $\nu=1$  modes, as shown in Table I. The  $b$  and  $c$  hyperfine parameters for <sup>24</sup>MgF also refine those determined from the ESR/matrix studies.<sup>17</sup> Spectroscopic parameters for <sup>26</sup>MgF and <sup>24</sup>MgF ( $\nu=2$  and  $\nu=3$ ) have not been previously measured, and hence there are no other values for comparison.

For <sup>25</sup>MgF, the spectra had to be fit considering the interactions of two nuclear spins. Hence,  $b$  and  $c$  hyperfine constants were determined for both the <sup>19</sup>F and <sup>25</sup>Mg nuclei. An electric quadrupole constant eq  $Q$  was derived as well for the magnesium 25 spin. The matrix elements used for coupling two nuclear spins are those of Ryzlewicz

*et al.*,<sup>6</sup> who use the basis  $|NSJ_1F_1I_2F\rangle$ . The nuclear-spin rotation term could not be well determined in the fit, so this constant was set equal to zero. Because the transitions of <sup>25</sup>MgF were obtained at high  $N$ , the data fit was not particularly sensitive to the value of eq  $Q$ . Our determination of this constant was based primarily on goodness of the fit. Because the error assigned to eq  $Q$  is purely statistical, it may not indicate the true uncertainty of the constant. The value of eq  $Q = -20.02$  MHz derived in the fit, however, is close to that of MgOH [eq  $Q = -41$  (17) MHz].<sup>21</sup> Hence, the number obtained here is likely to be a reasonable estimate of the actual value. These are the first measurements of the spectroscopic parameters for <sup>25</sup>MgF.

TABLE II. Hyperfine constants for alkaline-earth monofluorides.

Molecule	Nucleus	$\mu_I^a$	$b$ (MHz)	$c$ (MHz)	$Q^b$	eq $Q$ (MHz)
$^{138}\text{BaF}$	$^{19}\text{F}$	+2.627	60(6) <sup>c</sup>	8 <sup>d</sup>	...	...
$^{88}\text{SrF}^e$			97.6670(30)	29.846(24)		
$^{40}\text{CaF}^f$			107.7687(6)	41.175(3)		
$^{24}\text{MgF}^g$			154.7(1.4)	178.5(3.0)		
$^{137}\text{BaF}^e$	$^{137}\text{Ba}$	+0.927	2301(9)	75(6)	0.28	-117(12)
$^{87}\text{SrF}^e$	$^{87}\text{Sr}$	-1.089	-555.641(8)	-20.631(21)	0.36	-145.8(5)
$^{25}\text{MgF}^g$	$^{25}\text{Mg}$	-0.855	-309.01(26)	14.72(22)	0.22	-20.02(50)

<sup>a</sup>Reference 25, in units of nuclear magnetons.<sup>b</sup>Reference 26, in units of  $10^{-24}$  cm<sup>2</sup>.<sup>c</sup>Reference 6.<sup>d</sup>Reference 17.<sup>e</sup>References 11 and 12.<sup>f</sup>Reference 14.<sup>g</sup>This work.

The errors assigned to the constants in Table I are purely statistical, based on the goodness of the fit. There are other possible sources of uncertainty in the values, include the frequency stability of the spectrometer source, and line blending. The constants given in Table I for the most part reproduce the observed transition frequencies to better than 100 kHz. In fact these constants reproduce the measured frequencies to a mean  $\nu_{\text{obs}} - \nu_{\text{calc}}$  of 0.000 MHz, for both  $^{24}\text{Mg}$  and  $^{26}\text{Mg}$  isotopic species with a standard deviation of 0.028, 0.058, 0.063, 0.051, and 0.058 MHz for  $^{24}\text{MgF}$  ( $\nu=0$ ),  $^{24}\text{MgF}$  ( $\nu=1$ ),  $^{24}\text{MgF}$  ( $\nu=2$ ),  $^{24}\text{MgF}$  ( $\nu=3$ ), and  $^{26}\text{MgF}$ , respectively. For the  $^{25}\text{MgF}$  data, so many blends of lines occur that determining frequencies for individual hyperfine components is difficult. On the other hand, the differences between  $\nu_{\text{obs}}$  and  $\nu_{\text{calc}}$  for the  $^{25}\text{MgF}$  data are, on the average, less than 500 kHz, with the largest deviation being no more than 1.1 MHz. The mean deviation is  $0.229 \pm 0.421$  MHz for the values of  $\nu_{\text{obs}} - \nu_{\text{calc}}$ .

From  $B_e$ , the equilibrium bond length for  $^{24}\text{MgF}$  was calculated to be  $r_e = 1.7499$  Å. In comparison, the  $r_e$  bond lengths for CaF, SrF, and BaF are 1.9516, 2.0744, and 2.1592 Å, respectively.<sup>15,22,10</sup> The values of  $r_e$  thus decrease as the size of the metal atom gets smaller.

## V. DISCUSSION

The alkaline-earth monofluorides are considered to have highly ionic bonding with a  $\text{M}^+\text{F}^-$  configuration.<sup>17</sup> The unpaired electron is thought to reside on the metal in a partially antibonding  $\sigma$ -type orbital. However, the  $\text{F}^-$  electron cloud distorts this orbital such that the unpaired  $s$ -type electron also may have  $p$  and  $d$  character. In addition, there is thought to be an increase in covalency from BaF up the periodic table to SrF, CaF, and MgF. Magnesium fluoride is supposed to be the most covalent of the alkaline-earth monofluorides.

Ionic and covalent trends in bonding in these fluorides are readily apparent in their hyperfine parameters, which are summarized in Table II. The hyperfine  $b$  and  $c$  constants have been determined for the  $^{19}\text{F}$  fluorine atom ( $I=1/2$ ) for BaF through MgF. In barium fluoride, the most ionic of these compounds, both constants are small ( $b \sim 60$  MHz;  $c \sim 8$  MHz), indicating that only a small percentage of the unpaired electron density exists at the fluorine nu-

cleus. However, the values of  $b$  and  $c$  steadily increase in magnitude from SrF to CaF, and are the largest for MgF. In fact, magnesium fluoride has a  $c$  parameter larger than  $b$ , indicating that the lone electron has a highly anisotropic distribution at the F nucleus, suggestive of a hybridized orbital that can participate in covalent bonding. This pattern in the fluorine atom hyperfine parameters was also noted by Knight *et al.*<sup>17</sup>

There is also a trend in the hyperfine parameters associated with the metal nuclei. The less abundant isotopes barium 137, strontium 87, and magnesium 25 all have nuclear spins with magnetic moments that are comparable in value within 15% (see Table II). The spin for  $^{137}\text{Ba}$  is  $I=3/2$  and  $I(^{87}\text{Sr})=9/2$ . As Table II illustrates, the hyperfine  $b$  constant, which contains the Fermi contact term, steadily decreases in value from  $^{137}\text{BaF}$  ( $b=2,301$  MHz) to  $^{87}\text{SrF}$  ( $b=-555.6$  MHz) and then to  $^{25}\text{MgF}$  ( $b=-309.0$  MHz). Hence, there is considerable electron density at the  $^{137}\text{Ba}$  nucleus, as expected for  $\text{M}^+\text{F}^-$  ionic structure, but it decreases for the strontium nucleus in SrF and even more so for  $^{25}\text{Mg}$  in MgF. This behavior suggests a trend toward greater covalency as the alkaline-earth atom becomes smaller. The  $c$  constant is also relatively large for BaF ( $c=75$  MHz), but decreases for SrF and MgF.

It should be additionally noted that the  $b$  hyperfine constant for the  $^{25}\text{Mg}$  nucleus is larger than that of fluorine in  $^{25}\text{MgF}$  (see Table I). Comparing just the Fermi contact contribution, the values are  $b_F(^{25}\text{Mg}) = -304.1$  MHz vs  $b_F(^{19}\text{F}) = 221.5$  MHz. Because the  $^{19}\text{F}$  atom has a larger magnetic moment than the  $^{25}\text{Mg}$  nucleus (+2.627 vs -0.855; see Table II), the difference between the relative  $b_F$  values is actually larger. Consequently, it is clear that there is much more electron density of the unpaired electron at the magnesium nucleus, as opposed to being located at fluorine atom. Hence, the ionic  $\text{Mg}^+\text{F}^-$  configuration must still be the dominant structure in MgF, although the species does exhibit more covalency than its heavier alkaline-earth counterparts. In fact, the value of the Fermi contact term for MgF is quite close to that of the isoelectronic MgOH, which has  $b_F = -304.4(4.6)$  MHz.<sup>21</sup> The bonding in MgOH is thought to be primarily ionic, but to have a significant covalent component as well.

The quadrupole constant is an indicator of the electric

field gradient across the nucleus, and hence should be larger for more ionic species. For comparison, the quadrupole constants for  $^{137}\text{BaF}$ ,  $^{87}\text{SrF}$ , and  $^{25}\text{MgF}$  are listed in Table II along with the corresponding nuclear quadrupole moment. For  $^{137}\text{BaF}$ ,  $\text{eq } Q = -117(12)$  MHz, and the quadrupole constant for  $^{87}\text{SrF}$  is  $-145.8(5)$  MHz. These are both much larger than that of  $^{25}\text{MgF}$ , which has  $\text{eq } Q = -20.02(50)$  MHz, although this value must be viewed with some caution. On the other hand, the respective nuclear quadrupole moments  $Q$  vary by less than 40%. Hence, there appears to be less of a field gradient across  $^{25}\text{MgF}$  than the heavier alkaline-earth species, at least to an order of magnitude approximation.

If the bonding in these metal fluorides is largely ionic, then these  $^2\Sigma$  molecules should correlate with the separated ions  $\text{M}^+ (^2S)$  and  $\text{F}^- (^1S)$ . An indication of the bonding is then given by how closely the orbital of the unpaired electron on the metal atom in the molecule resembles the same electron in the  $\text{M}^+$  ion. This comparison can be done by examining the hyperfine constants of the  $^{25}\text{Mg}^+$  ion vs those of the  $^{25}\text{Mg}$  nucleus in  $\text{MgF}$ . The atomic hyperfine constant  $A$  for  $^{25}\text{Mg}^+$  in its  $3s^2S_{1/2}$  state has been determined by Itano and Wineland<sup>23</sup> and has the value  $A = -594.25438(16)$ . Comparing  $A$  for the  $3s^2S_{1/2}$  state of  $^{25}\text{Mg}^+$  and  $b_F$  for  $^{25}\text{MgF}$  yields a ratio of  $b_F/A = 0.51$ , indicating that 49% of the original  $s$  character of the electron in the  $\text{Mg}^+$  ion has been lost in the formation of the  $\text{MgF}$  molecule. In contrast, this ratio is 0.58 for  $^{137}\text{BaF}$  (Ref. 6) and 0.57 for  $^{87}\text{SrF}$ .<sup>11</sup> Therefore, roughly 42% and 43% of the  $s$  character has been lost in these species, apparently less than that for  $\text{MgF}$ . Thus, there is less  $s$  character in the lone electron of magnesium fluoride than the other fluorides, once again suggesting that the bond in the lighter species is more covalent.

The wave function  $\psi$  of the unpaired electron on the metal atom in the fluorides can be expressed as

$$a_s\psi_{ns} + a_p\psi_{np} + a_d\psi_{(n-1)d}, \quad (2)$$

where  $a_s^2 + a_p^2 + a_d^2 = 1$ .<sup>6</sup> The wave function is therefore a mixture of  $s$ ,  $p$ , and  $d$  orbitals. For magnesium fluoride, however, the unpaired electron lies in the  $n=3$  shell, and hence there can be no  $d$  character in its wave function using the above approximation, unlike  $\text{SrF}$  and  $\text{BaF}$ . The coefficient  $a_s^2$  is given by the  $b_F/A(^2S)$  ratio, and consequently has the value of 0.512(2) for  $\text{MgF}$ . It follows then that  $a_p^2$  for the  $\text{MgF}$  wave function is 0.488(2). Hence, the orbital of the unpaired electron in this fluoride atom has almost 50%  $p$  and 50%  $s$  character. In contrast,  $\text{BaF}$  (Ref. 6) has  $a_s^2 = 0.580(3)$ ,  $a_p^2 = 0.18(5)$ , and  $a_d^2 = 0.24(5)$ .<sup>6</sup> For  $\text{SrF}$ ,  $a_s^2$  is estimated to be 0.57.<sup>11,17</sup> The wave functions for both barium and strontium fluoride consequently have somewhat larger  $s$  character than that of  $\text{MgF}$ . The wave function for  $\text{BaF}$  has also considerably less  $p$  character, and most of the anisotropy of the unpaired electron orbital arises from the  $d$  contribution.

The quadrupole term and hence electric field gradient in the fluoride radicals consists of two contributions: polarization of the closed shells of the metal atom by the  $\text{F}^-$

ligand, and non- $s$  character of the orbital of the unpaired electron;<sup>6</sup> hence,

$$\text{eq } Q = (\text{eq } Q)_{\text{el}} + (\text{eq } Q)_{\text{pol}}. \quad (3)$$

The first term  $(\text{eq } Q)_{\text{el}}$ , is related to the hyperfine  $c$  parameter because both constants are proportional to the term  $[(3 \cos^2 \theta - 1)/r^3]_{\text{av}}$ . Therefore,  $(\text{eq } Q)_{\text{el}}$  can be calculated from  $c$  of  $^{25}\text{Mg}$  nucleus from the following formula:<sup>6</sup>

$$(\text{eq } Q)_{\text{el}} = -c(\text{Mg}^{25})e^2Q/3g_I\mu_0\mu_N, \quad (4)$$

where  $g_I$  is the spin  $g$  factor,  $Q$  is the quadrupole moment of the  $^{25}\text{Mg}$  nucleus, and  $\mu_0$  and  $\mu_N$  are the Bohr and nuclear magnetons, respectively. From this expression, we calculate  $(\text{eq } Q)_{\text{el}} = 15.5 \pm 0.4$  MHz for  $^{25}\text{MgF}$ . It then follows from Eq. (3) that  $(\text{eq } Q)_{\text{pol}} = -35.7 \pm 0.6$  MHz. Hence, the dominant contributor to the electric field gradient in  $\text{MgF}$  is the polarization of the closed shells. In comparison,  $(\text{eq } Q)_{\text{pol}} = -62(13)$  MHz and  $(\text{eq } Q)_{\text{el}} = -55(5)$  MHz for  $^{137}\text{BaF}$ ,<sup>6</sup> i.e., more than 50% of the field gradient arises from the polarization term. For  $^{87}\text{SrF}$ , the polarization term is  $(\text{eq } Q)_{\text{pol}} = -97$  MHz and  $(\text{eq } Q)_{\text{el}} = -48$  MHz.<sup>11</sup> Thus, in this case the polarization contribution is  $\sim 66\%$ , similar to that of magnesium fluoride.

Another comparison of interest is to  $\text{NaF}$ , which has  $\text{eq } Q = -8.4$  MHz.<sup>24</sup> Because  $\text{NaF}$  is closed shell, the polarization term is the only contributor to the quadrupole constant. Considering that the nuclear quadrupole moment of sodium is smaller than that of  $^{25}\text{Mg}$  by a factor of 2,<sup>24</sup> the  $\text{eq } Q$  polarization terms of  $\text{MgF}$  and  $\text{NaF}$  are roughly comparable.

## VI. CONCLUSIONS

The pure rotational spectrum of  $^{24}\text{MgF}$  in its  $v=0$ , 1, 2, and 3 vibrational modes, as well as its  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$  isotopomers, has been recorded using mm/sub-mm direct absorption techniques. In addition to the rotational and fine structure constants, the hyperfine parameters for  $\text{MgF}$  have been accurately determined for both the  $^{19}\text{F}$  and  $^{25}\text{Mg}$  nuclei. Comparing these hyperfine constants with those of the other heavier alkaline-earth monofluorides suggests that the electron density of the unpaired electron in  $\text{MgF}$  is slightly more concentrated on the fluorine nucleus than on the metal atom, indicating a greater degree of covalent bonding. The wave function for the unpaired electron appears to be composed of almost equal  $s$  and  $p$  character, while for  $\text{BaF}$  and  $\text{SrF}$ , the  $s$  character is more than 50%. The spectroscopic parameters determined here for  $\text{MgF}$  should aid in testing models of bonding in highly ionic metal compounds.

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