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Microwave spectroscopic detection of transition metal hydroxides: CuOH and AgOH

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Pure rotational spectra of transition metal hydroxides have been reported. Millimeter wave spectra of CuOH and AgOH were recorded in a direct current discharge absorption cell in the range of 200–390 GHz. The spectra of both molecules correspond to that of a near prolate asymmetric top and only *a*-type *R* branch transitions were observed. The rotational and centrifugal distortion constants of CuOH and AgOH were precisely determined. Centrifugal distortion terms up to $N^2N_z^{10}$ were required to fit the observed line frequencies of $^{63}\text{CuOH}$. A preliminary analysis showed that AgOH is also strongly bent like CuOH with a bond angle smaller by about 2° .

Rotational spectra of a number of metal hydroxide molecules have been previously studied. Examples include the alkali metal hydroxides NaOH to CsOH,^{1–4} the alkali earth hydroxides MgOH to BaOH,^{5–8} and more recently, AlOH (Ref. 9) and InOH.¹⁰ Linearity or nonlinearity of the metal hydroxide depends on a balance between ionic and covalent structures. The spectra of most of the alkali and alkali earth hydroxides indicate linear structures and have been rationalized in terms of the low ionization potentials and electronegativities of the metals.¹¹ The exceptions are MgOH, AlOH, and InOH which show features suggestive of quasilinear behavior. In contrast, there has been no previous microwave spectroscopy of transition metal hydroxides and only CuOH has been the subject of rotationally resolved electronic spectroscopic studies.^{12–14} The electronic spectra showed clearly that CuOH was strongly bent in its electronic ground state as opposed to the other molecules. A shift of the balance in the bonding seems to be taking place in transition metal hydroxides. Given the importance of metal–water interactions in the corrosion of transition metal surfaces where the formation of metal–OH bonds are often implicated,¹⁵ there is a need for rotational spectroscopy of such molecules in order to characterize their structure and electronic properties.

In this communication we report the first observation of pure rotational millimeter wave spectra of CuOH and AgOH produced in a direct current (dc) discharge absorption cell. This also constitutes a spectroscopic detection of AgOH.

Measurements in the range of 200–400 GHz were made using a 2-m-long single pass absorption cell spectrometer¹⁶ and a liquid helium cooled InSb detector. Millimeter wave radiation was generated by free running klystrons operating in the 75–110 GHz region and the required frequencies were produced by subsequent harmonic generation. The metal bearing molecules were produced in a dc electric discharge

inside the cell by sputtering from hollow cathode copper or silver electrodes. Prior to searches for the hydroxides, spectral lines of the corresponding oxide^{17,18} were optimized in intensity. For the initial hydroxide searches, a few millitorr of H_2 was added; however, this proved to be unnecessary. The optimum conditions found were, a discharge current of 200–400 mA, a cell temperature of -50 to -120°C (with the lower temperature favoring low K_a transitions) and a 10–20 mTorr gas mixture of 3:1 $\text{He}:\text{O}_2$. It was found that including water vapor in the gas mixture gave no improvement in the signal. However, flowing around 100 mTorr of water vapor through the cooled cell in the absence of a discharge prior to observations resulted in a significant improvement in the hydroxide signal. It seems likely therefore that surface conditions and/or surface reactions are important in producing the gas phase CuOH and AgOH species.

CuOH: Electronic spectra of CuOH indicated a closed shell near prolate asymmetric top ground state with a Cu–O–H bond angle of about 110° .¹³ A recent *ab initio* calculation gave a large dipole moment along the Cu–O bond (which is almost parallel to the *a* axis) with a much smaller dipole moment perpendicular to it.¹⁹ A search was therefore made for *a*-type *R* branch rotational transitions using the rotational constants of Ref. 13 and a number of strong absorption lines were seen with the correct K_a sub level pattern and ^{63}Cu – ^{65}Cu isotopic separation for an assignment to CuOH to be made. A total of 58 $^{63}\text{CuOH}$ and 30 $^{65}\text{CuOH}$ *a*-type rotational lines were measured to an accuracy of around 15–20 kHz. Transitions ranged from $N=10$ –9 to $N=17$ –16 and $K_a=0$ –0 to $K_a=6$ –6 with no *b*-type transitions being observed [Fig. 1(a) shows a typical line]. Although both copper isotopes possess a nuclear spin of $3/2$, no electric quadrupole structure was resolved, even for the lowest transition observed, $N=6$ –5 at 139.6 GHz. No CuOH signals were observable at lower frequencies and these might show a quadrupole structure.

AgOH: A complete active space self-consistent field cal-

FIG. 1. (a) The $12_1 11^-11_1 10$ transition of $^{63}\text{CuOH}$ observed in a dc discharge cell, with a 10 mTorr mixture of 3:1 He/O_2 and a cylindrical copper cathode. The integration time was 8 s. (b) The $20_1 19^-19_1 19$ transition of $^{107}\text{AgOH}$ observed with silver sheets inserted inside a hollow cathode. The other experimental conditions were similar to (a).

ulation of CuOH and AgOH by Bauchlicher²⁰ predicted a similar structure for both molecules, though the calculated CuOH bond angle (130°) deviated considerably from the value measured in Ref. 13. With this in mind, predictions of the rotational constants were made using the *ab initio* bond lengths and the 110° CuOH bond angle, and a search for *a*-type transitions undertaken. A total of 48 *a*-type transitions were assigned for both $^{107}\text{AgOH}$ and $^{109}\text{AgOH}$ isotopic molecules, with transitions ranging from $N=16-15$ to $N=22-21$ and $K_a=0-0$ to $K_a=5-5$. Both the K_a sublevel pattern and the $^{107}\text{Ag}-^{109}\text{Ag}$ isotope separations were in good agreement with those expected for the AgOH molecule. Figure 1(b) shows an example of a AgOH line.

The transition frequencies for each isotopomer were fitted using a Watson *S* reduced Hamiltonian.²¹ K_a asymmetry doubling was only observed for $K_a=1$ and 2 transitions. For $K_a=3$ the predicted doubling was somewhat larger than the measurement uncertainty, so the observed lines were fitted to the mean of the two calculated transitions. Centrifugal distortion terms up to $N^2N_z^{10}$ were required to fit the $K_a=6$ transitions observed for $^{63}\text{CuOH}$. This is understandable, since these levels possess a considerable amount of rotational energy due to the large *A* rotational constant. For CuOH , the *A*, D_K , H_K , and L_K parameters were held fixed to the values determined in Ref. 13 since they only have small effects on the observed transition frequencies. In the case of AgOH , *A* was floated, D_K held fixed to the CuOH value, and H_K and L_K were fixed at zero. This produced an estimated uncertainty in *A* of about 1 GHz, large compared to the *B* and *C* uncertainties, but quite small compared to the

size of *A*. An example of the fits for CuOH and AgOH is shown in Table I and the fitted parameters are shown in Tables II and III.

A full analysis of the CuOH and AgOH results including measurement of the CuOD and AgOD species and a determination of harmonic force field information is currently being undertaken and will be reported later. This will enable a vibrationally averaged structure to be determined for both molecules. We note here that the similarity of the inertial defects of CuOH and AgOH^- ($0.104 \text{ amu } \text{\AA}^2$) is good evidence that the vibrational effects on the rotational constants are also similar. In this case, we may use the rotational constants to determine the difference in geometry between CuOH and AgOH . The main assumption made was to fix r_{OH} to the r_0 value of OH (Ref. 22) for both molecules ($0.9741 \text{ \AA}$). Using $B+C$ and *A* or $B+C$ and $B-C$ gives slightly different values for the metal-oxygen distance and the bond angle due to the inertial defect. The results give: $r_{\text{AgO}} - r_{\text{CuO}} = 0.247(2) \text{ \AA}$ and $\theta_{\text{AgOH}} - \theta_{\text{CuOH}} = -1.9(2)^\circ$ where we have used the *A* and $B+C$ combination because $B-C$ is quite small and not so sensitive to the bond angle as *A*. The agreement of our CuOH *B* and *C* constants with those of Ref. 13 is very good (to within 1–3 MHz). This suggests that the partial *r_s* structure they derived should be reasonably reliable and we use this structure together with our differences to provide a geometry for AgOH shown in Table IV.

The Ag–O bond length of $2.017 \text{ \AA}$ is consistent with the isoelectronic fluorides. The Ag–F bond is $0.238 \text{ \AA}$ longer than Cu–F due to the larger ionic radius for silver,²³ which compares well with the $0.247 \text{ \AA}$ increase for AgOH compared to CuOH . The bond angles of bent hydroxides are particularly interesting as they reflect the competing ionic and covalent contributions to the metal-oxygen bond. The similarity of the two bond angles indicates that the metal-oxygen bonds are also quite similar in character. This is perhaps to be expected noting that copper and silver have similar ionization potentials and electronegativities. The ionic charge-dipole interaction will tend to increase the bond angle towards linearity, but this is offset by more favorable orbital overlap for bent structures. The decrease in the AgOH bond angle compared to CuOH may reflect the longer metal-oxygen bond length which should reduce the charge-dipole electrostatic interaction somewhat allowing the bond angle to become slightly more bent. Like CuOH , the AgOH bond angle calculated in Ref. 20 is about 20° too large. The geometries of the hydroxides therefore provide a very good test for calculations of transition metal molecules.

Finally, the significant higher order centrifugal distortion constants observed for $^{63}\text{CuOH}$ reflect the distortion of the molecule caused by the considerable rotational energy about the *a* axis for high values of K_a . Beyond $K_a=4$, each K_a state requires an additional distortion term to account for the *a*-type transitions. This can be interpreted as a kind of quasilinear behavior at high K_a where the separation between K_a levels becomes comparable to the vibrational energy differences. A good example of a bent quasilinear molecule is HNCO (Ref. 24) where a strong negative perturbation in the effective rotational constant is seen around $K_a=7$. The lower *A* rotational constant and higher bending vibrational fre-

TABLE I. Selection of the transition frequencies of CuOH and AgOH (MHz).

$N'_{Ka'Kc'}-N''_{Ka''Kc''}$	$^{63}\text{CuOH}$ $\nu_{\text{obs}}(\Delta\nu)^a$	$^{65}\text{CuOH}$ $\nu_{\text{obs}}(\Delta\nu)$	$N'_{Ka'Kc'}-N''_{Ka''Kc''}$	$^{107}\text{AgOH}$ $\nu_{\text{obs}}(\Delta\nu)$	$^{109}\text{AgOH}$ $\nu_{\text{obs}}(\Delta\nu)$
14 ₀₁₄ -13 ₀₁₃	325 841.795(-8)	323 738.573(5)	20 ₀₂₀ -19 ₀₁₉	329 888.850(-8)	329 066.457(-21)
14 ₁₁₄ -13 ₁₁₃	324 262.076(22)	322 178.829(-19)	20 ₁₂₀ -19 ₁₁₉	328 712.709(-30)	327 896.114(7)
14 ₁₁₃ -13 ₁₁₂	327 392.297(-33)	325 268.929(-14)	20 ₁₁₉ -19 ₁₁₈	331 030.594(-10)	330 202.417(-26)
14 ₂₁₃ -13 ₂₁₂	325 730.648(27)	323 628.540(12)	20 ₂₁₉ -19 ₂₁₈	329 777.367(-2)	328 955.351(-19)
14 ₂₁₂ -13 ₂₁₁	325 754.967(0)	323 652.145(-34)	20 ₂₁₈ -19 ₂₁₇	329 797.112(-26)	328 974.914(-27)
14 ₃ -13 ₃	325 577.006(-8)	323 476.783(13)	20 ₃ -19 ₃	329 626.293(-22)	328 804.925(-3)
14 ₄ -13 ₄	325 358.844(21)		20 ₄ -19 ₄	329 412.773(-20)	328 592.300(-30)
14 ₅ -13 ₅	325 089.945(10)		20 ₅ -19 ₅	329 148.918(-21)	328 329.652(9)
14 ₆ -13 ₆	324 773.581(-35)		20 ₆ -19 ₆		
15 ₀₁₅ -14 ₀₁₄	349 081.623(-14)	346 828.624(-37)	21 ₀₂₁ -20 ₀₂₀	346 348.047(22)	345 484.759(44)
15 ₁₁₅ -14 ₁₁₄	347 392.639(-25)	345 161.041(-8)	21 ₁₂₁ -20 ₁₂₀	345 115.148(-42)	344 257.907(6)
15 ₁₁₄ -14 ₁₁₃	350 745.293(-14)	348 470.706(19)	21 ₁₂₀ -20 ₁₁₉	347 548.058(-4)	346 678.666(5)
15 ₂₁₄ -14 ₂₁₃	348 965.932(8)	346 714.093(0)	21 ₂₂₀ -20 ₂₁₉	346 232.838(9)	345 369.898(0)
15 ₂₁₃ -14 ₂₁₂	348 995.863(-9)	346 743.217(30)	21 ₂₁₉ -20 ₂₁₈	346 255.707(1)	345 392.554(6)
15 ₃ -14 ₃	348 802.440(-9)	346 552.566(-4)	21 ₃ -20 ₃	346 074.833(7)	345 212.516(-16)
15 ₄ -14 ₄	348 568.441(-6)		21 ₄ -20 ₄	345 850.536(34)	345 989.192(14)
15 ₅ -14 ₅	348 280.249(-16)		21 ₅ -20 ₅	345 573.443(41)	344 713.300(-5)
15 ₆ -14 ₆	347 941.349(34)		21 ₆ -20 ₆		
16 ₀₁₆ -15 ₀₁₅	372 314.342(21)	369 911.736(31)	22 ₀₂₂ -21 ₀₂₁	362 802.033(1)	361 897.811(-8)
16 ₁₁₆ -15 ₁₁₅	370 516.865(-5)	368 136.936(10)	22 ₁₂₂ -21 ₁₂₁	361 512.796(10)	360 614.850(-15)
16 ₁₁₅ -15 ₁₁₄	374 091.616(-9)	371 665.852(-10)	22 ₁₂₁ -21 ₁₂₀	364 060.509(-25)	363 149.908(-9)
16 ₂₁₅ -15 ₂₁₄	372 194.752(-26)	369 793.280(-15)	22 ₂₂₁ -21 ₂₂₀	362 683.381(-20)	361 779.568(7)
16 ₂₁₄ -15 ₂₁₃	372 231.116(-8)	369 828.806(202) ^b	22 ₂₂₀ -21 ₂₁₉	362 709.719(22)	362 805.619(24)
16 ₃ -15 ₃	372 021.647(-15)	369 622.232(5)	22 ₃ -21 ₃	362 518.557(20)	361 615.370(11)
16 ₄ -15 ₄	371 771.794(-11)		22 ₄ -21 ₄	362 283.399(8)	361 381.236(4)
16 ₅ -15 ₅	371 464.318(8)		22 ₅ -21 ₅	361 993.017(-21)	361 092.147(-17)
16 ₆ -15 ₆	371 102.689(-31)		22 ₆ -21 ₆		

^a $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$ in kHz. ν_{calc} is obtained from the molecular constants in Tables II and III.^bNot included in the fit.

TABLE II. Parameters from least-squares fit to CuOH transitions.

Parameter ^a	$^{63}\text{CuOH}^b$	$^{65}\text{CuOH}^c$
A/GHz^d	690.693	690.659
$1/2(B+C)/\text{MHz}$	11 644.9965(5)	11 569.7706(8)
$(B-C)/\text{MHz}$	224.1400(25)	221.2492(37)
B/MHz	11 757.0655(18)	11 680.3952(27)
C/MHz	11 532.9265(18)	11 459.1460(27)
D_N/kHz	17.5686(11)	17.3460(19)
D_{NK}/kHz	1206.35(23)	1191.12(47)
D_K/MHz^d	692	692
d_1/kHz	-0.3486(15)	-0.3354(22)
d_2/kHz	-0.0422(4)	-0.0444(5)
H_{NK}/Hz	0.52(9)	0.98(43)
H_{KN}/kHz	5.443(62)	5.19(14)
H_K/MHz^d	4.53	4.53
L_{KN}/Hz	-96.4(53)	-64.(11)
P_{KN}/Hz	1.45(19)	
T_{KN}/Hz	-0.0108(24)	
$\Delta_0/\text{amu } \text{\AA}^2$	0.10372	0.10366
σ/kHz	19.6	15.7

^a $H_{KN}, L_{KN}, P_{KN}, T_{KN}$ are coefficients of $N^2N_z^4, N^2N_z^6, N^2N_z^8, N^2N_z^{10}$, respectively. Δ_0 is the inertial defect. σ is the standard deviation of the fit.^bFit to 61 transitions with $N=10-9$ to $17-16$ and $K_a=0-0$ to $6-6$.^cFit to 29 transitions with $N=12-11$ to $16-15$ and $K_a=0-0$ to $3-3$.^dParameter constrained to value reported in Ref. 13.

TABLE III. Parameters from least-squares fit to AgOH transitions.

Parameter	$^{107}\text{AgOH}^a$	$^{109}\text{AgOH}^a$
A/GHz	666.1(8)	666.7(7)
$1/2(B+C)/\text{MHz}$	8255.4170(6)	8234.8136(6)
$(B-C)/\text{MHz}$	116.3036(25)	115.7302(23)
B/MHz	8313.5688(19)	8292.6787(18)
C/MHz	8197.2652(19)	8176.9485(18)
D_N/kHz	9.60380(44)	9.555 95(37)
D_{NK}/kHz	817.16(43)	813.30(38)
D_K/MHz^b	692.	692.
d_1/kHz	-0.1278(8)	-0.1287(7)
d_2/kHz	-0.001 146(42)	-0.001 106(37)
H_{KN}/kHz	2.93(7)	2.86(7)
H_K/MHz^b	4.53	4.53
L_{KN}/Hz	-35.0(45)	-31.5(40)
P_{KN}/Hz	0.29(9)	0.22(8)
$\Delta_0/\text{amu } \text{\AA}^2$	0.1038(10)	0.1045(10)
σ/kHz	15.5	14.3

^aFit to 48 transitions with $N=16-15$ to $22-21$ and $K_a=0-0$ to $5-5$ for both species.^bParameter constrained to CuOH value.

TABLE IV. Geometrical parameters for CuOH and AgOH.

Parameter	CuOH ^a	AgOH ^b
$r_{M-O}/\text{\AA}$	1.7689(2)	2.016(2)
θ/degree	110.24(8)	108.3(2)
$r_{OH}/\text{\AA}$	0.952(5)	0.952

^aPartial r_s structure obtained from Ref. 13.^bGeometry derived from CuOH–AgOH geometry differences obtained in this work and CuOH r_s structure, r_{OH} are assumed to be equal.

quency for CuOH mean that the equivalent perturbation should not be seen until higher K_a levels. The K_a dependence of the effective $1/2(B+C)$ constant for CuOH does not show a negative deviation due to quasilinear behavior at least up $K_a=6$, though there is a noticeable reduction in the positive slope at the highest levels. As an alternative method of studying quasilinear behavior, it would be interesting to study the spectra of these metal hydroxides in the excited bending mode.

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