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Millimeter-wave spectrum of MgSH

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Abstract

The pure rotational spectrum of MgSH was observed for the first time, using millimeter-wave absorption spectroscopy in the 280–365 GHz region. This short-lived gas phase free radical was produced in a high-temperature cell by the reaction of Mg metal vapor with H_2S in the presence of an electrical discharge. The spectrum was analyzed using an *S*-reduced asymmetric rotor Hamiltonian to obtain molecular parameters, including rotational, centrifugal distortion, and spin-rotation constants. The analysis of the spectrum indicated that MgSH is bent, in agreement with an ab initio calculation. The ∠Mg–S–H angle obtained from the analysis was 87.5 ± 6.7°, as compared to a calculated ab initio value of 91.1°.

1. Introduction

Alkaline-earth monohydroxides (M–OH, M = Mg, Ca, Sr, Ba) have been thoroughly investigated by high-resolution optical [1–9] and millimeter-wave [10–15] spectroscopic techniques. The studies clearly demonstrated that these radicals, with the exception of MgOH, are linear, as is inherent in the ionic character of the M–OH bond. MgOH was instead shown to be quasi-linear, as characterized by the presence of a quartic bending potential [10,11,15]. In contrast to these hydroxides, very little is known about the alkaline-earth monohydrosulfides, M–SH. The only such radical that has been the subject of several high-resolution spectroscopic studies is CaSH [16–19]. From these studies it was shown that, unlike the alkaline-earth monohydroxides, CaSH is nonlinear, as indeed predicted by ab initio calculations [20]. The bent structure is indicative of a significant amount of covalent bonding in Ca–SH.

To gain more insight into the structure and bonding of alkaline-earth monohydrosulfides, we have investigated the pure rotational spectrum of MgSH using millimeter-wave absorption spectroscopy. We have also performed ab initio calculations in order to assist in the analysis of the spectrum and shed further light on the geometry of MgSH. In this Letter, we present the measurement of the millimeter-wave spectrum and its analysis in terms of spectroscopic constants, including the spin-rotation parameters. Preliminary structural results are also given.

2. Experimental

The rotational spectrum of MgSH was measured using a millimeter-wave absorption

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spectrometer [21] consisting of a tunable source of millimeter-wave radiation, an electric discharge high-temperature absorption cell, and a helium-cooled InSb detector. The millimeter-wave radiation was obtained by harmonic generation from a phase-locked Gunn oscillator (80–110 GHz) and signals were detected using tone burst modulation [22]. The absorption cell was similar to that used in the study of CaSH [19].

The MgSH radical was produced by heating magnesium metal in the high-temperature cell, and reacting the vapor with H_2S in the presence of a DC electrical discharge. The cell pressure was about 75 mTorr, with a mixture of magnesium vapor and 10% H_2S in argon carrier gas. The best absorption signals were obtained at a temperature of 600°C and a discharge current of 80 mA.

3. Results and discussion

The spectroscopic studies of CaSH [16,19] indicated that this radical is bent, with $\angle$Ca–S–H = 91°, and it seemed reasonable to assume a similar geometry for MgSH as a starting point for spectral searches. However, for a more precise prediction of the millimeter-wave spectrum of MgSH we carried out an ab initio geometry optimization calculation. This was done at the MP2/6-311+G(3df,2pd) level using the GAUSSIAN92 program [23]. The result was indeed a nonlinear structure, with Mg–S = 2.333 Å, S–H = 1.339 Å, and $\angle$Mg–S–H = 91.1°.

Using the above results, we searched for the R-branch of the a-type spectrum of MgSH in the 345–361 GHz region. Several transition doublets with splittings varying between 50 and 60 MHz were identified. These doublets are very likely to arise from the spin-rotation interaction, in analogy with CaSH, for which the average splitting in the spin-rotation doublets was about 42 MHz [19]. Additional members of the series were found using the simple $(N+1)/N$ ratio of frequencies, which is appropriate in this case because the above ab initio results indicate that MgSH is a nearly prolate asymmetric top, with $\kappa = -0.9989$. We then identified the $K_a = 1$ asymmetry doublets which are more widely split away from the main cluster of $K_a = 0$ and $K_a \geqslant 2$ transitions. The general pattern was similar to that observed in the case of CaSH.

A total of 86 a-type transitions with $K_a \leqslant 6$ were measured and assigned, and these are listed in Table 1. Although not listed in Table 1, some transitions with $K_a > 6$ were also observed. Transition frequencies were measured by averaging two scans taken up in frequency together with two scans down. The observed linewidths were typically 1.5–2.0 MHz, and the frequencies are believed to be accurate to ±30 kHz. A sample spectrum is shown in Fig. 1. The transitions listed in Table 1 showed no evidence of hyperfine splitting or broadening. For the case of MgOH, the hyperfine structure was observed in the $N = 3 \leftarrow 2$ transition [10], and it is likely that hyperfine structure for MgSH would be observable for rotational transitions with much lower N-values than those in Table 1.

The transitions in Table 1 were analyzed using the S-reduced effective Hamiltonian of Brown and Sears [24]. Spectroscopic parameters obtained from the fit are given in Table 2. For comparison, the rotational and quartic centrifugal constants obtained from the ab initio calculation are also listed in Table 2. The observed A constant is in good agreement with that obtained from the calculation. The relatively large uncertainty in the experimental A constant is due to the absence of b-type transitions in the fit, and the fact that MgSH is an only slightly asymmetric top. The observed B and C constants are each about 100 MHz larger than the ab initio values. This difference meant that our observed R-branch transitions were shifted up in frequency by ~5.5 GHz from the original predicted positions. The observed distortion parameters (D_N, D_{NK}, d_1, d_2) are in reasonable agreement with the ab initio values, as calculated using the Kivelson and Wilson method [25]. We were unable to extract the parameter D_K from the fit for the same reasons that resulted in the poor determination of A, and we therefore fixed it to the ab initio value of 15.1 MHz, as shown in Table 2. Two sextic distortion constants, H_{NK} and H_{KN}, were also derived from the fit. The zero-point inertial defect, derived from the observed rotational constants, was found to

Table 1
Observed rotational transitions (in MHz) of MgSH

$N' K'_a K'_c - N'' K''_a K''_c$	$J = N - 1/2$		$J = N + 1/2$	
	ν_{obs}	$\Delta\nu^a$	ν_{obs}	$\Delta\nu^a$
21 0 21 – 20 0 20	–		281643.993	0.085
21 1 20 – 20 1 19	283431.656	−0.115	283491.552	0.074
23 1 22 – 22 1 21	310358.280	−0.048	310418.027	−0.079
24 0 24 – 23 0 23	321680.825	−0.041	321735.158	0.018
24 1 24 – 23 1 23	319761.209	−0.041	319812.203	0.046
24 1 23 – 23 1 22	323814.577	0.018	323874.166	0.027
25 0 25 – 24 0 24	335032.727	−0.024	–	
25 1 25 – 24 1 24	333045.598	−0.028	333096.522	0.026
25 1 24 – 24 1 23	337265.804	−0.011	337325.369	0.014
25 2 24 – 24 2 23	335098.555	0.016	335154.394	0.032
25 2 23 – 24 2 22	335292.670	−0.057	335349.508	−0.146
25 3 23 – 24 3 22	335028.047	−0.034	–	
25 3 22 – 24 3 21	335029.679	−0.015	–	
25 4 22 – 24 4 21	334841.837	0.012	334899.962	−0.028
25 4 21 – 24 4 20	334841.837	0.007	334899.962	−0.033
25 5 21 – 24 5 20	334611.911	0.051	334671.532	−0.003
25 5 20 – 24 5 19	334611.911	0.051	334671.532	−0.003
25 6 20 – 24 6 19	334335.256	0.046	334396.710	−0.042
25 6 19 – 24 6 18	334335.256	0.046	334396.710	−0.042
26 0 26 – 25 0 25	348378.210	0.052	348432.115	−0.066
26 1 26 – 25 1 25	346325.129	0.021	346375.936	−0.006
26 1 25 – 25 1 24	350711.914	0.027	350771.362	−0.026
26 2 25 – 25 2 24	348460.631	−0.014	348516.398	−0.002
26 2 24 – 25 2 23	348678.826	0.022	348735.877	0.002
26 3 24 – 25 3 23	348392.034	−0.066	348448.932	−0.090
26 3 23 – 25 3 22	348394.119	0.056	348450.986	−0.020
26 4 23 – 25 4 22	348197.811	0.054	348255.709	−0.012
26 4 22 – 25 4 21	348197.811	0.047	348255.709	−0.019
26 5 22 – 25 5 21	347958.366	−0.062	348017.834	0.050
26 5 21 – 25 5 20	347958.366	−0.062	348017.834	0.050
26 6 21 – 25 6 27	347670.762	−0.040	347731.890	0.009
26 6 20 – 25 6 27	347670.762	−0.040	347731.890	0.009
27 0 27 – 26 0 26	361716.924	0.027	361770.792	−0.027
27 1 27 – 26 1 26	359599.535	0.031	359650.321	0.019
27 1 26 – 26 1 25	364152.641	0.074	364211.984	−0.045
27 2 26 – 26 2 25	361817.730	0.035	361873.351	−0.036
27 2 25 – 26 2 24	362061.867	0.048	362118.942	0.013
27 3 25 – 26 3 24	361751.549	−0.042	361808.381	−0.040
27 3 24 – 26 3 23	361753.957	−0.005	361810.818	0.003
27 4 24 – 26 4 23	361549.085	−0.000	361606.888	0.017
27 4 23 – 26 4 22	361549.085	−0.009	361606.888	0.008
27 5 23 – 26 5 22	361300.368	0.012	361359.449	0.021
27 5 22 – 26 5 21	361300.368	0.012	361359.449	0.021
27 6 22 – 26 6 21	361001.708	−0.034	361062.441	0.031
27 6 21 – 26 6 20	361001.708	−0.034	361062.441	0.031

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

be $\Delta_0 = 0.158(4)$ u Å^2. This value can be modeled fairly accurately using a simple formula due to Watson [26], which gave in this case $\Delta_0 = 0.139$ u Å^2. Interestingly, a similar discrepancy of 0.019 u Å^2 between the observed and calculated inertial defects was also obtained for CaSH [19].

The analysis also yielded the principal components of the spin-rotation tensor, ε_{aa}, ε_{bb}, and ε_{cc},

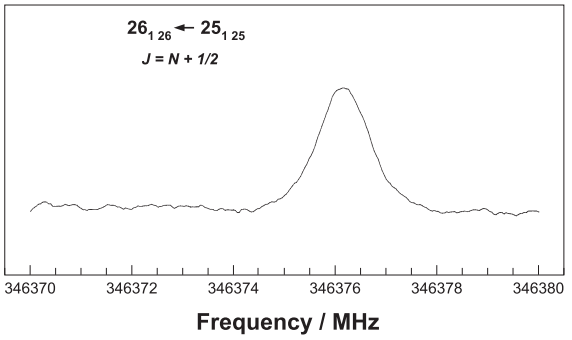

Fig. 1. An example showing one spin component of an R(25) pure rotational transition of MgSH. The spectrum is the average of 100 scans over a 10 MHz wide region.

Table 2
Spectroscopic constants of MgSH

	Millimeter-wave	ab initio
A (MHz)	289001.8(250)[a]	289019.8
B (MHz)	6799.698(3)	6679.4
C (MHz)	6629.659(5)	6528.5
D_N (kHz)	7.618(1)	7.24
D_{NK} (kHz)	506.00(11)	472.77
D_K (MHz)	15.1[b]	15.1
d_1 (kHz)	−0.199(1)	−0.167
d_2 (kHz)	−0.0263(2)	−0.018
H_{NK} (kHz)	0.00332(8)	
H_{KN} (kHz)	0.0876(9)	
ε_{aa} (MHz)	−51.2(6)	
ε_{bb} (MHz)	64.028(43)	
ε_{cc} (MHz)	46.652(45)	
$\lvert\varepsilon_{ab}+\epsilon_{ba}\rvert/2$ (MHz)	<0.060	
Δ_0 (u Å^2)	0.158(4)	
n[c]	86	
$\Delta\nu_{rms}$[d] (kHz)	47	

[a] Uncertainties are 1σ.
[b] Fixed to the ab initio value (see text).
[c] Number of transitions fitted.
[d] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

as shown in Table 2. The quantity $(\varepsilon_{bb} + \varepsilon_{cc})/2$, which correlates with the spin-rotation parameter γ for a linear molecule, is 55.34 MHz for MgSH compared to 41.93 MHz for CaSH. This is similar to the trend observed for MgOH ($\gamma = 37.56$ MHz) and CaOH ($\gamma = 34.76$ MHz). Having determined the three spin-rotation parameters for MgSH we can calculate the g tensor according to Curl's formula [27]. The result (with $g_e = 2.00232$) for MgSH is: $g_{aa} = 2.00241$, $g_{bb} = 1.99761$ and $g_{cc} = 1.99880$. These data will be useful for studies of the Zeeman effect in MgSH.

In the case of CaSH, an off-diagonal spin-rotation parameter, $|\varepsilon_{ab} + \varepsilon_{ba}|/2 = 3.38$ MHz, could be determined through small perturbations of transitions involving $(J = N + 1/2,\ K_a = 1,\ K_c = N - 1)$ and $(J = N - 1/2,\ K_a = 0)$ energy levels [19]. In the present case of MgSH, we might expect a similar effect around $J = 20.5$, as determined from the approximate expression $J \approx (A - B - C)/(B + C)$ [28]. However, no evidence of such a perturbation was observed here. We estimate that an upper value of 60 kHz can be assigned to the parameter $|\varepsilon_{ab} + \varepsilon_{ba}|/2$ for MgSH, based on the precision of our millimeter-wave measurements.

We also searched for b-type transitions, but no obvious candidates were found. The search range took into account the uncertainties of the spectroscopic constants in Table 2. The absence of b-type transitions is likely a result of a relatively small μ_b dipole moment component. This would be consistent with the values of μ_a and μ_b determined in our ab initio calculation, 2.92 and 0.47 D, respectively.

The assignment of the MgSH millimeter-wave spectrum has enabled us to produce an approximate r_0 structure. The least-squares fit of the three observed rotational constants yielded the structural parameters given in Table 3. We have also repeated the least-squares fit of two rotational constants at a time, namely (A, B) and (A, C) pairs. The fit of each of these two pairs of constants led to identical r_0 structures within the uncertainty limits given in Table 3. Due to the absence of

Table 3
Observed and calculated ab initio structures of MgSH

	Observed (r_0)	ab initio (r_e)
Mg–S (Å)	2.316(5)	2.333
S–H (Å)	1. 339[a]	1.339
∠Mg–S–H (deg)	87.5(67)	91.1
ΔI_{rms} (u Å^2)[b]	0.025	

[a] Fixed to the ab initio value (see text).
[b] $\Delta I = I_{obs} - I_{calc}$.

isotopic data, we were forced to constrain the S–H bond length to the ab initio value (Table 3). The observed Mg–S bond length and ∠Mg–S–H angle are in fairly good agreement with the ab initio values. The right angle shape of MgSH is very similar to that of CaSH [19], and this explains the fact that the observed A rotational constants for MgSH and CaSH are of the same order of magnitude. Future investigation of various isotopic species of MgSH would be useful in obtaining a more precise r_0 structure.

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