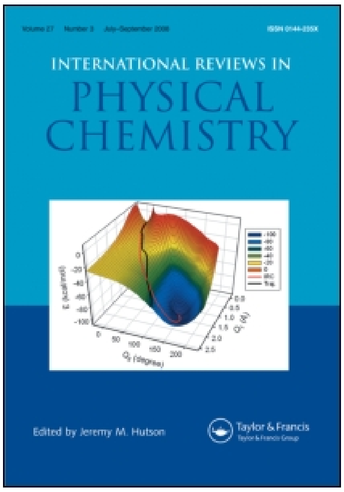

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# The equilibrium OH bond length

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# The equilibrium OH bond length

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The equilibrium structure of 36 small molecules containing OH bonds, including molecules with an internal hydrogen bond, is reviewed from the literature. The structures are redetermined or determined, if necessary, using high level *ab initio* calculations at the CCSD(T) level of theory with basis sets of quintuple zeta quality and with a correction for the core correlation. The possibility of calculating accurate *ab initio* OH bond lengths at different levels of theory (MP2/VTZ, MP2/VQZ, CCSD(T)/VTZ, and CCSD(T)/AVTZ) is examined. All methods agree provided a small offset correction is taken into account. In most cases, the addition of diffuse functions does not improve the results. The MP2 method appears to be satisfactory whenever the non-dynamical electron correlation is small, which is the most typical situation. The various results are merged to demonstrate the following quantitative correlation between $r_e$(OH) and 'isolated' OH stretching frequencies, relevant for predictive use: $r_e(\mathrm{OH})\ [\text{Å}] = 1.2261(76) - 7.29(21) \times 10^{-5}\ \nu_{is}(\mathrm{OH})\ [\mathrm{cm}^{-1}]$.

## Contents

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## 1. Introduction

The hydroxyl group (OH) is extremely important in chemistry and biochemistry. It is the functional group in alcohols, carboxylic acids, amino acids, hydroxides, and carbohydrates. It also plays a key role in many intra- and intermolecular hydrogen bonds. Detailed studies have demonstrated that the variation of the equilibrium OH bond length, $r_e$(OH), is strongly dependent on the intramolecular electronic environment. Large changes result for instance from hydrogen bonding. The goal of this paper is to search for a correlation between $r_e$(OH) and the corresponding isolated stretching frequency $\nu_{is}$(OH). Such a relationship, known to occur for CH [1] and NH [2], was predicted by Cox *et al.* [3] for OH bonds.

However, related data in the literature are still scarce and, sometimes not that accurate. We therefore first critically review the existing data on the O–H bond length, in a way as exhaustive as possible. We then improve the available information, if needed, and extend it to additional species by calculating the OH bond lengths using high level *ab initio* methods, in particular. The new set of species considered ensures optimal relevance of the results in various research areas, thus selecting each time prototype molecules.

In this paper, we shall concentrate on the determination of O–H bond lengths, on the one hand, and of isolated OH stretching frequencies, on the other. As far as the geometrical structure is concerned, one can calculate it in various ways. It may for instance be determined from rotational constants if one knows these for the substituted X–D species, as well. Such a H $\rightarrow$ D substitution unfortunately usually considerably modifies the vibration–rotation interaction parameters. The constants from different isotopologues can therefore not be easily merged in a single procedure, preventing access to reliable empirical $r_0$, $r_s$, and even $r_m$ structures [4]. Concerning the isolated OH stretching frequency, $\nu_{is}$(OH), there are two main methods. One can first use selective deuteriation, this time of all XH bonds but the relevant OH one. One therefore decouples the OH group of interest from the rest of the molecule in order to make sure that the OH stretching frequency (usually labeled $\nu_1$) is not affected. The main difficulty is often to synthesize a molecule where all hydrogens but one have been replaced by deuterium. Literature results actually indicate that the coupling between the OH stretch and the remaining vibrational modes is generally weak. In a few cases, however, the stretch vibration is perturbed by some resonance and, except if a detailed vibration–rotation analysis was carried out to provide a deperturbed stretching frequency, another method is required.

The second method for determining isolated OH stretching frequencies relies on data from overtone bands, i.e. resulting from the multiexcitation of a single vibration mode. It is well known that the motions of the individual bonds become increasingly localized upon increasing excitation and thus decreasingly affected by internal couplings [5]. The band origin of as many overtones of the OH stretch as possible needs to be measured and inserted into a so-called Birge–Sponer plot [6]:

$$\nu = v\tilde{\omega} - v(v+1)\tilde{\omega}x \tag{1}$$

where $\tilde{\omega}$ is the mechanical frequency, $\tilde{\omega}x$ the first anharmonic correction term, and $v$ the vibrational quantum number. This procedure thus also allows the frequency of the ‘unperturbed’ fundamental band, $\nu_{is}$(OH), to be determined:

$$\nu_{is} = \tilde{\omega} - 2\tilde{\omega}x \tag{2}$$

The major advantage of this second method is to avoid isotopic labelling. In addition, OH stretching overtone bands happen to be quite narrow, and their origin can be precisely determined, actually more precisely compared to other X–H bond overtone bands (X=C or N).

The paper is organized as follows. Section 2 provides a description of the *ab initio* methods used to calculate equilibrium structures. Section 3 reviews accurate structures available in the literature. Section 4 is devoted to structure calculations intended to both improve some of the literature results and address additional species. Various complementary information is reviewed at the same time. In section 5 is presented the resulting correlation between OH bond length and stretching frequency. The internal hydrogen bond issue is discussed in section 6, before concluding in section 7.

## 2. Methods of computation

Most correlated-level *ab initio* electronic structure computations of the present study have been carried out at two levels of calculation: second-order Møller–Plesset perturbation theory (MP2) [7] and coupled cluster (CC) theory with single and double excitation [8] augmented by a quasi-perturbative analysis for triple excitations [CCSD(T)] [9]. We extensively used correlation-consistent polarized *n*-tuple zeta basis sets cc-pV*n*Z [10] with $n \in \{D, T, Q, 5, 6\}$, that are abbreviated as V*n*Z in the text. We also used mixed basis sets composed of, for example, V5Z on all non-hydrogen atoms and VQZ on H atoms, denoted as V(Q, 5)Z. Such basis sets are not supposed to significantly reduce the accuracy compared to the use of the full set on all atoms while reducing the computation time significantly [11]. However, this mixed basis set artificially increases the X–H bond length by about 0.0006 Å. To account for the electronegative character of some atoms, the augmented V*n*Z (aug-cc-pV*n*Z, AV*n*Z in short) basis sets were also used [12]. Inclusion of diffuse functions is indeed expected to be of particular relevance to account for the electronegative character of O atoms. This statement actually holds for relatively small basis sets (as VTZ) but it has been found that, at the V5Z level, the effect of diffuse functions is negligible [13–15]. This result will be confirmed in this work. The core–core and core–valence correlation effects on the computed equilibrium geometries [16] were estimated thanks to the correlation-consistent polarized weighted core-valence *n*-tuple zeta (cc-pwCV*n*Z, abbreviated hereafter as wCV*n*Z) [17, 18] and the original CV*n*Z [19] basis sets. As to the effect of inclusion of diffuse functions in the basis, it is sufficient to use the MP2 method to estimate this correction [20]. The frozen core approximation (hereafter denoted as *fc*), *i.e.*, for instance, keeping the 1s orbital of first-row atoms doubly occupied during correlated-level calculations, was used extensively. Some geometry optimizations were also carried out by correlating all electrons (hereafter denoted as *ae*). The coupled-cluster $T_1$ diagnostic value was systematically calculated. When it is significantly smaller than the usual cut-off value, 0.020, it indicates dominant single-reference character [21] and highlights the reliability of the CCSD(T) results. It is convincingly small in most of the cases presently studied.

The CCSD(T) calculations were performed with the MOLPRO electronic structure program package [22–24], while most other calculations utilized the GAUSSIAN03 program [25]. Most calculations were performed on the HP-XC4000 cluster of the ULB/VUB computing centre.

Two different methods were used depending on the size of the molecule. In the first method, more appropriate for small molecules, the structure was calculated at the CCSD(T)/wCVQZ(*ae*) level of theory. Then a small correction accounting for basis set enlargement was added. In most cases, the correction was calculated at the MP2 level, only, because there is a large documented evidence [13, 20, 26] that the basis sets effects are similar at the MP2 and CCSD(T) levels. A second method was used for larger molecules. The structure was calculated at the CCSD(T)/VQZ(*fc*) level of theory, and corrected for core–core and core–valence correlations effects. This correction was generally calculated at the MP2 level. Whenever possible, the effect of larger basis sets (V5Z) was taken into account at the MP2 level. The results from the two methods were compared for several of the molecules considered in this study. A very good agreement was found, better than 0.002 Å in most cases, thus both approaches deliver reliable equilibrium structures.

Table 1. Isolated stretching frequencies, $\nu_{is}$(OH) ($cm^{-1}$) and equilibrium distances $r_e$(OH) (Å).

| Molecule | $r_e$(O–H) | Ref. | $\nu_{is}$(OH) | Ref.[a] | Acc.[b] |
|---|---|---|---|---|---|
| $OH^+$ ($^3\Sigma$) | 1.028 | 29 | 2947 | 29 | A |
| Proline I | 0.991 | 82 | 3238 | 83 | B |
| $HOC^+$ | 0.990 | c | 3268 | 95 | A |
| Glycine IIn | 0.992 | 78 | 3295 | 79 | B |
| $HOCO^+$ | 0.983 | c | 3375 | 100 | A |
| *c*-HONO | 0.974 | c | 3426 | 49 | B |
| HC(O)COOH | 0.970 | 75 | 3510 | 76 | B |
| *c*-$COHCH_2OH$ | 0.965 | c | 3549 | 132 | B |
| $HNO_3$ | 0.968 | 67 | 3549 | 68–71 | A |
| $OH^-$ | 0.964 | 30 | 3556 | 30 | A |
| *t*-HCOOH | 0.966 | 14 | 3565 | 59 | A |
| OH ($^2\prod$) | 0.970 | 28 | 3570 | 28 | A |
| HOF | 0.967 | c | 3578 | 88 | A |
| Glycine Ip | 0.966 | 78 | 3585 | 79 | B |
| *t*-HONO | 0.965 | 45 | 3587 | 46–47 | A |
| HOCl | 0.962 | 38 | 3610 | 39 | A |
| HOCN | 0.963 | c | 3610 | 96 | B |
| $H_2SO_4$ | 0.964 | 72 | 3609 | 73 | A |
| $H_2O_2$ | 0.961 | 51 | 3612 | 52 | A |
| HOBr | 0.963 | 40 | 3615 | 41 | B |
| *c*-HCOOH | 0.961 | 14 | 3618 | 60 | B |
| HOSH | 0.961 | 53 | 3626 | 54 | A |
| $CH_2$=CHOH | 0.960 | c | 3634 | 124–125 | B |
| *t*-HOCO | 0.962 | 42 | 3638 | 43 | A |
| $CH_2OH$ ($^2A''$) | 0.960 | 56 | 3675 | 58 | B |
| $NH_2OH$ | 0.958 | c | 3652 | 52 | A |
| *t*-$CH_3CH_2OH$ | 0.958 | c | 3676 | 140–143 | A |
| $CH_3OH$ | 0.957 | c | 3684 | 112 | A |
| $H_2O$ | 0.958 | 32 | 3706 | 33–34 | A |
| $BF_2OH$ | 0.957 | 13 | 3714 | 106 | B |
| LiOH | 0.949 | 35 | 3830 | 35 | B |
| MgOH | 0.946 | 37 | 3851 | 37 | B |

[a] See also text.
[b] Accuracy of the frequency: A = better than 10 $cm^{-1}$, B = worse than 10 $cm^{-1}$.
[c] This work.

## 3. Review of existing data on OH bonds

The $r_e$(OH) bond length in simple molecules, determined from accurate geometries, and the corresponding isolated stretching frequencies, $\nu_{is}$(OH), are listed in table 1. The accuracy of the bond lengths usually relies on the level of calculation. Only accurate results were retained as further detailed in this section. As far as $\nu_{is}$(OH) is concerned, the accuracy relies on the quality of the experimental data available. If it is determined from a series of overtone bands or from a fundamental band origin either perturbation-free or corrected for well characterized couplings, as previously explained, the accuracy is optimal and better than 10 $cm^{-1}$ (referred to as category A in table 1). If it is determined from less refined gas-phase investigations, the role of anharmonic corrections, different from one species to another, can hardly be quantified and the accuracy is obviously lower (referred to as category B in table 1). The same statement applies to matrix data (also referred to as category B in table 1). Jacox [27] has compared the position of vibrational fundamentals in the gas phase with those in rare gas matrices. She found that the matrix shift is usually to longer wavelengths and smaller for neon-matrices (a few $cm^{-1}$). For the molecules considered in this work, the median value of argon-matrix shifts is $18.8\,cm^{-1}$, the smallest value being $5.9\,cm^{-1}$ for HOF and the largest value $32.8\,cm^{-1}$ for *trans*-HOCO.

The results listed in table 1 are reviewed hereafter molecule by molecule, in order of increasing number of constituting atoms.

### 3.1. *Diatomic and triatomic species*

The equilibrium structure and fundamental vibrational frequency of the diatomic species OH [28], $OH^+$ [29], and $OH^-$ [30] have been very accurately determined in the literature.

The very important $H_2O$ species has been the subject of many studies [31]. Its equilibrium structure is accurately known [32]. Overtone spectroscopy has been performed on $H_2O$ and HDO. From the local mode parameters derived for $H_2O$ by Kjaergaard *et al.* [33], one finds $\nu_{is}(OH) = 3705.5(40)\,cm^{-1}$. It seems, however, more reliable to use results on HDO since the OH stretch is now better decoupled from other modes of vibration. From the known $\nu_{oh}$, $3\nu_{oh}$, and $4\nu_{oh}$ overtones in this isotopologue, one can derive $\nu_{is}(OH) = 3707.1(20)\,cm^{-1}$ [34], very close to the value of the fundamental: $\nu_1 = 3707.3\,cm^{-1}$.

The simplest hydroxide molecule, lithium hydroxide, LiOH, provides an example of a structure intermediate between bent $H_2O$ and linear $Li_2O$. For this reason, it has been the subject of many experimental and theoretical studies (see Ref. [35] for an extensive literature review). Recently, Higgins *et al.* [35] combined millimeter wave rotational spectroscopy and high level *ab initio* calculations to explore the potential energy surface of LiOH and LiOD. They found that the molecule is extremely non-rigid and that the structure is linear at equilibrium with $r_e(OH) = 0.949(2)\,\text{Å}$. They also predicted fundamental vibrational frequencies: $\nu(OH) = 3829.8\,cm^{-1}$ and $\nu(OD) = 2824.2\,cm^{-1}$. These are the most accurate values available, in the absence of gas phase measurement. Infrared spectra of LiOH and LiOD crystals were actually measured [36] giving $\nu(OH) = 3678\,cm^{-1}$ and $\nu(OD) = 2731\,cm^{-1}$, both values demonstrating typical crystal shift with respect to the previously listed values.

The equilibrium structure and potential energy surface of magnesium monohydroxide, MgOH, in the ground electronic state ($X^2\Sigma^+$) have been determined using the CCSD(T) method and basis sets up to quintuple zeta quality [37], leading to $r_e(OH) = 0.946\,\text{Å}$ and $\nu(OH) = 3851\,cm^{-1}$. The accuracy of the vibrational frequency is likely to be similar to that of LiOH, i.e. a few $cm^{-1}$.

Hypochlorous acid, HOCl, has been the subject of extensive research. It is a temporary reservoir of chlorine atoms in the stratosphere and is believed to be an important intermediate in the reaction mechanisms leading to the depletion of ozone. Moreover, HOCl is small enough to allow for accurate *ab initio* potential energy surfaces (PES) to be calculated, as achieved by Peterson *et al.* [38]. These authors used the electron correlation at the multi-reference configuration interaction (MRCI) level of theory. At each point calculated on the surface, three basis sets were used (AVDZ, AVTZ, and AVQZ) permitting extrapolation to an approximate complete basis set limit. The minimum of this PES gives an accurate equilibrium geometry, with $r_e(\mathrm{OH}) = 0.9624\,\text{Å}$. The overtone spectrum of HOCl has been measured by several groups. The measurements are summarized, up to $v_{\mathrm{oh}} = 6$, by Skokov *et al.* [39]. The OH stretch mode appears to be weakly coupled with the other modes and the fundamental $\nu_1$ is thus well isolated. A Birge–Sponer plot gives $\tilde{\omega} = 3778.49(96)\,\mathrm{cm}^{-1}$ and $\tilde{\omega}x = 84.35(16)\,\mathrm{cm}^{-1}$ which gives $\nu_{\mathrm{is}}(\mathrm{OH}) = 3609.79\,\mathrm{cm}^{-1}$ indeed very close to the value of the fundamental: $\nu_1 = 3609.48\,\mathrm{cm}^{-1}$.

### 3.2. *Tetraatomic species*

Hypobromous acid, HOBr, is very similar to HOCl and also plays an important role in atmospheric chemistry. Its PES and equilibrium structure have been determined by Peterson [40] in the same way as for HOCl. The frequency of the $\nu_1$ band, from Cohen *et al.* [41], is likely to be close to the value for $\nu_{\mathrm{is}}(\mathrm{OH})$ since the analysis of the rovibrational spectrum did not indicate any strong perturbation.

*Trans*-HOCO radical is a critical intermediate involved in the reaction of OH with CO. Its structure has been determined at the CCSD(T)/AV5Z level of theory [42]. The $\nu_1$ stretch has been measured in gas-phase [43]. The frequency corrected for Fermi resonance ($3637.7(1)\,\mathrm{cm}^{-1}$), is selected in table 1. For completeness, one should also mention Ar and Ne [44] matrix values of $\nu_1$, of respectively 3602.9 and $3628\,\mathrm{cm}^{-1}$.

The structure of *trans*-nitrous acid, HONO, has been accurately determined using three different methods: experimental, semi-experimental, and *ab initio* [45]. Due to inadequate treatment of electron correlation, the single-reference CCSD(T) method gives a N–O bond length that is significantly too short. However, a much more elaborate treatment of electron correlation at the CCSDTQ level solves this problem. The overtone spectrum has been measured up to $\mathrm{v}_{\mathrm{oh}} = 7$ [46, 47] giving $\tilde{\omega} = 3746.9(10)\ \mathrm{cm}^{-1}$ and $\tilde{\omega}x = 80.14(14)\,\mathrm{cm}^{-1}$ and leading to $\nu_{\mathrm{is}}(\mathrm{OH}) = 3586.6(10)\,\mathrm{cm}^{-1}$. This value is close to the experimental value of the fundamental band, $3590.11\,\mathrm{cm}^{-1}$ [48].

The structure of the *cis*-conformer of HONO has been determined in the same way as for the *trans*-isomer but only the fundamental OH stretch and its first overtone have been measured [49]. In the absence of more accurate information, the origin of the $\nu_1$ fundamental band at $3426.2\,\mathrm{cm}^{-1}$ is selected in table 1, despite the band was found to be perturbed.

Hydrogen peroxide, $H_2O_2$, is one of the simplest molecules performing a large amplitude motion. It is believed to play an important role in the chemistry of the Earth's stratospheric ozone. Its equilibrium structure and anharmonic force field have been determined several times (see e.g. [50]). The most accurate structure was calculated by Feller and Dixon [51], at the CCSD(T)/AV6Z level of theory including a correction for the core correlation. Many studies have also been devoted to the OH stretch overtone frequencies. Particularly, Scott *et al.* [52] used a Birge–Sponer plot based on data up to $\mathrm{v}_{\mathrm{OH}} = 6$, leading to $\tilde{\omega} = 3791.5\,\mathrm{cm}^{-1}$ and $\tilde{\omega}x = 90.5\,\mathrm{cm}^{-1}$, and therefore $\nu_{\mathrm{is}}(\mathrm{OH}) = 3611.5\,\mathrm{cm}^{-1}$.

The equilibrium structure of sulfenic acid, HOSH, was calculated at the CCSD(T)(*ae*)/CVQZ level of theory by Baum *et al.* [53]. In the same paper, these authors also determined an accurate semi-experimental structure from the rotational constants of four isotopologues. The frequency of the OH stretch was recently measured in gas phase as well as in Ar matrix [54]. The results are 3625.6 cm$^{-1}$ (gas phase) and 3608.3 cm$^{-1}$ (Ar matrix). From the calculated anharmonic force field, it may be concluded that this frequency is not significantly perturbed.

### 3.3. *Pentaatomic species*

The hydroxymethyl radical, $CH_2OH$, is one of the most studied organic free radicals due to its important role in astrophysics, combustion chemistry, photochemistry, and chemistry of the atmosphere [55]. Its equilibrium structure has been calculated at the CCSD(T) level by Marenich and Boggs [56] and matrix isolation infrared studies were reported by Jacox [57]. The fundamental OH stretch was measured at 3650 cm$^{-1}$ in Ar-matrix and at 3637 cm$^{-1}$ in $N_2$-matrix. The overtone spectra were also measured up to $v_{\mathrm{OH}} = 4$ [58] giving $\tilde{\omega} = 3857.7(29)$ cm$^{-1}$ and $\tilde{\omega}x = 91.4(10)$ cm$^{-1}$, leading to $\nu_{\mathrm{is}}(\mathrm{OH}) = 3674.9$ cm$^{-1}$. The linearity of the Birge–Sponer relationship indicates that the OH stretching reasonably behaves as a local mode.

The structures of the *cis*- and *trans*-conformers of formic acid, HCOOH, have been determined at the CCSD(T) level of theory using a basis set of quintuple zeta quality. These *ab initio* results were found in perfect agreement with a semi-experimental structure, confirming their accuracy [14]. The OH-stretching overtone spectrum of the *trans*-conformer was measured up to $v_{\mathrm{oh}} = 4$ giving $\tilde{\omega} = 3728(4)$ cm$^{-1}$ and $\tilde{\omega}x = 81.6(9)$ cm$^{-1}$ which leads to $\nu_{\mathrm{is}}(\mathrm{OH}) = 3565(4)$ cm$^{-1}$ [59] to be compared with the frequency of the fundamental band, 3570.5 cm$^{-1}$. The former value was selected in table 1.

The fundamental OH band of the *cis*-conformer of formic acid was measured in Ar-matrix [60]. A harmonic force field calculation does not indicate any particular perturbation [61]. Thus, this vibration may be considered as isolated.

Nitric acid, $HNO_3$, is a reservoir molecule for both the $NO_x$ and $HO_x$ species in the stratosphere and, therefore, plays a key role in the destruction of stratospheric ozone. For this reason, numerous studies of $HNO_3$ have been recently performed in the infrared, far infrared, and microwave regions [62–64]. An approximate equilibrium structure was extrapolated from the average ($r_z$) structure [65]. There are, however very few published high level *ab initio* calculations except for the recent contribution of Feierabend *et al.* [66] who calculated a CCSD(T)/ANO structure and determined the anharmonic force field. The accuracy of their structure is unfortunately difficult to estimate, particularly because the $T_1$ diagnostic is rather large: 0.018 (CCSD(T)/VQZ level of theory). The equilibrium structure was very recently redetermined by combining high level *ab initio* calculations and experimental rotational constants [67]. The new bond lengths are significantly shorter than those of Feierabend *et al.* Furthermore, an internal hydrogen bond H...Oc seems likely to occur, the distance between the H and O atoms, 2.15 Å, being shorter than the sum of the van der Waals radii, 2.72 Å. This is in agreement with a rather long OH bond $r(\mathrm{OH}) = 0.968$ Å, see Section 6. On the other hand, the OH stretching vibration, leading to strong overtone bands, has been extensively studied because overtone excitation (by photolysis) of the OH chromophore leads to the dissociation of $HNO_3$ in the stratosphere [68–71]. A Birge–Sponer plot of the data $1 \le v_{\mathrm{oh}} \le 6$ leads to $\tilde{\omega} = 3707$ cm$^{-1}$ and $\tilde{\omega}x = 79$ cm$^{-1}$, and to $\nu_{\mathrm{is}}(\mathrm{OH}) = 3549$ cm$^{-1}$. This value, selected in table 1, is close to the fundamental band origin (3549.8 cm$^{-1}$).

### 3.4. *Larger species*

The structure of sulfuric acid, $H_2SO_4$ has been very recently calculated at the CCSD(T) level using a basis set of quadruple zeta quality [72]. The accuracy of this structure was confirmed by comparison with results on similar molecules and by estimating the effects of basis set enlargement and of diffuse functions, as well as by calculating a semi-experimental structure. The fundamental and the first and second OH stretching overtone bands have been identified [73], leading to $\tilde{\omega} = 3768.2(13)\,\mathrm{cm}^{-1}$ and $\tilde{\omega}x = 79.5(4)\,\mathrm{cm}^{-1}$. The resulting value $\nu_{\mathrm{is}}(\mathrm{OH}) = 3609.2(13)\,\mathrm{cm}^{-1}$ is identical to the fundamental band origin, $3609.2\,\mathrm{cm}^{-1}$. The vibration is thus well isolated, as further confirmed by the similarity with the OH stretch frequency in $HDSO_4$ ($3611.3\,\mathrm{cm}^{-1}$) [74].

The structure of *trans* 1 glyoxylic acid, HCOCOOH, the simplest $\alpha$-oxoacid, has been determined at the CCSD(T)/VQZ level of theory [75]. This planar conformer is the most stable one and has the two C=O groups in *anti-periplanar* position (*trans*) to one another. The infrared spectrum has been measured in gas, solution, and solid phases by Fleury and Tabacik [76]. The OH stretching vibration is at $3510\,\mathrm{cm}^{-1}$. It is probably well isolated, although some anharmonic resonance with the first overtones of the two C=O stretching vibrations cannot be excluded, their fundamentals being at $1809\,\mathrm{cm}^{-1}$ for the aldehyde C=O and $1755\,\mathrm{cm}^{-1}$ for the acid C=O groups. The infrared spectrum was later measured in Ar-matrix [77]. The carboxyl group has an anti-periplanar conformation with the hydrogen atom forming an intramolecular bond with the hydroxyl group. Indeed, the sum of the van der Waals radii $r(\mathrm{H}) + r(\mathrm{O}) = 2.72\,\text{Å}$ is larger than the distance between the H and O atoms which is calculated to be only 2.09 Å. Moreover, the value of $r_e(\mathrm{OH})$ (0.970 Å), is significantly longer than that of the median value of $r_e(\mathrm{OH})$ bond length calculated from table 1. As discussed in Section 6, this indicates that this hydrogen bond stabilizes the *trans* 1 conformer. Another planar conformer (*trans* 2) where the carboxyl group has a *syn*-periplanar conformation is 5.0 kJ/mol less stable and not further considered here.

Glycine is the simplest amino acid and a very important biological molecule. It may exist in the gas-phase in a non-ionized form, $NH_2CH_2COOH$. Internal rotations lead to several conformers. The equilibrium structures of the two forms of lowest energy ($\mathrm{I_p}$ with a bifurcated $O\cdots NH_2$ intramolecular hydrogen bond and $\mathrm{II_n}$ with a OH…N intramolecular hydrogen bond) have been calculated at the CCSD(T)/VTZ level of theory [78]. Their cubic force fields have been calculated at the MP2/6-31G* level of theory resulting in semi-experimental equilibrium rotational constants and improving the accuracy of the *ab initio* structure. The OH stretching vibration was measured for both forms in Ar- and Ne-matrices as well as in liquid helium clusters [79]. Gas-phase values were determined by extrapolation of the matrix data. The results are $3585(2)\,\mathrm{cm}^{-1}$ and $3295(3)\,\mathrm{cm}^{-1}$ for $\mathrm{I_p}$ and $\mathrm{II_n}$, respectively. The OH stretching vibration was also measured in the deuteriated species $ND_2CH_2COOH$ [80] and the isotopic shift of $4\,\mathrm{cm}^{-1}$ may be considered as negligible indicating that a strong resonance is unlikely to affect these values. Thus, so far, the OH stretching vibration of glycine $\mathrm{I_p}$ may be considered as almost isolated.

Proline, *c*-$C_4NH_8COOH$, is a natural amino acid whose imino group is fixed within a pyrrolidine ring which constrains conformational flexibility. It is a favourite organocatalytic agent for assembling stereochemically complex molecules from achiral building blocks. These properties have prompted many experimental and theoretical investigations on this species [81]. The molecular structure of the lowest-energy conformer, Pro-I, has been determined by combining high level *ab initio* calculations and rotational spectroscopy [82]. It gives $r_e(\mathrm{OH}) = 0.991$ Å. This conformer is found to have a strong internal hydrogen bond OH···N. The distance between N and H is indeed only 1.88 Å whereas the sum of the van der Waals radii is 2.75 Å. The infrared spectrum was measured in Ar-matrix [83]: $\nu(\mathrm{OH}) = 3025\,\mathrm{cm}^{-1}$. This value was selected in table 1. This vibrational frequency is actually lower than that of the NH stretching ($3393\,\mathrm{cm}^{-1}$) due to strong hydrogen bonding. There is a significant discrepancy between the experimental and *ab initio* ($3238\,\mathrm{cm}^{-1}$) OH stretch values.

## 4. Determination of new data on OH bonds

Despite the already extensive set of information available in the literature on OH bond lengths and stretch frequencies, summarized in section 3, further information can be generated considering other relevant species. Such additional data are required to better assess the relationship between OH bond lengths and stretching frequencies addressed in section 5.

### 4.1. *Hypofluorous acid*

Hypofluorous acid, HOF, is a light triatomic molecule. It is an important test case to check the accuracy of the *ab initio* determination of $r_e(\mathrm{OH})$, in particular. The equilibrium structure has been determined by various authors. Experimentally, Halonen and Ha [84] found $r_e(\mathrm{OH}) = 0.9657(16)$ Å. *Ab initio*, the values $r_e(\mathrm{OH}) = 0.9665$ [85] and 0.9657 [86] Å were obtained using high level calculations, CCSD(T)/VQZ(*ae*) and CCSD(T)/CVQZ(*ae*), respectively. There is also a semi-experimental determination by Pawlowski *et al.* [87]: $r_e(\mathrm{OH}) = 0.96862(8)$ Å. This semi-experimental structure, although apparently precise, is not compatible with the previous determinations, see table 2. In order to check if convergence was achieved at the CVQZ level, we calculated the structure variation induced by the VQZ → V5Z → AV5Z changes, at the MP2 level. The results are given in table 2. They confirm that the CCSD(T)/CVQZ(*ae*) level of theory should provide a reliable structure, therefore indicating that the stated precision of the semi-experimental structure might be too optimistic. Actually, the $A$ rotational constants for the various isotopologues are extremely large and, thus, difficult to determine with good accuracy. For the same reason, it is not obvious that the perturbational treatment to calculate $A_e - A_0$ is applicable. It thus turns out that, in the semi-empirical procedure, the three structural parameters are determined from only six $B$ and $C$ rotational constants, explaining why the standard deviation is unreliable. To make things worse, there is no isotopic substitution available for fluorine, and both fluorine and oxygen atoms have a very small $b$-coordinate ($b(\mathrm{F}) = 0.006$ Å and $b(\mathrm{O}) = -0.063$ Å). This further hinders accurate structure determination [4]. The reliability of the *ab initio* results is confirmed by the $T_1$ diagnostic, which is only 0.012 at the CCSD(T)/VTZ level of theory.

Table 2. Structure of hypofluorous acid, HOF (distances in Å, angles in degrees).

| Method | Basis | $r$(OH) | $r$(OF) | ∠(HOF) |
|---|---|---|---|---|
| $r_e$[a] | | 0.9657(16) | 1.4350(31) | 97.54(50) |
| $r_e$[b] | | 0.96862(8) | 1.43447(11) | 97.86(2) |
| CCSD(T) | VQZ(ae)[c] | 0.9648 | 1.4324 | 97.86 |
| MP2 | VQZ | 0.9663 | 1.4226 | 97.918 |
| | V5Z | 0.9666 | 1.4219 | 98.005 |
| | AV5Z | 0.9671 | 1.4225 | 98.036 |
| | wCVQZ | 0.9664 | 1.4223 | 97.92 |
| | wCVQZ(ae) | 0.9655 | 1.4203 | 98.00 |
| CCSD(T) | VQZ | 0.9665 | 1.4347 | 97.78 |
| | CVQZ | 0.9666 | 1.4345 | 97.78 |
| | CVQZ(ae) | 0.9657 | 1.4326 | 97.85 |
| $r_e$[d] | | 0.9665 | 1.4325 | 97.97 |
| $r_e$[e] | | 0.9664 | 1.4327 | 97.97 |

[a] Experimental [84].
[b] Semi-experimental [87].
[c] Ref. [85].
[d] This work: CCSD(T)/CVQZ(*ae*) + MP2/[AV5Z − VQZ].
[e] This work, CCSD(T)/VQZ + CCSD(T)[VQZ(*ae*) − VQZ] + MP2/[AV5Z − VQZ].

The $\nu_1$ band has been measured by FTIR spectroscopy. The analysis explicitly accounted for the anharmonic resonance coupling the $1^1$ and $2^2 3^1$ states, leading to an unperturbed band origin $\nu_1 = 3577.9\,\mathrm{cm}^{-1}$ [88], selected in table 1.

## 4.2. *Isoformyl ion*

The isoformyl ion, $HOC^+$, is an isomer of $HCO^+$. It has been detected in several molecular clouds [89]. Its rotational spectrum has been extensively studied [90] and an experimental $r_s$ structure has been determined [91]. An *ab initio* structure has been reported at the CCSD(T) level by several authors. Martin *et al.* [92] used a triple zeta basis set and an empirical correction with the result: $r_e(\mathrm{OH}) = 0.9882(10)$ Å. Later, Mladenovic and Schmatz [93] recalculated the structure with VQZ basis set in the frozen core approximation and found $r_e(\mathrm{OH}) = 0.9904$ Å. Finally, Grunenberg *et al.* [94] calculated the structure with the AVQZ basis set, all electrons being correlated. Their result is: $r_e(\mathrm{OH}) = 0.9891$ Å. The latter is probably the most accurate result available but may still be affected by a small error since the AVQZ basis set is not appropriate when all electrons are correlated. We therefore recalculated the structure at the CCSD(T)/wCVQZ level of theory. The improved results are provided in table 3. The coupled cluster $T_1$ diagnostic (0.018) is, however, close to the cut off value (0.020) and the values are therefore likely to be less accurate than those presently obtained for other molecules.

The OH stretching vibration was measured in gas phase by difference frequency laser spectroscopy [95] at $\nu_1 = 3268.026\,\mathrm{cm}^{-1}$. From the analysis of the rotational structure and from the *ab initio* anharmonic force field [92], it may be concluded that this vibration is well isolated.

Table 3. Structure of $HOC^+$ (distances in Å).

| Method | Basis[a] | $r$(H–O) | $r$(C–O) | Ref. |
|---|---|---|---|---|
| $r_s$ | | 0.9641 | 1.1595 | 91 |
| $r_e$[b] | | 0.9882 | 1.1579 | 92 |
| CCSD(T) | VQZ(ae) | 0.9904 | 1.1547 | 93 |
| CCSD(T) | AVQZ(ae) | 0.9891 | 1.1553 | 94 |
| MP2 | VTZ | 0.9950 | 1.1593 | |
| | VQZ | 0.9934 | 1.1555 | |
| | V5Z | 0.9935 | 1.1549 | |
| CCSD(T) | VTZ | 0.9916 | 1.1621 | |
| | AVTZ | 0.9918 | 1.1622 | |
| | VQZ | 0.9900 | 1.1579 | |
| | wCVQZ | 0.9901 | 1.1575 | |
| | wCVQZ(ae) | 0.9895 | 1.1549 | |
| $r_e$[c] | | 0.9896 | 1.1544 | This work |
| $r_e$[d] | | 0.9895 | 1.1547 | This work |

[a] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.
[b] CCSD(T)/VTZ + correction.
[c] CCSD(T)/wCVQZ(*ae*) + MP2/V5Z – MP2/VQZ.
[d] CCSD(T)/VQZ + CCSD(T)[wCVQZ(*ae*) – wCVQZ] + MP2[V5Z – VQZ].

## 4.3. *Cyanic acid*

Cyanic acid, HO–CN, is an unstable isomer of isocyanic acid, HNCO, and of fulminic acid, HCNO. Its infrared spectrum was measured in Ar- ($3569.6\,m^{-1}$) and Ne- ($3610\,cm^{-1}$) matrices [96], the frequency of the $\nu$(OH) stretch in Ne-matrix being $38\,cm^{-1}$ higher. The *ab initio* structure was calculated at the CCSD(T)/VQZ level of theory [97]. However, we noticed that this structure is not compatible with the value of $\nu$(OH) stretch just mentioned. For this reason, we recalculated the structure, given in table 4, improving the correlation to be discussed in Section 5. The $T_1$ diagnostic is 0.0145 at the CCSD(T)/VQZ level of theory.

## 4.4. *Hydroxyoxomethylium*

Protonated carbon dioxide (or hydroxyoxomethylium), $HOCO^+$, is one of the key ions assumed to be intermediates in a variety of gas phase reactions occurring in interstellar clouds. Its rotational lines were observed in the interstellar medium [98] before being measured in the laboratory [99]. The OH stretching fundamental has been studied in the gas phase [100] giving $\nu(OH) = 3375.37\,cm^{-1}$. From the analysis of the rotational structure, it may be concluded that this frequency is well isolated. The band centre has also been measured in Ne-matrix [101]. Surprisingly, the frequency is $95\,cm^{-1}$ below the gas-phase value. This shift may be explained by a proton sharing effect in the matrix, $HOCO^+$ forming a complex with a single Ne atom. There are many *ab initio* calculations available for this ion (see Ref. [101] for an extensive list of references) but, apparently, no accurate equilibrium structure. We therefore calculated it. The results are listed in table 5. At the CCSD(T)/wCVQZ(*ae*) level of theory, the coupled cluster $T_1$ diagnostic is 0.0149.

Table 4. Structure of cyanic acid, HOCN (distances in Å, angles in degrees).

| Method | Basis[a] | $r$(CN) | $r$(CO) | $r$(OH) | ∠(COH) | ∠(NCO) |
|---|---|---|---|---|---|---|
| $r_e$[b] | | 1.1601 | 1.3031 | 0.9638 | 109.340 | 176.810 |
| MP2 | VTZ | 1.1723 | 1.3032 | 0.9663 | 108.969 | 176.624 |
| | VQZ | 1.1691 | 1.2995 | 0.9646 | 109.512 | 176.550 |
| | V5Z | 1.1685 | 1.2986 | 0.9646 | 109.670 | 176.563 |
| | wCVQZ | 1.1687 | 1.2992 | 0.9647 | 109.515 | 176.548 |
| | wCVQZ(*ae*) | 1.1657 | 1.2965 | 0.9638 | 109.689 | 176.566 |
| CCSD(T) | VTZ | 1.1650 | 1.3078 | 0.9656 | 108.765 | 176.842 |
| | VQZ | 1.1615 | 1.3035 | 0.9638 | 109.337 | 176.790 |
| | wCVQZ(*ae*) | 1.1586 | 1.3005 | 0.9630 | 109.504 | 176.810 |
| $r_e$[c] | This work | 1.1580 | 1.2996 | 0.9630 | 109.662 | 176.823 |
| $r_e$[d] | This work | 1.1579 | 1.2999 | 0.9629 | 109.669 | 176.822 |

[a] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.
[b] Ref. [97].
[c] CCSD(T)/wCVQZ(*ae*) + MP2/V5Z – MP2/VQZ.
[d] CCSD(T)/VQZ + MP2/[V5Z – VQZ + wCVQZ(*ae*) – wCVQZ].

Table 5. Structure of *anti*-$HOCO^+$ (distances in Å, angles in degrees).

| Method | Basis[a] | $r(HO_1)$ | $r(O_1C)$ | $r(CO_2)$ | $\angle(HO_1C)$ | $\angle(O_1CO_2)$ |
|---|---|---|---|---|---|---|
| $r_0$[b] | | 0.9766 | 1.2085 | 1.1400 | 119.38 | 174.39 |
| MP2 | VTZ | 0.9866 | 1.2283 | 1.1352 | 117.623 | 173.933 |
| | VQZ | 0.9850 | 1.2245 | 1.1318 | 118.188 | 174.042 |
| | V5Z | 0.9850 | 1.2239 | 1.1312 | 118.306 | 174.087 |
| CCSD(T) | VTZ | 0.9852 | 1.2309 | 1.1292 | 117.257 | 174.140 |
| | VQZ | 0.9835 | 1.2266 | 1.1254 | 117.882 | 174.278 |
| | wCVQZ | 0.9837 | 1.2263 | 1.1250 | 117.877 | 174.288 |
| | wCVQZ(*ae*) | 0.9828 | 1.2237 | 1.1229 | 118.176 | 174.326 |
| $r_e$[c] | | 0.9828 | 1.2231 | 1.1224 | 118.294 | 174.371 |
| $r_e$[d] | | 0.9826 | 1.2234 | 1.1227 | 118.299 | 174.361 |

[a] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.
[b] Ref. [99].
[c] CCSD(T)/wCVQZ(*ae*) + MP2/V5Z – MP2/VQZ.
[d] CCSD(T)/VQZ + CCSD(T)[wCVQZ(*ae*) – wCVQZ] + MP2[V5Z – VQZ].

## 4.5. *Hydroxylamine*

*Trans*-hydroxylamine, $NH_2OH$, is a molecule relevant for industrial applications. It is also prototype for theoretical investigations since it is composed of only two functional groups, $-NH_2$ and $-OH$, which both exhibit large amplitude motions. Hydroxylamine has been the subject of many *ab initio* investigations [51, 102, 103]. However, as there is some inconsistency between the published structures, we recalculated it. The results are listed in table 6. The $T_1$ diagnostic at the CCSD(T)/wCVQZ(ae) level of theory is only 0.0082. It is worth noting that the effect of diffuse functions is small but not negligible at the quadruple zeta level (the largest variations are +0.0012 Å for the OH bond length and 0.23 degrees for the $\tau$(HONH) dihedral angle). On the other hand, as expected, their effect is negligible at the quintuple zeta level. Likewise, the extension of the basis set from V5Z to V6Z has negligible effects on the structure. The equilibrium structure has been calculated in two different ways which are in very good agreement. This is

Table 6. Structure of *trans*-hydroxylamine, $NH_2OH$ (distances in Å, angles in degrees).

| Method | Basis[a] | $r$(NO) | $r$(NH) | $r$(OH) | ∠(ONH) | ∠(NOH) | $\tau$(HNOH) |
|---|---|---|---|---|---|---|---|
| $r_0$ Ref. [104] | | 1.453(3) | 1.016(9) | 0.962(5) | 103.3(7) | 101.4(7) | [b] |
| MP2 | VQZ | 1.4369 | 1.0127 | 0.9586 | 103.727 | 101.757 | 124.916 |
| | AVQZ | 1.4370 | 1.0133 | 0.9598 | 103.833 | 101.979 | 124.755 |
| | V5Z | 1.4355 | 1.0126 | 0.9589 | 103.850 | 101.968 | 124.759 |
| | AV5Z | 1.4357 | 1.0129 | 0.9593 | 103.872 | 102.019 | 124.721 |
| | V6Z | 1.4350 | 1.0127 | 0.9592 | 103.883 | 102.014 | 124.722 |
| | wCVQZ | 1.4364 | 1.0128 | 0.9588 | 103.745 | 101.777 | 124.908 |
| | wCVQZ(*ae*) | 1.4330 | 1.0115 | 0.9578 | 103.906 | 101.914 | 124.763 |
| CCSD(T) | VTZ | 1.4486 | 1.0167 | 0.9598 | 103.228 | 101.454 | 125.463 |
| | VQZ | 1.4422 | 1.0151 | 0.9584 | 103.573 | 101.925 | 125.096 |
| | V5Z | 1.4406 | 1.0150 | 0.9586 | 103.685 | 102.136 | 124.951 |
| | wCVQZ | 1.4416 | 1.0152 | 0.9585 | 103.589 | 101.944 | 125.088 |
| | wCVQZ(*ae*) | 1.4384 | 1.0139 | 0.9576 | 103.742 | 102.067 | 124.951 |
| $r_e$[c] | | 1.4369 | 1.0137 | 0.9580 | 103.872 | 102.304 | 124.776 |
| $r_e$[d] | | 1.4365 | 1.0138 | 0.9582 | 103.898 | 102.324 | 124.756 |

[a] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.
[b] $\angle_0$(HNH) = 107.1(10) degrees, to be compared with $\angle_e$(HNH) = 105.78 degrees.
[c] CCSD(T)/V5Z + CCSD(T)/wCVQZ(*ae*) – CCSD(T)/wCVQZ + MP2/V6Z – MP2/V5Z.
[d] CCSD(T)/wCVQZ(*ae*) + MP2/[V6Z – VQZ].

demonstrated in table 6 where the empirical $r_0$ structure is also given for the sake of comparison [104].

Scott *et al.* [52] measured the overtone spectrum up to $v_{oh} = 5$. The Birge–Sponer plot gives $\tilde{\omega} = 3833.6(30)\,\mathrm{cm}^{-1}$ and $\tilde{\omega}x = 90.6(5)\,\mathrm{cm}^{-1}$, leading to $\nu_{is}(\mathrm{OH}) = 3652.4\,\mathrm{cm}^{-1}$. This value is listed in table 1. It is close to the fundamental band origin, $3650\,\mathrm{cm}^{-1}$, found to be very slightly perturbed ($< 0.1\,\mathrm{cm}^{-1}$) by anharmonic resonances [105].

## 4.6. *Hydroxyboranes*

Among the hydroxyboranes, difluorohydroxyborane, $BF_2OH$, was studied in great details because it is an intermediate in the hydrolysis of $BF_3$ and because it is isovalent with nitric acid ($HONO_2$). The equilibrium geometry was determined at the CCSD(T)/V5Z level of theory and a semi-experimental structure was calculated to check the accuracy of the *ab initio* structure [13]. Nearly all fundamental vibrational bands were analyzed from high resolution spectra [106]. From the analysis of the anharmonic force field, it was found that $\nu_1$, measured at $3714.5\,\mathrm{cm}^{-1}$, is not significantly perturbed. This frequency was also measured in Ne-matrix, at $3712.5\,\mathrm{cm}^{-1}$ [107]. We found it interesting to evaluate the effects of isotopic substitution on the OH bond lengths in this class of molecules and determined the *ab initio* structure of the other simple hydroxyboranes: fluorohydroxyborane, BHFOH, borinic acid, $BH_2OH$, and boronic acid, $BH(OH)_2$. For these molecules, there is no experimental infrared spectrum available and the published *ab initio* calculations, which are rather old, use a low level of theory [108].

The microwave spectra of BHFOH and $BH(OH)_2$ were measured by Kawashima *et al.* [109] in the hydrolyses of diborane and $BF_3$. They derived $r_s$ as well as $r_0$ structures and found that, for BHFOH the two hydrogens are in *syn* position. In $BH(OH)_2$,

Table 7. Structure of boronic acid, $BH(OH)_2$ (distances in Å, angles in degrees).

| Method | | MP2 | | | | CCSD(T) | |
|---|---|---|---|---|---|---|---|
| Basis[a] | $r_s$[b] | VQZ | V5Z | wCVQZ | wCVQZ(*ae*) | VQZ | $r_e$[c] |
| $r$(B–H) | 1.1972(3) | 1.1886 | 1.1881 | 1.1884 | 1.1861 | 1.1923 | 1.1895 |
| $r$(B–$O_a$) | 1.359(9) | 1.3579 | 1.3576 | 1.3573 | 1.3539 | 1.3574 | 1.3537 |
| $r$(O–$H_a$) | 0.9590(8) | 0.9611 | 0.9610 | 0.9612 | 0.9603 | 0.9608 | 0.9598 |
| $r$(B–$O_s$) | 1.365(9) | 1.3678 | 1.3677 | 1.3673 | 1.3638 | 1.3672 | 1.3636 |
| $r$(O–$H_s$) | 0.9498(4) | 0.9573 | 0.9573 | 0.9575 | 0.9565 | 0.9569 | 0.9559 |
| ∠($HBO_a$) | 118.2(12) | 118.436 | 118.517 | 118.434 | 118.435 | 118.503 | 118.585 |
| ∠($BOH_a$) | 111.8(13) | 111.657 | 111.774 | 111.654 | 111.775 | 111.716 | 111.954 |
| ∠($HBO_s$) | 122.8(12) | 122.329 | 122.332 | 122.330 | 122.296 | 122.276 | 122.245 |
| ∠(OBO) | 119.1(13) | 119.236 | 119.151 | 119.236 | 119.269 | 119.222 | 119.170 |
| ∠($BOH_s$) | 113.3(17) | 112.563 | 112.715 | 112.571 | 112.711 | 112.630 | 112.922 |

[a] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.
[b] Ref. [109].
[c] CCSD(T)/VQZ + MP2/[V5Z − VQZ + wCVQZ(*ae*) − wCVQZ].

Table 8. Structure of fluorohydroxyborane, BHFOH (distances in Å, angles in degrees).

| Method | MP2 | | | | | CCSD(T) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Basis[a] | VQZ | V5Z | AV5Z | wCVQZ | wCVQZ(*ae*) | VQZ | wCVQZ(*ae*) | $r_e$[b] | $r_e$[c] | $r_e$(se)[d] |
| $r$(B–H) | 1.1883 | 1.1878 | 1.1881 | 1.1881 | 1.1858 | 1.1920 | 1.1896 | 1.1894 | 1.1895 | 1.1899(2) |
| $r$(B–F) | 1.3239 | 1.3238 | 1.3244 | 1.3235 | 1.3205 | 1.3224 | 1.3191 | 1.3196 | 1.3199 | 1.3183(10) |
| $r$(B–O) | 1.3510 | 1.3508 | 1.3512 | 1.3505 | 1.3470 | 1.3503 | 1.3464 | 1.3466 | 1.3472 | 1.3473(9) |
| $r$(O–H) | 0.9580 | 0.9579 | 0.9581 | 0.9581 | 0.9572 | 0.9576 | 0.9568 | 0.9569 | 0.9568 | 0.95853(6) |
| ∠(HBF) | 119.355 | 119.384 | 119.396 | 119.353 | 119.334 | 119.356 | 119.338 | 119.380 | 119.378 | 119.74(42) |
| ∠(HBO) | 123.450 | 123.479 | 123.490 | 123.450 | 123.422 | 123.401 | 123.365 | 123.406 | 123.413 | 123.06(42) |
| ∠(FBO) | 117.196 | 117.137 | 117.114 | 117.197 | 117.244 | 117.243 | 117.296 | 117.215 | 117.209 | 117.200(9) |
| ∠(BOH) | 112.478 | 112.619 | 112.664 | 112.479 | 112.638 | 112.539 | 112.677 | 112.863 | 112.884 | 112.663(52) |

[a] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.
[b] CCSD(T)/wCVQZ(*ae*) + MP2/AV5Z − MP2/VQZ.
[c] CCSD(T)/VQZ + MP2/[AV5Z − VQZ + wCVQZ(*ae*) − wCVQZ].
[d] Semi-experimental equilibrium structure, see text.

one hydrogen is *syn* with respect to the hydroxyl hydrogen, whereas the other one is *anti* and forms an internal hydrogen bond with the oxygen of the other hydroxyl group. The structure of $BH(OH)_2$ as we calculated it is given in table 7. The $T_1$ diagnostic is 0.012 at the CCSD(T)/VQZ level of theory. From the results, it may be argued that the *syn–anti* form is stabilized by an internal $H_a \cdots O$ hydrogen bond. Actually, the distance between the H and O atoms, which is calculated to be 2.40 Å, is only slightly smaller than the sum of the van der Waals radii $r(H) + r(O) = 2.72$ Å. Moreover, the $r_e(OH_a)$ bond length, 0.960 Å, is still rather short, as further discussed in section 6.

The structure of BHFOH we have calculated is given in table 8. The effect of diffuse functions at the V5Z level is quite small, even for the BF bond length (+0.0006 Å). The $T_1$ diagnostic is 0.011 at the CCSD(T)/wCVQZ(*ae*) level of theory. The rotational constants of ten isotopologues of BHFOH have been experimentally determined [109]. We derived a semi-experimental structure to check the accuracy of the

Table 9. Structure of borinic acid, $BH_2OH$ (distances in Å, angles in degrees).

| Method | | MP2 | | | | | | | | CCSD(T) |
|---|---|---|---|---|---|---|---|---|---|---|
| Basis[a] | $r_0$[b] | VTZ | VQZ | V5Z | wCVQZ | wCVQZ(*ae*) | VQZ | wCVQZ(*ae*) | $r_e$[c] | $r_e$[d] |
| $r$(B–O) | 1.352(4) | 1.3570 | 1.3540 | 1.3539 | 1.3534 | 1.3498 | 1.3535 | 1.3495 | 1.3494 | 1.3498 |
| $r(B–H_s)$[e] | 1.200[f] | 1.1939 | 1.1927 | 1.1922 | 1.1925 | 1.1901 | 1.1969 | 1.1944 | 1.1939 | 1.1940 |
| $r(B–H_a)$[e] | 1.200[f] | 1.1884 | 1.1872 | 1.1867 | 1.1870 | 1.1846 | 1.1913 | 1.1888 | 1.1883 | 1.1884 |
| $r$(O–H) | 0.967(14) | 0.9610 | 0.9591 | 0.9590 | 0.9592 | 0.9583 | 0.9589 | 0.9581 | 0.9580 | 0.9579 |
| $\angle(OBH_s)$[e] | 121.8(8) | 120.685 | 120.510 | 120.447 | 120.514 | 120.526 | 120.468 | 120.483 | 120.421 | 120.417 |
| $\angle(OBH_a)$[e] | 117.2(8) | 116.562 | 116.652 | 116.651 | 116.651 | 116.689 | 116.766 | 116.814 | 116.813 | 116.803 |
| ∠(HBH) | 121.0 | 122.752 | 122.839 | 122.902 | 122.835 | 122.785 | 122.766 | 122.703 | 122.766 | 122.780 |
| ∠(BOH) | 112.0(17) | 112.309 | 112.661 | 112.762 | 112.670 | 112.809 | 112.724 | 112.849 | 112.950 | 112.964 |

[a] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.

[b] Ref. [110].

[c] CCSD(T)/wCVQZ(*ae*) + MP2/V5Z – MP2/VQZ.

[d] CCSD(T)/VQZ + MP2/[V5Z – VQZ + wCVQZ(*ae*) – wCVQZ].

[e] s = *syn* with respect to the hydroxyl hydrogen, t = *anti*.

[f] Assumed value.

*ab initio* structure. We have calculated the anharmonic force field at the MP2/VTZ level of theory and predicted semi-experimental equilibrium rotational constants. The semi-experimental equilibrium structure was obtained from a least squares fit of the rotational constants. It is also given in table 8. It is in good agreement with the *ab initio* structure. The B–F and B–O distances and the angles ∠(HBF) and ∠(HBO) are, however not precise because: (i) there is no isotopic substitution available for fluorine; and (ii) the Cartesian coordinates of three atoms are small ($a(B) = 0.033$ Å; $b(F) = 0.18$ Å; and $a(H_B) = 0.026$ Å).

The microwave spectrum of $BH_2OH$, a transient intermediate in the reaction between diborane and water, was measured by Kawashima *et al.* [110] who also determined a partial empirical structure. We have calculated the structure, which is given in table 9. The $T_1$ diagnostic is 0.012 at the CCSD(T)/wCVQZ(*ae*) level of theory.

In the series $BH_2OH$, BHFOH, $BF_2OH$, substitution of each additional fluorine atom shortens the BO bond by about 0.002 Å while the lengths of both B–H and OH bond remain almost constants. In $BH(OH)_2$, the $\angle(HBO_s)$ angle (122.2 degrees) is larger than the $\angle(HBO_a)$ angle (118.6 degrees). This favours the formation of an internal hydrogen bond $O_s–H\cdots O_a$.

## 4.7. *Methanol*

Methanol, $CH_3OH$, is the simplest alcohol. It served as a model for the study of large amplitude motions [111] as well as for intramolecular vibrational energy redistribution. It is also an important interstellar molecule. The infrared spectrum, including overtones up to $v_{OH} = 7$ is well known [112] A Birge–Sponer plot gives $\tilde{\omega} = 3855.7\,cm^{-1}$ and $\tilde{\omega}x = 86.1\,cm^{-1}$ leading to $\nu_{is}(OH) = 3683.5\,cm^{-1}$. This value, selected in table 1, is to be compared with the frequency of the fundamental, $3681\,cm^{-1}$. The experimental structure has been determined by microwave spectroscopy ($r_s$ structure) [113] and by electron diffraction ($r_z$ structure) [114]. The *ab initio* structure has also been calculated

Table 10. Structure of methanol, $CH_3OH$ (distances in Å, angles in degrees).

| Method | Basis[b] | $r$(C–O) | $r$(O–H) | $r$(C–$H_s$) | $r$(C–$H_a$) | ∠(COH) | ∠($OCH_s$) | ∠($OCH_a$) | $\tau$($HOCH_a$) |
|---|---|---|---|---|---|---|---|---|---|
| $r_s$[a] Ref. [113] | | 1.421 | 0.963 | 1.094 | 1.094 | 108.0 | | | |
| $r_z$[a] Ref. [114] | | 1.428 | 0.975 | 1.098 | 1.098 | 107.6 | | | |
| $r_e$[a] Ref. [115] | | 1.416 | 0.956 | 1.090 | 1.090 | 108.4 | | | |
| MP2 | VQZ | 1.4174 | 0.9578 | 1.0842 | 1.0897 | 107.973 | 106.687 | 112.136 | 61.488 |
| MP2 | V5Z | 1.4182 | 0.9578 | 1.0837 | 1.0892 | 108.168 | 106.619 | 111.984 | 61.442 |
| MP2 | wCVQZ | 1.4171 | 0.9579 | 1.0841 | 1.0897 | 107.977 | 106.695 | 112.129 | 61.479 |
| MP2 | wCVQZ(*ae*) | 1.4143 | 0.9569 | 1.0826 | 1.0881 | 108.099 | 106.748 | 112.157 | 61.483 |
| MP2 | CVTZ | 1.4181 | 0.9590 | 1.0853 | 1.0911 | 107.433 | 106.787 | 112.341 | 61.512 |
| MP2 | CVTZ(*ae*) | 1.4157 | 0.9582 | 1.0841 | 1.0899 | 107.539 | 106.833 | 112.366 | 61.515 |
| CCSD(T) | VQZ | 1.4192 | 0.9577 | 1.0877 | 1.0933 | 107.974 | 106.803 | 112.077 | 61.442 |
| CCSD(T) | wCVQZ(*ae*) | 1.4163 | 0.9569 | 1.0861 | 1.0917 | 108.083 | 106.860 | 112.097 | 61.437 |
| $r_e$[c] | This work | 1.4171 | 0.9569 | 1.0856 | 1.0912 | 108.278 | 106.792 | 111.945 | 61.391 |
| $r_e$[d] | This work | 1.4172 | 0.9567 | 1.0857 | 1.0912 | 108.291 | 106.788 | 111.953 | 61.400 |

[a] $C_{3v}$ symmetry was assumed for the methyl group.
[b] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.
[c] CCSD(T)/wCVQZ(*ae*) + MP2/V5Z − MP2/VQZ.
[d] CCSD(T)/VQZ + MP2/[V5Z − VQZ + wCVQZ(*ae*) − wCVQZ].

at the CCSD(T)/VQZ level [115]. However, the core correction was calculated with the CVTZ basis set which is known to recover only partially the core correlation [116]. Furthermore, in these previous calculations, the methyl group was assumed to present $C_{3v}$ symmetry, which is a very poor approximation in this particular case. For these reasons, we recalculated the structure of $CH_3OH$. The results are given in table 10. The $T_1$ diagnostic is 0.008 at the CCSD(T)/wCVQZ(*ae*) level of theory. One can check that, despite the wCVTZ basis set does not recover all the core correlation, the differences with the wCVQZ basis set are small. The largest difference is only 0.0004 Å for the $r$(C–O) bond length and 0.122 degrees for the ∠(COH) bond angle. Going from VQZ to V5Z has very small effects on the structure: the $r$(C–O) bond length increases by 0.0008 Å, ∠(COH) and ∠($OCH_a$) bond angles increase by 0.195 degrees and decreases by −0.152 degrees, respectively. The asymmetry of the methyl group is noticeable: the $r$(C–$H_a$) bond length is longer by 0.0056 Å than the $r$(C–$H_s$) bond length and the ∠($OCH_a$) bond angle is larger by 5.15 degrees than the ∠($OCH_s$) angle. For this reason, a comparison with the previous literature structures is not meaningful. The isolated CH stretching frequencies confirm this asymmetry [117]. The values are: $\nu(CH_s) = 2979.2\,\mathrm{cm}^{-1}$ giving $r_e(CH_s) = 1.087$ Å and $\nu(CH_a) = 2920.6\,\mathrm{cm}^{-1}$ giving $r_e(CH_a) = 1.091$ Å [1], in perfect agreement with the *ab initio* structure.

## 4.8. *Vinyl alcohol*

Vinyl alcohol (ethenol), $CH_2{=}CHOH$, is the simplest enol compound. It was first identified in gas phase by Saito in 1976 [118]. Only the *syn* conformer was observed. Later, Rodler and Bauder measured the microwave spectra of nine isotopologues and determined a complete $r_s$ structure [119]. Rodler [120] measured the microwave spectrum of the *anti* rotamer which is 4.5(6) kJ mol$^{-1}$ higher in energy. The *syn* conformer was identified in the molecular cloud Sgr B2 by Turner and Apponi [121]. The *ab initio* structure was calculated at the MP2 level in the literature and the results

Table 11. Structure of *syn*-ethenol, $CH_2=CHOH$ (distances in Å, angles in degrees).

| Method | CCSD(T) | MP2 | | | | |
|---|---|---|---|---|---|---|
| Basis set[a] | VQZ | VQZ | V5Z | wCVQZ | wCVQZ(*ae*) | $r_e$[b] |
| $r$(C–O) | 1.3621 | 1.3582 | 1.3582 | 1.3579 | 1.3551 | 1.3593 |
| $r$(O–H) | 0.9612 | 0.9620 | 0.9620 | 0.9622 | 0.9612 | 0.9602 |
| $r$(C–$H_g$)[c] | 1.0813 | 1.0792 | 1.0790 | 1.0792 | 1.0777 | 1.0796 |
| $r$(C=C) | 1.3340 | 1.3307 | 1.3302 | 1.3303 | 1.3271 | 1.3303 |
| $r$(C–$H_c$)[c] | 1.0832 | 1.0801 | 1.0799 | 1.0801 | 1.0786 | 1.0815 |
| $r$(C–$H_t$)[c] | 1.0789 | 1.0760 | 1.0758 | 1.0759 | 1.0744 | 1.0772 |
| ∠(COH) | 108.439 | 108.408 | 108.583 | 108.414 | 108.533 | 108.734 |
| ∠(OC$H_g$)[c] | 110.955 | 110.903 | 110.905 | 110.910 | 110.944 | 110.991 |
| ∠(OCC) | 126.441 | 126.619 | 126.529 | 126.616 | 126.622 | 126.356 |
| ∠(CC$H_g$)[c] | 122.603 | 122.478 | 122.566 | 122.474 | 122.434 | 122.652 |
| ∠(CC$H_c$)[c] | 121.931 | 121.898 | 121.897 | 121.896 | 121.899 | 121.933 |
| ∠(CC$H_t$)[c] | 119.625 | 119.387 | 119.353 | 119.393 | 119.424 | 119.622 |
| ∠($H_c$C$H_t$)[c] | 118.644 | 118.715 | 118.750 | 118.712 | 118.677 | 118.645 |

[a] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.
[b] CCSD(T)/VQZ + MP2/[{wCVQZ(*ae*) – wCVQZ} + {V5Z – VQZ}].
[c] g, geminal; c, *cis* to OH; t, *trans* to OH.

dismissed the experimental $r_s$ structure [122]. We recalculated the structure at the CCSD(T) level of theory. The results are listed in table 11. The $T_1$ diagnostic is 0.012 at the CCSD(T)/VQZ level of theory.

These results may be compared to the equilibrium structures of vinyl halides [123]. The $r$(C=C) bond length (1.3303 Å) is almost identical to the value found for ethene (1.3307 Å). The $r$(C–$H_t$) length (1.0072 Å) is as small as in vinyl fluoride (1.0774 Å). Likewise, the ∠(CC$H_t$) bond angle (119.62 degrees) is smaller than 120 degrees as in vinyl fluoride (118.97 degrees). The large value of the ∠(CCO) bond angle (126.36 degrees) has to be noted. The distance between the hydrogen of the OH group and the centre of the double bond is 2.10 Å. It is smaller than 2.90 Å which is the sum of the van der Waals radii of hydrogen and the half-thickness of an aromatic molecule (1.70 Å). This indicates a possible internal hydrogen bond. However, this conclusion is not confirmed by the $r$(OH) bond length, which is rather short (0.960 Å), as discussed in sections 5 and 6.

The fundamental OH stretch was measured in gas phase by Koga *et al.* [124] and by Joo *et al.* [125]. Their results ($3633.5\,cm^{-1}$), are in perfect agreement and close to a measurement in Ar-matrix ($3620\,cm^{-1}$) [126]. The related accuracy is, however low, in the absence of high resolution investigation of this band.

### 4.9. *Glycolaldehyde*

Glycolaldehyde, $CHOCH_2OH$, is the simplest sugar. It was first studied in vapor phase in the infrared by Michelsen and Klaboe [127]. The microwave spectrum was later measured by Marstokk and Møllendal [128]. Only the *cis*-conformer stabilized by an intramolecular hydrogen bond was observed. It was recently detected in the interstellar cloud Sgr B2 [129]. It is also active in atmospheric chemistry. For these reasons, the study of its rotational spectrum was extended to the millimeter wave range [130].

Table 12. Structure of glycolaldehyde, $HCOCH_2OH$ (distances in Å, angles in degrees).

| Method | CCSD(T) | MP2 | | | | |
|---|---|---|---|---|---|---|
| Basis set[a] | VQZ | wCVQZ | wCVQZ(*ae*) | VQZ | V(Q,5)Z | $r_e$[b] |
| $r$(C=O) | 1.2105 | 1.2121 | 1.2098 | 1.2125 | 1.2123 | 1.2080 |
| $r$(C–C) | 1.5060 | 1.499 | 1.4953 | 1.4995 | 1.4988 | 1.5016 |
| $r$(C–O) | 1.3984 | 1.3957 | 1.3929 | 1.3960 | 1.3959 | 1.3955 |
| $r$(O–H) | 0.9662 | 0.9672 | 0.9663 | 0.9671 | 0.9679 | 0.9653 |
| $r$(C–H) ($CH_2$) | 1.0974 | 1.0945 | 1.0930 | 1.0946 | 1.0949 | 1.0959 |
| $r$(C–H) (CHO) | 1.1026 | 1.1003 | 1.0988 | 1.1003 | 1.1007 | 1.1011 |
| ∠(C–C=O) | 121.660 | 121.657 | 121.671 | 121.651 | 121.655 | 121.677 |
| ∠(C–C–O) | 111.665 | 111.795 | 111.835 | 111.786 | 111.828 | 111.747 |
| ∠(C–O–H) | 105.650 | 105.454 | 105.558 | 105.435 | 105.679 | 105.754 |
| ∠(CCH) ($CH_2$) | 107.810 | 107.753 | 107.737 | 107.751 | 107.820 | 107.794 |
| ∠(CCH) (CHO) | 116.827 | 116.837 | 116.829 | 116.837 | 116.851 | 116.819 |
| $\tau$[c] | 57.541 | 57.435 | 57.392 | 57.441 | 57.498 | 57.555 |

[a] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.
[b] CCSD(T)/VQZ + MP2/[{wCVQZ(*ae*) − wCVQZ} + {V(Q,5)Z − VQZ}].
[c] dihedral angle C–C–H[CHO]–H($CH_2$). Derived parameter: $\angle_e$(HCH) = 106.879 degree.

From the microwave Fourier transform spectrum, the nuclear spin–spin constant between the two hydrogens of the methylene group was determined [131]. The infrared spectrum was also studied and the Fermi resonance between the C=O fundamental stretching state and the first overtone of the C–C stretching was analyzed [132]. The resulting gas-phase frequency of the OH stretching is $3549\,\mathrm{cm}^{-1}$. The potential energy surface and the torsional spectrum were calculated at the MP2/AVTZ [133] and MP4/VQZ [134] levels of theory, respectively.

The equilibrium structure was recalculated here using the CCSD(T) method. The results are given in table 12. The $T_1$ diagnostic is 0.014 at the CCSD(T)/VQZ level of theory. The C–H bond lengths are large. This is particularly true for the H attached to the C=O group. This behaviour seems typical of this type of bonding and indeed quite close to the value found in $H_2CO$, $r_e(CH) = 1.1007$ Å [87]. In the particular case of the methylene group, there is an inverse, non linear correlation between the C–H bond length and the ∠(HCH) bond angle as can be seen in table 13 and figure 1. The correlation is statistically significant, despite of the species, $H_2CO$ ($r_e(CH) = 1.100$ Å and ∠(HCH) = 116.7 degrees) does not seem to obey the rule. The Spearman rank correlation coefficient is indeed high ($\rho = 0.925$). This correlation is easy to explain, at least qualitatively. Because of the stretch–bend interaction, the bonds stretch out when the angle between them is reduced and shrink when that angle is increased [135]. For the methylene group in glycolaldehyde, the distance $d(H\cdots H) = 1.76$ Å is quite small, which explains why the spin–spin coupling could be observed in the rotational spectrum.

The occurrence of an internal hydrogen bond between the hydroxy hydrogen and the $sp^2$ oxygen atom is probable. Indeed, the sum of the van der Waals radii $r(H) + r(O) = 2.72$ Å is larger than the distance between the H and O atoms which is calculated to be only 2.07 Å. Another evidence comes from the $r_e(OH)$ bond length (0.966 Å), which is slightly longer than the median value of $r_e(OH)$ bond lengths, as discussed in section 6.

Table 13. *r*(C–H) bond length (Å) as a function of the ∠(HCH) bond angle (degrees) in the methylene group of a few molecules.

| Molecule | ∠(HCH) | *r*(C–H) | *d*(H···H) | Ref. |
|---|---|---|---|---|
| $H_2C{=}C{=}O$ | 121.78 | 1.076 | 1.880 | 156 |
| $c$-$H_2CN_2$ | 119.86 | 1.077 | 1.864 | 157 |
| $c$-$C_3H_6$ | 114.93 | 1.079 | 1.819 | 26 |
| $H_2C{=}CH_2$ | 117.12 | 1.081 | 1.844 | 26 |
| $H_2C{=}C{=}CH_2$ | 118.32 | 1.081 | 1.856 | 26 |
| $c$-$C_2H_4O$ | 116.20 | 1.082 | 1.837 | 26 |
| $CH_3Br$ | 111.17 | 1.083 | 1.786 | 158 |
| $H_2C{=}C{=}C{:}$ | 117.60 | 1.083 | 1.853 | 26 |
| $CH_3Cl$ | 110.48 | 1.084 | 1.781 | 158 |
| $CH_2BrF$ | 113.03 | 1.084 | 1.808 | 159 |
| $c$-$C_3H_4$ | 114.24 | 1.086 | 1.823 | 20 |
| $CH_4$ | 109.47 | 1.086 | 1.773 | 160 |
| $CH_3NC$ | 109.47 | 1.086 | 1.774 | 20 |
| $CH_3CN$ | 109.10 | 1.087 | 1.770 | 161 |
| $CH_3F$ | 110.24 | 1.087 | 1.784 | 162 |
| $CH_2F_2$ | 108.36 | 1.087 | 1.763 | 163 |
| $CH_3CCH$ | 108.31 | 1.089 | 1.765 | 26 |
| $\mathbf{CH}_3CH_2OH$ | 108.40 | 1.089 | 1.766 | a |
| $CH_3CH_3$ | 107.67 | 1.089 | 1.758 | 145 |
| $CH_3CH{=}CH_2$ | 107.01 | 1.091 | 1.754 | a |
| $CH_3OH$ | 109.04 | 1.091 | 1.777 | a |
| $CH_3NH_2$ | 107.21 | 1.093 | 1.760 | 15 |
| $CH_3\mathbf{CH_2}OH$ | 107.94 | 1.094 | 1.769 | a |
| $CH_3OCH_3$ | 108.43 | 1.095 | 1.777 | 15 |
| $CHOCH_2OH$ | 106.88 | 1.096 | 1.761 | a |
| Range | 14.90 | 0.020 | 0.126 | |

[a] This work.

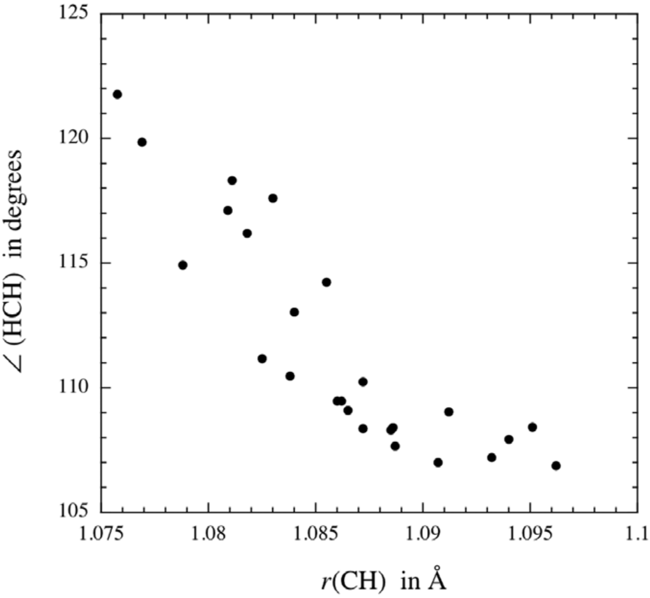

Figure 1. *r*(C–H) bond length (Å) as a function of the ∠(HCH) bond angle (degrees) in the methylene group of a few molecules.

Table 14. Structure of *anti*-ethanol, $CH_3CH_2OH$ (distances in Å, angles in degrees).

| Method | MP2 | | | | CCSD(T) | | | |
|---|---|---|---|---|---|---|---|---|
| Basis[a] | VQZ | wCVQZ | wCVQZ[d] | V(Q,5)Z | VTZ | VQZ | $r_e$[b] | $r_s$[c] |
| $r$(C–C) | 1.5075 | 1.5071 | 1.5036 | 1.5068 | 1.5158 | 1.5131 | 1.5089 | 1.512 |
| $r$(C–O) | 1.4226 | 1.4223 | 1.4196 | 1.4232 | 1.4257 | 1.4242 | 1.4221 | 1.431 |
| $r$(O–H) | 0.9588 | 0.959 | 0.958 | 0.9595 | 0.9601 | 0.9583 | 0.9580 | 0.971 |
| $r(C_2–H_s)$ | 1.0874 | 1.0873 | 1.0857 | 1.0877 | 1.0918 | 1.0908 | 1.0895 | 1.098 |
| $r(C_2–H_a)$ | 1.0865 | 1.0864 | 1.0848 | 1.0867 | 1.0910 | 1.0900 | 1.0886 | 1.088 |
| $r(C_1–H)$ | 1.0920 | 1.0919 | 1.0903 | 1.0922 | 1.0960 | 1.0954 | 1.0940 | 1.091 |
| $\angle$(CCO) | 107.366 | 107.363 | 107.410 | 107.370 | 107.517 | 107.544 | 107.596 | 107.77 |
| $\angle$(COH) | 108.277 | 108.287 | 108.403 | 108.441 | 107.755 | 108.261 | 108.541 | 105.43 |
| $\angle(C_1C_2H_s)$ | 110.522 | 110.527 | 110.559 | 110.472 | 110.561 | 110.489 | 110.471 | 110.49 |
| $\angle(C_1C_2H_a)$ | 110.190 | 110.192 | 110.208 | 110.209 | 110.198 | 110.224 | 110.258 | 110.13 |
| $\angle(C_2C_1H)$ | 110.171 | 110.181 | 110.169 | 110.257 | 109.990 | 110.135 | 110.210 | 110.72 |
| $\angle(HC_1H)$ | 107.918 | 107.915 | 107.874 | 107.994 | 107.815 | 107.906 | 107.941 | 107.97 |
| $\angle(H_sC_2H_a)$ | 108.722 | 108.718 | 108.699 | 108.723 | 108.709 | 108.718 | 108.699 | 108.79 |
| $\angle(H_aC_2H_a)$ | 108.441 | 108.440 | 108.415 | 108.454 | 108.413 | 108.415 | 108.403 | 108.45 |

[a] Frozen core approximation, unless otherwise stated: *ae* = all electrons correlated.
[b] CCSD(T)/VQZ + MP2/[{wCVQZ(*ae*) – wCVQZ} + {V5Z – VQZ}].
[c] Ref. [138]
[d] All electrons correlated.

## 4.10. *Ethanol*

Ethanol (or ethyl alcohol), $CH_3CH_2OH$, is known to exist in two distinct conformations. The lowest energy form has the hydroxyl group in the *anti* conformation. The rotational spectrum has been studied extensively and was observed in several interstellar molecular clouds [136, 137]. The empirical substitution ($r_s$) structure has been determined by microwave spectroscopy [138, 139]. The overtone spectrum was measured by Fang *et al.* [140], Lange *et al.* [141], Weibel *et al.* [142], and Hu *et al.* [143] up to $v_{OH} = 6$. From their work, it is possible to derive $\tilde{\omega} = 3846.2(16)\,\mathrm{cm}^{-1}$ and $\tilde{\omega}x = 85.20(26)\,\mathrm{cm}^{-1}$ which leads to $\nu_{is}(\mathrm{OH}) = 3675.8\,\mathrm{cm}^{-1}$. This value is almost identical to the fundamental band origin ($\nu_1 = 3676\,\mathrm{cm}^{-1}$), which is therefore not significantly perturbed. This is confirmed by additional infrared measurements demonstrating that the band does not shift by more than $0.2\,\mathrm{cm}^{-1}$ upon deuteriation of CH bonds [144].

The calculated equilibrium structure of the *anti* conformer is reported in table 14. The $T_1$ diagnostic is 0.009 at the CCSD(T)/VQZ level of theory. It is compared with the experimental substitution structure of Culot [138]. With the exception of the $\angle_s$(COH) angle, which is more than two degrees too small, the overall agreement is satisfactory, taking into account the limited accuracy of the $r_s$ structure. Contrary to $CH_3OH$, table 10, the methyl group is almost symmetric and, as usual, the $r_s$ structure greatly exaggerates the asymmetry. This is confirmed by the isolated stretching frequencies [144]: $\nu(CH_s) = 2949\,\mathrm{cm}^{-1}$ giving $r_e(CH_s) = 1.089$ Å, and $\nu(CH_a) = 2964\,\mathrm{cm}^{-1}$ giving $r_e(CH_a) = 1.088$ Å [1]. These methyl bond lengths are close to the value found in ethane (1.089(1) Å) [145]. On the other hand, the CH bond in the $CH_2OH$ group (1.094 Å) is significantly longer. This value agrees with the one derived from the isolated stretching frequency which was determined from the infrared spectra of the $CD_3CHDOH$ and

$CD_3CHDOD$ [146]. The experimental value $\nu(CH) = 2896\,cm^{-1}$ indeed gives $r_e(CH) = 1.093\,Å$ [1]. The CC bond length (1.509 Å) is much shorter than in ethane (1.522(2) Å). Finally, the ∠(CCH) angles ($\angle(C_1C_2H_s) = 110.47$; $\angle(C_1C_2H_a) = 110.26$; and $\angle(C_2C_1H) = 110.21$, all values in degrees) are slightly smaller than in ethane (111.2(1) degrees). The CO bond length (1.422 Å), is longer than in $CH_3OH$ (1.417 Å). Actually, it is the longest CO bond length determined so far in alicyclic molecules [15], see also table 17.

## 5. The OH bond length

### 5.1. *Relationship r(OH) vs. v(OH)*

The stretching force constants are related to the bond strength and one can expect a good correlation between the length of a bond and the corresponding diagonal stretching force constant to occur, as shown for instance by Badger [147, 148]. In principle, such a correlation might be used to determine bond lengths, but it is often more difficult to accurately determine force constants than bond lengths because the number of force constants, $(1/2)n_{vib}(n_{vib}+1)$, is usually larger than the number of fundamental vibrations, $n_{vib}$, and additional information (vibrational frequencies of isotopic species,…) is required to determine the force constants. There are however a few cases in which the bond length vs. diagonal force constant correlation is relevant. One is when the molecule is simple enough and this correlation has been for instance used to determine the Au–Au bond length in several molecules [149].

More generally, when a vibrational mode $i$ has characteristic frequency far from the others, $i'$, it may be considered as isolated. In other words, the non-diagonal force constants $f_{ii'}$ are then negligible compared to the corresponding energy differences $E_i - E_{i'}$. Thus, in this particular case, a relationship between the bond length and the corresponding stretching vibrational frequency is to be expected. Such a relationship was first pointed out by Bernstein [150] and considerably developed by McKean [151], for CH bonds. The method previously exposed, replacing all hydrogens by deuterium but one in a molecule was extensively used. It efficiently decouples the remaining lone CH stretch from the other stretching motions in the molecule as well as from the first overtone of the bending modes, actually except for $CHX_3$ molecules where X is an halogen atom [152].The 'resolution' of the correlation is at the level of a shift in the isolated CH stretching fundamental frequency of $10\,cm^{-1}$, corresponding to a bond length change of about 0.001 Å[1], –C–H bond lengths can thus be determined with a precision of about 0.002 Å, from this correlation. This method was extended by McKean to SiH and GeH bond lengths [153]. Such a linear relationship was also suggested to exist between $r(OH)$ and $\nu(OH)$ [3] and between $r(NH)$ and $\nu(NH)$ [2]. A non-linear relationship between $r(N{=}O)$ and $\nu(N{=}O)$ was also pointed out [154].

The equilibrium values of the OH bond lengths and the corresponding 'isolated' stretching frequencies $\nu_{is}(OH)$ were listed in table 1, for all molecules discussed in sections 3 and 4. Within this selected set of species, the maximum and minimum bond lengths are 1.028 Å for $OH^+$ and 0.946 Å for MgOH, respectively. They thus range over some 0.082 Å. The median value of all listed bond lengths is $r_e(OH) = 0.963\,Å$. Similarly, the maximum and minimum stretching frequencies are $3851\,cm^{-1}$ for MgOH

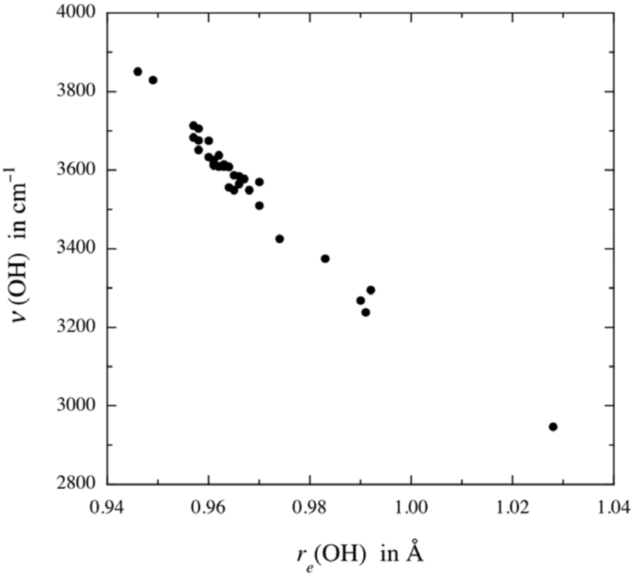

Figure 2. Correlation between isolated stretching frequencies, $\nu$(OH) (cm$^{-1}$) and equilibrium distances $r_e$(OH) (Å) in a selected set of compounds (see table 1).

and 2947 cm$^{-1}$ for OH$^+$, respectively. These values thus extend over some 904 cm$^{-1}$, with a median value of $\nu_{is}$(OH) = 3610 cm$^{-1}$. A plot of $r_e$(OH) as a function of $\nu_{is}$(OH) is presented in figure 2. It demonstrates a very good, linear correlation, as anticipated. The very few discrepancies with this very regular behaviour, concerning OH, OH$^+$ and Glycine IIn, are discussed hereafter:

- OH$^+$ is specific because the bonding is expected to be of rather different nature in this open shell ion.
- OH also presents an open shell structure, thus again supporting a behaviour different from the majority of compounds.
- Glycine IIn data is less than optimally reliable. On the one hand, it is indeed not clear whether the OH stretching frequency provided is truly isolated. On the other hand, the listed O–H bond length, predicted to be 0.005 Å shorter from figure 2, could suffer from various approximations. The semi-experimental structure is actually difficult to determine because there are 24 independent structural parameters. Five constraints had to be introduced. Furthermore, the rotational constants of the –OD species had to be excluded from the procedure. The accuracy of the semi-experimental $r_e$(OH) bond length might thus be worse than the standard deviation obtained from the least squares fit, 0.002 Å. This conclusion is strengthened by the fact that the CCSD(T)/VTZ(*ae*) value, expected to be close to the true $r_e$ value [155], is only 0.977 Å.

Excluding OH, OH$^+$ and Glycine IIn, one can least squares fit the remaining 28 data points, resulting into the following expression

$$r_e(\mathrm{OH})\ [\text{Å}] = 1.2261(76) - 7.29(21) \times 10^{-5}\ \nu_{is}(\mathrm{OH})\ [\mathrm{cm}^{-1}] \qquad (3)$$

with a correlation coefficient $\rho = 0.979$ and a standard deviation $\sigma = 0.0015$ Å. A variation in OH bond length of 0.001 Å thus corresponds to a variation in OH stretching frequency of 13 $cm^{-1}$.

High level *ab initio* calculations can deliver accurate $r_e$(OH) bond lengths but at a high computational cost, which is not affordable for large molecules. The correlation between $r_e$(OH) and of $\nu_{is}$(OH), from equation (3) thus provides a cheap alternative to predict O–H bond lengths.

### 5.2. *Lower level* ab initio *calculations*

Unfortunately, an estimate of $\nu_{is}$(OH) cannot always be obtained. It is therefore interesting to check the accuracy of lower level *ab initio* calculations to replace the suggested procedure in order to estimate O–H bond lengths. Such lower level calculations are indeed readily accessible and, if the electron correlation is correctly taken into account (at least at the MP2 level) and if the basis size is large enough, there is an offset, generally almost constant for a given bond, which can thus be corrected by comparing to similar molecules whose structure is accurately known. The equilibrium values of the O–H bond lengths of a few molecules are summarized in table 15 together with the *ab initio* values calculated at four different levels of theory: CCSD(T)/AVTZ, CCSD(T)/VTZ, MP2/VQZ, and MP2/VTZ. The mean, standard deviation, median, standard deviation, range and largest (absolute) value of the residuals are also given at the bottom of table 15. The MP2/VQZ level of theory gives the smallest offset (mean value of the residuals). The CCSD(T)/VTZ level of theory gives the smallest standard deviation, the smallest range, and the smallest maximum deviation. The CCSD(T)/AVTZ level of theory gives the largest offset and the largest maximum deviation. There are very few exceptions. The only one at the MP2 level is $HOC^+$ which is not surprising because the $T_1$ diagnostic is large indicating that the MP2 method is not expected to be accurate in this case. On the other hand, this species is no more an outlier at the CCSD(T) level. At the CCSD(T)/VTZ level, the largest outlier is $OH^-$ (0.003 Å), probably revealing a too small basis set in the calculations. It therefore appears that, in most cases, it is possible to obtain a reliable structure using the MP2 method provided that a single-reference treatment is appropriate. The VQZ basis set is to be preferred to the smaller VTZ basis set, however, the improvement is not great. On the other hand, the inclusion of diffuse functions (with the AVTZ basis set) does not improve the prediction. As a conclusion, lower level calculations indeed do provide an interesting method to predict O–H bond lengths, whenever $\nu_{is}$(OH) cannot be estimated. It requires accounting for specific offsets, whose typical values are provided in table 15.

## 6. Hydrogen bond

Some molecules studied in this work present intramolecular hydrogen bonding $OH\cdots X$ (X=N, O, F) which can be highlighted by three flags: the short distance $d(H\cdots X)$, the large value of $r_e$(OH) and the red shift of $\nu_{is}$(OH). The known related values are gathered in table 16 for all relevant species investigated here. It is interesting to note, in figure 2, that the presence of the hydrogen bond has no effect on the

Table 15. Equilibrium and *ab initio* OH bond lengths (in Å).

| | | CCSD(T) | | MP2 | |
|---|---|---|---|---|---|
| | $r_e$(O–H)[a] | AVTZ | VTZ | VQZ | VTZ |
| LiOH | 0.9490 | 0.9515 | 0.9497 | 0.9495 | 0.9507 |
| $NH_2OH$ | 0.9580 | 0.9621 | 0.9598 | 0.9586 | 0.9600 |
| $BH(OH)_2$ *cis* | 0.9559 | 0.9600 | 0.9587 | 0.9573 | 0.9591 |
| BHFOH | 0.9567 | 0.9607 | 0.9595 | 0.9580 | 0.9598 |
| $CH_3OH$ | 0.9569 | 0.9611 | 0.9595 | 0.9578 | 0.9595 |
| $BF_2OH$ | 0.9574 | 0.9613 | 0.9600 | 0.9585 | 0.9603 |
| $H_2O$ | 0.9578 | 0.9616 | 0.9594 | 0.9577 | 0.9591 |
| $BH_2OH$ | 0.9580 | 0.9619 | 0.9609 | 0.9591 | 0.9610 |
| *t*-$CH_3CH_2OH$ | 0.9580 | 0.9617 | 0.9601 | 0.9588 | 0.9605 |
| $BH(OH)_2$ *trans* | 0.9598 | 0.9640 | 0.9627 | 0.9611 | 0.9629 |
| $CH_2{=}CHOH$ | 0.9602 | 0.9644 | 0.9632 | 0.9620 | 0.9639 |
| HOSH | 0.9606 | 0.9631 | 0.9616 | 0.9620 | 0.9632 |
| $H_2O_2$ | 0.9609 | 0.9665 | 0.9640 | 0.9631 | 0.9644 |
| c-HCOOH | 0.9610 | 0.9650 | 0.9633 | 0.9624 | 0.9639 |
| HOCl | 0.9624 | 0.9673 | 0.9652 | 0.9653 | 0.9665 |
| HOBr | 0.9625 | 0.9671 | 0.9651 | 0.9658 | 0.9669 |
| HOCN | 0.9629 | 0.9669 | 0.9656 | 0.9646 | 0.9663 |
| $H_2SO_4$ | 0.9640 | 0.9680 | 0.9662 | 0.9666 | 0.9680 |
| $OH^-$ | 0.9643 | 0.9678 | 0.9676 | 0.9627 | 0.9653 |
| *t*-HONO | 0.9650 | 0.9689 | 0.9664 | 0.9665 | 0.9677 |
| *c*-$COHCH_2OH$ | 0.9653 | 0.9694 | 0.9679 | 0.9671 | 0.9687 |
| *t*-HCOOH | 0.9660 | 0.9701 | 0.9686 | 0.9678 | 0.9695 |
| HOF | 0.9665 | 0.9703 | 0.9677 | 0.9663 | 0.9674 |
| $HNO_3$ | 0.9681 | 0.9722 | 0.9701 | 0.9697 | 0.9710 |
| HC(O)COOH | 0.9697 | 0.9735 | 0.9723 | 0.9722 | 0.9739 |
| *c*-HONO | 0.9743 | 0.9784 | 0.9765 | 0.9771 | 0.9785 |
| $HOCO^+$ | 0.9828 | 0.9865 | 0.9851 | 0.9850 | 0.9866 |
| $HOC^+$ | 0.9896 | 0.9918 | 0.9916 | 0.9934 | 0.9950 |
| Mean | | −0.0039 | −0.0023 | −0.0015 | −0.0031 |
| Median | | −0.0040 | −0.0026 | −0.0015 | −0.0031 |
| Standard deviation | | 0.0007 | 0.0007 | 0.0011 | 0.0010 |
| Range | | 0.0034 | 0.0026 | 0.0054 | 0.0045 |
| Max | | 0.0056 | 0.0033 | 0.0038 | 0.0054 |

[a] For references, see table 1.

Table 16. $r(H\cdots X)$ distance, sum of van der Waals radii[a] $r(H)+r(X)$, $r_e(OH)$ bond length[b] (in Å) and $\nu(OH)$ stretching frequencies[b] (in $cm^{-1}$) in molecules with an intramolecular H bond.

| Molecule | X | $r(H\cdots X)$ | $r(H)+r(X)$ | $r_e(OH)$ | $\nu(OH)$ |
|---|---|---|---|---|---|
| $BF_2OH$ | F | 2.44 | 2.55 | 0.957 | 3713 |
| $H_2SO_4$ | O | 2.42 | 2.72 | 0.962 | 3609 |
| $BH(OH)_2$ | O | 2.40 | 2.72 | 0.960 | |
| *t*-HCOOH | O | 2.31 | 2.72 | 0.966 | 3565 |
| Glycine Ip | O | 2.28 | 2.72 | 0.966 | 3585 |
| $HNO_3$ | O | 2.13 | 1.55 | 0.968 | 3549 |
| *c*-HONO | O | 2.11 | 2.72 | 0.974 | 3426 |
| $CH_2{=}CHOH$ | C=C | 2.10 | 2.90 | 0.960 | 3634 |
| HCOCOOH | O | 2.09 | 2.72 | 0.970 | 3510 |
| $CHOCH_2OH$ | O | 2.07 | 2.72 | 0.966 | 3549 |
| Glycine IIn | N | 1.90 | 2.75 | 0.992 | 3295 |
| Proline I | N | 1.88 | 2.90 | 0.991 | 3025 |

[a] Ref. [164].

[b] For references, see table 1.

Table 17. Angle ∠(COH) (in degrees) and distances $r_e$(C–O) and $r_e$(OH) in molecules[a] with an intramolecular H bond H···O.

| Molecule | ∠(COH) | $r_e$(C–O) | $r_e$(O–H) |
|---|---|---|---|
| HOCN | 109.7 | 1.300 | 0.963 |
| *c*-HCOOH | 109.3 | 1.348 | 0.961 |
| $CH_2$=CHOH | 108.7 | 1.359 | 0.960 |
| *t*-$CH_3CH_2OH$ | 108.5 | 1.422 | 0.965 |
| $CH_3OH$ | 108.3 | 1.417 | 0.957 |
| $CH_2OH$ | 108.2 | 1.370 | 0.958 |
| *t*-HCOOH | 106.9 | 1.341 | 0.966 |
| HCOCOOH | 106.7 | 1.332 | 0.970 |
| $CHOCH_2OH$ | 106.0 | 1.396 | 0.966 |
| Glycine Ip | 106.0 | 1.353 | 0.966 |
| Glycine IIn | 105.2 | 1.333 | 0.992 |
| Proline I | 102.2 | 1.328 | 0.991 |

[a] For references, see table 1.

correlation $r_e$(OH) vs. $\nu_{is}$(OH). The parameters in the hydrogen-bonded species fit the same correlation curve and it is thus still possible to accurately predict the length of the OH bond. Likewise, either the MP2 method or the CCSD(T) method with the relatively small VTZ basis set, give satisfactory results although the offset seems to be a little bit larger (in absolute value) in presence of a hydrogen bond.

Another criterion of the existence of intramolecular hydrogen bonding is the shortening of the C–O bond to which the hydrogen is attached. However, the C–O bond length is affected by many factors (partial double bond character,...) and this specific effect is therefore difficult to highlight. The ∠(COH) (or ∠(XOH)) angle which should be smaller in presence of hydrogen bonding probably provides a more reliable criterion. Its value which is typically around 108.3 degrees (for $CH_3OH$) indeed becomes significantly smaller in presence of hydrogen bonding, the shortening being correlated with the lengthening of the OH bond, see table 17.

## 7. Conclusions

The equilibrium length of the O–H bond has been reviewed and accurately determined, in various molecules. The compounds selected for the present study actually constitute the smallest and most distinguished group of organic and inorganic molecules that contain the OH bond. It is found that for the $r$(OH) bond length, a quadruple zeta basis set is large enough, the improvement brought by larger basis sets (V5Z, AV5Z) being almost negligible. Furthermore the core correction is small and practically constant, its value being −0.0009 Å. We also demonstrated that, in most case, the MP2 method is accurate enough provided a small offset correction is added. Finally, the following accurate correlation is confirmed between $r_e$(OH) bond lengths and corresponding $\nu_{is}$(OH) stretching frequencies: $r_e(\mathrm{OH})\ [\text{Å}] = 1.2261(76) - 7.29(21) \times 10^{-5}\ \nu_{is}(\mathrm{OH})\ [\mathrm{cm}^{-1}]$. This correlation may be used to predict $r_e$(OH) bond lengths or, inversely $\nu_{is}$(OH) stretching frequencies, provided the other parameter can be reliably determined.

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