Role of vibrational anharmonicity in atmospheric radical hydrogen-bonded complexes

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Abstract

Harmonic and anharmonic vibrational frequency calculations are reported for the most stable hydrogen bonded complexes formed between the hydroperoxyl radical and formic, acetic, nitric, and sulphuric acids which are of atmospheric interest. A comparison between the calculated IR spectra of the hydrogen bonded complexes with the corresponding separate monomers is also reported with the aim to facilitate a possible experimental identification of these complexes. The calculations have been carried out using the second-order vibrational perturbative treatment implemented by Barone applied to the PES obtained with the B3LYP functional using the 6-31+G(d,p) and 6-311+G(2d,2p) basis sets. Our calculations for the separate monomers predict vibrational frequencies with a quite good agreement with the experimental values. The anharmonic contribution results in differences of around 40 cm^{-1} with respect to the harmonic values; although in some cases involving, highly anharmonic modes, these differences can rise up to of 300 and 450 cm^{-1}.

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1) Introduction

In recent years an increased interest has been observed in the study of the free radicals because of their key role in different fields of science, such as atmospheric chemistry, catalysis, and biological processes.[1-5] For instance, in Earth's atmosphere the reactions including free radicals are generally fast compared to reactions with closed-shell species. Furthermore, it has been shown that the formation of pre-reactive complexes involving hydrogen bonds has an important role in the kinetic behavior of atmospheric reactions,[4,6,7] the photochemistry of the species,[8,9] the spread of contamination through the atmosphere, and the formation of aerosols.[10-13] Therefore, the description of pre-reactive hydrogen-bonded complexes formed between radical and neutral molecules becomes essential to understand the atmospheric reactions.[14-17]

One of the relevant atmospheric radicals is the hydroperoxyl radical (HOO·). A large amount of research work has been devoted to the hydrogen-bonded complexes between HOO· and neutral molecules of atmospheric relevance.[18-36] The great deal of interest in these hydroperoxyl radical complexes resides on the large stability of the hydrogen bond formed, which is even larger than their corresponding water counterpart (changing the HOO· for water and maintaining the neutral molecule). On the basis of these stabilities, it has been theoretically predicted the existence of HOO·-neutral molecule complexes in the atmosphere.[3-5]

One of the main purposes of the papers reported in the literature on this subject is to provide accurate theoretical data to assist in the experimental identification of these complexes. The formation of these hydrogen bonded complexes provokes changes in the vibrational frequencies of the separate monomers and in their intensities as well, which are especially relevant for the IR bands associated to the hydrogen bonds. Moreover, new IR bands arise as a result of the intermolecular interaction.

The majority of the theoretical infrared spectra of these HOO·-neutral molecule complexes published are evaluated using the harmonic approximation. However, it is well-know the relevance of the vibrational anharmonicity in the hydrogen-bonded systems.[37-40] In addition, and as far as we know, the few theoretical works about the IR spectra of these type of complexes[24,30-32] that took into account the anharmonic effects did not included the coupling between normal modes. Nevertheless, the calculation of the non diagonal anharmonic mode-mode coupling is essential for the accurate simulation of the IR spectra. Fortunately in the last years many different methodologies have been implemented to evaluate vibrational wavefunctions including both the diagonal and non diagonal (*i.e.* mode-mode coupling) anharmonicity. Among them, it is important to remark the vibrational self-consistent field (VSCF)[41-44] and the second-order vibrational perturbative vibrational treatment (VPT2).[45-49]

In the VSCF procedure each mode vibrates in the average potential generated by all other modes. The correlation between modes can be introduced through post-VSCF procedures such as perturbation theory (VMP2),[50-52] configuration interaction (VCI),[53-55] and coupled-cluster techniques (VCC).[56,57] Although the VSCF and post-VSCF have been successfully applied for a large variety of systems,[58-62] the present work is focused on the Barone implementation of the VPT2 method,[48] which has become an effective choice to investigate vibrational properties of semirigid molecules[63-67] and systems involving hydrogen bonds.[68-71] Moreover, it is worth noting that alternative implementations of the VPT2 approach have been also reported on the literature and successfully applied to a large set of harmonic and anharmonic systems.[46,49,72,73] These methods essentially differ from the Barone VPT2 in the scaling of the force constants, the truncation of the PES used, and the selection of the Fermi resonances explicitly included.

In the Barone VPT2 method, the zeroth-order vibrational wavefunctions are obtained from the harmonic approximation. The anharmonic vibrational wavefunctions and energies are obtained by second-order perturbation theory using all non resonant harmonic energy terms followed by a variational treatment of the relevant resonant interactions. The second-order perturbation theory correction is applied to a potential energy surface (PES) approximated by a Taylor series in normal coordinates, q_i, that includes the quadratic, and all cubic, and semidiagonal quartic force constants.

$$V(q_1, q_2, \ldots, q_N) \cong \frac{1}{2}\sum_i w_i q_i^{\,2} + \frac{1}{6}\sum_{ijk} f_{ijk} q_i q_j q_k + \frac{1}{24}\sum_{ijk} f_{ijkk} q_i q_j q_k q_k \ . \qquad (1)$$

At this point it is important to remark that harmonic force constants are not scaled and all the 3N-6 normal modes are included in the fourth-order semidiagonal PES used in the Barone VPT2 approach. The cubic and semidiagonal quartic force constants are computed by a finite difference approach, which scales linearly with the number of normal modes. The second-order perturbation theory correction includes also a kinetic contribution arising from the vibrational angular momentum. Furthermore, the Coriolis couplings and Fermi resonances are also taken into account in the VPT2 approach. In order to determine which Fermi resonances are included Barone VPT2 algorithm uses the simple formulas of Martin *et al.*[74] that give quite good estimations of the difference between including explicitly a Fermi resonance and absorbing it into the anharmonic constants (10 cm^{-1} is used as default value for maximum allowed difference).

Using the VPT2 methodology Carbonniere *et al.*[66] found that excellent harmonic and anharmonic frequencies for semirigid molecules can be obtained with the B3LYP/6-31+G(d,p) level. This is one of the levels of calculation used in the present work.

Two are the main goals of the present work. First, provide theoretical anharmonic vibrational spectra for the hydroperoxyl radical-neutral molecule hydrogen-bonded complexes more accurate than their harmonic counterparts. This theoretical data may assist in experimental detection of the complexes using infrared spectroscopy. As far as we know, it has never been reported on the literature neither VSCF nor VPT2 calculations for complexes involving hydrogen bonds between the hydroperoxyl radical and a neutral molecule. Secondly, test the performance of the B3LYP/6-31+G(d,p) level to evaluate the anharmonic contributions using the VPT2 methodology for highly anharmonic systems. The selected complexes for the present study are the most stable hydrogen bonded complexes formed between the hydroperoxyl radical and formic ($HCOOH$), acetic (CH_3COOH), nitric (HNO_3), and sulphuric (H_2SO_4) acids, all these systems playing a fundamental role in the atmospheric chemistry, *e.g.* H_2SO_4 and HNO_3 are components of the acid rain.[75,76]

2) Computational details

The B3LYP[77,78] exchange-correlation functional with 6-31+G(d,p) and 6-311+G(2d,2p) basis sets[79,80] have been used to optimize the geometries of the monomers and complexes and to calculate their frequencies. The calculations for the open-shell systems have been done within the unrestricted formulation, whereas for the closed-shell system the restricted approach has been followed. The spin contamination for all the radical systems is very small with $\left\langle S^2 \right\rangle$ values always smaller than 0.755. The anharmonic corrections have been evaluated by the second-order perturbative treatment implemented by Barone,[48,81] and the requested third and fourth energy derivatives with respect to normal coordinates have been calculated by numerical differentiation of the analytical Hessians. All calculations have been carried out using Gaussian 03.[82]

The effect of extending the basis set, by including diffuse functions on the hydrogen atoms, and the functional, was also checked by performing additional calculations on one hydrogen bonded complex and its reactants at B3LYP/6-311++G (2d,2p), MP2/6-311++G(2d,2p), and M05-2X/6-311++G(2d,2p) and the results are included in the supplementary information.[83,84]

3) Results and Discussion

a) Structures and vibrational frequencies of the monomers

Figure 1 displays the theoretical and experimental geometrical parameters for the isolated systems studied in this work. One can notice that the optimized geometrical parameters evaluated at B3LYP/6-311+G(2d,2p) level quantitatively agree with the experimental results obtained from literature,[85-88] showing a maximum difference of 0.04 Å for distances and 7° for angles, both maxima for the sulfuric acid structure. The optimized geometrical parameters at B3LYP/6-31+G(d,p) level are not reported on Figure 1, but they also show a good agreement with the largest basis set, displaying maximum deviations of 0.03 Å and 2° for distances and angles, respectively.

(Please insert Figure 1 around here)

In order to check if this agreement between theoretical and experimental geometrical parameters for the isolated systems can also be extrapolated to their spectroscopic counterpart, the Tables 1-3 contain the calculated harmonic and anharmonic vibrational frequencies and their experimental counterparts for the 5 monomers studied in this work. In addition, these Tables also include the mean absolute deviation, Δ_{mean}, and the maximum deviation, $\Delta_{\max}$, values of the theoretical vibrational frequencies with respect to the experimental values. The Δ_{mean} has been calculated as the sum over all the normal modes of the absolute difference between the theoretical frequency and the experimental ones divided by the total number of normal modes, *i.e.* $\sum_{i=1}^{N}\left(\left|v_i(theor)-v_i(\exp)\right|/N\right)$.

(Please insert Tables 1-3 around here)

The first important conclusion obtained from the Tables 1-3 is that the theoretical vibrational frequencies are converged with respect to the size of the basis set. Thus the increase of 6-31+G(d,p) to 6-311+G(2d,2p) basis sets is not crucial for the evaluation of the infrared anharmonic spectra of the monomers. This fact can be noticed by comparing the harmonic and anharmonic frequencies obtained using the two basis sets with respect to the experimental values. For instance, the anharmonic Δ_{mean} using the 6-311+G(2d,2p) basis set lies in the range from 7.4 to 34.8 cm^{-1}, while the 6-31+G(d,p) basis set lies in the range from 9.1 to 49.1 cm^{-1} (similar conclusions can be also obtained from the harmonic contributions and from the $\Delta_{\max}$ values).

The introduction of the anharmonicity through the VPT2 methodology provokes an important reduction of Δ_{mean} and $\Delta_{\max}$ values, indicating the key role of the anharmonicity in the evaluation of vibrational states. As one can see in the Tables 1-3, Δ_{mean} ($\Delta_{\max}$) values for the harmonic vibrational frequencies using 6-311+G(2d,2p) basis set lie in the range from 36.6 (169.5) to 99.8 (211.3) cm^{-1}. But when the VPT2 anharmonic contribution is taking into account Δ_{mean} ($\Delta_{\max}$) interval goes from 7.4 (13.4) to 34.8 (116.7) cm^{-1}. Thus the differences of the theoretical frequencies with respect to the experimental values are reduced an average of 1/3 when the anharmonicity is included through the VPT2 method. The VPT2 method results especially effective predicting the vibrational frequencies of formic and nitric acids and hydroperoxyl radical with calculated $\Delta_{\max}$ always smaller than 50 cm^{-1}. For most of the normal modes of the sulfuric and acetic acids the vibrational perturbation theory also presents an important improvement of the harmonic approximation, although some specific anharmonic normal modes differ in about 100 cm^{-1}, *e.g.* the C-O-H bending of the CH_3COOH, with respect to the experimental values. One possible approach to try to improve the worst results could be to separate the low frequency modes (*i.e.* bellow 500 cm^{-1}) from the remaining modes, which is out of the Barone code capabilities..

It is important to remark that the good performance of the VPT2 methodology to reproduce the IR spectrum of these monomers is observed even in the case with the largest perturbation correction to the harmonic frequencies, *i.e.* the O-H stretching of the hydroperoxyl radical. In this mode, the anharmonic perturbation correction is -206.1 cm^{-1} (3410.8 minus 3616.9 cm^{-1}), but whereas the difference between the anharmonic frequency and the experimental value is only -25.4 cm^{-1}, its harmonic counterpart is 180.7 cm^{-1}.

To sum up, these results lead us to conclude that the VPT2 methodology with a potential energy surface obtained at B3LYP/6-31+G(d,p) level represents an effective and reliable choice to reproduce the experimental spectra of the monomers studied in this work. In the incoming sections, we will also use this level of methodology to provide accurate geometries, stabilities, and mainly vibrational spectra for the hydroperoxyl radical-neutral complexes.

b) Structures and stabilities of the hydrogen-bonded complexes

The geometrical parameters for the 4 hydrogen bonded complexes optimized at

B3LYP level using the 6-31+G(d,p) and 6-311+G(2d,2p) basis sets are displayed in Figure 2. The names used to refer each studied complexes is also reported on the Figure 2. Table 4 collects their relative electronic energetic stabilities, ΔE, relative electronic energies with their harmonic, $ZPVE_{har}$, and anharmonic, $ZPVE_{anhar}$, zero-point vibrational energy contributions, enthalphies with harmonic, ΔH_{har}, and anharmonic contributions, ΔH_{anhar}, and Gibbs free energy also with harmonic, ΔG_{har}, and anharmonic, ΔG_{anhar}. Our results with respect to geometrical, energetic stabilities, and harmonic ZPVE, enthalphies, and Gibbs free energies compare very well with those previously reported in the literature.[18-22] Then, we will only discuss their main features.

(Please insert Figure 2 and Table 4 around here)

First of all, notice that the complexes studied present cyclic seven member ring structures, stabilized by two hydrogen bonds. One hydrogen bond is formed with the hydrogen of the hydroperoxyl radical and the oxygen of the carbonyl group (sulfonyl and nitro groups in the cases of sulphuric and nitric acids, respectively, OOH···OXOH). The other hydrogen bond is formed between the acidic hydrogen and the terminal oxygen of the hydroperoxyl radical (OXOH···OOH). Thus, each moiety of the complex acts as hydrogen donor and acceptor simultaneously. The results displayed in Figure 2 show again a good agreement between the geometrical parameters obtained using the two basis sets with maximum deviations of 0.02 Å and 2º for the distances and angles, respectively, both maxima for **C4**. Then from now on, the only geometrical parameters discussed in the text are those obtained with the largest basis set.

The computed distances for the OOH···OXOH hydrogen bond vary among 1.612 and 1.773 Å, whereas for the OXOH···OOH hydrogen bond the distances vary among 1.680 and 1.740 Å. Please note that for the **C1** and **C2** complexes the OOH···OXOH bond lengths are shorter than the OXOH···OOH bond distances, while for **C3** and **C4** holds the contrary. As pointed out by Steiner,[89,90] these OH···O hydrogen bond interactions can be understood as an incipient proton transfer reaction, so that the different hydrogen bond distances reflect, and in some way form a phenomenological point of view about, the distinct acidic character of each monomer.

Regarding the energetic stability, the $\Delta(E + ZPVE_{anhar})$ values from Table 4 indicate that the stability of these complexes ranges among -9.30 and -13.59 kcal/mol (among -14.09 and -9.74 kcal/mol considering enthalpies and among -3.52 and 0.65 kcal/mol considering Gibbs free energies). In addition the high stability of these complexes is reflected in their geometries in three different ways: short hydrogen bond distances (from 1.622 to 1.773 Å), directionality of the hydrogen bonds (from 158.7º to 178.5º), and perturbations that the complex formation provoke in the monomers structures (especially in the ·O-OH and C/S/N=O distances). Notice that the geometry of the most stable complex, **C2**, presents one very short (1.612 Å) and strong hydrogen bond and a second one larger and weaker (1.740 Å), instead to present two intermediate hydrogen bonds, *e.g.* the **C4** complex.

Finally, it is worth noting that the introduction of the harmonic ZPVE, enthalpic and Gibbs free energy corrections in the calculation of the energetic stabilities is quite relevant whereas the additional consideration of the anharmonic effects is irrelevant. For instance, the $\Delta(E + ZPVE_{har})$ and $\Delta(E + ZPVE_{anhar})$ values differ in less than 0.2 kcal/mol (see Table 4). Consequently, we conclude that that *the effect of the anharmonicity in estimating the stabilization energies of these complexes is very small*. On the other hand, the change of the 6-31+G(d,p) to the 6-311+G(2d,2p) basis set shows an effect in the ΔE values of around 0.5 kcal/mol. Then the basis set superposition error (BSSE) will show a important role in the stabilization energy of these complexes (around 2 kcal/mol), as it has been pointing out in the literature.[21,22] Nevertheless, although the BSSE for basis set with diffuse functions included could cause changes in the anharmonic vibrational frequencies of hydrogen-bonded dimmers between 1-20 cm^{-1},[91] these corrections would not change the conclusions of this paper about the important role of the anharmonic corrections.

c) Anharmonicity of the hydrogen-bonded complexes

This section will be devoted on the analysis of the basis set dependency and the anharmonicity character of the vibrational spectra of hydrogen-bonded complexes. The harmonic and anharmonic vibrational frequencies and harmonic intensities of the four complexes studied using the 6-311+G(2d,2p) basis set are listed in Tables 5-8. The values obtained with the 6-31+G(d,p) basis set are also reported in the supporting information.

As it has been noticed in the isolated molecules, the calculation of the harmonic vibrational frequencies shows a good convergence with respect to the basis set size. Then the use of the 6-311+G(2d,2p) instead of 6-31+G(d,p) basis set is not essential for the evaluation of the harmonic vibrational frequencies. For instance, the average of the differences between the harmonic vibrational frequencies evaluated using the two basis sets lies in the range from 7.0 (**C2**) to 13.3 (**C4**) cm^{-1}, although some specific vibrational modes, *e.g.* the OO-H stretching of the complex **C2**, can have a difference of around 50 cm^{-1}. On the other hand, the anharmonic VPT2 vibrational frequencies show a slightly larger basis set dependency. The values of the average of the differences between the anharmonic vibrational frequencies using the two basis sets vary from 12.6 (**C2**) to 18.3 (**C4**) cm^{-1}. At this point we want to stress the effect of the basis set on the stretching of the OO-H bond and the bending of the hydroperoxyl radical of the complex **C2**. For these modes the improvement of the basis set employed (from 6-

31+G(d,p) to 6-311+G(2d,2p)) provokes a change in the VPT2 vibrational frequencies of 68.1 and 79.5 cm^{-1}, respectively.[83] However, as we will show in the incoming paragraphs, this basis set dependency in the vibrational frequencies is small with respect to the effect of the inclusion of the anharmonicity.

(Please insert Tables 5-8 around here)

The values displayed in Tables 5-8 indicate that the anharmonic contribution provokes differences of around 40 cm^{-1} with respect to the harmonic values. However, in some cases (highly anharmonic modes) these differences can rise up to of 300 and 450 cm^{-1}. These highly anharmonic modes are mostly vibrations associated to hydrogen bond interactions (*e.g.* the stretching frequencies of C/N/S(O)-H and OO-H bonds, the bending of the hydroperoxyl monomer, or the C/N/S(O)-H and O-(O)H waggings out of the plane). The O-H stretchings involved in the hydrogen bonds could be considered the most relevant, with displacements larger than 250 cm^{-1} from the harmonic ones at VPT2 level of theory. For instance, Table 6 shows that the O-H stretchings in **C2** present anharmonicity effects of -314.5 cm^{-1} (2920.5 minus 3235.0 cm^{-1}) and -449.0 cm^{-1} (2468.0 minus 2917.0 cm^{-1}) at the B3LYP/6-311+G(2d,2p) level, indicating the important anharmonicity of this complex. Another interesting system to be analyzed is complex **C4** (see Table 8), which shows the clear link between the anharmonicity of the O-H stretchings and the hydrogen bond interaction. Whereas the VPT2 anharmonic correction for the frequency of the stretching of the isolated SOH group is -169.0 cm^{-1}, its counterpart for the stretching of the complex SOH group, which forms the hydrogen bond with the hydroperoxyl radical, is -368.3 cm^{-1}. There are several other vibrational modes that also show a high anharmonicity degree. For instance, the bending of the hydroperoxyl moiety presents differences between the computed harmonic and anharmonic values of 95.8 cm^{-1} for **C1** complex. These results illustrate the relevance of the VPT2 correction in the evaluation of vibrational spectra for species with weak interactions. Indeed the important effect of the VPT2 correction is more evident if one focus on the shift between the frequencies of the monomers and their counterparts in the complexes (see section d).

Last but not least, it is important pointing out that some of the largest anharmonic corrections to vibrational frequencies have to be taken with *caution* since they have been evaluated using a truncated PES and the perturbation theory.[84] The coupling between anharmonic low and high frequency modes generate very large cubic and quartic force constants, which could be a handicap for the convergence of the perturbation method. Nevertheless, VPT2 procedure leads to an excellent theoretical simulation of the experimental spectra for all the monomers (*vide supra*). This very good performance of VPT2 for the monomers make us believe that the VPT2 results for the largest anharmonic corrections to vibrational frequencies of the hydrogen-bonded complexes will represent at least an improvement of the approximate harmonic ones. In order to validate the VPT2 results for these highly anharmonic systems it would be necessary to apply vibrational variational methods, *i.e.* VCI or VCC, and using a full PES, although this point is out of scope and possibilities of this work. In any case, we are confident that the anharmonic effects computed in this way will help experimentalists to identify and characterize these hydrogen bonded complexes.

d) The importance of the anharmonic effects in the shifts between hydrogen bounded complexes and monomers IR spectra.

The IR spectra have been proven to be an important tool for identifying and characterizing hydrogen bonded complexes when compared with those of the separated monomers. Conventional hydrogen bonds of the type O-H···O, considered in the present work, produce a red-shift in the O-H stretching band in an amount that depends on the strength of the hydrogen bond. Moreover the O-H stretching intensities are enhanced according to the changes in the associated dipole moments. These shifts are very useful for the complex identification, but the formation of the complexes can also produce significant changes in other IR frequencies. In addition, as it has been pointed out above, new bands appear as a consequence of the interactions occurring in the formation of the complex, which can be also considered as a signature of the complexes. The predictions derived from the theoretical works constitute an important help for the identification of the spectra and in what follows we will focus our attention on the anharmonic effects, with the aim of helping possible experimental work. In Tables 5-8 we have collected, in parentheses, the shift of the vibrational frequencies of the complexes relative to the monomers and the ratios between the intensity of the complexes and their corresponding monomers, according to the calculations performed at the B3LYP/6-311+G(2d,2p) level of theory.

The first point we have analyzed is the effect of the anharmonicity in the $\Delta\nu$ values. The results from Tables 5-8 show that, in many cases, the effect of the anharmonicity on $\Delta\nu$ is larger than on ν. For instance, on one hand the CO-H stretching of **C1** is computed to be $\nu(har) = 3201.9$ cm^{-1} and $\nu(anhar) = 2873.5$ cm^{-1} with an anharmonic effect of -328.4 cm^{-1}, which represents around 10% of the ν values. On the other hand the predicted red-shifts for this vibrational mode are $\Delta\nu(har) = -537.7$ cm^{-1} and $\Delta\nu(anhar) = -673.7$ cm^{-1} with an anharmonic effect of -136.0 cm^{-1}, which represents around 20% of the $\Delta\nu$ values (see Table 5). For the other complexes considered, similar differences are also observed, with the maximum value between $\Delta\nu(har)$ and $\Delta\nu(anhar)$ being -242.9 cm^{-1} for the OO-H stretching of **C2** ($\Delta\nu(har) = -699.9$ cm^{-1} and $\Delta\nu(anhar) = -942.8$ cm^{-1}; see Table 6). These results exclude a possible cancellation effect in the prediction of the IR-shifts due to the fact that the anharmonic effects have been considered in both, the complex and the monomers, and points out that the anharmonicity effects becomes very important in the evaluation of the vibrational shifts of these complexes.

After this analysis we will mainly focus on the anharmonic values and we will discuss $\Delta\nu$ on four main groups of vibrational modes, namely (a) the O-H stretchings associated to the hydrogen bond interactions such as those of the acidic C/N/S(O)-H and OO-H groups; (b) the OOH and XOH bending modes; (c) the X=O stretching, and (d) the new IR modes that appear in the complex formation.

(a) Tables 5-8 show that our calculations predict very large red-shifts for these O-H stretching modes, ranging among 310 cm^{-1} (**C3**) and 943 cm^{-1} (**C2**) in the case of the OO-H stretching, and among 654 cm^{-1} (**C2**) and 896 cm^{-1} (**C4**) in the case of the C/N/S(O)-H groups, whereas the corresponding intensities are enhanced among 4 and 44 times (SO-H and OO-H modes in **C4**, respectively). Another point of interest refers the absolute intensities of these bands in the complexes. For **C1** and **C2** the acidic XO-H band is considerably more intense and it is located at higher vibrational frequencies than the OO-H band, while the contrary holds for **C4** and **C5**. These results are related to the different acidic character of both groups in the complexes as reflected in the corresponding hydrogen bond distances (*vide supra*).

(b) The calculations predict important blue-shifts in the OOH and XOH bending modes ranging from 8 (37 excluding the symmetric bending SOH) cm^{-1} to 290 cm^{-1}. The changes in the intensities of these bands relative to those of the monomers vary a factor among 5.7 and 0.4. These facts combined with the absolute intensity values in each complex allow us to predict that only the OOH bending in **C1**, **C2**, **C3**, and **C4** and the XOH bending in **C3** and **C4** will be easily distinguishable with respect to their monomers in the IR spectra.

(c) The X=O stretchings are predicted to be red-shifted among 42 and 95 cm^{-1} (excluding the asymmetric stretching of the $N=O_2$ with only 1.6 cm^{-1}) and their intensities are expected to diminish in a factor among 0.6 and 0.8, although in the asymmetric stretching of the $S=O_2$ the intensity is increased by a factor of 2.6. However, in all the complexes the absolute intensity value of these bands is quite high (around 250 km mol^{-1}), which allow distinguishing them.

(d) Tables 5-8 show that among the new IR bands originated as a consequence of the complex formation, the H(O)O wagging will be the most easily distinguishable. It will appear in the region between 590 and 800 cm^{-1}, where no other relevant IR bands are predicted. Their intensities are computed to be around 10% of the maximum of each complex.

4) Conclusions

The harmonic and anharmonic vibrational spectra of the most stable hydrogen bonded complexes formed between the hydroperoxyl radical and formic, acetic, nitric, and sulphuric acids and their corresponding monomers have been reported. The potential energy surface of these systems has been evaluated at B3LYP level using the 6-31+G(d,p) and 6-311+G(2d,2p) basis sets and approximated by a Taylor series in normal coordinates including the quadratic, cubic, and semidiagonal quartic forces, while the second-order vibrational perturbative treatment implemented by Barone in the Gaussian package has been used to calculate the anharmonic vibrational frequencies.

Regarding the separate monomers, namely the different acids and the HOO radical considered, our calculations taking into account the VPT2 anharmonic contribution predict vibrational frequencies with a quite good agreement with the experimental values, with Δ_{mean} ($\Delta_{\max}$) interval going from 7.4 (13.4) to 34.8 (116.7) cm^{-1}. The theoretical data show a systematic improvement of the VPT2 results with respect to their harmonic counterparts.

Regarding the different hydrogen bond complexes several points can be stressed: (a) the contribution of the anharmonic effects to the stabilization energy is predicted to be insignificant, with a value of about 0.2 kcal/mol. (b) The anharmonic contribution results in differences of around 40 cm^{-1} with respect to the harmonic frequencies; although in some cases involving highly anharmonic modes these differences can rise up to of 300 and 450 cm^{-1}. (c) The computed vibrational frequencies of the **C1-C4** complexes have been analyzed in comparison with those of the separate monomers which will help the experimental identification of these complexes. Among others, our calculations predict very large red-shifts for the OH stretching modes and important blue-shifts for the OOH and XOH bending modes. (d) Furthermore, the apparition of new IR bands originated as a consequence of the complex formation may act as also as a signature of these hydrogen bond complexes.

Finally, our VPT2 calculations could be improved and validated using more accurate full PES and variational vibrational wavefunctions. On one hand, the quality of the PES could be improved interpolating the data obtained from a fine grid that should include the explicit coupling between the modes. On the other hand, variational methods as VCI o VCC could be used to obtain a very accurate variational wavefunctions. But these type calculations for the systems studied in this work are out of our computational capabilities due to their high computational cost. Nevertheless, in the future we plan to perform such type of calculations taking profit of efforts that are currently in progress in order to reduce their cost.

Supporting information available: Tables S1-S2 with the harmonic and harmonic vibrational frequencies calculated at B3LYP/6-311++G(2d,2p), MP2/6-311++G(2d,2p), and M052X/6-311++G(2d,2p) levels for the ·OOH, HCOOH, and **C1** systems.Tables S3-

S6 with the harmonic and anharmonic vibrational frequencies and intensities calculated at B3LYP using the 6-31+G(d,p) and 6-311+G(2d,2p) for the 4 complexes studied are reported with the Cartesian coordinates of all studied structures in this paper.

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84 For the C1 complex and their isolated monomers (acid formic and hydroperoxyl) the effect of the electronic correlation on the PES and in the evaluation of the harmonic and anharmonic vibrational spectra was checked with the analysis of additional results obtained using B3LYP/6-311++G(2d,2p), MP2/6-311++G(2d,2p), and M052X/6-

311++G(2d,2p) levels of theory (see supporting information). It is important to remark here, that for the monomers the anharmonic frequencies computed at B3LYP are those comparing better with the experimental vibrational spectra. On the other hand, for the C1 complex the B3LYP and MP2 anharmonic vibrational frequencies compare well (maximum differences less than 150 cm^{-1}), but they are quite different from those obtained using the M052X functional (with a maximum differences of about 300 cm^{-1}).

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FIGURE CAPTIONS

Figure 1. Selected geometrical parameters of the B3LYP/6-311+G(2d,2p) optimized and the experimental[85-88] (in bold) geometries for the isolated systems studied in this work. Distances are given in Ångstroms and angles in degrees.

Figure 2. Selected geometrical parameters of the B3LYP/6-311+G(2d,2p) and B3LYP/6-31+G(d,p) (in parentheses) optimized geometries for the radical complexes studied in this work. Distances are given in Ångstroms and angles in degrees.

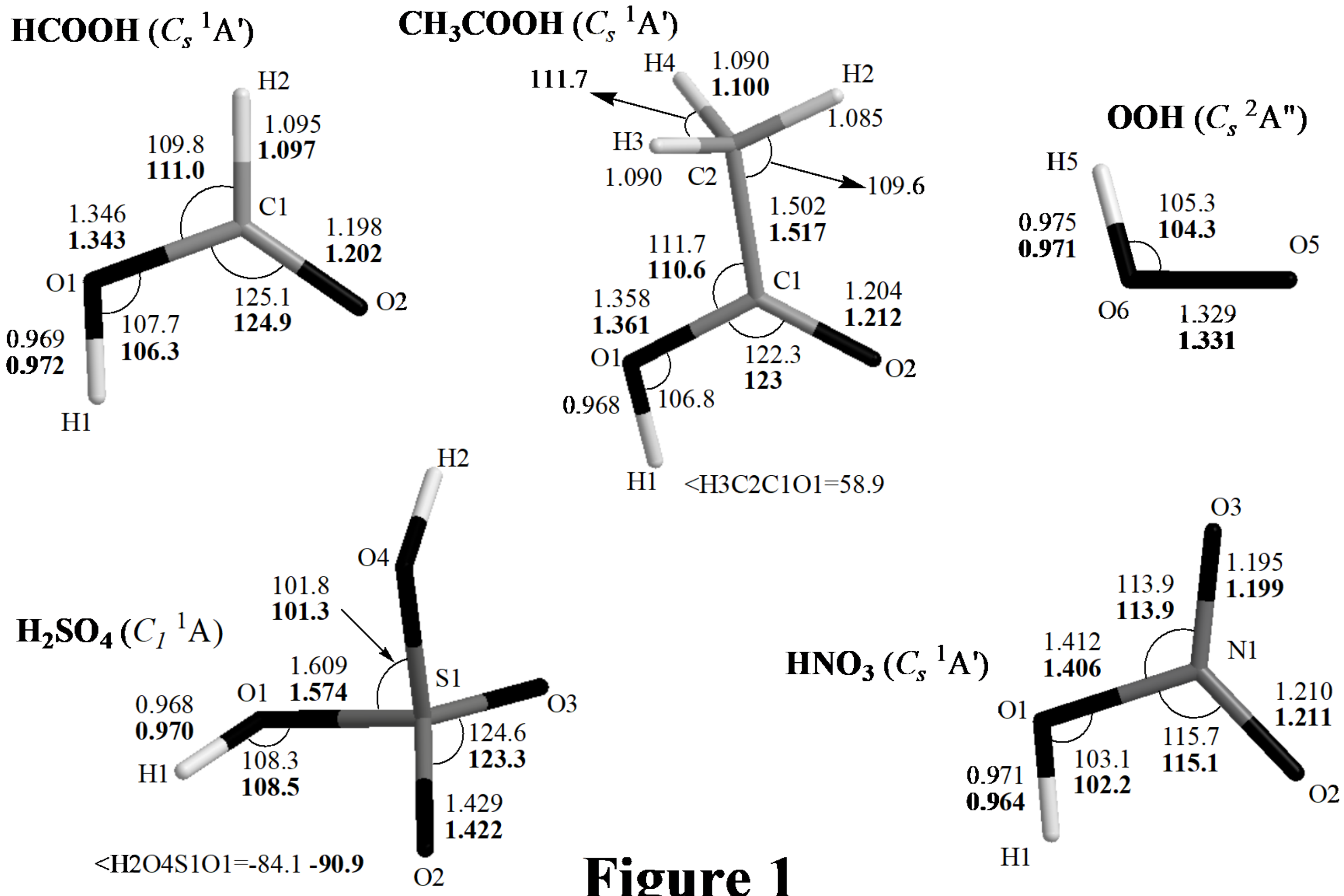
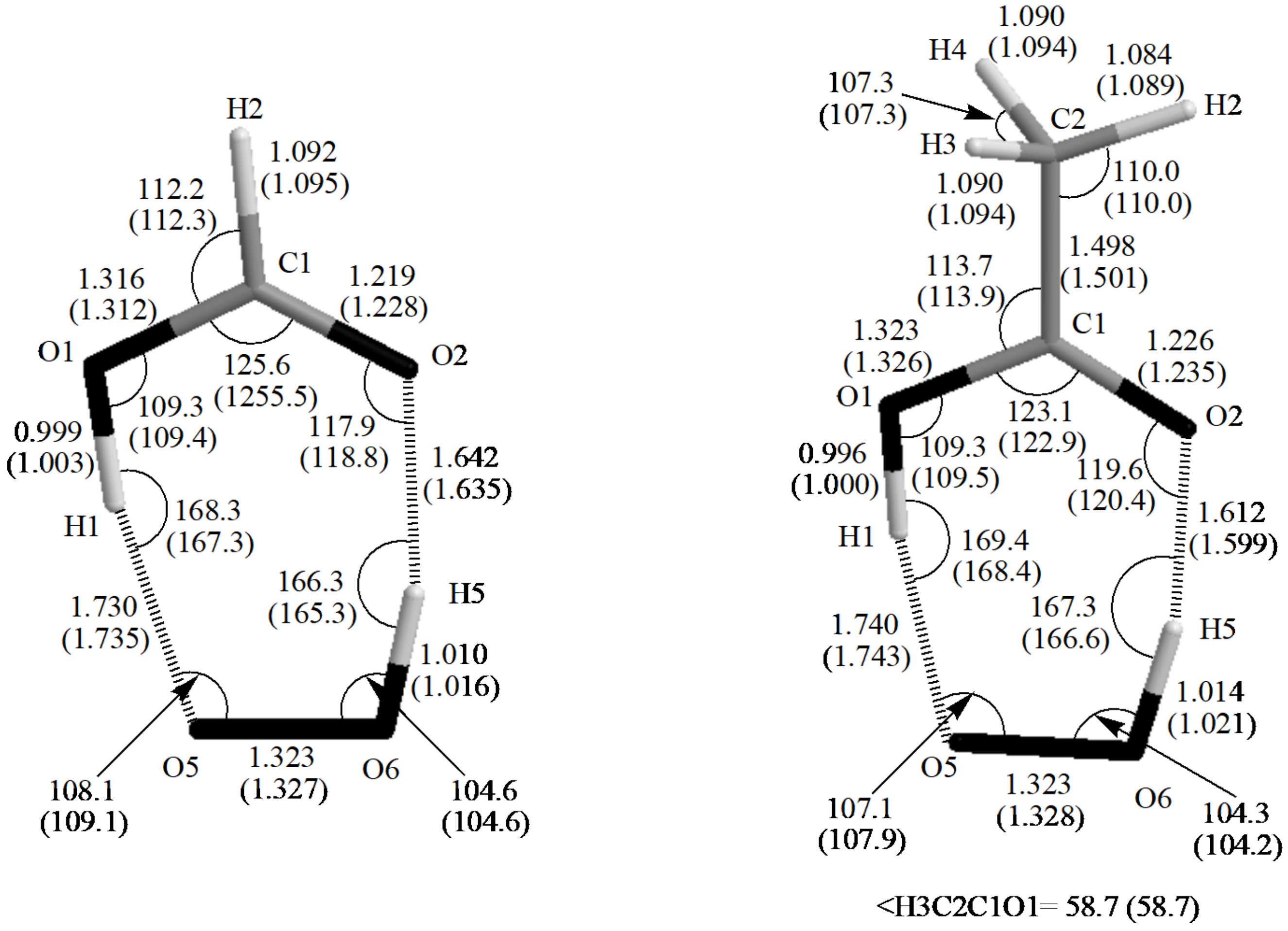

HCOOH (C_s $^1A'$)
H2
1.095
1.097
109.8
111.0
C1
1.346
1.343
1.198
1.202
O1
125.1
124.9
O2
0.969
0.972
107.7
106.3
H1
CH$_3$COOH (C_s $^1A'$)
111.7
H4
1.090
1.100
H2
1.085
H3
1.090
C2
109.6
1.502
1.517
111.7
110.6
C1
1.358
1.361
1.204
1.212
O1
122.3
123
O2
0.968
106.8
H1
<H3C2C1O1=58.9
OOH (C_s $^2A''$)
H5
105.3
104.3
0.975
0.971
O5
O6
1.329
1.331
H2
O4
101.8
101.3
H$_2$SO$_4$ (C_1 ^1A)
1.609
1.574
S1
0.968
0.970
O1
O3
124.6
123.3
H1
108.3
108.5
1.429
1.422
<H2O4S1O1=-84.1 -90.9
O2
O3
1.195
1.199
113.9
113.9
1.412
1.406
N1
HNO$_3$ (C_s $^1A'$)
1.210
1.211
O1
115.7
115.1
103.1
102.2
0.971
0.964
O2
H1

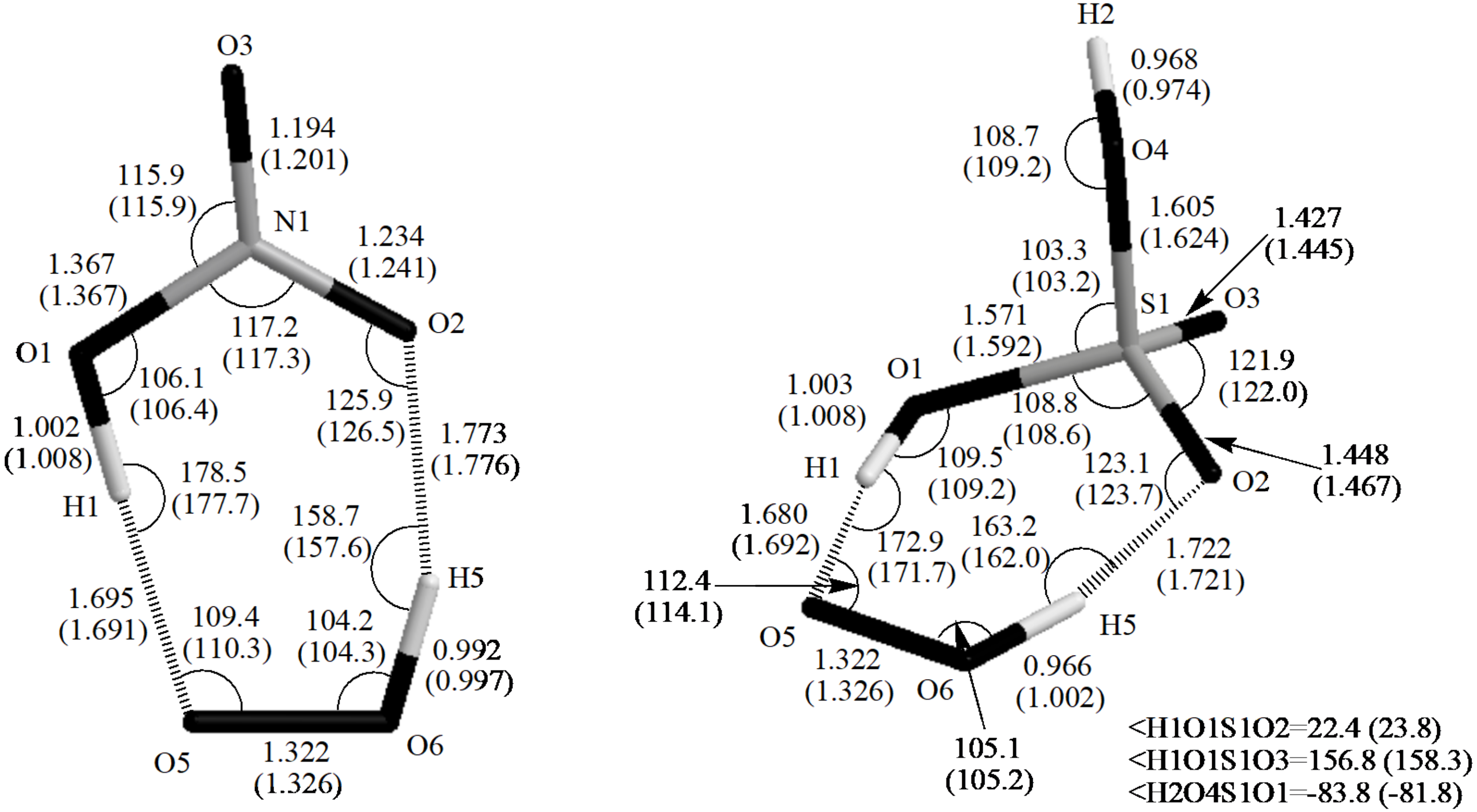
Figure 1



C1 (C_s $^2A''$)

C2 (C_s $^2A''$)

Figure 2a



<H1O1S1O2=22.4 (23.8)
<H1O1S1O3=156.8 (158.3)
<H2O4S1O1=-83.8 (-81.8)

C3 (C_s ^{2}A")

C4 (C_1 ^{2}A)

Figure 2b

Table 1: Experimental and calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the HCOOH and HNO_3 systems. The values in parentheses are at B3LYP/6-31+G(d,p) level.

Molecule	**Mode**		**I(har)**	**ν(har)**	**ν(anhar)**	**ν(exp)**[a]
HCOOH	O-H st	A'	63.8 (61.1)	3739.5 (3733.3)	3547.2 (3548.7)	3570.0
	C-H st	A'	38.7 (39.2)	3057.3 (3088.8)	2902.5 (2926.3)	2942.8
	C=O st	A'	381.0 (394.0)	1809.5 (1819.8)	1776.5 (1786.4)	1770.0
	H-C-O bend	A'	2.4 (2.6)	1402.8 (1402.6)	1386.5 (1390.6)	1387.0
	H-O-C bend	A'	7.0 (15.9)	1305.7 (1293.5)	1257.5 (1207.7)	1229.0
	C-O st	A'	271.7 (264.2)	1120.8 (1133.5)	1088.7 (1101.0)	1105.3
	H(C) out wag	A"	2.3 (2.5)	1050.9 (1048.0)	1031.0 (1026.0)	1033.0
	H(O) out wag	A"	145.1 (160.9)	675.4 (683.8)	616.6 (646.6)	638.0
	O-C=O bend	A'	41.4 (46.7)	628.6 (623.2)	622.2 (617.0)	625.0
Δ_{mean}				54.5 (58.9)	15.7 (11.9)	
$\Delta_{\max}$				169.5 (163.3)	40.3 (21.3)	
HNO_3	O-H st	A'	99.7 (100.4)	3733.8 (3717.4)	3545.4 (3538.0)	3550.0
	$N=O_2$ st asy	A'	414.8 (416.2)	1738.4 (1766.6)	1696.2 (1722.8)	1709.6
	$N=O_2$ st sy	A'	303.7 (316.6)	1346.8 (1354.5)	1319.3 (1324.2)	1325.7
	N-O-H bend	A'	74.5 (50.5)	1323.7 (1321.7)	1295.3 (1299.2)	1303.5
	O-N st	A'	185.2 (190.9)	902.4 (900.0)	879.6 (875.7)	879.1
	N out wag	A"	9.3 (8.3)	782.5 (765.7)	770.0 (754.3)	763.2
	NO_2 scissors	A'	14.0 (10.2)	650.1 (647.5)	634.8 (632.3)	646.8
	NO_2 rock	A'	7.4 (8.5)	586.0 (580.0)	574.2 (568.9)	580.3
	H(O) out wag	A'	121.9 (138.1)	482.3 (475.1)	449.2 (470.9)	458.2
Δ_{mean}				36.6 (34.7)	7.4 (9.1)	
$\Delta_{\max}$				183.8 (167.4)	13.4 (14.6)	

[a] The HCOOH and HNO_3 experimental vibrational frequencies are from Refs. 92 and 93-95, respectively.

Table 2: Experimental and calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the ·OOH and H_2SO_4 systems. The values in parentheses are at B3LYP/6-31+G(d,p) level.

Molecule	**Mode**		**I(har)**	**ν(har)**	**ν(anhar)**	**ν(exp)**[a]
·OOH	O-H st	A'	29.4 (28.4)	3616.9 (3600.2)	3410.8 (3395.1)	3436.2
	O-O-H ben	A'	38.3 (34.4)	1441.5 (1424.1)	1399.9 (1384.5)	1391.8
	O-O st	A'	28.7 (30.2)	1166.5 (1166.6)	1142.9 (1143.7)	1097.6
Δ_{mean}				99.8 (88.4)	26.3 (31.5)	
$\Delta_{\max}$				180.7 (50.1)	45.3 (46.0)	
H_2SO_4	O-H st sy	A	49.2 (57.1)	3774.3 (3755.3)	3599.0 (3579.8)	3563
	O-H st asy	B	203.1 (196.3)	3770.2 (3751.3)	3594.9 (3575.7)	3566.7
	$S=O_2$ st asy	B	297.1 (302.9)	1436.4 (1411.7)	1407.3 (1382.6)	1452.4
	$S=O_2$ st sy	A	80.2 (148.2)	1185.1 (1165.9)	1160.1 (1142.4)	1216.1
	S-O-H bend asy	B	87.2 (89.0)	1184.4 (1148.3)	1151.5 (1122.4)	1156.9
	S-O-H bend sy	A	160.0 (103.0)	1174.1 (1138.7)	1150.9 (1117.6)	1135.9
	$S-O_2$ st asy	B	332.8 (348.4)	831.1 (823.4)	810.3 (805.0)	881.7
	$S-O_2$ st sy	A	112.0 (118.6)	775.0 (765.5)	757.2 (748.2)	834.1
	$S=O_2$ wagg	B	20.3 (22.7)	529.9 (511.1)	521.5 (502.8)	558.0
	$S=O_2$ bend	A	36.4 (44.2)	519.3 (506.0)	513.7 (500.0)	548.1
	O-S=O rock	B	41.4 (48.0)	478.2 (460.9)	470.4 (454.0)	506
	O-S=O bend	A	17.6 (27.0)	423.2 (412.0)	390.7 (361.3)	421.7
	O-S=O twist	A	2.8 (5.7)	356.1 (348.6)	334.5 (325.3)	378.5
	H(O) out asy	B	57.7 (68.5)	326.9 (310.8)	287.1 (229.8)	287.7
	H(O) out sy	A	96.1 (95.1)	245.8 (246.0)	229.9 (198.6)	224
Δ_{mean}				53.8 (55.0)	34.8 (49.1)	
$\Delta_{\max}$				211.3 (192.3)	76.9 (85.9)	

[a] The ·OOH and H_2SO_4 experimental vibrational frequencies are from Refs. 96-98 and 67, 99, respectively.

Table 3: Experimental and calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the CH_3COOH system. The values in parentheses are at B3LYP/6-31+G(d,p) level.

Mode		**I(har)**	**ν(har)**	**ν(anhar)**	**ν(exp)**[a]
O-H st	A'	63.5 (60.5)	3760.3 (3754.5)	3575.0 (3566.1)	3583
C-H st	A'	4.3 (4.2)	3166.8 (3180.6)	3021.3 (3029.6)	3051
C-H st	A"	3.6 (3.7)	3115.4 (3129.1)	2973.0 (2976.5)	2996
C-H st	A'	1.5 (2.1)	3059.8 (3063.8)	2949.6 (2952.7)	2944
C=O st	A'	351.2 (358.6)	1810.6 (1822.1)	1778.5 (1789.6)	1788
H-C-H bend	A"	8.6 (11.1)	1482.7 (1482.6)	1429.8 (1440.6)	1430
H-C-H bend	A'	16.9 (16.5)	1477.7 (1475.8)	1439.4 (1437.6)	1430
H-C-H bend	A'	44.3 (57.4)	1413.3 (1414.1)	1374.1 (1375.9)	1382
H-O-C bend	A'	29.6 (51.1)	1342.0 (1335.9)	1380.7 (1321.9)	1264
C-O st	A'	223.1 (211.1)	1206.3 (1205.6)	1166.0 (1162.0)	1182
CH_3 torsion	A"	7.4 (7.5)	1072.1 (1067.4)	1045.6 (1049.8)	1048
CH_3 torsion	A'	80.3 (68.5)	1000.4 (1001.8)	982.0 (985.5)	989
C-C st	A'	4.6 (3.4)	857.3 (862.5)	838.9 (844.9)	847
H(O) out wag	A'	90.7 (107.0)	664.8 (667.5)	737.5 (646.5)	657
O=C-O bend	A"	36.4 (40.2)	584.3 (580.4)	577.9 (572.6)	642
HOC=O torsion	A'	30.3 (27.5)	545.9 (544.9)	533.3 (532.4)	581
O-C-C bend	A"	4.8 (4.8)	425.3 (422.4)	424.8 (423.0)	534
CH_3 twist	A"	0.2 (0.3)	74.7 (69.6)	73.6 (44.5)	93
Δ_{mean}			58.8 (64.3)	31.4 (26.4)	
$\Delta_{\max}$			177.3 (171.5)	116.7 (158.0)	

[a] The CH_3COOH experimental vibrational frequencies are from Ref. 92.

Table 4: Calculated relative electronic energies, ΔE, relative electronic energies with harmonic, $\Delta(E + ZPVE_{har})$, and anharmonic, $\Delta\left(E + ZPVE_{anhar}\right)$, ZPVE contributions enthalpies with harmonic, ΔH_{har}, and anharmonic contributions, ΔH_{anhar}, and Gibbs free energy with harmonic, ΔG_{har}, and anharmonic, ΔG_{anhar}, contributions at B3LYP/6-311+G(2d,2p) level for the complexes studied in this work. The values in parentheses are at B3LYP/6-31+G(d,p) level. All values are in kcal/mol.

	C1	**C2**	**C3**	**C4**
ΔE	-14.83 (-15.31)	-15.53 (-16.06)	-11.23 (-11.68)	-13.70 (-14.29)
$\Delta(E + ZPVE_{har})$	-12.44 (-13.01)	-13.40 (-14.02)	-9.20 (-9.70)	-13.70 (-12.35)
$\Delta(E + ZPVE_{anhar})$	-12.62 (-13.16)	-13.59 (-14.22)	-9.30 (-9.81)	-11.84 (-12.42)
ΔH_{har}	-13.19 (-13.75)	-13.97 (-14.59)	-9.68 (-10.17)	-12.25 (-12.87)
ΔH_{anhar}	-13.31 (-13.85)	-14.09 (-14.76)	-9.74 (-10.25)	-12.36 (-13.01)
ΔG_{har}	-2.26 (-2.83)	-3.17 (-3.84)	0.82 (0.32)	-1.58 (-2.18)
ΔG_{anhar}	-2.51 (-3.03)	-3.52 (-4.22)	0.65 (0.13)	-1.68 (-2.18)

Table 5: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the HCOOH···OOH (**C1**) complex.

Mode		***I(har)*** [a]	***ν(har)*** [b]	***ν(anhar)*** [b]
CO-H st	A'	1490.2 (23.4)	3201.9 (-537.7)	2873.5 (-673.7)
C-H st	A'	122.2 (3.2)	3093.3 (36.0)	2933.6 (31.1)
OO-H st	A'	356.9 (12.1)	2975.1 (-641.9)	2608.7 (-802.1)
C=O st	A'	292.7 (0.8)	1730.7 (-78.8)	1698.9 (-77.6)
O-O-H bend	A'	156.6 (4.1)	1626.2 (184.7)	1530.4 (130.5)
H-O-C bend	A'	2.5 (0.4)	1474.0 (168.3)	1456.1 (198.6)
H-C-O bend	A'	17.3 (7.2)	1395.9 (-6.9)	1363.0 (-23.5)
C-O st	A'	181.1 (0.7)	1248.3 (127.5)	1220.5 (131.8)
O-O st	A'	12.1 (0.4)	1223.0 (56.4)	1200.3 (57.4)
H(C) out wag	A"	13.6 (5.9)	1079.3 (28.3)	1054.1 (23.1)
H(O)-C out wag	A"	51.9 (0.4)	966.3 (290.9)	922.7 (306.1)
unique mode H(O)-O out wag	A"	163.4	849.5	753.7
O-C=O bend	A'	22.5 (0.5)	709.3 (80.7)	702.0 (79.7)
unique mode	A'	76.9	329.8	315.6
unique mode	A'	4.8	246.0	234.2
unique mode	A"	1.0	232.8	223.1
unique mode	A'	3.7	194.6	180.9
unique mode	A"	1.2	110.6	108.0

[a] Numbers in parentheses are the ratios between the intensity of the complex and the corresponding in the monomer, displayed in Tables 1 and 2.

[b] The values in parentheses are shift relative to the monomers, displayed in Tables 1 and 2.

Table 6: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the $CH_3COOH\cdots OOH$ (**C2**) complex.

Mode		***I(har)***[a]	***ν(har)***[b]	***ν(anhar)***[b]
CO-H st	A'	1540.2 (24.3)	3235.0 (-525.4)	2920.5 (-654.4)
C-H st	A'	10.9 (2.5)	3168.9 (2.1)	3018.1 (-3.2)
C-H st	A"	1.8 (0.5)	3116.9 (1.5)	2970.6 (-2.4)
C-H st	A'	0.2 (0.2)	3061.6 (1.7)	2951.3 (1.7)
OO-H st	A'	702.9 (23.9)	2917.0 (-699.9)	2468.0 (-942.8)
C=O st	A'	253.2 (0.7)	1732.4 (-78.2)	1685.4 (-93.2)
O-O-H bend	A'	217.4 (5.7)	1633.6 (192.1)	1576.1 (176.2)
H-C-H bend	A"	24.3 (2.8)	1486.1 (3.4)	1430.2 (0.4)
H-C-H bend	A'	9.1 (0.5)	1482.2 (4.5)	1439.6 (0.2)
H-O-C bend	A'	34.1 (1.2)	1466.5 (124.5)	1417.8 (37.1)
H-C-H bend	A'	36.1 (0.8)	1407.1 (-6.2)	1370.9 (-3.2)
C-O st	A'	203.0 (0.9)	1326.8 (120.6)	1293.1 (127.1)
O-O st	A'	10.5 (0.4)	1222.7 (56.2)	1200.4 (57.5)
CH_3 torsion	A"	8.4 (1.1)	1077.4 (5.4)	1051.5 (5.9)
CH_3 torsion	A'	21.6 (0.3)	1033.1 (32.7)	1018.5 (36.5)
H(O)-C out wag	A"	30.6 (0.3)	949.1 (284.3)	905.6 (168.1)
C-C st	A'	2.0 (0.4)	904.8 (47.5)	889.3 (50.4)
unique mode H(O)-O out wag	A"	171.3	869.9	798.8
O=C-O bend	A'	29.0 (0.8)	636.7 (52.4)	621.7 (43.8)
HOC=O torsion	A"	0.7 (0.0)	603.3 (57.4)	595.2 (61.9)
O=C-C bend	A'	29.9 (6.2)	466.3 (41.0)	465.8 (41.0)
unique mode	A'	54.1	312.1	304.9
unique mode	A'	3.9	222.7	212.1
unique mode	A'	6.0	176.2	168.6
unique mode	A"	0.3	114.1	112.0
unique mode	A"	0.4	95.1	90.4
CH_3 twist	A"	0.7 (3.7)	55.0 (-19.6)	46.7 (-26.9)

[a] Numbers in parentheses are the ratios between the intensity of the complex and the corresponding in the monomer, displayed in Tables 2 and 3.

[b] The values in parentheses are shift relative to the monomers, displayed in Tables 2 and 3.

Table 7: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the $HNO_3\cdots HOO$ (**C3**) complex.

Mode		***I(har)*** [a]	***v(har)*** [b]	***v(anhar)*** [b]
OO-H st	A'	954.5 (32.5)	3352.7 (-264.2)	3100.8 (-310.0)
NO-H st	A'	796.6 (8.0)	3104.7 (-629.1)	2828.6 (-716.8)
N=O_2 st asy	A'	265.3 (0.6)	1741.3 (2.9)	1697.8 (1.6)
O-O-H bend	A'	149.0 (3.9)	1547.1 (105.6)	1550.3 (150.4)
N-O-H bend	A'	260.6 (3.5)	1497.3 (173.6)	1513.7 (218.3)
N=O_2 st sy	A'	226.6 (0.7)	1299.8 (-47.0)	1267.2 (-52.1)
O-O st	A'	14.8 (0.5)	1218.3 (51.8)	1192.3 (49.4)
O-N st	A'	120.8 (0.7)	968.8 (66.4)	942.2 (62.6)
H(O)-N out wag	A''	50.8 (0.4)	859.4 (377.2)	819.8 (370.6)
N out wag	A''	16.8 (1.8)	787.4 (4.8)	777.0 (6.9)
NO_2 scissors	A'	5.7 (0.4)	696.0 (45.8)	683.4 (48.5)
unique mode H(O)-O out wag	A'	160.3	646.6	593.4
NO_2 rock	A''	2.0 (0.3)	644.2 (58.2)	631.0 (56.7)
unique mode	A'	66.5	280.6	269.8
unique mode	A'	10.9	205.9	194.9
unique mode	A'	0.7	175.7	160.6
unique mode	A''	3.2	96.1	94.2
unique mode	A''	0.0	73.1	72.7

[a] Numbers in parentheses are the ratios between the intensity of the complex and the corresponding in the monomer, displayed in Tables 1 and 2.

[b] The values in parentheses are shift relative to the monomers, displayed in Tables 1 and 2.

Table 8: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the $H_2SO_4\cdots HOO$ (**C4**) complex.

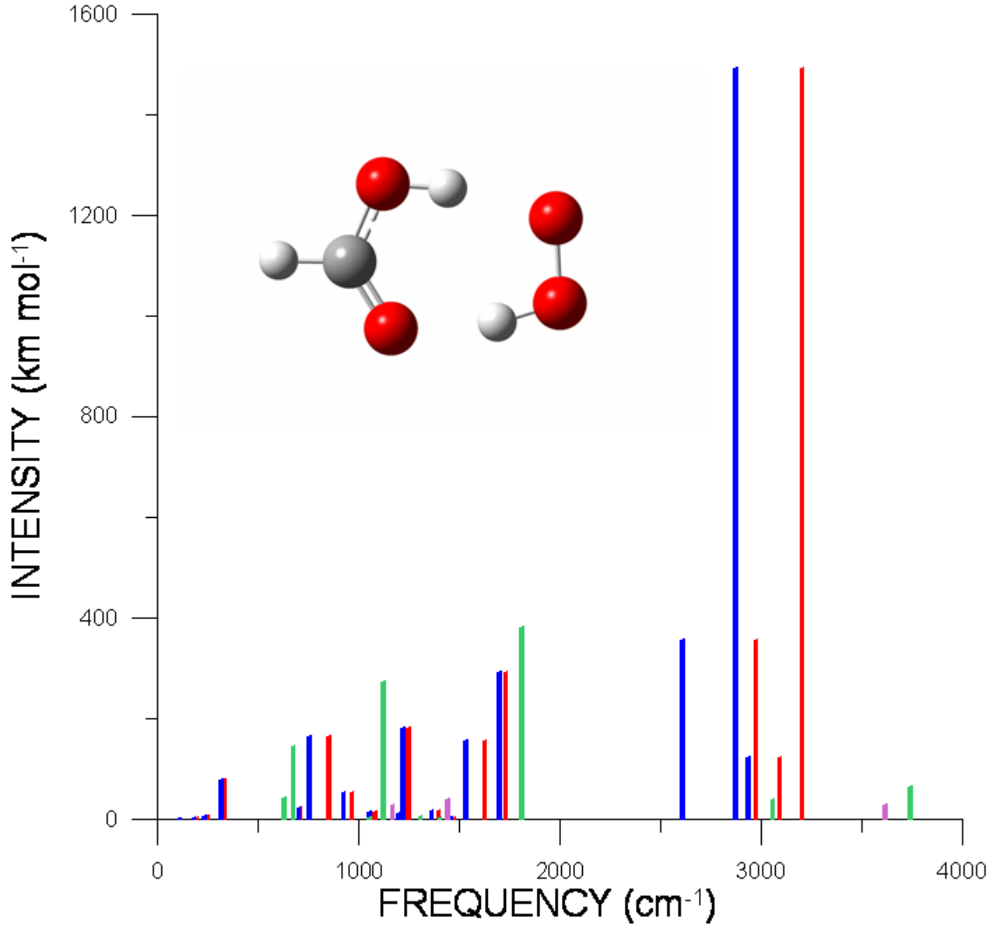
Mode		***I(har)*** [a]	***ν(har)*** [b]	***ν(anhar)*** [b]
SO-H st [c]	A	133.9 (2.7)	3769.9 (-4.4)	3600.9 (1.9)
OO-H st	A	1292.4 (44.0)	3281.9 (-335.1)	3021.2 (-389.7)
SO-H st [d]	A	791.6 (3.9)	3067.2 (-703.0)	2698.9 (-896.0)
O-O-H bend	A	29.8 (0.8)	1580.9 (139.4)	1609.1 (209.1)
S-O-H bend asy	A	273.0 (3.1)	1446.4 (262.0)	1442.0 (290.5)
$S=O_2$ st asy	A	185.3 (0.6)	1343.6 (-92.8)	1311.9 (-95.4)
O-O st	A	9.2 (0.3)	1222.3 (55.8)	1198.5 (55.6)
S-O-H bend sy	A	41.7 (0.3)	1185.4 (11.2)	1159.4 (8.4)
$S=O_2$ st sy	A	210.3 (2.6)	1140.9 (-44.1)	1117.8 (-42.3)
$S-O_2$ st asy	A	294.2 (0.9)	890.1 (59.0)	871.9 (61.6)
H(O)-S out asy	A	43.8 (0.8)	821.1 (494.1)	761.6 (474.5)
$S-O_2$ st sy	A	111.9 (1.0)	796.7 (21.7)	777.7 (20.5)
unique mode H(O)-O out wag	A	141.3	667.3	616.6
$S=O_2$ wagg	A	46.5 (2.3)	547.8 (17.9)	541.4 (19.8)
$S=O_2$ bend	A	18.1 (0.5)	527.5 (8.3)	523.6 (9.8)
O-S=O rock	A	4.3 (0.1)	502.9 (24.8)	497.6 (27.2)
O-S=O bend	A	29.0 (1.6)	419.6 (-3.6)	397.8 (7.1)
O-S=O twist	A	3.2 (1.1)	360.9 (4.8)	343.5 (9.0)
unique mode	A	75.1	292.9	283.5
H(O)-S out sy	A	74.2 (0.8)	255.2 (9.4)	232.6 (2.7)
unique mode	A	6.2	189.9	181.6
unique mode	A	9.8	169.6	161.0
unique mode	A	1.8	88.7	89.8
unique mode	A	1.3	45.1	47.6

[a] Numbers in parentheses are the ratios between the intensity of the complex and the corresponding in the monomer, displayed in Table 2.

[b] The values in parentheses are shift relative to the monomers, displayed in Table 2.

[c] The H does not interact with the hydroperoxyl radical.

[d] The H interacts with the hydroperoxyl radical.



Text: Harmonic and anharmonic vibrational frequency calculations are reported for the most stable hydrogen bonded complexes formed between the hydroperoxyl radical and formic, acetic, nitric, and sulphuric acids which are of atmospheric interest.