High resolution spectroscopy of MgOH (X 2 Σ +) in its V 2 mode: Further evidence for quasilinearity

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High resolution spectroscopy of MgOH ($X\,{}^2\Sigma^+$) in its V_2 mode: Further evidence for quasilinearity

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Pure rotational spectra of the MgOH and MgOD radicals have been recorded in the v_2 bending vibration of their $X\,{}^2\Sigma^+$ ground electronic states using millimeter-wave direct absorption spectroscopy. Multiple rotational transitions arising from the $v_2^l = 1^1$, 2^2, 2^0, 3^1, 3^3, 4^2, and 4^4 substates have been measured in the frequency range 240–520 GHz for these species. Both the spin-rotation and l-type doubling interactions have been resolved in the spectra. The complete data sets for MgOH and MgOD have been analyzed using a linear model for the Hamiltonian which takes into account higher order ($l = \pm 4$) l-type interactions. The global analyses were adequate, but anomalous behavior was apparent in both molecules. In particular, the B_v vs v_2 relation was found to be highly nonlinear, large variations in the l-type doubling constant q were observed with vibrational level, and r_0, r_s, and $\tilde{r}_e$ structures determined differed substantially. Such findings suggest that MgOH is highly quasilinear, comparable to HNCO. The competition between ionic and covalent bonding is therefore becoming apparent in the lighter alkaline earth hydroxide species. © *1999 American Institute of Physics.* [S0021-9606(99)00648-0]

I. INTRODUCTION

Extensive high resolution studies of metal monohydroxide molecules have been conducted in the past 30 years, in particular of alkali and alkaline earth species, revealing some unique aspects of their bonding characteristics and dynamic motions.[1–4] The bonding for these species is expected to be ionic (M^+OH^-), with the OH^- ligand behaving as a halide ion. Because of this ionic nature, the structure of these species is predicted to be linear.[5,6] As covalent bonding begins to play a role, however, the structure changes, becoming bent, in analogy to water. Such a structure has been recently observed in the F excited state of CaOH,[7] as well as in the ground states of CuOH and AgOH.[8] The MOH bond angles for the two transition metal species, in fact, were found to be 110° and 108°, respectively. Because the formation of M–OH bonds is thought to be important in the corrosion of metal surfaces,[9] examining the structural trends in the monohydroxides is of interest.

The competition between ionic and covalent bonding, however, does not always produce a clearly linear or bent molecule. Subtle deviations from linearity were first observed in the pure rotational spectra of CsOH and RbOH.[10,11] In particular, the variation of the effective rotational constant B_v with respect to v_2, the quantum number for the degenerate bending mode, was strongly nonlinear with an initial negative slope. These inconsistencies were attributed to large amplitude motions (LAM) of the low frequency bending vi-

bration. Later pure rotational studies conducted for the lighter alkali species KOH and NaOH showed even more pronounced anomalous behavior. For example, Kuijpers, Törring, and Dymanus[12] had to use fourth-order corrections to fit the rotational spectra of the vibrational satellite lines of KOH, while Pearson, Winnewisser, and Trueblood[13] could only do a state-by-state analysis of their KOH data. In the case of NaOH, Kuijpers, Törring, and Dymanus[14] were not able to confidently assign many of the vibrational satellite lines of this species, including the (02⁰0) state. To our knowledge, the pure rotational spectrum of NaOH has never been fully analyzed. While the irregularities in the KOH spectra are thought to again arise from the large amplitude v_2 bending motions, those of NaOH are far more extreme and could be an indication that the molecule is quasilinear.

The alkaline earth monohydroxides are another class of molecules where the competition between bonding types is becoming evident. Studies of the pure rotational spectra of these species in their $X\,{}^2\Sigma^+$ electronic states were first conducted by our group, which carried out measurements of the ground vibrational state lines of MgOH, CaOH, SrOH, and BaOH.[15–18] These data were successfully analyzed assuming the molecules to be linear. Recording the spectra of the less abundant ^{25}MgOH and ^{137}BaOH isotopomers of these radicals enabled the metal hyperfine structure to be investigated, which indicated that the unpaired electron in these species resides primarily on the metal nucleus. Such data supported the M^+OH^- ionic (and therefore linear) structure proposed for these molecules.[5,6] Subsequent studies of the vibrationally excited states, in contrast, revealed additional complications, particularly in the v_2 bending mode.[19–21] The $v_2 = 1, 2$, and, in certain cases, 3, states of CaOH and its deuterium isotopomer, SrOH, and BaOH were readily analyzed

with a linear model, with small corrections to account for contamination of the Π and Δ vibronic levels by excited electronic states of the same symmetry. For MgOH and MgOD, however, only the $v_2 = 1$ state could be fitted with this model with comparable residuals. Moreover, many of the $v_2 > 1$ states for the magnesium species could not be confidently assigned, unlike the other hydroxides.

In an effort to aid in these identifications, Bunker et al.[22] used the MORBID (Morse oscillator rigid bender for internal dynamics) Hamiltonian to derive a full ground state potential surface for MgOH. The surface was optimized to fit some of the rotational data (0° and six vibrationally excited substates 1^{1d}, 1^{1c}, 2^{2d}, 2^{2c}, 2^0, 3^{1d}), as well as vibrational energies of several quanta of the bend deduced from laser induced fluorescence (LIF) measurements. This study showed that MgOH is linear at equilibrium with a flat, quartic bending potential. A small barrier to linearity of ~ 10 cm^{-1} could not be excluded, however, given the precision of the fitting. Hence, the calculations of Bunker et al. suggested that MgOH is indeed quasilinear.

The modeling of the potential surface by Bunker et al. enabled predictions of rotational constants for the vibrationally excited states of MgOH. Additional predictions by Bunker[22] were also carried out for MgOD, which were subsequently followed by further laboratory measurements on both species in our group. In this paper we present our complete pure rotational data set for MgOH and MgOD with accurate vibrational satellite assignments. For MgOH, the 2^0, 2^2, 3^1, 3^3 and 4^2 states were investigated, and for MgOD the 2^0, 2^2, 3^1, 3^3 and 4^4 states. These data extend the 1^1 measurements published in Fletcher et al.[19] and Nuccio, Apponi, and Ziurys.[21] The pure rotational satellite spectra have been analyzed assuming both molecules to be linear but accounting for l-type doubling, l-type resonance, and anharmonicity effects. Rotational, spin–rotation, and l-type doubling constants have been determined for each vibrational state. Anomalies have been found in the spectra that are consistent with MgOH and MgOD being quasilinear. Here we present the data and its analysis, and discuss the interesting behavior of these unusual species.

II. EXPERIMENT

The rotational spectra of MgOH and MgOD were recorded using one of the quasioptical millimeter-wave spectrometers of the Ziurys group, which are described in detail elsewhere.[23] The instrument consists of a Gunn oscillator/varacter multiplier source operating in the range 65–530 GHz, a gas cell incorporating a Broida-type oven, and an InSb detector.

MgOH and MgOD were synthesized in the gas phase by the reaction of metal vapor with the appropriate precursor. About 50% H_2O_2 in H_2O was used as the precursor for MgOH, and pure D_2O for MgOD. Magnesium was heated in the oven and the vapor entrained in 10–20 mTorr of argon carrier gas and flowed into the gas cell. Approximately 50 mTorr of the reactant material was then added to the metal vapor/argon mixture over the top of the oven. For MgOD, a dc discharge was run continuously through these gases using a cathode placed above the grounded oven. The discharge

conditions were optimized to obtain maximum signal to noise. Typical settings used were 500–1000 mA at 3–20 V. In the case of MgOH, H_2O_2 was sufficiently reactive that no dc discharge was required.

Initially, scans covering 100 MHz in frequency were recorded to sort out the various spectral features. Part of this process included measurements of the relative intensities of spectral features. Because the spectrometer source power varies in a nonuniform manner as a function of frequency, intensity calibration was conducted on the basis of signal-to-noise ratio per spectral line. An accurate baseline removal was carried out to obtain such ratios. Also, when possible, spectra were recorded that had several features on one single scan. Then, when going to a nearby frequency, one of the ''calibrated'' lines was left in the new spectrum for scaling purposes. Actual transition frequencies were measured using scans 3–4 MHz in coverage, depending on the linewidth. The linewidths were typically 700–1000 kHz over the range 240–520 GHz. The estimated error on the measurements is ±50 kHz.

III. RESULTS

The data obtained for MgOH and MgOD in their ground electronic $^2\Sigma^+$ state are given in the EPAPS database.[24] To summarize, rotational transitions arising from nine excited vibrational substates of MgOH in the degenerate v_2 bending mode were recorded ($v_2^l = 2^0, 2^{2c}, 2^{2d}, 3^{1c}, 3^{1d}, 3^{3c}, 3^{3d}, 4^{2c}, 4^{2d}$). Multiple substates per quantum v_2 arise because of the effects of l-type doubling and l-type resonance (e.g., Refs. 25–27), where $l = v_2$, $v_2 - 2$, $v_2 - 4,...$ $- v_2$ (c and d indicate substates with respect to $\pm l$). Five transitions consisting of two spin–rotation components were measured for each state (except for the 4^2 level, where only four transitions were recorded). Previously, only the 1^{1c} and 1^{1d} and the $v_1 = 1$ data had been reported,[19,20] in addition to the ground ($v=0$) state. The same set of vibrationally excited states were observed for MgOD, with the exception of the substate 4^2. In addition, lines from the $v_2^l = 4^{4c}$ and 4^{4d} levels were recorded as well. For MgOD, six to nine transitions were observed for each vibrational state, all which consist of spin–rotation doublets. Similarly, measurements of only the ground and 1^1 states for MgOD had been previously published.[21]

Assignment of the spectra of MgOH and MgOD was not trivial. Although harmonic relationships were readily established between features arising from different rotational transitions, careful intensity studies, as described previously, were critical for proper identifications. Also, predictions of rotational constants for MgOH from Bunker et al.[22] and for MgOD from separate calculations aided in the assignments. Stick figures illustrating the final vibrational assignments and observed relative intensities are shown in Figs. 1 and 2. Figure 1 presents data for the $N = 11 \rightarrow 12$ transition of MgOH near 353 GHz. (The spin–rotation splittings have been omitted for simplicity.) The inset panel shows a close-up view of a cluttered region near 352 GHz. Because α_2 is positive for MgOH, unlike most linear triatomic molecules,[25] the vibrational satellite lines lie to lower frequency relative to the ground state, as Fig. 1 illustrates. Also, while the centroids of
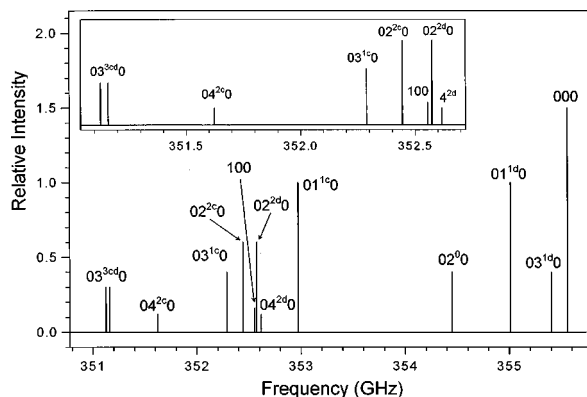
FIG. 1. A stick diagram showing the vibrational progression in the $N=11 \to 12$ transition of MgOH near 353 GHz and the approximate relative intensities. The magnitude of the spin–rotation interactions is sufficiently small to be neglected here. The inset panel is a close-up view of the region near 352 GHz. The large shifts of the 2^0, 3^1, and 4^2 substates relative to the 2^2 and 3^3 states suggests that MgOH is quasilinear.

the $v_2^l = 1^1$, 2^2, and 3^3 states are spaced at somewhat regular frequency intervals relative to the 0^0 state, as expected for a linear molecule, the 2^0, 3^1, and 4^2 states are shifted considerably from their v_2 counterparts, in the direction of the 0^0 line. For example, the 2^0 satellite line lies almost 2 GHz to higher frequency relative to the 2^{2c} and 2^{2d} features, while the centroid of the 3^1 state is shifted ~2.5 GHz to higher frequency from the 3^3 lines. Similarly, the 4^2 features lie to much higher frequency relative to where the $v_2 = 4$ state is expected in the vibrational progression. For a strictly linear molecule, the l-type substates of a given v_2 quantum number should occur relatively close to each other in frequency.[25] Fermi resonance cannot account for such frequency shifts, either, as the $v_1 = 1$ and $v_3 = 1$ stretching modes are at sufficiently higher (and different energies) relative to the v_2 states, as predicted by Bunker et al.

The vibrational progression for the $N = 12 \to 13$ transition of MgOD near 350 GHz is shown in Fig. 2. Again the effects of spin–rotation interactions are suppressed for clar-
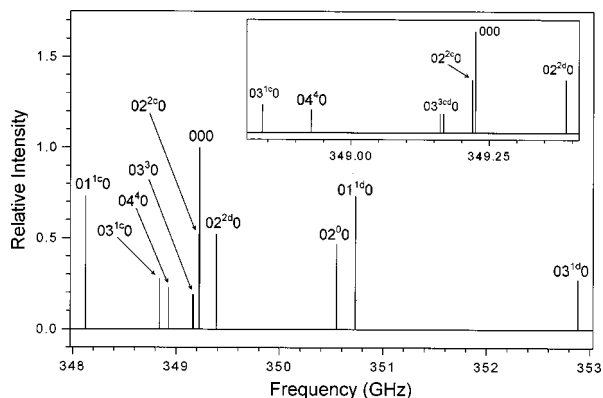

FIG. 2. A stick figure showing the progression and relative intensities of the vibrational satellites in the $N = 12 \to 13$ transition of MgOD. (The effects of spin–rotation here are negligible and hence not shown.) The region near 349 GHz is shown in detail in the upper right-hand corner. Because MgOD has a small negative α_2 value, the pattern is different from that of MgOH, where $\alpha_2 \sim 100$ MHz, but large frequency shifts are still seen in the 2^0 and 3^1 substates.
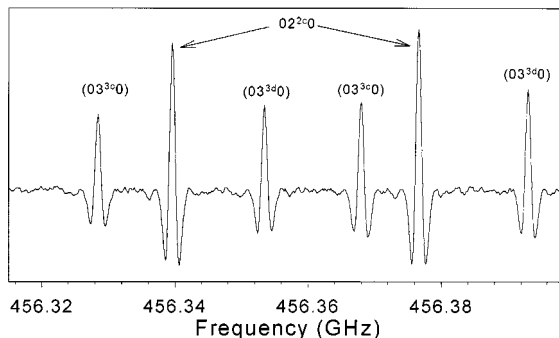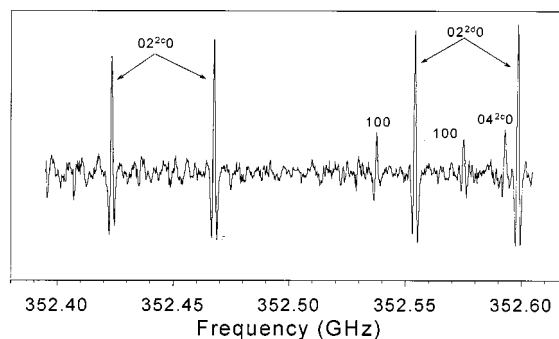

FIG. 3. Representative satellite line spectra of the $N = 11 \to 12$ transition of MgOH and the $N = 16 \to 17$ transition of MgOD near 352 and 456 GHz, respectively. The magnitude of the spin rotation vs l-type interactions is clearly illustrated in the spectra. The MgOH figure is a composite of two separate 110 MHz scans, each with an acquisition time of 1 min, the MgOD data are from a single 100 MHz scan with a 1 min duration. Baselines were removed from each spectrum.

ity, and the inset at the upper right magnifies a congested region of the spectrum. Similarly, the centroids of the 1^1, 2^2, 3^3, and, in this case, 4^4 states lie at fairly regular spacings relative to the ground state (except for MgOD, α_2 is small and negative). However, the 2^0 lines and the centriod of the 3^1 features are shifted relative to their 2^2 and 3^3 counterparts. (The 4^2 state was never confidently assigned in MgOD.) In Fig. 3, representative vibrational spectra for MgOH and MgOD are presented. The top panel shows the spin–rotation doublets for the 2^{2c}, 2^{2d}, and $v_1 = 1$ states and one fine structure component of the 4^{2c} level for the $N = 11 \to 12$ transition of MgOH. The l-type doubling interaction for the 2^2 state is significantly larger than that arising from spin–rotation, as is generally the case for most substates observed for MgOH except the 3^3 level. These data cover 210 MHz in frequency space. The lower panel shows a part of $N = 16 \to 17$ transition of MgOD near 456 GHz, spanning nearly 100 MHz. The spin–rotation components of the 2^{2c}, 3^{3c}, and 3^{3d} levels are visible in these data. For the 3^3 lines, the spin–rotation and l-type doubling splittings are comparable in magnitude.

IV. ANALYSIS

Despite the irregularities in the spectrum, the data were analyzed assuming both molecules to be linear. Hence, the following Hamiltonian was used:

$$\hat{H} = \hat{H}_{\text{rot}} + \hat{H}_{\text{cd}} + \hat{H}_{\text{sr}} + \hat{H}_{\text{ld}}. \tag{1}$$

The first two terms are simply those for molecular frame rotation and its centrifugal distortion corrections, which need no further comment. The other two terms, which concern spin–rotation and l-type interactions, are more complicated and will be discussed briefly. The l-type interactions for the $v_2 = 1$, 2, and 3 states were analyzed using the matrix elements formulated by Amat and Nielsen,[27] but considering the differences in parity of the two spin rotation levels F_1 and F_2, as outlined by Presunka and Coxon.[28] In the Amat and Nielsen representation, the most general form of l-type interactions is l-type resonance with l-type doubling being a special case occurring only in Π vibronic states i.e., for $l = \pm 1$). The l-type interactions appear in the energy matrix only as off-diagonal terms of the form:

$$\langle v', l | \hat{H} | v, l \pm 2 \rangle, \tag{2}$$

$$\langle v', l | \hat{H} | v, l \pm 4 \rangle, \tag{3}$$

where $\hat{H}$ is the perturbing Hamiltonian. The first matrix element here characterizes the l-type doubling parameter q_v, and the second element, the higher order constant, ρ_v. Explicit expressions for these elements can be found in Maki and Lide.[29] In addition, the diagonal terms for the unperturbed energies need to include $g_{ll} l^2$, the contribution of the angular momentum l to the vibrational energy, where g_{ll} is the anharmonicity constant. Differences between these factors characterize the splitting between l substates of a given v_2 bending mode. For example, the 2^0 and 2^2 states will be separated by the energy $4g_{22}$. Consequently, the energy splittings between the different l substates for a given level v_2 must be known to explicitly solve for the l-type parameters. Therefore, while l-type interactions for the 1^1 state are simply described by

$$\Delta E = \pm \tfrac{1}{2} q_v N(N+1), \tag{4}$$

not including centrifugal distortion corrections, those for the $v_2 = 2$ and 3 states must be expressed in matrix form. For the $v_2 = 2$ state, the matrix representation is

$$\begin{vmatrix} E_\Delta & W_{20} & W_{22} \\ W_{20} & E_\Sigma & W_{20} \\ W_{22} & W_{20} & E_\Delta \end{vmatrix}, \tag{5}$$

where E_Δ indicates the energy of the $l = 2$ states and E_Σ, the $l = 0$ state. The W_{22} off-diagonal term in this matrix involves the higher order constant ρ_v, which was not needed to fit the $v_2 = 2$ data set and therefore was set to zero in the analysis.

This matrix becomes further simplified as a result of parity selection rules, which play a role because the spin–rotation interaction separates out every rotational level into F_1 and F_2 components. The $l \pm 2$ levels also have F_1 and F_2 parities, and only states of the same parity can interact. Consequently, the F_1 and F_2 states become separated into two parity blocks (e.g., see Refs. 19 and 28), each which loose half of their off-diagonal terms. Moreover, diagonalization of these final matrices can only be done with knowledge of the separation between the 2^0 and 2^2 levels, namely $4g_{22}$. For MgOH, this separation was set to that derived by Bunker

et $al.$ (10.5 cm^{-1}) while 11.8 cm^{-1} was used for MgOD, also based on calculations by Bunker. These energy separations gave reasonable fits for both molecules.

For the $v_2 = 3$ state, the l-type interactions are expressed by a 4×4 matrix of the form

$$\begin{vmatrix} E_\Phi & W_{31} & W_{3\text{-}1} & 0 \\ W_{31} & E_\Pi & W_{1\text{-}1} & W_{3\text{-}1} \\ W_{3\text{-}1} & W_{1\text{-}1} & E_\Pi & W_{31} \\ 0 & W_{3\text{-}1} & W_{31} & E_\Phi \end{vmatrix}, \tag{6}$$

where $W_{1\text{-}1}$ and W_{31} represent l-type interactions linking states varying by $l = \pm 2$ (q parameter). $W_{3\text{-}1}$ is the energy term for states differing by $l = \pm 4$ (ρ parameter). Again, this matrix had to be separated into F_1 and F_2 parity blocks, and the energy splitting between the 3^1 and 3^3 substates had to be estimated, also using values of Bunker et $al.$ In these cases, the higher order l-type resonance term ρ had to be used to account for splittings in the 3^3 states.

The $v_2 = 1$, 2, and 3 data were analyzed in a single, global fit using these representations. For the 4^2 and 4^4 substates of MgOH and MgOD, respectively, other $v_2 = 4$ levels were not securely identified. Hence, l-type interactions with the other sublevels were not considered, and the data were fit separately with an effective l-type doubling term q_{eff}, according to the following equation:[27]

$$\Delta E_{l\ \text{type}} = \pm \tfrac{1}{2} q_{\text{eff}} \{ [N(N+1) - l(l+1)]$$
$$\times [N(N+1) - (l+1)(l+2)] \}^{1/2}. \tag{7}$$

The spectroscopic constants derived from this analysis are listed in Table I. The rms given in Table I applies to the global fit of the $v_2 = 1$, 2, and 3 data. For both molecules, the observed spectra are relatively well described by B, D, H, γ, γ_D (the centrifugal distortion correction to γ, the spin–rotation constant), and, when l-type doubling is involved, the corresponding constant q, its centrifugal distortion correction q_D, and, in the case of the 3^1 substate, q_H as well. As mentioned, ρ, the l-type resonance parameter, was needed to fit the 3^3 data. Finally, the 1^1 and 3^1 states required the constant p_Π, to account for the differences in spin–rotation splittings between the l-type doublets. This parameter has the same functional form as the lambda-doubling constant p in a $^2\Pi$ electronic state, and probably arises from the mixing of low-lying $^2\Pi$ electronic states with the $v_2 = 1$ Π vibronic level. The constant was needed to fit the 1^1 and 3^1 data for CaOH, SrOH, and BaOH.[19] Similar p_Δ and p_Γ terms were also necessary in the 4^2 MgOH and 4^4 MgOD analyses, of identical vibronic origins. The rms of the global MgOH fit is 274 kHz, with residuals to the fit as high as 900 kHz—above the estimated experimental uncertainty of ± 100 kHz. The rms of the MgOD global analysis was similar: 257 kHz, with comparable residuals. Some systematic errors were present in the 3^1 data as well, which cannot be accounted for by the l-type, spin–rotation, and vibronic interactions modeled here. Clearly the quality of these analyses are not nearly as good as those carried out for comparable data sets for CaOH, SrOH, and BaOH, where the rms of the fits were 15–35 kHz.[19]

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TABLE I. Molecular constants for MgOH and MgOD ($X\,{}^2\Sigma^+$).[a]

(v_1, v_2^l, v_3)		MgOH	MgOD
(01^10)	B	14 757.1807(66)	13 446.4037(51)
	D	0.026 546(25)	0.020 263(17)
	γ	42.23(27)	36.76(22)
	γ_D	$-0.004\ 10(72)$	$-0.002\ 01(52)$
	q	$-85.134(13)$	$-100.885(10)$
	q_D	0.000 413(49)	0.001 468(34)
	p_Π	$-2.16(13)$	$-1.68(12)$
(02^00)	B	14 771.018(15)	13 483.435(11)
	D	0.026 860(57)	0.021 470(50)
	H	$\cdots$	$\cdots$
	γ	40.15(39)	35.68(59)
	γ_D	0.0008(10)	0.0013(17)
(02^20)	B	14 698.0383(87)	13 444.6864(89)
	D	0.026 346(33)	0.020 106(44)
	H	$\cdots$	$-6.5(6.5)\times10^{-8}$
	γ	50.60(27)	40.51(15)
	γ_D	$-0.014\ 20(72)$	$-0.003\ 77(23)$
	q	$-79.96(12)$	$-84.601(39)$
	q_D	0.002 39(54)	0.001 015(94)
(03^10)	B	14 744.7103(68)	13 498.7655(81)
	D	0.020 136(25)	0.021 271(37)
	H	$\cdots$	$-1.31(52)\times10^{-7}$
	γ	43.15(28)	37.35(14)
	γ_D	$-0.003\ 81(72)$	$-0.000\ 81(19)$
	q	$-65.859(30)$	$-78.2716(82)$
	q_D	0.002 22(24)	0.001 073(38)
	q_H	0.000 016 28(63)	$\cdots$
	p_Π	6.14(36)	3.94(30)
(03^30)	B	14 644.3711(61)	13 439.0084(83)
	D	0.033 143(24)	0.020 380(40)
	H	$\cdots$	$-6.9(5.9)\times10^{-8}$
	γ	64.08(28)	47.16(24)
	γ_D	$-0.032\ 71(71)$	$-0.009\ 02(51)$
	ρ	0.032 686(59)	$-0.000\ 332(54)$
(04^20)	B	14 679.9365(88)	$\cdots$
	D	0.029 672(38)	$\cdots$
	γ	43.389(75)	$\cdots$
	q_{eff}	0.9236(38)	$\cdots$
	$q_{D,\mathrm{eff}}$	$-0.008\ 922(71)$	$\cdots$
	$q_{H,\mathrm{eff}}$	0.000 041 00(48)	$\cdots$
	$q_{I,\mathrm{eff}}$	$-7.42(11)\times10^{-8}$	$\cdots$
	p_Δ	3.188(75)	$\cdots$
(04^40)	B	$\cdots$	13 430.1957(77)
	D	$\cdots$	0.032 673(41)
	H	$\cdots$	$1.920(61)\times10^{-6}$
	γ	$\cdots$	52.53(14)
	γ_D	$\cdots$	$-0.011\ 30(19)$
	q_{eff}	$\cdots$	$-5.01(93)\times10^{-5}$
	$q_{D,\mathrm{eff}}$	$\cdots$	$2.45(19)\times10^{-7}$
	p_Γ	$\cdots$	$-0.003(28)$
rms of fit[b]		0.274	0.257

[a]In MHz. Errors are 3σ and apply to the last quoted decimal places.
[b]Excludes $v_2=4$ mode.

The vibrational dependence of B_v with respect to v_2 for linear triatomic molecules exhibiting large amplitude motions is given by[11]

$$B_v = \tilde{B}_e - \alpha_2(v_2+1) + \gamma_{22}(v_2+1)^2 + \gamma_{ll}l^2, \qquad (8)$$

where $\tilde{B}_e = B_e - \frac{1}{2}(\alpha_1+\alpha_3)$. This expression was used by Lide and Matsumura[11] to describe the nonlinear behavior of B_v with respect to v_2 for RbOH and CsOH. This equation has also been used to model the spectra for MgOH and MgOD using the $v_2=0$, 1, 2, and 3 states, not including the 3^1 level. The resulting α_2, γ_{22}, and γ_{ll} parameters are given in Table II, along with those determined for CaOH, CaOD, and NaOH. It is interesting to note that α_2 is positive for MgOH, unlike most linear triatomic molecules. Positive α_2 values have been routinely found for alkali and alkaline earth hydroxide species,[10,11,19] and have been thought to arise from substantial anharmonic terms in the bending potential. The α_2 constant for MgOH, however, is unusually large (110.5 MHz), indicating a severe degree of anharmonicity. Values for α_2 of less than 50 MHz have been measured for CaOH, SrOH, BaOH, KOH, CsOH, and RbOH. On the other hand, the MgOH value is comparable to that of NaOH ($\alpha_2=97$), another species whose vibrational satellite pattern is complex and not completely understood.[14] The α_2 parameter for MgOD, in contrast, is small and negative ($\alpha_2 = -5.43$ MHz), and follows the trend of alkali/alkaline earth hydroxide species on deuterium substitution (e.g., Ref. 21). Another irregularity in the vibrational dependence of MgOH (and MgOD) is the unusually large values of the higher order terms γ_{22} and γ_{ll}. For MgOH, the constants are $\gamma_{22} = 21.18$ MHz and $\gamma_{ll} = -18.27$ MHz. To our knowledge, these are the highest values of these parameters found in the literature for any molecule, and deviate from the trend of the other alkaline earth monohydroxides, where $\gamma_{22} = 1.3$–2.8 MHz and $\gamma_{ll} = -1.5$ to -3.6 MHz.[19] They are also much larger than most alkali monohydroxide values, which are typically a few megahertz or less.[13,21] The only molecule that has remotely similar constants is NaOH, where $\gamma_{22} = 9(2)$ MHz and $\gamma_{ll} = -10(2)$ MHz.[14]

V. DISCUSSION

Many molecular species undergo large amplitude motions (LAM), which result in peculiarities in their spectra. Only a subset of such molecules are truly quasilinear, i.e., have a potential with a minimum at other than linearity. Furthermore, the energy required to access the linear configuration for a quasilinear species is lower than the zero point energy of the bending vibration.

The millimeter-wave studies of MgOH presented here provide very good experimental evidence that this molecule is indeed a quasilinear species. First of all, assignment of the vibrational satellite states proved extremely difficult, even when aided by careful intensity studies and theoretical predictions. In fact, there are several rotational progressions of lines with the typical spin–rotation splittings for both MgOH and MgOD whose identity cannot be confidently established. Of the assignments made, the substates that appear shifted relative to their expected positions (2^0, 3^1, and 4^2 states) are those that correlate with excited vibrational levels in the bent limit. In fact, the 2^0, 3^1, and 4^2 levels become the $K_a=0$, 1, and 2 levels of the first vibrationally excited state ($v_2=1$) of the bent molecule (see, e.g., Ref. 26). In contrast, the 1^1, 2^2, 3^3, and 4^4 substates, which follow a fairly regular pattern for

TABLE II. Vibrational dependence of B_v.[a]

Parameter	MgOH	MgOD	CaOH[d]	CaOD[d]	NaOH[e]
$\tilde{B}'_e$[b]	15 036.85(10)	$\cdots$	10 085.12(10)	9109.440(25)	$\cdots$
$\tilde{B}_e$[c]	14 911.76(10)	13 428.65(10)	$\cdots$	$\cdots$	12 654(22)
α_1	250.17(5)	$\cdots$	66.725(4)	55.707(25)	$\cdots$
α_2	110.47(5)	$-5.43(5)$	31.518(3)	$-0.357(20)$	97(20)
γ_{22}	21.18(3)	4.28(3)	2.849(3)	1.209(5)	9(2)
γ_{ll}	$-18.27(3)$	$-9.80(3)$	$-3.361(1)$	$-1.818(5)$	$-10(2)$

[a]Values quoted are in MHz.
[b]$\tilde{B}'_e = B_e - 1/2\alpha_3$.
[c]$\tilde{B}_e = B_e - 1/2(\alpha_1 + \alpha_3)$.
[d]From Refs. 19 and 21.
[e]From Ref. 14.

MgOH and MgOD, correlate with the $K_a = 1, 2, 3,$ and 4 levels in the bent molecule's ground state ($v_2 = 0$). In other words, $v_2(\text{bent}) = \frac{1}{2}$ [$v_2(\text{linear}) - |l|$], and $K_a(\text{bent}) = l(\text{linear})$. Therefore, the vibrational progressions of MgOH and MgOD are those exactly expected for a molecule whose structure is in between the linear and bent limits.

Other indications of quasilinear behavior are rotational constants that do not depend linearly on v_2, as expected from the usual definition of B_v, and large variations in q_{v_2}, the l-type doubling constant for the v_2 mode.[26] Both effects are found in MgOH As previously discussed and shown in Table II, the vibrational expansion of B_v in terms of v_2 has large nonlinear terms. The γ_{22} and γ_{ll} parameters established for MgOH are significantly greater than any others found in the literature. These values were derived by fitting the rotational constants of the 0^0, 1^1, 2^0, 2^2, and 3^3 substates for both MgOH and MgOD. However, the fit as it stands does not reproduce the 3^1 data for either species, or the 4^2 spectra for MgOH, with reasonable accuracy. Even higher order terms would be needed in these cases—additional evidence for quasilinear behavior.

Large differences in the l-type doubling constants are also apparent in MgOH and MgOD, as illustrated in Table III. This table presents the l-type parameter q of the $v_2 = 1, 2,$ and 3 states for these two molecules, as well as those for CaOH, CaOD, SrOH, and HNCO. The percent charge in q in going from the 1^1 to the 2^2 substate is less than 2.5% for CaOH, CaOD, and SrOH. In comparison, the difference in the MgOH and MgOD values are 6% and 16%, respectively. An even more pronounced effect is observed in going from $v_2 = 1$ to $v_2 = 3$, where the difference is 22% for MgOH and MgOD, as opposed to 5% for SrOH. For MgOH, for ex-

ample, $q(1^1) = -85.13$ MHz, while $q(3^1) = -65.86$ MHz, a considerable decrease. In contrast, $q(1^1) = -11.85$ MHz and $q(3^1) = -12.48$ MHz for SrOH. Such changes in the l-type constant for the magnesium hydroxide species are comparable to that of highly quasilinear HNCO in its v_5 mode, which are about 22% as well.[30] Indeed, using the predictions of Bunker et al.,[22] MgOH and MgOD have quasilinear parameters similar to HNCO (-0.72 and -0.71 vs -0.66^{26}). Consequently, common trends in q for the lowest energy bending modes of these molecules might be expected.

Another interesting effect found for MgOH is the large positive value of α_2, which decreases to a small, negative number for MgOD. As previously mentioned, this is a common pattern for metal monohydroxide species, as illustrated by KOH, CsOH, RbOH, CaOH, SrOH, and BaOH.[10,11,13,19,21] Each of these species undergoes a large isotope shift when replacing hydrogen with a deuterium, which decreases the value of α_2. Only for the lighter species does α_2 actually become negative. Lide and Matsumura[11] have attributed this property as arising from a large (and positive) anharmonic term in the bending potential, which is particularly prominent in the OH species, but decreases with deuterium substitution. The isotope shifts also become larger with decreasing mass of the metal atom, as expected. For cesium, rubidium, calcium, potassium, and magnesium, the shifts are -16, -22, -32, -34, and -114 MHz, respectively.

The final evidence for quasilinear behavior in MgOH is found in a comparison of the r_0, r_s, and $\tilde{r}_e$ structures, which can be obtained because deuterium and two magnesium substitutions have been carried out, and because α_2 has been determined. (The term $\tilde{r}_e$ in this case corrects for α_2 but not α_1 or α_3.) These structures are given in Table IV. The r_0 structure does not account for zero-point vibrational energy.

TABLE III. Comparison of l-type doubling constants.[a]

Molecule	$q(1^1)$	$q(2^2)$	$q(3^1)$	Reference
MgOH	$-85.134(13)$	$-79.96(12)$	$-65.859(30)$	This work
MgOD	$-100.885(10)$	$-84.601(39)$	$-78.2716(82)$	This work
CaOH	$-21.649(10)$	$-21.131(51)$	$\cdots$	19
CaOD	$-22.983(17)$	$-23.425(25)$	$\cdots$	21
SrOH	$-11.855(12)$	$-11.934(48)$	$-12.4840(60)$	19
HNCO[b]	34.6391(3)	$\cdots$	27.091 65(12)	30

[a]In MHz.
[b]For v_5 mode instead of v_2.

TABLE IV. Structures for MgOH.[a]

	r_0[b]	r_s[c]	$\tilde{r}_e$[d]
r_{Mg-O}	1.780	1.777	1.767
r_{O-H}	0.871	0.873	0.940

[a]In angstroms.
[b]From Ref. 21.
[c]Using ^{25}Mg, ^{26}Mg, and deuterium substitutions.
[d]Corrected for α_2 only.

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The r_s structure, which considers changes in center of mass with isotopic substitution, is thought to be closer to the true equilibrium structure than the r_0 one. Because it takes out the contribution of the low-lying bending mode, the $\widetilde{r}_e$ structure is corrected for some of the zero-point vibrations, and is nearest to the true r_e geometry. (For MgOH, the $v_2 = 1$ level lies ~ 160 cm^{-1} above ground state.[22]) As can be deduced from Table IV, there are significant differences between the O–H bond length for the r_0, and r_s, and $\widetilde{r}_e$ structures. The O–H bond distance is $r_{O-H} = 0.871$ Å for the r_0 calculation and 0.873 Å for the r_s structure, which is unusually short for this bond, as noted by Nuccio, Apponi, and Ziurys.[21] This decrease in apparent bond length likely arises from the projection of the O–H bond of the bending molecule on the equilibrium linear axis. In comparison, the $\widetilde{r}_e$ value is $r_{O-H} = 0.94$ Å. This number is more typical of O–H bond lengths and similar to the distances of $r_{O-H} = 0.92 – 0.93$ Å found for linear CaOH, SrOH, and BaOH from r_0 and r_s structure determinations.[21] Obviously correcting for the zero-point contribution of the bending motion makes a significant change in the structure of MgOH.

VI. CONCLUSION

Analysis of the pure rotational spectra of the v_2 vibrational satellite transitions of MgOH and MgOD indicates that both molecules are quasilinear. This property is apparent in several of the spectroscopic constants determined in this study, as well as in structural calculations. Moreover, the spectra themselves show deviations from patterns expected for a linear molecule. Quasilinear behavior has already been suggested by theoretical calculations,[22] which predict that MgOH has a quartic bending potential perhaps containing a small barrier. The ionic bonding of the linear species CaOH, SrOH, and BaOH obviously acquires a more significant covalent component with substitution of the lighter alkaline and alkali metals Mg and Na. However, MgOH and NaOH are not predominantly covalent compounds or they would be bent like CuOH or AgOH. Clearly it would be interesting to investigate other metal monohydroxides in order to examine further structural trends.

ACKNOWLEDGMENTS

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