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Microwave spectra of CuOD and AgOD: Molecular structure and harmonic force field of CuOH and AgOH

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Pure rotational spectra are reported for the deuterated species of copper and silver hydroxide, ^{63}CuOD, ^{107}AgOD, and ^{109}AgOD. Together with the CuOH and AgOH data previously reported, a number of harmonic force constants were determined. These constants are interpreted in terms of the balance between competing ionic and covalent interactions. The harmonic force field allowed the r_z structures to be determined. Both molecules are strongly bent indicating considerable covalent character.

I. INTRODUCTION

There is now a considerable amount of high resolution spectroscopic data on diatomic transition metal radicals such as oxides, halides, nitrides, and hydrides.[1–5] Gas phase data of this type is helpful in understanding the often complex role the *d* electrons play in bonding. In contrast, polyatomic transition metal molecules have received much less attention. Some examples of recent polyatomics that have been studied include FeCO,[6] WCH,[7] $CuCl_2$,[8] and $NiCl_2$.[9] The lack of data is particularly true for the hydroxides. In a recent communication,[10] we reported rotational spectra of CuOH and AgOH obtained in a dc discharge absorption cell millimeter wave spectrometer. The only previous gas phase spectroscopic study of a transition metal hydroxide has been the electronic spectroscopy of CuOH.[11–13] Yet, metal hydroxides are an important class of radicals. As well as playing an important role in the interactions of water with metal surfaces,[14] they are also interesting from a theoretical point of view. Being isoelectronic with metal fluorides, they offer a simple extension of bonding models from diatomics to polyatomics. In particular, the M–O–H bond angle is a sensitive probe of ionic vs covalent interactions in the M–O bond. Highly ionic molecules like NaOH, KOH, and CaOH are found to be linear,[15–17] whilst at the other extreme, covalent molecules like H_2O and CH_3OH have strongly bent hydroxide bonds. The group III hydroxides, AlOH and InOH, lie somewhere in between being quasilinear, i.e., slightly bent but with a low barrier to linearity.[18,19] The influence of *d* electrons can be expected to play a major role in determining the structure of transition metal hydroxides perhaps leading to a wide range of geometries and there is therefore a need for rotational spectroscopic studies of these molecules.

The first rotationally resolved spectrum of a transition metal hydroxide was reported by Trkula and Harris in 1983,[11] who recorded an electronic spectrum of CuOH around 540 nm. Their spectrum showed clear evidence for a bent structure. Subsequent high resolution electronic spectra by Bernath and co-workers[12,13] resulted in more accurate rotational constants for the ground $\tilde{X}\,^1A'$ state and two electronically excited states labeled $\tilde{A}\,^1A'$ and $\tilde{B}\,^1A''$. From the partial r_s structure, they determined the bond angle to be about 110° in the ground state, indicating considerable covalent interaction in the Cu–O bond.

A number of *ab initio* calculations of CuOH have been reported,[20–22] of which the most recent by Mochizuki *et al.* was in reasonable agreement with the r_s structure. It was found that the effects of correlation among the Cu *d* electrons are very important for the calculation of the correct bond angle and also the electronic excitation energies. The importance of correlation seems to be a feature of transition metal bonding, earlier lower level calculations on CuOH overestimated the bond angle by about 20°.

In this paper, we report millimeter wave spectra of CuOD and AgOD. Together with our CuOH and AgOH data,[10] we have been able to determine a harmonic force field using the centrifugal distortion constants. Vibrationally averaged structures were calculated for CuOH and AgOH by correcting the observed rotational constants for the harmonic vibrational contributions. We found that the AgOH bond angle is very similar to that of CuOH indicating that the metal–oxygen bond is also similar in both molecules. A slightly smaller value for the AgOH angle may be the result of the longer Ag–O bond compared to Cu–O.

II. EXPERIMENT

The CuOD and AgOD spectra were recorded under similar conditions to the CuOH and AgOH spectra.[10] The molecules were produced in a 2 m long absorption cell by sputtering from copper or silver cathode electrodes in a dc discharge of a 20 mTorr 3:1 He/O_2 gas mixture. The optimum signals required flowing about 100 mTorr of D_2O through the cooled cell (held below 223 K) for 10–20 min before starting the measurements. Reactions at the metal surface would therefore seem to be important for production of the gas phase hydroxides. Millimeter wave radiation in the range 200–370 GHz was generated using free running klystrons and frequency multipliers and modulated at 50 kHz.[23] After passing through the cell, radiation was detected

TABLE I. Parameters from least-squares fit to CuOD transitions.

Parameter[a]	^{63}CuOD[b]
A/GHz[c]	372.5
$1/2\,(B+C)$/MHz	10 797.063 5(7)
$(B-C)$/MHz	343.9759(42)
B/MHz	10 969.0515
C/MHz	10 625.0760
D_N/kHz	14.9792(15)
D_{NK}/kHz	475.86(13)
D_K/MHz[c]	192
d_1/kHz	−0.5952(22)
d_2/kHz	−0.0851(4)
H_{NK}/Hz	1.47(15)
H_{KN}/kHz	0.046(12)
L_{KN}/Hz	−2.6(3)
Δ_0/amu Å^2	0.1350
σ/kHz	19.8

[a] H_{KN}, L_{KN}, are coefficients of $N^2N_z^4$, $N^2N_z^6$, respectively. Δ_0 is the inertial defect. σ is the standard deviation of the fit.

[b] Fit to 38 transitions with $N=12-11$ to $17-16$ and $K_a=0-0$ to $5-5$.

[c] Parameter constrained to value reported in Ref. 12.

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

Parameter	^{107}AgOD[a]	^{109}AgOD[a]
A/GHz	357.25(2)	357.27(3)
$1/2\,(B+C)$/MHz	7677.5924(3)	7657.5798(4)
$(B-C)$/MHz	180.8048(18)	179.8614(24)
B/MHz	7767.9948	7747.5104
C/MHz	7587.1900	7567.6490
D_N/kHz	8.1251(3)	8.0824(6)
D_{NK}/kHz	351.99(8)	349.80(10)
D_K/MHz[b]	180	180
d_1/kHz	−0.2099(4)	−0.2071(6)
d_2/kHz	−0.0241(1)	−0.0238(2)
H_{NK}/Hz	0.088(30)	0.16(3)
H_{KN}/kHz	0.147(7)	0.141(8)
L_{KN}/Hz	−1.24(20)	−1.21(20)
Δ_0/amu Å^2	0.1358	0.1358
σ/kHz	10	12

[a] Fit to 46 transitions with $N=19-18$ to $24-23$ and $K_a=0-0$ to $5-5$. for both species.

[c] Parameter estimated from the force field calculation.

at 100 kHz with a liquid helium cooled InSb detector. Measurement accuracy was estimated to be about 10–20 kHz.

III. RESULTS AND SPECTROSCOPIC ANALYSIS

All the observed spectra correspond to that of a closed shell near prolate asymmetric top. Predictions of a-type rotational transitions were made for ^{63}CuOD using the electronic spectra rotational constants.[12] A total of 39 a-type R branch transitions were measured ranging from $N=12-11$ to $17-16$ and $K_a=0-0$ to $5-5$ (i.e., $\Delta N=1$, $\Delta K_a=0$). As for CuOH, no quadrupole splitting was observed from the $I=3/2$ Cu nucleus.

For ^{107}AgOD and ^{109}AgOD (both silver isotopes are in roughly 50% abundance), predictions were made using the structure derived in our previous communication.[10] A total of 48 a-type rotational transitions were measured for both isotopic species, ranging from $N=19-18$ to $24-23$ and $K_a=0-0$ to $5-5$. Both silver isotopes have $I=1/2$ so no hyperfine splittings were expected. Two transitions, $22_{0,22}-21_{0,21}$ and $22_{3,20}-21_{3,19}$ were found to overlap for both isotopomers, and so were excluded from the least squares analysis.

As for our previous CuOH and AgOH spectra, the CuOD and AgOD transition frequencies were fitted to a standard Watson S reduced Hamiltonian, incorporating centrifugal distortion terms up to $N^2N_z^6$. The $K_a=3$ asymmetry splitting is calculated to be quite significant for the deuterated species (over 100 kHz); so although no splitting was observed, the mean of the two asymmetry components was used in the calculations. The CuOD A and D_K constants were held fixed to the values determined in Ref. 12 and H_K was set to zero. For AgOD, A was fitted and D_K set to 180 MHz, the value suggested by our force field calculations; the results being very insensitive to the value of D_K.

The results of the fits are shown in Tables I and II. The transition frequencies and residuals for all the observed isotopic species of CuOH and AgOH are given in tables in EPAPS.[24] Note that the A rotational constant is more precisely determined for AgOD than for AgOH because of the larger asymmetry.

IV. FORCE FIELD ANALYSIS

Information on the harmonic force field is desirable for two reasons. First, the force constants themselves provide useful data on the strengths of bonds and the response to deformations in the molecule. Secondly, they can also be used to correct the observed rotational constants for harmonic vibrational effects to produce zero point average rotational constants.[25–27] All the calculations were performed using the ASYM20 program of Hedberg and Mills,[28] which is capable of fitting a force field to a variety of experimental data.

An unsymmetrical bent triatomic molecule MOH has six independent force constants with respect to the internal coordinates, $\Delta r_{\mathrm{OH}}(\mathrm{r}_1)$, $\Delta\theta(\mathrm{r}_2)$, and $\Delta r_{\mathrm{MO}}(\mathrm{r}_3)$. For CuOH, five quartic centrifugal distortion parameters are available for ^{63}CuOH and ^{63}CuOD (though only four of them are independent in the harmonic approximation for a planar molecule). The ^{65}CuOH parameters are not so useful as they differ only slightly from those of ^{63}CuOH. In addition, bending vibrational frequencies were assigned for CuOH and CuOD from the gas phase emission spectra of Trkula and Harris.[11] Together, these constitute a data set sufficient to determine the force field. However, because of the lack of additional vibrational frequencies, it is advisable to be guided by previous work on related molecules in which a more extensive data set was available. Anderson *et al.*[29] reported calculations on ClOH using all three vibrational frequencies and centrifugal distortion constants for a number of isotopic species. We repeated the ClOH calculations using ASYM20 for a data set equivalent to that obtained for CuOH. This produced very little change in the force constants except for a 20% reduction in the O–H stretch f_{11}. Accordingly, we decided to fix this force constant in CuOH to the value for OH$^-$ (7.8 aJ Å^{-2}),[30] noting that the OH stretch force constants are very

TABLE III. Observed and calculated centrifugal distortion constants and vibrational frequencies of CuOH.

	^{63}CuOH		^{63}CuOD	
Parameter	obs	calc	obs	calc
D_N /kHz	17.57	17.68	14.98	15.05
D_{NK} /kHz	1206.3	1206.3	475.9	476.4
D_K /MHz	692[a]	590.0	192.0	192.8
d_1 /kHz	−0.349	−0.300	−0.595	−0.538
d_2 /kHz[b]	−0.042	−0.0237	−0.085	−0.057
ω_1 /cm^{-1}		3738		2718
ω_2 /cm^{-1}	743[c]	744	537[c]	535
ω_3 /cm^{-1}		628		633

[a] Value given weight of zero in the fit.

[b] d_2 commonly has larger errors than other parameters because the five calculated centrifugal constants are necessarily constrained by the planarity condition.

[c] Observed value from gas phase emission spectrum of Ref. 11.

TABLE IV. Harmonic force field for CuOH.

Force constant[a]	CuOH	*ab initio*[b]
f_{11} /aJ Å^{-2}	7.8[c]	9.15
f_{12} /aJ Å^{-1} rad^{-1}	0.464(21)	0.55
f_{22} /aJ rad^{-1}	0.3046(40)	0.24
f_{13} /aJ Å^{-2}	0.0[c]	
f_{23} /aJ Å^{-1} rad^{-1}	0.162(2)	0.28
f_{33} /aJ Å^{-2}	3.106(40)	3.03

[a] The internal coordinates used are $r_1 = \Delta r(\mathrm{OH}), r_2 = \Delta\theta(\mathrm{CuOH}), r_3 = \Delta r(\mathrm{CuO})$. The geometry used was the r_s structure of Ref. 12; $r_{\mathrm{CuO}} = 1.7689$ Å, $r_{\mathrm{CuO}} = 0.952$ Å, $\theta = 110.2°$.

[b] From Ref. 22.

[c] Parameter constrained in the fit.

similar for a range of molecules, such as OH^-, OH, ClOH, and H_2O. The calculations used the partial r_s structure previously determined for CuOH (Ref. 12) and the geometry derived for AgOH in our communication.[10]

From trial fits it became apparent that the stretch–stretch interaction force constant f_{13} was very poorly determined and so was constrained to zero. It was then found that removing a single item of data had very little effect on the fit except for the D_K parameter for the ^{63}CuOH isotopic species, which is by far the largest distortion parameter used (692 MHz) and is therefore likely to have the largest nonharmonic contribution (the value calculated for this parameter, on removing it from the fit, 590 MHz, has a 15% error). This assumption is consistent with related studies on other molecules. There is a clear correlation between the quasilinearity of a molecule, as estimated by the ratio of the A rotational constant to the lowest bending vibrational frequency, and the error in the calculated D_K parameter for the H-isotopic species (the errors for the D-isotopomer are much smaller by comparison). For ClOH, which is less quasilinear than CuOH, the calculated value of D_K for the ^{35}ClOH isotopic species (119 MHz) has an error of 8% compared to the observed value (130 MHz).[29] For the more quasilinear molecule HNCO, the percentage error for D_K was larger (26%).[31] For this reason, we believe that D_K for the ^{63}CuOH isotopomer contains a significant nonharmonic contribution and was omitted from the final fit. It should also be noted that, with this parameter removed, including f_{11} in the fit produced little change in the other force constants. Because the fitted value had a large uncertainty, 8.0 ± 0.7 aJ Å^{-2}, it was decided to keep it constrained to the OH^- value. The resulting fit to four force constants was quite satisfactory, with the data shown in Table III, and the force constants given in Table IV.

For AgOH, the lack of any vibrational data means that a general force field determination is not possible. However, the AgOH and AgOD inertial defects are virtually identical to those of CuOH and CuOD (0.104 and 0.135 amu Å^2, respectively), and as the bending vibration gives the largest contribution to the inertial defect, this suggests that the bending force constants f_{22} are also very similar. When the AgOH and AgOD centrifugal distortion constants were calculated using the CuOH force field, good agreement was achieved with the exception of D_N. As the Ag–O stretch f_{33} gives the largest contribution to D_N, this was then floated in a least squares fit and a value of 2.32(2) aJ Å^{-2} was determined. We believe the fit gives a reliable value for f_{33} and reasonable values for the harmonic corrections to the rotational constants (from the reasonable conclusion that all the other force constants are very similar to those of CuOH). It is possible to float other force constants simultaneously; however, because of strong correlations between f_{22}, f_{12}, and f_{23} their reliability would be difficult to acertain. The three vibrational frequencies calculated from the AgOH force field are 3738, 738, 517 cm^{-1} (AgOH) and 2718, 552, 498 cm^{-1} (AgOD).

V. VIBRATIONALLY AVERAGED STRUCTURE

The vibrationally averaged, or r_z structure is calculated by correcting the observed rotational constants for harmonic vibrational effects.[25–27] The resulting constants have very small residual inertial defects (for planar molecules) and so give a more consistent molecular geometry. The harmonic corrections were calculated using the relation

$$B_z^r - B_0^r = \sum_v 1/2\alpha_v^r(\mathrm{har}), \tag{1}$$

where the sum is over all vibrational modes v, and r refers to the inertial axes x,y,z. α_v^r(har), the harmonic contributions to the vibration-rotation constants, were calculated from the molecular force constants using the ASYM20 program by the standard method.[28]

In addition, small corrections due to centrifugal distortion contributions to the S reduced rotational constants were also made.[32,33] The resulting vibrationally averaged constants A_z, B_z, C_z for CuOH and AgOH are given in Tables V and VI. The residual inertial defects are satisfactorily small, indicating that the force fields used give a reliable estimate of the harmonic contributions.

The r_z geometry was determined by a fit of the averaged constants, for the various isotopic species, to the parameters r_{MO}, r_{OH}, and θ. In general, it is necessary to account for a slight reduction in the averaged r_{OD} bond length compared to r_{OH} due to anharmonic effects,[34] (typically 0.002–0.004 Å). However, the data set is not very sensitive to such effects and

TABLE V. Vibrationally averaged rotational constants of CuOH.

Constant	^{63}CuOH	^{65}CuOH	^{63}CuOD
A_z/GHz[a]	667.27	667.25	362.36
B_z/MHz[b]	11 719.426	11 643.165	10 931.743
C_z/MHz[b]	11 515.89	11 442.258	10 611.092
Δ_z[c]/amu Å^2	0.0047	0.0047	0.0023

[a] Estimated reliability of harmonic corrections, 1 GHz.
[b] Estimated reliability of harmonic corrections, 1 MHz.
[c] Residual inertial defect.

the minimum standard deviation of the fit was achieved with the same value for r_{OH} and r_{OD}. The geometrical parameters from the fits are given in Table VII.

VI. DISCUSSION

The CuOH r_z structure is consistent with the partial r_s structure of Ref. 12. The slightly longer r_z CuO and OH distances (by 0.003 and 0.013 Å, respectively) are similar to that observed in other molecules and are due to vibrational anharmonicity.[26] The two values for the bond angle are remarkably similar. In our previous communication,[10] we determined the difference in the AgOH and CuOH geometry from just one isotopic species assuming the OH bond length was the same for both molecules. The present determination makes no such assumption and gives a more precise and reliable AgOH geometry, but does not differ appreciably from that in Ref. 10. The OH bond length is found to be almost identical in both molecules (0.964 Å), which is consistent with a similar electronic structure (largely OH^-). Thus both molecules would seem to be fairly ionic ($\mathrm{M}^+ - \mathrm{OH}^-$) but with similar amounts of covalent character giving rise to a bent geometry.

The similarity of the AgOH and CuOH bond angles is good evidence that the balance between ionic and covalent interactions is roughly the same. This is understandable given that both the copper and silver ionization potentials (7.725 and 7.576 eV) and the Pauling electronegativities (1.9 and 1.93, respectively) are similar. Although the dominant metal atom configurations for the covalent structure are $3d^{10}4s^1$ (Cu) and $4d^{10}5s^1$, (Ag) SCF calculations using this configuration gave bond angles of 130°, about 20° too large.[21] The effects of electron correlation for the metal d electrons are important and have the effect of mixing in excited configurations (e.g., $3d^9 4s^2$), enhancing covalent overlap and reducing the bond angle.[22]

The difference in the Ag–O and Cu–O bond lengths (0.247 Å) is mainly due to the larger ionic radius of Ag compared to Cu. The difference compares favorably with that between AgF and CuF (0.238 Å).[1] Although similar, there is a noticable decrease of about 2.3° in the AgOH bond angle from CuOH. This may result from the larger metal–oxygen distance for AgOH. The bond angle is the result of a balance between ionic repulsion between the positive charges on the metal and H atoms tending to increase the angle towards linearity and covalent orbital overlap tending to decrease the angle. The longer Ag–O bond means a reduced electrostatic repulsion between Ag and H, allowing the angle to decrease in order to enhance the covalent stabilization.

TABLE VI. Vibrationally averaged rotational constants of AgOH.

Parameter	^{107}AgOH	^{109}AgOH	^{107}AgOD	^{109}AgOD
A_z/GHz	645.64	646.24	348.52	348.54
B_z/MHz	8292.087	8271.282	7746.743	7726.357
C_z/MHz	8186.391	8166.112	7578.145	7558.642
Δ/amu Å^2	0.0041	0.0041	0.0013	0.0013

TABLE VII. The r_z structure for CuOH and AgOH.

Parameter	CuOH	AgOH
r_{M-O}/Å	1.77182(3)	2.01849(4)
θ/deg	110.12(30)	107.81(2)
r_{O-H}/Å	0.9646(3)	0.9639(1)

The force constants are best discussed by comparison with other related metal containing molecules, especially hydroxides and the isoelectronic fluorides. Table VIII lists the metal–F/O stretching force constants for a number of metal hydroxides and fluorides for which data is available.

The reduction in the M–O stretch force constant from CuOH to AgOH closely matches that between CuF and AgF. This is presumably due to the reduced ionic attraction for the longer Ag–O bond. In fact, this seems to be a general trend for all the metal hydroxides and fluorides, especially within a group; longer bond lengths mean smaller force constants. There is also a small but consistent reduction between the MF and MOH values, which again correlates with the slightly longer M–O vs M–F bond length (a difference of about 0.02 to 0.03 Å).

There are not very many MOH molecules with which to compare bending force constants. Those available are listed in Table IX, where we have derived the value for CaOH from the observed bending frequency.[35] All the linear metal hydroxides have very low force constants. This is understandable if the restoring force to deformation comes from the repulsion between the positive charges on the M and H

TABLE VIII. A comparison of metal stretch force constants and bond lengths for some hydroxides and fluorides.

Molecule	f_{MO} or f_{MF}/aJ Å^{-2}	r_{MO} or r_{MF}/Å
CuOH[a]	3.105	1.771
CuF[b]	3.33	1.75
AgOH[a]	2.32	2.016
AgF[b]	2.51	1.98
CaOH[c]	2.6	1.985
CaF[d]	2.63	1.952
KOH[e]	1.3	2.2
KF[b]	1.38	2.171
RbOH[f]	1.05	2.301
RbF[b]	1.29	2.27

[a] This work.
[b] Reference 1.
[c] Reference 35.
[d] Reference 36.
[e] Reference 37.
[f] Reference 38.

TABLE IX. Comparison of bending force constants for some hydroxides.

Molecule	f_b/aJ rad^{-1}
CuOH[a]	0.305
KOH[b]	0.05
RbOH[c]	0.046
CaOH[d]	0.05
ClOH[e]	0.796

[a]This work.
[b]Reference 37.
[c]Reference 38.
[d]Reference 35.
[e]Reference 29.

atoms, rather than a change in orbital overlap. At linearity, the rate of change of the M–H separation with the bond angle is zero. It is of interest to examine how this simple electrostatic model works for the linear hydroxides. In order to calculate the bending force constant, we assume that the bending potential is given by the electrostatic repulsion between two positive point charges on the metal (M) and the H atoms (δ_M, δ_H,) see Fig. 1.

Equation (2) gives the potential as a function of the M–H distance r, where $r^2 = r_{MO}^2 + r_{OH}^2 + 2r_{MO} \cdot r_{OH} \cdot \cos\phi$,

$$V(\phi) = \frac{\delta_M \delta_H}{4\pi\varepsilon r}. \tag{2}$$

For small values of ϕ the potential can be expanded to give

$$V = \frac{\delta_M \delta_H}{4\pi\varepsilon(r_{MO}+r_{OH})} + \frac{\delta_M \delta_H r_{MO} r_{OH} \phi^2}{8\pi\varepsilon(r_{MO}+r_{OH})^3}. \tag{3}$$

Hence, the bending force constant, which is derived from $V = \frac{1}{2} f_b \cdot \phi^2$, is

$$f_b = \frac{\delta_M \delta_H r_{MO} r_{OH}}{4\pi\varepsilon(r_{MO}+r_{OH})^3}. \tag{4}$$

Using RbOH as an example, $r_{MO} = 2.3$ Å, $r_{OH} = 0.957$ Å. Estimating δ_M as $+0.8\ e$ [values for the ionic character of alkali metal halides range from 70% to 100% (Ref. 31)] and δ_H as around $+0.3\ e$ [from an SCF charge calculated for CuOH (Ref. 22)], f_b is calculated to be 0.035 aJ rad^{-1}, compared to the observed value of 0.046. Considering its highly simplistic nature, the model seems to give a reasonable semiquantitative picture of the bending potential and certainly correctly predicts the low values of the bending force constant.

Clearly, the electrostatic model cannot be used for the bent CuOH and AgOH molecules. Their bending force constants lie between those of the linear molecules and strongly bent covalent hydroxides like ClOH.

The CuOH stretch–bend interaction force constants, f_{12}, f_{23}, are also interesting. Both are positive, which means that a stretching of either the Cu–O or O–H bonds results in a smaller bond angle. The explanation may be related to the explanation of the smaller bond angle of AgOH; when the Cu–O bond is stretched the Cu–H separation increases, reducing the electrostatic repulsion and allowing the bond angle to become smaller in order to enhance the covalent orbital overlap. If this was the sole effect, the stretch–bend constants for the Cu–O and O–H stretches should be similar (though not identical because of the different bond lengths). However, the O–H interaction constant is roughly three times larger. The main difference between the two bonds is that the OH^- subunit is largely covalent rather than largely ionic. *Ab initio* calculations for OH^- show a strong reduction in the dipole moment with internuclear distance, which indicates a reduction in the positive charge on the H atom.[39] This suggests that as the O–H bond is stretched, not only is the Cu–H distance increased, but the positive charge on the H atom is simultaneously decreasing giving a much stronger decrease in the electrostatic repulsion.

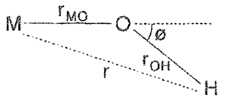

FIG. 1. The relationship between the M–H distance and the bending angle ϕ for a linear MOH molecule.

Finally, Table IV also lists the *ab initio* force constants calculated by Mochizuki *et al.*[22] There is reasonably good, in some cases semiquantitative, agreement, with our experimental values. This is consistent with the agreement with the geometry and electronic excitation energies, suggesting that the level of calculation (SDCI) gives a reasonable account of the complex electrostatic and covalent interactions in this molecule. It is desirable to carry out further investigations of the properties of CuOH and AgOH (such as dipole moment and electric quadrupole moments) and other transition metal hydroxides.

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