Pressure-induced OH frequency downshift in Brucite: frequency-distance and frequency-field correlations

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Abstract. The ordered Mg(OH)$_2$ crystal structure has been optimized for different pressures in the pressure range 0–21 GPa, within the trigonal P$ar{3}$m1 space group. Anharmonic frequencies for the Raman-active OH vibrational mode were calculated from potential energy curves obtained by B3LYP and PW91 calculations with the CRYSTAL06 program. We find that an external pressure leads to an OH frequency downshift, in agreement with experiment, but there are no hydrogen bonds involved. The frequency downshift depends linearly on the electric field exerted on the OH$^-$ ions from its neighbours in the "opposite" layer. In agreement with experiment we also find that the pressure-induced $\nu$(OH) vs. interlayer R(O • • • O) curve deviates from the well established correlation curves for hydrogen-bonded systems in the literature; the $\Delta\nu/\Delta R$ slope for high pressure conditions is much smaller. We also point out the merits of reporting both $\nu$(OH) and $\Delta\nu$gas-to-solid for comparison with experiment.

1. Introduction
IR and Raman spectroscopy, together with X-ray and neutron diffraction, are the most important techniques for identification and characterization of OH groups in the solid phase. The experimental literature for crystalline hydrates reveals a clear correlation between the intramolecular OH stretching vibrational frequencies and the intermolecular equilibrium R$_e$(O • • • O) distances, as shown in the lower part of Figure 1. Also hydroxides and oxohydroxides appear to fit quite well onto the same correlation curve [1]. In short, the correlation curve in Figure 1 communicates that the stronger the intermolecular interaction, the larger the $\nu$(OH) frequency downshift, or the "OH softening", at ambient conditions.

It has been noted in the literature that for non-zero pressures, the usual correlation curves for hydrogen-bonded systems do not necessarily hold. This was demonstrated by Besson et al. [6] for the correlation between R(O • • • O) and the intramolecular r(O–H) distance in ice VIII. Using neutron diffraction, they found that a substantial pressure-induced shortening of the R(O • • • O) distance is accompanied by a tiny change in r(O–H), much smaller than expected from traditional $R_e$ vs. $r'$ correlation curves. Silvi [7] rationalised this behaviour by calculating a (very small) value for the $\partial\Delta r/\partial R$ slope based on the electrostatic dipole-dipole interactions between a central water molecule and its neighbours within a large sphere.

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Metal hydroxides constitute a particularly interesting category of OH-containing compounds with respect to these correlations. An applied pressure is often found to induce a softening of the O-H bond (see, e.g., Ref. 8), but with "a smaller slope" than predicted by the regular \( \nu \) vs. Re' correlation curve.

The pressure-induced frequency shift of the Raman-active OH stretching mode in the brucite crystal, \( \text{Mg(OH)}_2 \), is shown as an example in the upper part of Fig. 1. The frequency downshift has often been referred to as pressure-induced hydrogen bonding in the literature, i.e. it is common to explain the observations in terms of traditional H-bond relationships. But the brucite structure consists of neutral \( \text{Mg(OH)}_2 \) sheets, held together by staggered weak O\( \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ ·\ −1 \cdot 10^6 \text{ atm} \cdot \text{ K}^{-1}

Numerous experimental investigations of structure, vibrations and other properties of brucite have been presented in the literature. Also the theoretical and computational literature is vast. Earlier work of particular relevance to the current study are the Mg(OH)\(_2\) ab initio calculations of Sherman [9], Baranek et al. [10] and of D'Arco et al. [11], the ab initio, B3LYP and DFT calculations of Pascale et al. [12] and Ugliengo et al. [13], the (static) DFT calculations by Winkler et al. [14] and the dynamic DFT calculations (CPMD) of Raugei et al. [15]. Out of these, Refs. 9 and 15 focus on non-zero pressure behaviour.

Here we have studied the Mg(OH)\(_2\) crystal at ambient and high pressure conditions with the help of ab initio calculations using the CRYSTAL06 [16] program. Section 2 describes the computational methods we used. Sections 3.1 and 3.2 report the optimized structure and (anharmonic) Raman-active OH frequency at 0 and high pressure, respectively. In Section 3.3, the virtues of presenting both absolute frequencies and gas-to-solid frequency shifts will be discussed.
2. Computational details

2.1 The Mg(OH)$_2$ crystal

Systems and overview. Calculations for the brucite bulk crystal were performed within the centrosymmetric P$3_1m1$ space group (trigonal, no. 164); see Figure 2. The crystal structure was optimized at different external pressures, and OH vibrational frequencies were calculated (see below). Calculations were also performed for crystalline fragments (clusters) taken out of the bulk, with the atomic positions kept at the optimized crystal values. The CRYSTAL06 program [16] was used.

Hamiltonians. The calculations were performed with the B3LYP hybrid method [17, 18] and with the Perdew-Wang 91 (PW91) [19-21] DFT functional. The main results presented here are calculated with the B3LYP method.

Basis sets. The 8-411G* and -31G* basis sets from Ojamäe et al. [22] for O and H, respectively, and the 8-511G basis from Catti et al. [23] for Mg, were used for most of the calculations. We will refer to these basis sets collectively as "TZVP".

Frequency calculations. Anharmonic OH frequencies, $\nu$(OH), were calculated using a normal-mode following procedure for the symmetric A$_{1g}$ mode. This mode consist of the simultaneous stretching of the two OH bonds in the crystallographic cell with a displacement coordinate $q = (\Delta r_{OH1} + \Delta r_{OH2})/2$, where $\Delta r_{OH} = r_{OH} - r_{e,OH}$. Potential energy curves were calculated and the time-independent Schrödinger equation in one dimension was solved, using the VIBRO program by Wójcik et al. [24].

The potential energy curve was calculated from 15 pointwise single-point energy calculations with the CRYSTAL program, allowing $q$ to vary with a step-size of 0.015 Å. The center of mass of each OH group was kept fixed during the displacements. A polynomial in $\Delta q$ was fitted to each curve (giving also the minimum-energy value, $r_e$) and transformed into so-called rho coordinates [25]. The vibrational Schrödinger equation was solved variationally using 15 harmonic oscillator functions as basis functions. The energy difference between the ground level and the first excited level in each case gives the 1-dimensional anharmonic vibrational frequencies reported in this paper. Harmonic frequencies, $\omega$(OH), were calculated from the second-order force constants.

In certain cases, $\nu$(OH) for Mg(OH)$_2$ was corrected for the basis-set superposition error (BSSE), using the counterpoise (CP) procedure of Boys and Bernardi [26]. The frequency was then calculated using a CP-corrected potential energy curve, where two types of BSSE contributions were added to the potential energy curve for the Mg(OH)$_2$ crystal, thereby accounting for the effect of the basis-set overlap from the OH neighbours onto OH, and vice versa. These estimates were derived with the help of energy calculations for supercells containing (i) one OH$^-$ ion in the supercell and all other atoms treated as ghosts, (ii) all atoms in the supercell except one OH$^-$ ion which was treated as ghost atoms, (iii) all atoms in the supercell except one OH$^-$ ion which was completely removed, and (iv) only one OH$^-$ in the supercell.

Electric field calculations. We define "the intermolecular electric field" at the H atom as the electric field arising from all cations and anions outside the OH$^-$ ion itself. We are only concerned with the field component along the OH bond since we have previously found that only this has an appreciable effect on the OH frequency [27]. The direction of the field is defined as positive for the most stable field orientation, namely as $+\text{O}\text{H}^+ -\text{H}^-$. We have calculated the field by using a 3 x 3 x 2 supercell, removing one OH$^-$ ion from the cell, and then calculating the field from the remainder of the crystal at the (old) H position.

2.2. The isolated ion

For the isolated OH$^-$ ion, the Gaussian03 program was used [28], with a range of basis sets and methods; references are given in the Table captions. Anharmonic and harmonic frequencies were calculated with the VIBRO program.
3. Results

3.1 Structure and frequency shift at ambient pressure

The optimized cell parameters and atomic coordinates resulting from the present B3LYP/"TZVP" and PW91/"TZVP" calculations at ambient pressure are given in Table 1. The results from the calculations by Baranek et al. [10] and Pascale et al. [12], where 8-511G*/8-411G*/-211G* bases were used for Mg/O/H, are given for comparison. The structures reported by the various authors are in good agreement and the agreement with experiment is also quite good, except for the \( c \) parameter resulting from B3LYP, which is too long, especially considering that BSSE effects underestimate the \( c \) axis by some 0.1 Å (Pascale et al. report a CP-corrected \( c \) parameter value of 4.957 Å at the B3LYP level).

Our calculated value for the bulk modulus (\( K_0 \)) of brucite is 33 GPa at the B3LYP level, smaller than (most of) the the experimental values reported; the more recent measurements appear to agree on a value around 40 GPa. Recent plane-wave DFT calculations of ours with the PW91 functional give a value of 39.7 GPa [31].

The interlayer interaction in Mg(OH)\(_2\) is weak. This was shown at the Hartree-Fock level by D’Arco et al. [11] who obtained an interlayer interaction energy of 5 kJ/mol (for an optimized \( c \) parameter of 5.35 Å). We also constructed an artificial crystal with elongated \( c \) axis and let the layers approach each other; the resulting potential energy curve has a minimum of \(-9\) kJ/mol (BSSE-uncorrected) at the B3LYP level.

Anharmonic OH frequencies were calculated in this study and are also given in Table 1. Our values at the B3LYP and PW91 levels are 3670 and 3456 cm\(^{-1}\), respectively. Both are seen to be in reasonable agreement with the corresponding results from Pascale et al. [12], but only the B3LYP value is in good agreement with the experimental value of 3654 cm\(^{-1}\).

In Figure 3 we show how the OH\(^-\) ion's electron density is distorted when neighbours are successively added around the ion, i.e. as the crystal is "built up" from the isolated OH\(^-\) ion to the \((\text{Mg}^{2+})_3\text{OH}^-\) cluster (Figure 3a) → the Mg(OH)\(_2\) slab (Figure 3b) → the Mg(OH)\(_2\) crystal (Figure 3c). The calculated OH frequencies for the same systems are also given in the figure. A comparison of Figures 3a and b shows that the hydroxide ion's next-nearest neighbours (and beyond) in the slab partially reverse the electron redistribution caused by the three nearest-neighbour Mg\(^{2+}\) ions. A comparison of Figures 3b and c confirms that the O–H - - - H–O interlayer interaction gives rise to only a small electron density rearrangement (cf. also Fig. 5e in Ref. 11). The interlayer interaction lowers the OH frequency by \(-85\) cm\(^{-1}\). The frequency follows the trend we have previously found for the isolated OH\(^-\) ion in an electric field [32, 33]; a weak electric field gives rise to an OH frequency
upshift, which turns into a large downshift as the field gradually increases.

\[ \Delta \rho(r) = \rho_{\text{cluster/slab/solid}} - \sum \rho(\text{isolated ions}) \]

**Figure 3.** Difference electron density (defined in the figure title; section through Mg-O-H plane) and OH frequency for brucite and fragments of the crystal. The isolated-ion frequency with the same method is 3511 cm\(^{-1}\). All atomic positions are taken from the optimized Mg(OH)\(_2\) crystal. Contour interval: \(\pm 0.01 \text{ e/Å}^3 = \pm 0.0675 \text{ e/Å}^3\). Solid lines indicate electron excess, dashed line electron loss; the zero contour is omitted. B3LYP/TZVP calculations.

### 3.2 Structure - frequency correlation at high pressure

The Mg(OH)\(_2\) crystal structure was optimized for a series of fixed volumes at the B3LYP level and the pressure and the Raman OH frequency were calculated. (Figure 4). The resulting structures at ~10 and ~20 GPa are compared with experiment in Table 2. The overall agreement is good.

The frequency vs. P dependence is plotted in Figure 4. As in experiment, we find an OH softening as pressure increases. The agreement with experiment is only qualitative, however. The experimental value for the \(d\nu/dP\) slope is \(-7.7 \text{ cm}^{-1}/\text{GPa}\) for the Raman-active mode [5]; our slope is about half of this value and our curve is markedly non-linear at higher pressures, contrary to experiment.

| Table 2. | Comparison of our optimized Mg(OH)\(_2\) structure (B3LYP/TVP method) with available experimental data at two selected pressures, ~10 GPa and ~20 GPa. |
|----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Ref.     | Method       | P (GPa) | a (Å)  | c (Å)  | \(z_o\) |
| This work | B3LYP        | 9.2     | 3.097  | 4.409  | .2354   |
| Catti95 [3] | ND         | 10.9    | 3.047  | 4.355  | .2357   |
| Parise94 [34] | ND      | 9.3     | 3.037  | 4.403  | .232    |
| Nagai 00 [4] | ND         | 8.9     | 3.053  | 4.475  | .246    |
| This work | B3LYP        | 21.1    | 3.021  | 4.238  | .2434   |
| Nagai 00 [4] | ND         | 18.0    | 2.984  | 4.294  | .25     |

\(\nu(\text{OH})\) is plotted against the "intermolecular electric field" in Figure 5. We find a linear correlation. This provides a clue to the OH softening, suggesting that the electric field from the hydroxide ion's neighbours play an important role in determining the OH frequency shift (together
with electronic overlap effects). In fact, the frequency-field variation is consistent in sign and magnitude with our earlier findings for the isolated OH$^-$ ion in an electric field [33]. For Mg(OH)$_2$, the field variation with pressure originates almost exclusively from the field variation caused by the "opposite layer" across the gap in the crystal. This field is positive (as seen on the x-axis in Figure 5) and, based on the results in Refs. 32-33, it is expected to give a downshift contribution, which indeed it does. This downshift will be partly, but only partly, counteracted by an upshift originating from intermolecular electronic overlap, and the net result is a downshift.

We will now return to the 'ν(OH) vs. R(O • • • O)' correlation curves discussed in the introduction. Our calculated data are shown as the uppermost curve in Figure 1 and agree with the experimental finding that the pressure-induced correlation is different from the usual hydrogen-bond correlation. The experimental and calculated slopes agree well.

3.3 Gas-to-solid frequency shifts
The experimental gas-to-crystal frequency shifts, Δν(OH), is approximately +100 cm$^{-1}$ (Table 3), while our B3LYP/TZVP value is quite a bit larger, namely approximately +160 cm$^{-1}$. The PW91/TZVP shift agrees well with experiment, but the absolute value does not, so that situation is not very satisfactory either. Also the basis set from Ref. 12 is seen to give unsatisfactory agreement with experiment for the frequency shifts. The free-ion frequencies are given in Table 4 for several basis sets and methods.

Table 3. Anharmonic frequency (in cm$^{-1}$) calculated for the A$_{1g}$ mode of the Mg(OH)$_2$ crystal. Values in parenthesis have been corrected for the BSSE using the CP-method. The gas-phase values are listed in Table 4.

| Method | Basis-set ref. | $\nu_{an}$ BSSE-corr. in ( ) | $\Delta\nu_{an}$, gas-to-crystal BSSE-corr. in ( ) | Ref. |
|--------|----------------|-----------------------------|--------------------------------------------------|------|
| B3LYP  | Baranek01 [10] | 3638                        | Not given.                                       | Baranek01 [10] |
| B3LYP  | Pascale04 [12] | 3663                        | Not given.                                       | Pascale04 [12] |
| B3LYP  | Pascale04 [12] | 3662 (3561)                 | +236 (+135)                                      | This work |
| B3LYP  | TZVP           | 3671 (3654)                 | +160 (+143)                                      | This work |
| PW91   | Pascale04 [12] | 3480                        | Not given.                                       | Pascale04 [12] |
| PW91   | Pascale04 [12] | 3460 (3371)                 | +97 (+8)                                         | This work |
| PW91   | TZVP           | 3457 (3476)                 | +16 (+34)                                        | This work |
| Experiment |                | 3654                        | +98                                              | Duffy95 [5] |
Table 4. Optimized $r_e$ distance, and vibrational frequencies, calculated for the isolated OH (g) ion with different methods and basis sets. Experimental values from velocity modulation laser spectroscopic measurements are given for comparison. Within each "method category", the entries are listed in descending energy order. Entries that are at, or close to, the respective basis-set limit are highlighted in bold.

| Method                  | Basis-set                  | $E$ at min. (Hartree) | $r_e$(OH$^-$) (Å) | $\omega_{harm}$ (cm$^{-1}$) | $\nu_{anh}$ (cm$^{-1}$) | Ref.            |
|-------------------------|----------------------------|----------------------|-------------------|-----------------------------|------------------------|-----------------|
| MP2                     | "Extended basis" [32]       | $-75.7027$           | 0.965             | 3816                        | 3672                   | Hermansson91 [32]|
| MP4                     | "Extended basis" [32]       | $-75.7158$           | **0.969**         | **3722**                    | **3562**               | Hermansson91 [32]|
| B3LYP Pascale04         |                            | $-75.7593$           | 0.973             | 3602                        | 3426                   | This work       |
| B3LYP Pascale04 + ghosts|                            | $-75.7921$           | 0.970             | 3572                        | 3501                   | This work       |
| B3LYP TZVP              |                            | $-75.7670$           | 0.971             | 3754                        | 3511                   | This work       |
| B3LYP TZVP + ghosts     |                            | $-75.7896$           | 0.970             | 3719                        | 3547                   | This work       |
| B3LYP aug-cc-pV5Z       | [35]                       | $-75.8318$           | 0.964             | 3732                        | 3556                   | This work       |
| B3LYP Extended basis    | [32]                       | $-75.8386$           | **0.969**         | **3763**                    | **3590**               | This work       |
| B3LYP aug-cc-pV6Z       | [36]                       | $-75.8444$           | **0.964**         | **3762**                    | **3589**               | This work       |
| PW91 Pascale04          | [12]                       | $-75.7678$           | 0.980             | 3536                        | 3363                   | This work       |
| PW91 Pascale + ghosts   |                            | $-75.8035$           | 0.977             | 3658                        | 3486                   | This work       |
| PW91 TZVP               |                            | $-75.7757$           | 0.977             | 3609                        | 3441                   | This work       |
| PW91 TZVP + ghosts      |                            | $-75.8035$           | 0.977             | 3644                        | 3475                   | This work       |
| PW91 aug-cc-pV5Z        | [35]                       | $-75.8058$           | 0.972             | 3638                        | 3459                   | This work       |
| PW91 Extended basis     | [32]                       | $-75.8158$           | **0.974**         | **3671**                    | **3501**               | This work       |
| PW91 aug-cc-pV6Z        | [36]                       | $-75.8216$           | **0.972**         | **3670**                    | **3500**               | This work       |

**Experiment**            |                            | 0.96431             | 3738.4            | 3555.61                     | Owrutsky85 [37]      |

Frequency shifts which have been CP-corrected for the BSSE are also listed in parentheses in Table 3. We now note that the B3LYP calculations with the TZVP basis set are in fair agreement with experiment, both for the absolute frequency and the gas-to-solid frequency shift. However, also such agreement should be interpreted with caution, and could still be a results of error cancellations. For example, it should be noted that we have not taken anharmonic couplings between the $A_{1g}$ and $A_{2u}$ modes into account in our vibrational model. Such effects may have considerable impact on the calculated Raman frequency in brucite.

4. Concluding remarks

It is important to understand the variation of OH frequencies with environment and pressure in metal hydroxides since vibrational spectroscopy is one of the major research tools in structural mineralogy and OH groups play a vital role for the functionality of many metal oxide surfaces. The focus of this paper is the understanding of frequency-structure correlations, in particular the frequency-structure correlations in brucite at higher pressure. We find a similar pressure-induced $dv/dR(O \cdots O)$ slope as in experiment, a slope which is much smaller than the $dv/dR_e(O \cdots O)$ slopes found for H-bonded crystals at ambient conditions. The pressure-induced frequency shift can largely be viewed as an effect of the variation of the electric field strength from the "opposite layer" as the crystal is compressed. Although electrostatic interactions do not necessarily exclude hydrogen bonding, H-bonds can nevertheless not be present in this structure because of the awkward staggered OH arrangement.

We have also discussed some of the difficulties involved in calculating OH frequency shifts. Despite such difficulties, it is important to report the shifts since they provide an additional probe by which to judge the quality of the calculated results.
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