The millimeter-wave spectrum of the SrOH and SrOD radicals

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Received 22 April 1992

The pure rotational spectra of the X $^2\Sigma^+$ ground states of the SrOH and SrOD radicals have been observed in the laboratory using millimeter/submillimeter direct absorption spectroscopy. The lesser abundant isotopically substituted species, ^{86}SrOH, has been observed as well. The molecules were produced in a Broida-type oven by the reaction of Sr metal vapor with either H_2O_2 or D_2O_2. The rotational and spin–rotation constants were determined for the radicals from a nonlinear least-squares fit to the data using a $^2\Sigma$ Hamiltonian. The millimeter-wave measurements support the picture that strontium hydroxide is linear in its ground electronic and vibrational state.

1. Introduction

Alkali metal monohydroxides such as RbOH and CsOH have been studied in great detail by microwave spectroscopy [1–4]. Hence their spectra have been measured at high resolution and very accurate spectroscopic constants have been determined for such species. These studies have concluded that most of the alkali metal hydroxides, which are closed-shell molecules, are nearly linear in their ground vibrational states. Their excited vibrational modes, however, exhibit anomalous behavior which can be explained by quasilinear effects [1]. In contrast, little work has been done on examining the high resolution spectra of alkaline-earth metal monohydroxides, probably because they are open-shell and highly reactive. Several of these species, however, have been studied at optical wavelengths. For example, Harris and co-workers have observed both the A $^2\Pi$–X $^2\Sigma^+$ and the B $^2\Sigma^+$–X $^2\Sigma^+$ systems of CaOH [5], and the B $^2\Sigma^+$–X $^2\Sigma^+$ system of SrOH and SrOD [6]. Also, Bernath and associates have detected the B $^2\Sigma^+$–X $^2\Sigma^+$ transitions of BaOH and BaOD [7] and the A $^2\Pi$–X $^2\Sigma$ transition of SrOH [8], as well as having performed additional studies of the B–X and A–X systems of CaOH [9]. Recently, Steimle et al. have measured the dipole moments of SrOH and CaOH as well [10]. The optical measurements suggest that the alkaline earth metal hydroxides are also generally linear.

A linear structure is expected in the ground state if the metal–hydroxide bond is ionic in character. In the ionic bonding scheme, the lone pair electron resides on the metal atom in an M^+OH^- type structure. If the bonding were covalent, then the geometry would be bent, resembling that of water. The past optical data therefore suggest strongly that bonding in the alkaline earth metal monohydroxides is primarily ionic.

Recently, Ziurys, Barclay, and Anderson [11,12] observed the pure rotational spectrum of both CaOH and MgOH in their ground electronic $^2\Sigma^+$ states at mm/sub-mm wavelengths. These authors measured rotational transitions originating in several of the low-lying vibrational modes as well [13]. Analysis of the transitions originating in the (0, 0, 0) mode suggests that both CaOH and MgOH are linear or very nearly linear in their ground states. However, in its excited vibrational states, MgOH shows some evidence of being quasilinear [13]. Hence, the bonding in MgOH may be more covalent than in CaOH.

It is therefore of interest to study other alkaline earth metal monohydroxides to examine if they are

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Elsevier Science Publishers B.V.

linear, quasilinear, or bent. In this paper, we present the first high-resolution measurements of the rotational spectrum of SrOH in its ground electronic and vibrational states, along with the less abundant strontium 86 isotopic species, ^{86}SrOH, and SrOD. Nineteen rotational transitions have been observed for ^{88}SrOH in the frequency range 89–370 GHz, and twelve rotational transitions have been measured for both ^{86}SrOH and ^{88}SrOD in the region 202–374 GHz. The absolute accuracy of these frequency measurements is ±50–100 kHz. Several rotational transitions originating in the (0, 1, 0), (0, 2, 0), and (1, 0, 0) vibrational modes of SrOH have also been observed and splittings arising from ℓ-type doubling have been resolved. The results of the vibrational analysis will be published in another paper [13]. Here we present spectroscopic constants and bond lengths for the strontium hydroxide radical in its (0, 0, 0) mode.

2. Experimental

The rotational transitions of SrOH and its isotopically substituted species were measured using a direct absorption spectrometer operating in the range 65–400 GHz. The details of this instrument are described elsewhere [14]. Briefly, the spectrometer consists of a tunable source of millimeter radiation (65–118 GHz) in this case Gunn oscillators (J.E. Carlstrom Co.), which are phase-locked to a 2 GHz signal generator (Fluke 6082A). In order to obtain higher frequencies, Schottky diode multipliers are employed (Millitech Corp.). The radiation from the source is quasi-optically sent into a gas absorption cell by use of a scalar feedhorn and several machined teflon lenses. The cell is 0.5 m in length and is a double pass system. After one pass through the cell, the beam is folded onto itself by a rooftop reflector, which rotates the linearly polarized radiation by 90°. The radiation passes back through the cell and after it exists is reflected into a detector by a wire grid. The detector is a helium cooled InSb hot-electron bolometer (Cochise Instruments). Phase sensitive detection is accomplished by fm modulation of the Gunn oscillators at a rate of 25–50 kHz and by using a lock-in amplifier (EG&G PAR5301).

The SrOH radical was produced in a Broida-type oven by the reaction of strontium metal vapor with hydrogen peroxide. The vapor was carried into the absorption cell by a flow of argon carrier gas. The argon pressure was typically 15 mTorr, while the H_2O_2 pressure used was about 20 mTorr. A bright orange chemiluminescence was observed when the vapor was reacted with H_2O_2, presumably arising from the $A\,^2\Pi^+$–$X\,^2\Sigma^+$ and/or $B\,^2\Sigma^+ \to X\,^2\Sigma^+$ electronic transitions of SrOH. It was found that signals arising from SrOH where maximized by optimizing the brightness of this chemiluminescence. The 86-isotopically substituted species was observed in its natural abundance (^{88}Sr: 82.56% and ^{86}Sr: 9.86%). In a similar manner, the SrOD radical was produced by reacting strontium vapor with D_2O_2. The deuterated hydrogen peroxide was made by adding D_2O to H_2O_2 and successively pumping off the H_2O. The intensities of the SrOD lines were typically one third of the main isotope SrOH transitions.

In past optical studies, SrOH and SrOD were produced by reacting strontium metal vapor with H_2O and D_2O [6] instead of peroxide. In these reactions an orange red chemiluminescence was detected. We were unable to observe signals arising from SrOH by reacting the strontium metal vapor with water. This may arise from the fact that the pressures used in these experiments ($\lesssim$50 mTorr) were much less than those employed in the optical studies (1–3 Torr). The dipole moment of SrOH in its $X\,^2\Sigma^+$ state is 1.9 D [10].

The temperature at which SrOH radicals were produced could only be estimated on a relative basis from the voltage applied to the oven. For the detection of the weaker isotopically substituted lines or lower rotational lines, the oven voltage was increased over its normal operating value to improve sensitivity. (The melting point of strontium is 1043 K.)

3. Results

Table 1 lists the rotational transitions measured for the main isotope lines of SrOH, while tables 2 and 3 show the transition frequencies determined for ^{86}SrOH and SrOD. As is apparent from the tables, the spin–rotation splitting was readily resolved in all these data. However, no evidence of hyperfine struc-

Table 1
Observed transition frequencies of ^{88}SrOH: X $^2\Sigma^+$ ($v=0$)

$N \to N'$	$J \to J'$	$F \to F'$	ν_{obs} (MHz)	$\nu_{obs}-\nu_{cal}$ (MHz)	$N \to N'$	$J \to J'$	$F \to F'$	ν_{obs} (MHz)	$\nu_{obs}-\nu_{cal}$ (MHz)
5→6	9/2→11/2	4→5 5→6	89607.872	0.023	16→17	31/2→33/2	15→16 16→17	253843.472	−0.002
	11/2→13/2	5→6 6→7	89680.597	−0.028		33/2→35/2	16→17 17→18	253916.241	−0.007
6→7	11/2→13/2	5→6 6→7	104546.194	0.011	17→18	33/2→35/2	16→17 17→18	268761.163	0.008
	13/2→15/2	6→7 7→8	104618.922	−0.036		35/2→37/2	17→18 18→19	268833.924	−0.006
8→9	15/2→17/2	7→8 8→9	134419.461	0.053	18→19	35/2→37/2	17→18 18→19	283676.005	−0.016
	17/2→19/2	8→9 9→10	134492.186	0.003		37/2→39/2	18→19 19→20	283748.806	0.009
9→10	17/2→19/2	8→9 9→10	149354.008	0.021	19→20	37/2→39/2	18→19 19→20	298587.908	−0.008
	19/2→21/2	9→10 10→11	149426.760	−0.003		39/2→41/2	19→20 20→21	298660.700	0.008
10→11	19/2→21/2	9→10 10→11	164287.027	0.026	20→21	39/2→41/2	19→20 20→21	313496.668	−0.012
	21/2→23/2	10→11 11→12	164359.769	−0.007		41/2→43/2	20→21 21→22	313569.467	0.011
11→12	21/2→23/2	10→11 11→12	179218.294	<0.001	21→22	41/2→43/2	20→21 21→22	328402.151	−0.010
	23/2→25/2	11→12 12→13	179291.031	−0.039		43/2→45/2	21→22 22→23	328474.959	0.023
12→13	23/2→25/2	11→12 12→13	194147.725	0.015	22→23	43/2→45/2	21→22 22→23	343304.173	−0.026
	25/2→27/2	12→13 13→14	194220.467	−0.019		45/2→47/2	22→23 23→24	343376.996	0.022
13→14	25/2→27/2	12→13 13→14	209075.093	<0.001	23→24	45/2→47/2	22→23 23→24	358202.620	−0.019
	27/2→29/2	13→14 14→15	209147.865	−0.003		47/2→49/2	23→24 24→25	358275.433	0.019
14→15	27/2→29/2	13→14 14→15	224000.282	−0.003	24→25	47/2→49/2	23→24 24→25	373097.295	−0.029
	29/2→31/2	14→15 15→16	224073.091	0.030		49/2→51/2	24→25 25→26	373170.128	0.029
15→16	29/2→31/2	14→15 15→16	238923.121	−0.009					
	31/2→33/2	15→16 16→17	238995.898	−0.007					

ture was observed in any of the spectra. This is not unexpected, since any hyperfine splittings should be small because if the molecule is linear, the unpaired electron resides on the metal atom as opposed to the proton. Thus, interactions between the electron and proton should be minimal. Substitution of H with D on the radical did not appear to change the magnitude of the hyperfine splitting, although D has a spin of 1 as opposed to 1/2. Also, there was no evidence of quadrupole splitting on SrOD, since linewidths of the spectra of this species were nearly identical to those of SrOH.

Fig. 1 shows spectra of the $N=24\to25$ transition of SrOH and ^{86}SrOH. Fig. 2 displays the $N=25\to26$ transition of SrOD. Because of the modulation scheme employed, the spectra appear in emission as

Table 2
Observed transition frequencies of ^{86}SrOH: X $^2\Sigma^+$ ($v=0$)

N→*N*′	*J*→*J*′	*F*→*F*′	ν_{obs} (MHz)	$\nu_{\mathrm{obs}}-\nu_{\mathrm{cal}}$ (MHz)
13→14	25/2→27/2	12→13 13→14	209851.313	0.026
	27/2→29/2	13→14 14→15	209924.327	−0.022
14→15	27/2→29/2	13→14 14→15	224831.861	0.013
	29/2→31/2	14→15 15→16	224904.896	−0.014
15→16	29/2→31/2	14→15 15→16	239810.054	0.009
	31/2→33/2	15→16 16→17	239883.074	−0.033
16→17	31/2→33/2	15→16 16→17	254785.727	0.007
	33/2→35/2	16→17 17→18	254858.772	−0.010
17→18	33/2→35/2	16→17 17→18	269758.723	0.007
	35/2→37/2	17→18 18→19	269831.781	0.002
18→19	35/2→37/2	17→18 18→19	284728.887	0.011
	37/2→39/2	18→19 19→20	284801.936	−0.002
19→20	37/2→39/2	18→19 19→20	299696.037	−0.004
	39/2→41/2	19→20 20→21	299769.119	0.016
20→21	39/2→41/2	19→20 20→21	314660.042	−0.012
	41/2→43/2	20→21 21→22	314733.117	0.001
21→22	41/2→43/2	20→21 21→22	329620.758	0.001
	43/2→45/2	21→22 22→23	329693.829	0.009
22→23	43/2→45/2	21→22 22→23	344577.976	0.017
	45/2→47/2	22→23 23→24	344651.071	0.015
23→24	45/2→47/2	22→23 23→24	359531.588	−0.017
	47/2→49/2	23→24 24→25	359604.688	0.021
24→25	47/2→49/2	23→24 24→25	374481.408	−0.026
	49/2→51/2	24→25 25→26	374554.513	0.017

Table 3
Observed transition frequencies of SrOD: X $^2\Sigma^+$ ($v=0$)

N→*N*′	*J*→*J*′	*F*→*F*′	ν_{obs} (MHz)	$\nu_{\mathrm{obs}}-\nu_{\mathrm{cal}}$ (MHz)
14→15	27/2→29/2	13→14 14→15	202543.882	0.027
	29/2→31/2	14→15 15→16	202609.846	−0.016
15→16	29/2→31/2	14→15 15→16	216039.087	0.012
	31/2→33/2	15→16 16→17	216105.073	−0.009
16→17	31/2→33/2	15→16 16→17	229523.398	0.020
	33/2→35/2	16→17 17→18	229598.373	−0.013
17→18	33/2→35/2	16→17 17→18	243023.653	0.008
	35/2→37/2	17→18 18→19	243089.661	0.008
18→19	35/2→37/2	17→18 18→19	256512.776	0.021
	37/2→39/2	18→19 19→20	256578.748	−0.015
19→20	37/2→39/2	18→19 19→20	269999.517	−0.072
	39/2→41/2	19→20 20→21	270065.587	−0.010
20→21	39/2→41/2	19→20 20→21	283484.033	0.006
	41/2→43/2	20→21 21→22	283550.032	−0.003
21→22	41/2→43/2	20→21 21→22	296965.962	0.013
	43/2→45/2	21→22 22→23	297031.952	−0.005
22→23	43/2→45/2	21→22 22→23	310445.235	<0.001
	45/2→47/2	22→23 23→24	310511.286	0.043
23→24	45/2→47/2	22→23 23→24	323921.757	−0.009
	47/2→49/2	23→24 24→25	323987.767	−0.007
24→25	47/2→49/2	23→24 24→25	337395.410	−0.011
	49/2→51/2	24→25 25→26	337461.441	0.011
25→26	49/2→51/2	24→25 25→26	350866.067	−0.015
	51/2→53/2	25→26 26→27	350932.105	0.015

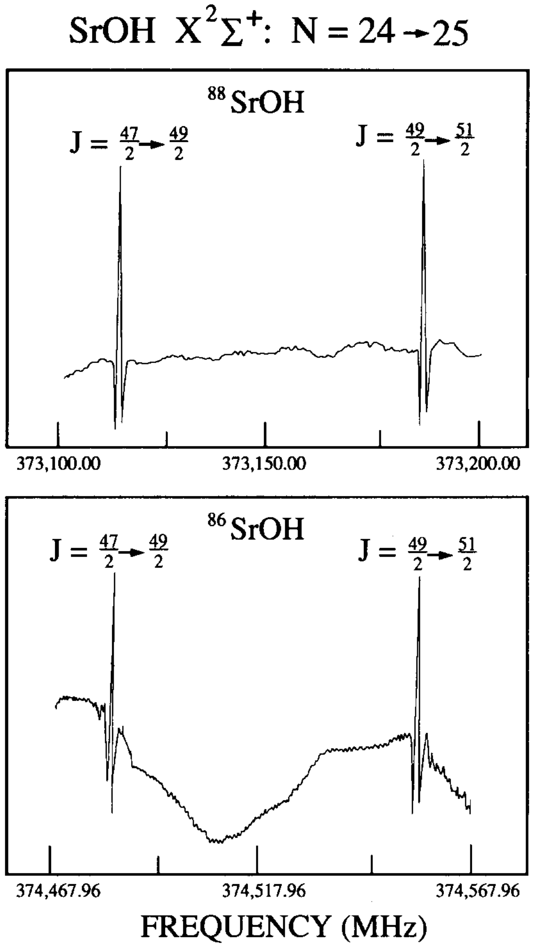

Fig. 1. Spectra of $N=24\rightarrow25$ rotational transition of the ^{88}SrOH and ^{86}SrOH radicals observed in this work near 373–374 GHz. Each spectrum represents about 6 min of scan time, covering a range of 100 MHz. The lines appear in emission because of the modulation scheme employed.

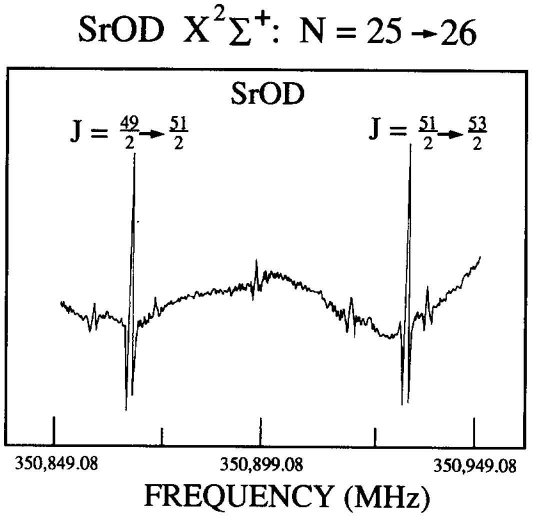

Fig. 2. Spectrum of the $N=25\rightarrow26$ rotational transition of SrOD detected in this work near 350 GHz. The spectrum represents about 6 min of integration, covering a range of 100 MHz. The smaller lines in the data arise from H_2O_2.

second derivatives. The data represent about 6 min of integration time per spectra, which cover the frequency range of 100 MHz. As the figures illustrate, SrOH has a much larger spin–rotation splitting than CaOH or MgOH. For example, $\gamma(\mathrm{SrOH})=72.78$ MHz, as opposed to 37.56 MHz for MgOH and 34.76 MHz for CaOH.

Table 4 gives the rotational constants B_0 and D_0 and the spin–rotation constant γ for all three species. This is the first determination of the spectroscopic constants for ^{86}SrOH. These values were derived from a nonlinear least-squares fit to the data, using a $^2\Sigma$ Hamiltonian. Since evidence of hyperfine splitting was not observed, the hyperfine constants b and c were set to zero in doing the least-squares analysis. As the table demonstrates, the millimeter-wave constants are in good agreement with those determined from optical data for SrOH and SrOD, especially in comparison with the work of Brazier and Bernath [8].

The errors quoted in table 4 are purely statistical errors (3σ) from the data fit. However, the constants reproduce the observed frequencies to, at worst, $\nu_{\mathrm{obs}}-\nu_{\mathrm{calc}}\leqslant72$ kHz. Other sources of error are the frequency stability of the 2 GHz synthesizer, and determining the center frequency of any given line. An overall uncertainty for these frequencies is probably $\approx\pm50$ kHz for the main lines and $\approx\pm100$ kHz for the isotopically substituted species.

Table 5 lists the Sr–O and O–H bond lengths determined for strontium hydroxide from the millimeter-wave measurements, using both the SrOH/SrOD and ^{88}SrOH/^{86}SrOH ratios. For comparison, bond distances derived from the optical work of Nakagawa et al. [6] are also given. The bond lengths determined from the SrOH/SrOD millimeter-wave data compare closely with the optical values, which used the same isotopic species. However, the O–H

Table 4
Molecular constants for ^{88}SrOH, ^{88}SrOD and ^{86}SrOH: $X\,^2\Sigma^+$ ($\nu=0$) [a]

	Constant	Millimeter wave (MHz)	Optical (MHz)
^{88}SrOH	B_0	7470.8224(6)	7471.1(6) [b]; 7470.9(2) [c]
	D_0	0.0065186(6)	0.0064(1) [b]; 0.00654(3) [c]
	γ	72.775(13)	75(9) [b]; 72.8(5) [c]
^{88}SrOD	B_0	6754.8083(8)	6754.9(6) [b]
	D_0	0.0049918(9)	0.0052(1) [b]
	γ	66.008(18)	84(21) [b]
^{86}SrOH	B_0	7498.5676(6)	-
	D_0	0.0065667(7)	-
	γ	73.063(14)	-

[a] Errors are 3σ and apply to the last quoted digits.
[b] Ref. [6]. The values originally reported in cm^{-1}.
[c] Ref. [8]. The values originally reported in cm^{-1}.

Table 5
Bond lengths for SrOH (in Å)

Millimeter wave		Optical [a]	
r_0(SrO)	r_0(OH)	r_0(SrO)	r_0(OH)
2.111 [b]	0.922 [b]	2.111	0.922
2.104 [c]	0.999 [c]		

[a] Ref. [6].
[b] Determined from ^{88}SrOH/^{88}SrOD.
[c] Determined from ^{88}SrOH/^{86}SrOH.

bond distance appears to be somewhat larger, when derived from the ^{88}SrOH/^{86}SrOH millimeter-wave data. The Sr–O length of ≈ 2.1 Å, however, is about the same from all calculations. This bond length is significantly smaller than either the Rb–O and Cs–O distances, which are 2.3 and 2.4 Å, respectively [1,2]. Nakagawa et al. [6] interpret the shorter metal–oxygen bond length in SrOH versus RbOH and CsOH as arising from the larger degree of covalent bonding in the strontium hydroxide radical.

4. Discussion

The ability to readily reproduce the observed transition frequencies with a $^2\Sigma$ Hamiltonian is further evidence that SrOH and SrOD are both linear molecules. Past optical work [6,8] had strongly suggested this behavior for strontium hydroxide. Also, lack of any observable hyperfine splitting supports this picture as well. The hyperfine structure should be small if the lone electron resides on the metal, far away from the proton, in an ionic M^+OH^- type linear configuration. However, the shorter metal–oxygen bond length in SrOH as opposed to CsOH and RbOH does suggest that alkaline earth hydroxides have a larger degree of covalent character in their bonding than their alkali metal counterparts.

Studies of alkaline earth metal hydroxides such as SrOH, CaOH [11], and MgOH [12] do seem to show that individual bonds to these metals with an OH group tend to be chiefly ionic in character. Studies of BeOH and BaOH could further characterize the nature of the bonding. Transition metal hydroxides such as AlOH and FeOH may exhibit a more covalent-type structure, however.

Acknowledgement

This research was supported by NSF grants No. AST-90-58467 (Presidential Young Investigator Award) and No. AST-91-10701, and NASA grant No. NAGW-2989. MAA acknowledges the NASA Space Grant Program at ASU for his support. LMZ thanks the staff at NRAO, Tucson, for their various equipment loans, and R. Claude Woods for the use of his $^2\Sigma$ Hamiltonian.

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