

FULL PAPER

How relevant are S=O and P=O Double Bonds for the Description of the Acid Molecules H_2SO_3 , H_2SO_4 , and H_3PO_4 , respectively?

Thorsten Stefan and Rudolf Janoschek

Institut für Theoretische Chemie, Karl-Franzens-Universität Graz, Strassoldogasse 10, A-8010 Graz, Austria.
Tel.: +43-316-380-8865; Fax: +43-316-380-9893. E-mail: rudolf.janoschek@kfunigraz.ac.at

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Abstract The acid molecules H_2SO_3 , H_2SO_4 , and H_3PO_4 are usually drawn using “Lewis structures” which exhibit the octet extension by 3d-orbitals on sulfur and phosphorus, respectively. Thus, S=O and P=O double bonds are assumed to be formed. The natural d-orbital occupancies on S and P, however, were calculated to be as low as 0.1 e, and therefore, an octet extension can hardly be expected. After the natural bond orbitals (NBO) search procedure was forced to attempt to form different Lewis structures of bonds and lone pairs, we defined the optimal Lewis structure, if a dominant structure exists at all, by the maximum electronic charge in Lewis orbitals. Indeed, sulfur obeys the octet rule in the optimal zwitterionic Lewis structures and does not form S=O double bonds. No dominant resonance structure could be found for H_3PO_4 where polarized PO π -bond and zwitterionic PO bond structures exhibit similar weights.

Keywords Acid molecules, Lewis structures, Natural bond orbitals, Octet rule

Introduction

Simple empirical rules of bonding such as the octet rule and Lewis structures can be found in well known textbooks which, as is stated, enable us to predict the correct structure that a molecule assumes [1]. That all potential bonding patterns of small molecules comprising only main group elements have not yet been discovered can be shown, for example, by the seemingly well understood sulfur dioxide molecule SO_2 , which prefers a bent geometry (C_{2v} , symme-

try). Different formulae for the distribution of four electrons in π -orbitals, sketched in Scheme 1, can be found in the literature:

a) The electronic structure of sulfur dioxide is **1a** because the sulfur atom makes use of a 3d-orbital in addition to 3s- and 3p-orbitals [2-6].

b) The polar structure **1b** is a useful Lewis structure; 3d-orbitals on sulfur are irrelevant [7,8].

c) The bonding patterns can be understood using 4-electron-3-center π -orbitals [9-11].

d) SO_2 should be described by semipolar resonance structures **1c**, where sulfur obeys the octet rule [3,9,10,12,13].

As will be shown later, only one of the four different descriptions of the SO_2 molecule can be favored to be the optimal Lewis structure. The authors of references [9-11] use the description c) as a paraphrase of d) without actually

Correspondence to: R. Janoschek

Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

calculating 3-center π -orbitals and their occupancies. Speculations about four-electron three-center bonding [9-11] for SO_2 can quickly be ruled out. The search for a resonance structure can be forced to occupy three-center orbitals. Doing this for SO_2 , a quite meaningless resonance structure results where non-Lewis orbitals exhibit high occupancies. The importance of so-called increased-valence structures [13] in terms of the valence bond (VB) theory can be ruled out by the NBO analysis. The oxygen free electron pairs of O^- in **1c** donate into the anti-bonding non-Lewis $\text{S}^+-\text{O}-\pi^*$ orbital. Accordingly, an increased valence on sulfur does not exist. Moreover, the importance of singlet diradical structures [13] for SO_2 can be seen as an artifact of qualitative VB theory. The multi-configuration SCF wave function of the type CAS(6,6) (complete active space where six electrons are distributed in six orbitals) and their subsequent NBO analysis unequivocally indicate the pronounced closed-shell character of SO_2 .

In contrast to SO_2 , the acid molecules H_2SO_3 , H_2SO_4 , and H_3PO_4 can be found uniformly described in the textbooks applying the octet extension and the formation of double bonds on sulfur and phosphorus, respectively. Nevertheless, the respective Lewis structures have been calculated employing the natural bond orbitals (NBO) analysis [14]. In addition, it is possible to override the automatic NBO search procedure and to force the NBO program to attempt to form a chosen resonance structure of bonds and lone pairs. Thus, an optimal Lewis structure can be defined out of a set of competing resonance structures ('boundary formulae' in the new literature). Concomitantly, the much discussed bond polarization (or lone pair delocalization) as well as the amount of d-orbital contribution on the atoms P and S to the wave function will be discussed.

Computational methods

Density functional theory calculations at the B3LYP level [15] with the 6-311G* and cc-pVQZ basis sets were carried out with the GAUSSIAN 94 program [16]. The results of geometry optimizations at both levels of theory are presented, but the NBO calculations are constrained to the 6-311G* basis set due to the consistency of the natural orbitals.

The analysis of a calculated wave function can be investigated by means of the NBO program [14]. Starting from the input basis set, different sets of localized orbitals can be achieved for different purposes:

BS \Rightarrow NAO's \Rightarrow NHO's \Rightarrow NBO's \Rightarrow NLMO's

The abbreviations have the following meanings:

BS: Input Basis Set

NAO's: Natural Atomical Orbitals

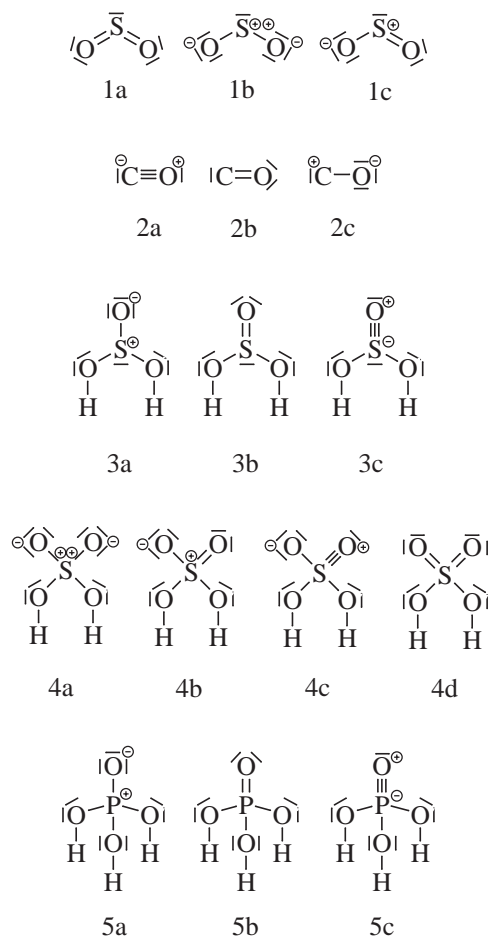
NHO's: Natural Hybrid Orbitals

NBO's: Natural Bonding Orbitals

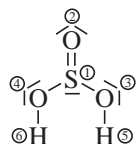
NLMO's: Natural Localized Molecular Orbitals

All these sets are derived from the input basis set by orthogonal transformations. The NAO's are the result of the diagonalization of the density matrix and are expressed by

atomic orbital symbols ($1s$, $2s$, $2p_x$, ...). The eigenvalues of the density matrix are occupation numbers which indicate the relevance of the corresponding NAO's for the description of the wave function. The NHO's are formed by linear combinations of NAO's of different types (s , p , d , ...) at the same atom. The NBO's are the base for the Lewis structure. Their occupation numbers can be found in the range between 0 and 2. In most of the molecules there are two more or less clearly separated sets of NBO's. These are the Lewis orbitals with occupation numbers near 2, and the non-Lewis orbitals with occupation numbers near 0. Four types of Lewis orbitals can be distinguished: core orbitals (one center), orbitals for free electron pairs (one center), two-center bond orbitals, and three-center bond orbitals. The latter can be introduced as elements of localization due to their large field of application. Summarizing, a set of high-occupation Lewis orbitals describes a Lewis structure. Non-Lewis orbitals (low-occupation orbitals) are Rydberg orbitals (one center) and two-center (or three-center) anti-bonding orbitals. High-occupation Lewis orbitals with occupation numbers considerably lower than 2, and, consequently, low-occupation non-Lewis



Scheme 1 Different formulae for the distribution of electrons in π -orbitals for sulfur dioxide **1**, carbon monoxide **2**, sulfurous acid **3**, sulfuric acid **4** and phosphoric acid **5**

Table 1a B3LYP calculated geometrical parameters [\AA , degree] of H_2SO_3 (C_s) with different basis sets

	6-311G*	cc-pVQZ
$r(\text{S1-O2})$	1.4720	1.4597
$r(\text{S1-O3})$	1.6601	1.6372
$r(\text{O3-H5})$	0.9733	0.9707
$\angle(\text{O2-S1-O3})$	105.7	105.8
$\angle(\text{O3-S1-O4})$	100.8	100.7
$\angle(\text{S1-O3-H5})$	110.2	108.7
$\angle(\text{O3-O2-S1-O4})$	106.4	106.2
$\angle(\text{O2-S1-O3-H5})$	22.1	20.0

Table 1b Natural net atomic charges of H_2SO_3

S1	O2	O3	H5
1.65	-0.89	-0.85	0.47

orbitals with occupation numbers considerably higher than 0, indicate electron delocalization which reduces the strict meaning of a single Lewis structure (resonance structure). The NLMO's are useful tools for the study of electron delocalization. In contrast to NBO's, the NLMO's are delocalized as little as necessary to achieve occupation numbers of exactly 2.

Optimal Lewis structures

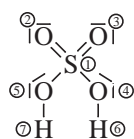
For most of the molecules, different Lewis structures can be drawn. For example, the carbon monoxide CO can be written either as **2a**, **2b** or **2c**. Formula **2a** emphasizes the relation to the isoelectronic N_2 molecule with respect to the dissociation energy, and the octet rule at both atoms. Formula **2b** seems to explain the low dipole moment of 0.1 D. Formula **2c** seems to be in agreement with the electronegativities of the contributing atoms and with calculated net atomic charges.

Different general definitions of the term 'Lewis structure' can be found in textbooks: "The most important boundary formulae are those with the least number of formal charges and with the least amounts for these charges. Boundary formulae without formal charges should be preferred. The distribution of positive and negative formal charges should be in agreement with the electronegativity of the atoms." [3] The above example (CO) indicates, however, that these rules for the definition of the optimal Lewis structure are dubious.

Table 2 Characterization of different Lewis structures for H_2SO_3 by the number of electron pairs in CR (core), BD (bond), and LP (lone pair) orbitals, and the valence Lewis charge (%). Lewis and non-Lewis orbitals are presented only for low (considerably lower than 2) and high (considerably higher than 0) occupancy, respectively

H_2SO_3	3a SB	3b DB	3c TB
CR, BD, LP	8, 5, 8	8, 6, 7	8, 7, 6
Val. Lewis charge	97.39	96.46	96.81
Lewis orbitals			
BD(1) S1-O2 σ	1.987	1.968	1.855
BD(2) S1-O2 π	-	1.931	1.931
BD(3) S1-O2 π	-	-	1.917
BD(1) S1-O3	1.989	1.882	1.847
BD(1) S1-O4	1.989	1.882	1.847
LP(2) O2	1.819	1.644	-
LP(3) O2	1.766	-	-
Non-Lewis orbitals			
BD*(1) S1-O2 σ^*	0.050	0.253	0.147
BD*(2) S1-O2 π^*	-	0.199	0.199
BD*(3) S1-O2 π^*	-	-	0.165
BD*(1) S1-O3	0.221	0.150	0.114
BD*(1) S1-O4	0.221	0.150	0.114

In the following, an alternative general definition for the optimal Lewis structure is proposed: The optimal Lewis structure is that one with the maximum amount of electronic charge in Lewis orbitals (Lewis charge). A low amount of electronic charge in Lewis orbitals indicates strong effects of electron delocalization or, in other words, the minor importance of the corresponding boundary formula (resonance structure). For example, the Lewis charge of the CO molecule in the formula **2a** is 99.93% of 14 electrons, whereas those of **2b** and **2c** are only 96.58% and 93.24%, respectively. According to the above definition, only the formula **2a** with the triple bond is a true Lewis structure. The formal charges in **2a**, are not in conflict with electronegativities, $\chi(\text{C}) = 2.55$, $\chi(\text{O}) = 3.41$, or natural net atomic charges, $Q(\text{C}) = 0.47$, $Q(\text{O}) = -0.47$, because the two-center bonds are strongly polarized towards the oxygen atom (σ : 71%, π : 77%). Many well known molecules, such as NH_3 or C_2H_4 , have dominant optimal Lewis structures, in the sense of Lewis charges. For this study, however, some of those molecules have been investigated where different boundary formulae are in competition. The following questions should be answered: Is one of the competing formulae favored and is, therefore, an optimal Lewis structure, or exist several boundary formulae with comparable Lewis charges? Does the violation of the octet rule for second row atoms (P, S) always take place where it is assumed in textbooks, and what is the meaning of d-functions?

Table 3a B3LYP calculated geometrical parameters [\AA , degree] of H_2SO_4 (C_2) with different basis sets and experimental data

	6-311G*	cc-pVQZ	Exp.
$r(\text{S1-O2})$	1.4376	1.4257	1.422
$r(\text{S1-O4})$	1.6220	1.5996	1.574
$r(\text{O4-H6})$	0.9696	0.9675	0.970
$\angle(\text{O2-S1-O3})$	124.8	124.0	123.3
$\angle(\text{O3-S1-O4})$	108.8	108.6	108.6
$\angle(\text{O3-S1-O5})$	105.3	105.7	106.4
$\angle(\text{O4-S1-O5})$	101.5	102.0	101.3
$\angle(\text{S1-O4-H6})$	110.4	109.0	108.5

Table 3b Natural net atomic charges of H_2SO_4

S1	O2	O4	H6
2.45	-0.87	-0.85	0.49

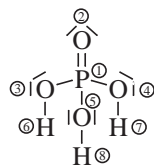
Table 4 Characterization of different Lewis structures for H_2SO_4 by the number of electron pairs in CR (core), BD (bond), and LP (lone pair) orbitals, and the valence Lewis charge (%). Lewis and non-Lewis orbitals are presented only for low and high occupancy, respectively

H_2SO_4	4a	4b	4c	4d
	SB SB	SB DB	SB TB	DB DB
CR, BD, LP	9, 6, 10	9, 7, 9	9, 8, 8	9, 8, 8
Val. Lewis charge	96.30	95.84	95.88	95.74
Lewis orbitals				
BD(1) S1-O2 σ	1.986	1.911	1.872	1.907
BD(2) S1-O2 π	-	-	-	1.934
BD(2) S1-O3 π	-	1.934	1.934	1.934
BD(3) S1-O3 π	-	-	1.931	-
BD(1) S1-O4	1.981	1.872	1.865	1.868
BD(1) S1-O5	1.981	1.974	1.863	1.868
LP(2) O2 π	1.783	1.782	1.782	1.728
LP(3) O2 π	1.778	1.725	1.725	-
LP(2) O3 π	1.783	1.728	-	1.728
LP(3) O3 π	1.778	-	-	-
Non-Lewis orbitals				
BD*(1) S1-O2 σ^*	0.140	0.159	0.125	0.155
BD*(2) S1-O2 π^*	-	-	-	0.228
BD*(1) S1-O3 σ^*	0.140	0.185	0.170	0.155
BD*(2) S1-O3 π^*	-	0.228	0.225	0.228
BD*(3) S1-O3 π^*	-	-	0.251	-
BD*(1) S1-O4	0.293	0.199	0.185	0.194
BD*(1) S1-O5	0.293	0.292	0.175	0.194

 H_2SO_3

SO_2 dissolves in water to give the phantom 'sulfurous acid', which according to Raman spectroscopy contains large amounts of solvated SO_2 as well as HSO_3^- , H_3O^+ , and $\text{S}_2\text{O}_5^{2-}$. The free acid molecule H_2SO_3 was detected in the gas phase in 1988, but experimental structural data are not available.[17] The calculated geometry is characterized by a non-planar structure where the sulfur atom is a center of pronounced pyramidal. The calculated structural data are presented in Table 1a. The extension of the basis set from 6-311G* to cc-pVQZ shows the well known sensitivity of the S–O bond lengths with respect to computational efforts. The calculated natural net atomic charges in Table 1b indicate a remarkably high positive charge of 1.65 on sulfur. This is in accord with the low total occupancy of natural 3d orbitals on sulfur of no more than 0.098. Therefore, the traditionally assumed violation of the octet rule on the sulfur atom is in conflict with the charge distribution as well as the 3d occupancy.

Three different possible Lewis structures for H_2SO_3 are given in **3a - c**. The octet rule on sulfur is fulfilled only for formula **3a**. Formula **3b**, which exhibits a formal S=O double bond, is that found in textbooks. The NBO analysis for the three structures **3a**, **3b**, and **3c** in Table 2 unequivocally favors structure **3a**, without multiple bonds, according to the maximum valence Lewis charge. The textbook structure **3b**, with a S=O double bond and without formal charges, is, in

Table 5a B3LYP calculated geometrical parameters [\AA , degree] of H_3PO_4 (C_3) with different basis sets

	6-311G*	cc-pVQZ
$r(\text{P1-O2})$	1.4739	1.4656
$r(\text{P1-O3})$	1.6036	1.5930
$r(\text{O3-H6})$	0.9644	0.9628
$\angle(\text{O2-P1-O3})$	116.3	116.1
$\angle(\text{O3-P1-O4})$	101.9	102.1
$\angle(\text{P1-O3-H6})$	114.0	112.3
$\angle(\text{O2-P1-O3-H6})$	-39.0	-33.3

Table 5b Natural net atomic charges of H_3PO_4

P1	O2	O3	H6
2.44	-1.05	-0.96	0.50

this sense, the most irrelevant description of H_2SO_3 . The SO π -bond in **3b** is composed of a pd-hybrid on the sulfur atom, but this π -bond is polarized by more than 90% towards oxygen so that the contribution of the d-functions is finally unimportant for the wave function. The most relevant formula **3a**, however, is not a good Lewis structure. Strong electron delocalization occurs, where two lone pairs on O2 donate 0.44 electronic charge into the antibonding non-Lewis orbitals $\text{BD}^* \text{S1-O3}$ and $\text{BD}^* \text{S1-O4}$.

H_2SO_4

Sulfuric acid is one of the most important acids in the chemical industry. In contrast to sulfurous acid, the structure of the free H_2SO_4 molecule is known from microwave spectroscopy.[18] The usually applied formula of H_2SO_4 exhibits a sulfur atom which forms six bonds, so that a violation of the octet rule occurs. The experimental as well as the calculated geometry adopt C_2 symmetry, where the sulfur atom is the center of a distorted tetrahedral environment. The calculated structural data are presented and compared with microwave data in Table 3a. The extension of the basis set from 6-311G* (and similar basis sets from the older literature [19]) to cc-pVQZ shows again the sensitivity of the S-O bond lengths with respect to computational efforts. The calculated natural net atomic charges in Table 3b show an in-

Table 6 Characterization of different Lewis structures for H_3PO_4 by the number of electron pairs in CR (core), BD (bond), and LP (lone pair) orbitals, and the valence Lewis charge (%). Lewis and non-Lewis orbitals are presented only for low and high occupancy, respectively

H_3PO_4	5a SB	5b DB	5c TB
CR, BD, LP	9, 7, 9	9, 8, 8	9, 9, 7
Val. Lewis charge	97.36	97.44	97.53
Lewis orbitals			
LP(2) O2 π	1.794	1.794	-
LP(3) O2 π	1.794	-	-
Non-Lewis orbitals			
$\text{BD}^*(2) \text{P1-O2 } \pi^*$	-	0.156	0.156
$\text{BD}^*(3) \text{P1-O2 } \pi^*$	-	-	0.156
$\text{BD}^*(1) \text{P1-O4}$	0.174	0.150	0.090
$\text{BD}^*(1) \text{P1-O5}$	0.174	0.159	0.090

creased positive charge of 2.45 on sulfur, compared with sulfurous acid, due to the additional oxygen atom. The total occupancy of natural 3d-orbitals on sulfur is slightly increased to 0.18. The traditionally assumed violation of the octet rule on the sulfur atom in H_2SO_4 is in disagreement with the charge distribution and the low 3d occupancy.

For H_2SO_4 four different possible Lewis structures can be drawn (**4a** - **d**). The octet rule on sulfur is fulfilled only for formula **4a**. Formula **4d**, where sulfur forms two S=O double bonds, is the well known textbook structure. The NBO analysis for the four structures **4a** - **d** in Table 4 favors structure **4a**, without multiple bonds, according to the maximum valence Lewis charge. In addition, this formula indicates strong electron deficiency on sulfur and the validity of the octet rule. The textbook structure **2d**, with S=O double bonds and without formal charges, is again the least relevant description of H_2SO_4 . The SO π -bonds in **2d** are composed of pd-hybrids on the sulfur atom, but these π -bonds are polarized by more than 90% towards oxygen so that the contribution of the d-functions is finally unimportant for the discussion of the wave function. The most relevant formula **4a** is not a good Lewis structure. Strong electron delocalization occurs, where two lone pairs on O2 and O3 donate 0.87 electronic charge mainly into the antibonding non-Lewis orbitals $\text{BD}^* \text{S1-O4}$ and $\text{BD}^* \text{S1-O5}$. This can easily be seen in Table 4.

The free acid molecules H_2SO_3 and H_2SO_4 were characterized at a common basis of bonding theory, where fundamental principles are retained. These are the consideration of charge distribution (electronegativity) and the octet rule. The sulfur atom requires d-orbitals initially for the construction of hybrids (NHO). The contribution of d-orbitals to the wave function, however, is negligibly small due to the strongly polarized bonds. The following question arises: Is sulfur prin-

Table 7 Natural localized molecular orbitals for lone pairs on X and X-Y bonds. Oxygen π -lone pairs, delocalized to sulfur (%); and phosphorus-oxygen π -bonds, polarized towards oxygen.

	NLMO	X	Y
H ₂ SO ₃	LP(2) O2	O2: 90.71	S1: 6.92
	LP(3) O2	O2: 87.83	S1: 9.10
H ₂ SO ₄	LP(2) O2	O2: 88.75	S1: 8.11
	LP(3) O2	O2: 88.23	S1: 8.59
	LP(2) O3	O3: 88.75	S1: 8.11
	LP(3) O3	O3: 88.23	S1: 8.59
H ₃ PO ₄	BD(2) P1-O2	O2: 88.92	P1: 10.54
	BD(3) P1-O2	O2: 88.93	P1: 10.50

cially unable for the violation of the octet rule? There is at least one example where the octet on sulfur seems to be extended - the octahedral SF₆ molecule.[20] The optimal Lewis structure exhibits six S-F bonds. The six octahedral sp³d²-hybrids on sulfur do not imply strong occupancy of d-orbitals in the bond orbitals because the S-F bonds are polarized by 78% towards fluorine; the natural net atomic charge on sulfur is 2.62. Therefore, the total d-orbital contribution to the wave function is only 0.19 electronic charge, similar to that in H₂SO₄. The formula for SF₆ with six S-F bonds is not a good Lewis structure because 0.96 electronic charge donates from the bonding orbitals into the antibonding non-Lewis orbitals. Thus, the violation of the octet rule in SF₆ should be seen with caution.

H₃PO₄

The geometry optimization of the phosphoric acid molecule yielded C₃ symmetry with the structural data in Table 5a. Two different P-O distances are known in the crystalline acid, $r(\text{P}=\text{O}) = 1.52 \text{ \AA}$ and $r(\text{P}-\text{OH}) = 1.57 \text{ \AA}$, and in the hydrated acid, $r(\text{P}=\text{O}) = 1.49 \text{ \AA}$ and $r(\text{P}-\text{OH}) = 1.55 \text{ \AA}$. [8] The textbook structure of H₃PO₄ indicates a violation of the octet rule on phosphorus, which forms three P-O single bonds and one P=O double bond. The calculated natural net atomic charges in Table 4b show a positive charge of 2.44 at phosphorus; and the total occupancy of natural 3d-orbitals on the P atom is 0.11.

For H₃PO₄, three possible Lewis structures are in competition (5a - c). The octet rule on phosphorus is fulfilled only for formula 5a; and 5b is the textbook structure, where phosphorus forms a P=O double bond. Up to here, the NBO analysis of phosphoric acid should not be expected to differ markedly from sulfuric acid. Surprisingly, the maximum Lewis charge can be found for formula 5c which exhibits a P⁺≡O: triple bond, and formula 5a with a P⁺≡O::: triple bond is

even worse than the textbook structure 5b. However, a dominant Lewis structure in the sense of our definition by the Lewis charge cannot be found. The Lewis charges of formulae 5a - c are more or less equal, as can be seen in Table 6. The result of the NBO analysis for H₃PO₄ is not surprisingly different from H₂SO₄, according to the NBO's. The three P-OH single bonds are polarized towards oxygen by 82% and the two P-O π -bonds in 5c are polarized towards oxygen by more than 91%. The bond polarization explains the same electron deficiency for phosphorus and sulfur in their respective acids. Thus, no extension of the octet occurs on phosphorus. The formulae 5a - c describe more or less the same electronic situation if we keep in mind that there is a fluid transition from slightly delocalized (to X) oxygen lone pairs to strongly polarized (towards O) X-O bonds (X = P, S).

Conclusions

The usual description of molecules by means of two-center bonds and lone pairs is not sufficient for characterizing the wide variety of bonding patterns. The search for Lewis structures should be accompanied by the calculation of net atomic charges, bond polarity and electron delocalization. The NBO analysis of a wave function is found to be capable of the calculation of Lewis structures and their characterization by Lewis orbitals and their occupancies. The NBO analysis can, therefore, be seen as a "tribunal" where different competing Lewis structures are being under discussion. For our introductory example, SO₂, four different structures could be found in different textbooks. According to the criterion of the maximum valence Lewis charge, the semi-ionic resonance structure d) is the only relevant description of SO₂. Irrelevant structures are, at the second rank a) the two double bonds structure, and at the third rank b) the two ionic bonds structure. The description by means of 4-electron-3-center orbitals c) fails dramatically. The formally non-bonding 3-center orbital is actually antibonding in its character so that meaningless occupancies occurred with the message 'excited state configuration'.

The sulfurous and sulfuric acid molecules are recommended to be described correctly by ionic bonds instead of covalent π -bonds. Thus, the electron deficiency, the negligibly low 3d occupancy, and the conservation of the octet rule on sulfur are retained. No dominant resonance structure could be found for the phosphoric acid molecule. Notwithstanding this fact, the bonding patterns of H₃PO₄ are closely related to those of H₂SO₄. This can be shown at best by means of the NLMO's in Table 7. There is still some arbitrariness in the terminology of the NBO analysis when going from delocalized lone pairs to polarized bonds.

The usefulness of the NBO analysis is not restricted to the calculation of Lewis structures for well known molecules. Unexpected structures, such as the nontetrahedral structure of SiLi₄ [21], or the polyacetylenic character of so-called heterocumulated double bond systems XC_nY [22], can be understood at best in terms of natural bond orbitals.

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