

Bonding Elucidation of the Three Common Acids H₂SO₄, HNO₃, and HClO₄Apostolos Kalemos[†] and Aristides Mavridis*

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The bonding nature of the non-hydroxyl oxygen atoms of the familiar acids sulfuric [(OH)₂SO₂], nitric (HONO₂), and perchloric (HOClO₃) is explained without using such ad hoc concepts of circular logic like “hypervalency”. It is proposed here for the first time and confirmed through the help of coupled-cluster RCCSD(T) calculations, that the S(–O)₂, N(–O)₂, and Cl(–O)₃ bonding occurs by transfer of the electron pair densities of the central atoms, S, N, and Cl to the first excited state, ¹D, of the non-hydroxyl O atoms.

1. Introduction

It sounds rather strange and parochial that the bonding (the “nature” of the chemical bond) is, at least questionable, in such banal chemical species like sulfuric [(HO)₂SO₂], nitric (HONO₂), and perchloric acid (HOClO₃) as the title above implies. We hasten to add, however, that the detailed experimental geometrical gas phase structures of these compounds are well-known; see Figure 1.

Figure 1a shows the “preferred” equilibrium microwave structure of H₂SO₄ obtained in 1981 by Kuczkowski et al.¹ The X-ray crystal structure of H₂SO₄ was determined in 1965 by Bascard-Billy but without the positions of the H-atoms.⁴ More recently, the complete X-ray structure of pure H₂SO₄ has been determined much more accurately,⁵ whereas in 1983 the H-positions were also pinpointed by neutron diffraction from polycrystalline H₂SO₄ near the melting point (10.4 °C) and at 10 K.⁶ In the gas phase, and disregarding the two hydrogen atoms, the four O atoms define a slightly distorted tetrahedron with the plane O₃–S–O₄ deviating from being perpendicular to the O₁–S–O₂ plane by 2°; see Figure 1a.¹ Finally, the energetics of the four rotamers of H₂SO₄ have been determined theoretically through MP2/6-31+G[d,p] calculations.⁷

The most accurate experimental geometry of HNO₃, determined by Ghosh et al.² through microwave spectroscopy, is displayed in Figure 1b, clearly of C_{2v} symmetry if omitting the light atom. The whole geometry is planar, the result of a remarkably strong H•••O₁ interaction (internal hydrogen bond), already explicitly referred to by Forsythe and Giauque as early as 1942.⁸ These workers estimated also accurately enough the rotational barrier around the N–O₃ axis to about 7 kcal/mol from entropic data at 298.1 K, and the first vibrational level of the restricted N–OH rotation to about 430 cm^{–1}.⁸ These values were more accurately redetermined later to 9.4⁹ and 9.74 kcal/mol,¹⁰ with corresponding torsional frequencies of 465⁹ and 486 cm^{–1},¹⁰ respectively.

Earlier, prior to 1981, experimental work related to the geometrical structure of HNO₃ is given in refs 11–14. Finally, the microwave zero point averaged structure (*r*_z) of HNO₃ has been reported by Cox et al.¹⁵

The detailed geometrical structure of HClO₄, Figure 1c, has been reported for the first time in 1994 the result of a combined

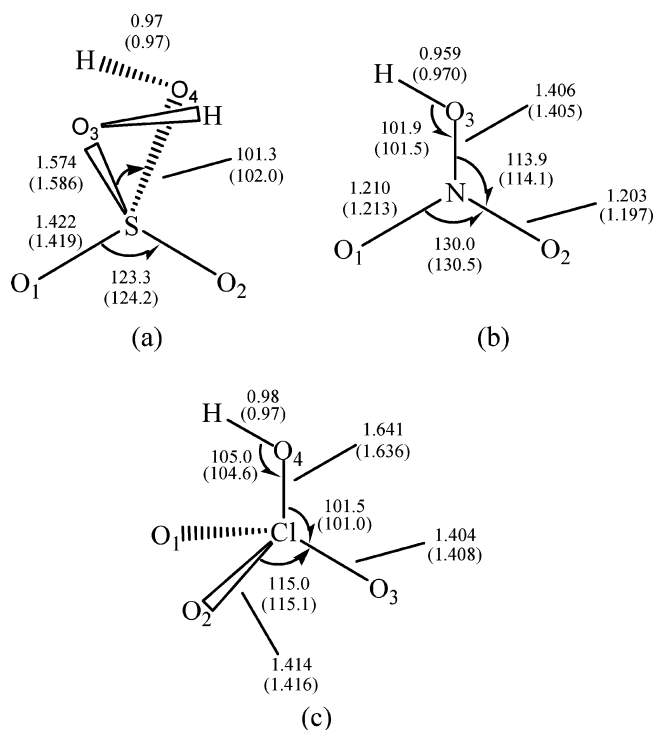


Figure 1. Equilibrium experimental geometries of H₂³²SO₄ (a), HNO₃ (b), and H³⁵ClO₄ (c) from refs 1, 2, and 3, respectively (bond distances in Å, angles in degrees). In parenthesis theoretical results of the present work at the CCSD(T) level; see text.

electron diffraction³ and microwave spectroscopic study;¹⁶ disregarding the H-atom the structure of ClO₄ resumes a T_d configuration. As is clearly displayed in Figure 1c, the HClO₄ molecule has two distinct rotamers, a staggered one (the Cl–O₄–H plane bisects the O₁–Cl–O₂ angle) and an eclipsed one (the H atom projected on top of an O atom), both of C_s symmetry. The staggered-eclipsed torsional barrier has been determined experimentally to be 0.67 kcal/mol as deduced from Figure 11 of ref 16.

Recent theoretical calculations (and references therein) on H₂SO₄ [CCSD(T)],¹⁷ HNO₃ [CCSD(T), MP2],¹⁸ and HClO₄ [CCSD(T), DFT]¹⁹ have been focused mainly on geometrical parameters of these systems.

The motivation of the present work is not, of course, the accurate theoretical structural determination of the three acids

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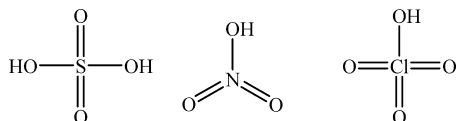


Figure 2. Traditional bonding pictures of H₂SO₄,¹⁷ HNO₃,²⁰ and HClO₄.³

or their molecular parameters,^{17–19} but the elucidation of the “binding mechanism”, as this engenders naturally from the basic tenets of molecular quantum theory. It is indeed remarkable that the bonding “explanation” is exhausted in such “historical” pictures as those shown in Figure 2.

Notice the double bonds between S, N, Cl, and the non-hydroxyl O atoms (*vide infra*). These bonding formulas allude to such entrenched concepts as “hypervalency” and “hypervalent bonds”, the VESPR model (see for instance ref 21 for a rationalization of the H₂SO₄ structure), or “resonance”. It is interesting also to see what Pauling has to say on the structure of the acids Si(OH)₄, O=P(–OH)₃, (O=)₂S(–OH)₂, (O=)₃Cl–OH in his authoritative book.²²

(Very recently Woon and Dunning published an article on the “hypervalent” molecule SF₆ by using mainly the RCCSD(T) approach.²³ The word hypervalent (or hypervalency) does not refer to a specific category of molecules or bonding theory. It is simply a tautology expressing ignorance of how the bonding occurs, clearly suggesting an “anomaly” of certain elements like sulfur, iodine, chlorine, etc. to form bonds with atoms like oxygen for instance, when such bonding cannot be described by the historical-conventional rules of bonding. See also the article by Musher who first quoted the term in 1969.²⁴ The SF₆ molecule, which certainly conforms to this definition, is of different type than the molecular systems examined presently. The Woon–Dunning paper²³ concludes after examining the sequence of species SF_{*n*}, *n* = 1–6, that the six equivalent S–F bonds are covalent in nature formed finally by an in situ septet (*S* = 3) sulfur atom coupled to a singlet with six F ground state ²P atoms.)

Guided by a conceptual parsimony as this is expressed, for instance, by Ockham’s dictum (*multiplicity ought not to be posited without necessity*²⁵), we believe that we do not need these “rationalizing principles” as rather ad hoc, cyclic, and finally obfuscating.

In what follows we present our view on the bonding of H₂SO₄, HNO₃, and HClO₄ based solely on fundamental principles and the symmetry of the “natural” fragments of which the molecules are composed of. To this end we have performed (valence) coupled-cluster+singles+doubles+quasi-perturbative connected triples [CCSD(T)] calculations,²⁶ in conjunction with correlation consistent basis sets of triple ζ quality (cc-pVTZ)²⁷ generally contracted to [5s4p3d1f/c_{LS} 4s3p2d1f/o_N 3s2p1d/h]. For reasons of completeness, complete active space self-consistent field (CASSCF) calculations have also been performed to bona fide secure our assumptions on the bonding situation on H₂SO₄ and HClO₄. In the case of the sulfuric acid and for the dissociation of both non-hydroxyl oxygen atoms a state-average CASSCF (SACASSCF) scheme has been adopted by distributing 10 electrons over 11 valence orbitals (10 e[–]/11 orb.) for a total of 7 states, the first two of which are shown in Figure 5. In the case of the HClO₄ molecule a CASSCF (12 e[–]/11 orb.) PEC along the dissociative coordinate of one oxygen atom has been computed correlating to an O(¹D) atom.

All calculations have been performed with the MOLPRO package.²⁸

2. Results and Discussion

Naming the –OH ($X(^2\Pi)$) group X, we are confronted with the problem of understanding the attachment (bonding) of 2, 2,

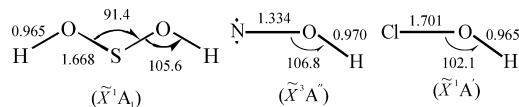
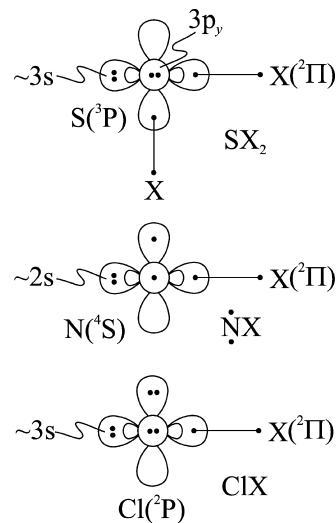
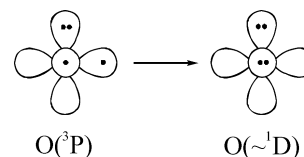


Figure 3. Ground state geometries of S(OH)₂ (SX₂), NOH (NX), and ClOH (CIX) (bond distances in Å, angles in degrees).

SCHEME 1



SCHEME 2



and 3 oxygen atoms to the central atoms S, N, and Cl of the species SX₂, NX, and CIX, respectively. The optimized geometries of S(OH)₂ (assuming C_{2v} symmetry), NOH (C_s), and ClOH (C_s) at the CCSD(T)/cc-pVTZ level are shown in Figure 3.

Using valence-bond-Lewis (vbL) diagrams the molecules of Figure 3 can be represented as shown in Scheme 1.

The ground state of the oxygen atom is of ³P symmetry, obviously unable to form strong (*vide infra*) bonds leading to closed shell molecules, either with SX₂ or CIX. Certainly two sigma N–O bonds can be formed with N–X(\tilde{X}^3A'') leading to a triplet or open singlet XNO₂, but not to a closed shell XNO₂ molecule. The only way to form X₂S–O, XN–O, or XCl–O bonds, is by considering the first excited state of O atom (¹D; 2p⁴) located 45.1 kcal/mol above the ³P term (Scheme 2).²⁹

What happens now is rather clear at least for the SX₂ and CIX species (Scheme 1). The two and three electron pairs of \ddot{X}_2 and \ddot{CIX} can form one, two, and three (CIX) dative (harpooning) σ bonds with the O atoms, through insertion to the empty 2p orbital of the oxygen ¹D state (Scheme 2). Observe that the resulting geometries of the O₂SX₂ and O₃CIX species are approximately tetrahedral.

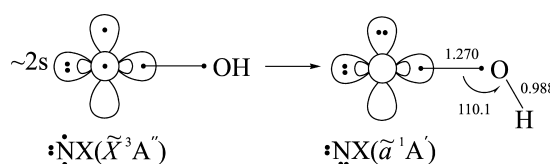
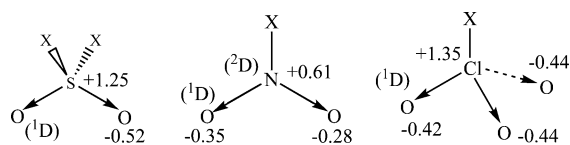


Figure 4. Excitation of \tilde{X}^3A'' to \tilde{a}^1A' of NX (bond distances in Å, angles in degrees).

SCHEME 3



The situation with the $N-X(\tilde{X}^3A'')$ is a little bit different: We need two electron pairs to form two dative bonds with two $O(^1D)$ atoms. The first excited state of $NX(\tilde{a}^1A')$ is exactly what we need, located 17.9 kcal/mol above the X-state (present calculations CCSD(T)/cc-pVTZ); see Figure 4.

Two 1D oxygen atoms can now be bonded to the \tilde{a}^1A' state of NX as previously described, attaching themselves to the available lone pair(s) of $NX(\tilde{a}^1A')$.

The discussion above is summarized in Scheme 3. Indicated charges are obtained from Mulliken populations at the Hartree–Fock (HF) level, whereas in parentheses we display the symmetry of the in situ O and N atoms.

The previous approach predicts and explains in a natural way the general molecular shape of the molecules in question, i.e., their (singlet) multiplicity, the strong charge transfer from the central atoms to the non-hydroxyl oxygen atoms, and of course single σ $S\rightarrow O$, $N\rightarrow O$, and $Cl\rightarrow O$ bonds. In addition, potential energy curves (PEC) with respect to $S(\rightarrow O)_2$, $N(\rightarrow O)_2$, and $Cl(\rightarrow O)_3$ bonds, can be constructed even at the HF level, or with any single reference post-HF approach. Our CCSD(T) and CASSCF calculations completely corroborate this bonding scenario (*vide infra*).

CCSD(T)/cc-pVTZ geometries shown in Figure 1 (present theoretical values in parentheses), are in excellent agreement with experiment. For HNO_3 the $H\cdots O_1$ interaction, or torsion barrier, is calculated to be 7.9 kcal/mol; experimental value 9–10 kcal/mol.^{9,10} For the torsion barrier of $HClO_4$ we calculate 0.69 kcal/mol as contrasted to ~ 0.67 kcal/mol obtained experimentally,¹⁶ indicating quasi-free rotation of the $-OH$ group around the $Cl-O$ axis.

For the H_2SO_4 and $HClO_4$ molecules we have constructed PECs along the $[(HO)_2SO\rightarrow O, (HO)_2S(\rightarrow O)_2]$ and $[HOClO_2\rightarrow O]$ dissociation channels at the CASSCF level of theory. The $(HO)_2SO_2 \rightarrow (HO)_2SO + O$ reaction smoothly dissociates to singlet fragments, i.e., $(HO)_2SO(^1A) + O(^1D)$, due to the conservation of spin angular momentum and with a binding energy of ca. 132 kcal/mol. When both oxygen atoms are pulled apart the dissociation pictures remain *in essence* identical. Due to energetic reasons, the adiabatic curve dissociates to two O atoms in their ground 3P state after suffering a severe avoided crossing at around 4.0 bohr with another adiabatic curve dissociating to two $O(^1D)$ excited state oxygen atoms; see Figure 5. The energy gap of the dissociation channels $\Delta E \sim 103$ kcal/mol reflects the excitation energy $\Delta E(^1D\leftarrow^3P) = 45.1^{29}$ kcal/mol of the O atom. The binding energy of the two non-hydroxyl oxygen atoms with respect to the $O(^1D)$ dissociation (diabatic) channel is ca. 131 kcal/mol per atom, in perfect agreement with the previous case and in harmony with the equivalency of these two O atoms.

Pulling apart an oxygen atom from the $HClO_4$ molecule leads to dissociation of the potential curve to an $O(^1D)$ with a binding energy of approximately 83 kcal/mol at the CAS level.

PECs (profiles) of $[(HO)_2SO\rightarrow O, (HO)_2S(\rightarrow O)_2]$, $[HONO\rightarrow O, HON(\rightarrow O)_2]$, and $[HOClO_2\rightarrow O, HOClO(\rightarrow O)_2, HOCl(\rightarrow O)_3]$ at the CCSD(T)/cc-pVTZ level are shown in Figures 6, 7, and 8, respectively. The populations of the oxygen atoms at infinity conform, as it should, to 1D symmetry; see Schemes 2 and 3. The profiles have been constructed by maintaining the remaining part at the calculated equilibrium geometry of the original

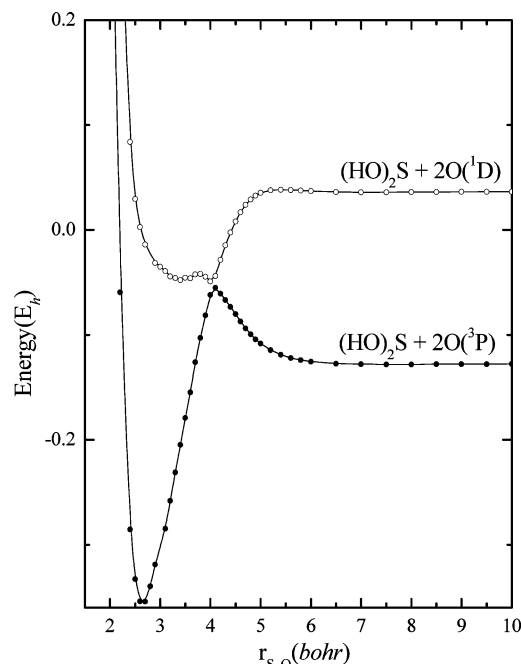


Figure 5. Potential energy profiles of $(HO)_2S(\rightarrow O)_2$ for two states of the same symmetry at the CASSCF level of theory. Energies have been shifted by $+698.0 E_h$.

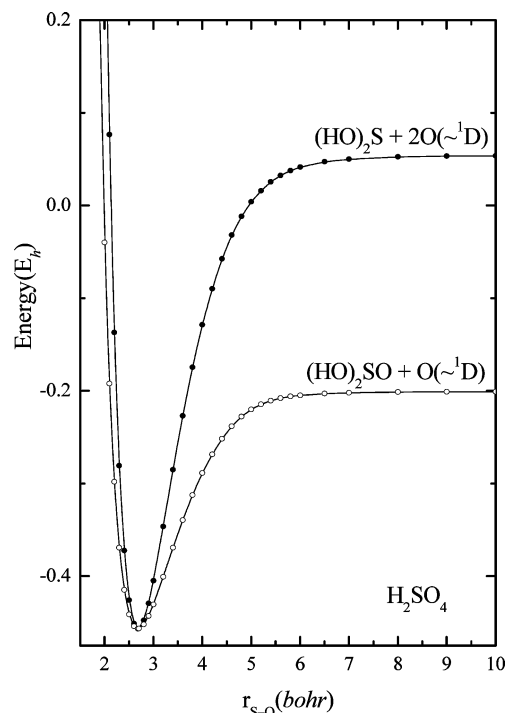


Figure 6. Potential energy profiles of $(HO)_2SO\rightarrow O$ and $(HO)_2S(\rightarrow O)_2$ at the CCSD(T) level of theory. Energies have been shifted by $+699.0 E_h$.

molecule(s) shown in Figure 1. The optimal geometries of the end species $S(OH)_2(\tilde{X}^1A_1)$, $NOH(\tilde{a}^1A')$, and $ClOH(\tilde{X}^1A')$ are shown in Figures 3 and 4.

Finally, the CCSD(T)/cc-pVTZ mean binding energies (\bar{D}_e), as far as we know reported for the first time, of $(HO)_2S(\rightarrow O)_2$, $HON(\rightarrow O)_2$, and $HOCl(\rightarrow O)_3$ with respect to $O(^1D) + [S(OH)_2(\tilde{X}^1A_1), NOH(\tilde{a}^1A'), ClOH(\tilde{X}^1A')]$ are $\bar{D}_e = 160, 162,$ and 99 kcal/mol, respectively. The calculated (experimental) $O(^1D)\leftarrow O(^3P)$ energy splitting is $50.9 (45.1^{29})$ kcal/mol; therefore with respect to $O(^3P)$ the corresponding \bar{D}_e values are 58

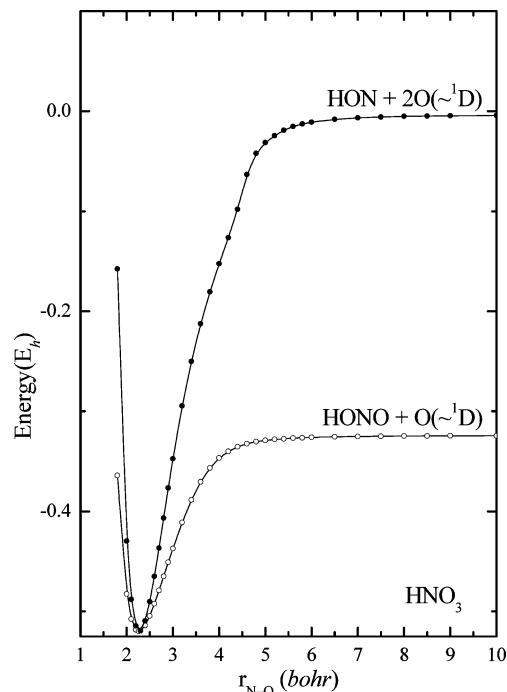


Figure 7. Potential energy profiles of HONO→O and HON(→O)₂ at the CCSD(T) level of theory. Energies have been shifted by +280.0 E_h .

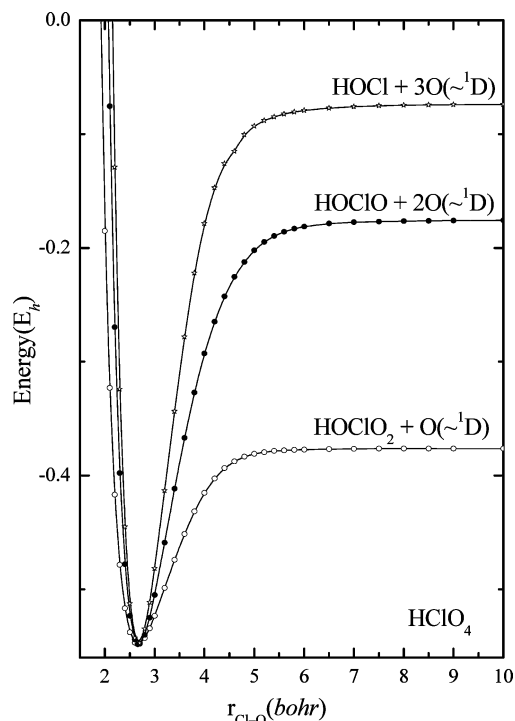


Figure 8. Potential energy profiles of HOCIO₂→O, HOCIO(→O)₂, and HOCI(→O)₃ at the CCSD(T) level of theory. Energies have been shifted by +760.0 E_h .

and 60 kcal/mol for (HO)₂SO₂ and HONO₂, whereas HOCIO₃ can be considered as slightly unbound.

3. Synopsis

Solving the Schrödinger equation by the coupled-cluster approach and without using extraneous concepts like hyper-valency, the VSEPR model, resonances, etc. we have explained, we believe for the first time, how the non-hydroxyl oxygen atoms are bonded to the common acids (HO)₂SO₂, HONO₂, and HOCIO₃. The upshot

of the present work is that the in situ O atoms are not the “same”; i.e., the hydroxyl ones are in their ground (³P) state, whereas the non-hydroxyl ones are in the first excited ¹D state. In addition, the in situ N atom in nitric acid is also in its first excited ²D state. Somehow the O ¹D atoms “button” to the available electron pairs of the central atomic unit. The “unbuttoning” process (leading to smooth potential energy profiles) can be achieved even at the HF level since no spin coupling-decoupling phenomena are at work. Of course, the same ideas can be applied to a plethora of similar type molecular systems, like, for instance, (HO)₃P→O, (HO)₃Br(→O)_n, (HO)₃I(→O)_n, $n = 1, 2, 3$, (O←)₃Cl—O—Cl(→O)₃, etc., where “hypervalency” concepts are usually invoked to rationalize the bonding of the non-hydroxyl oxygen atoms.

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