

Addressing the Hypervalent Model: A Straightforward Explanation of Traditionally Hypervalent Molecules

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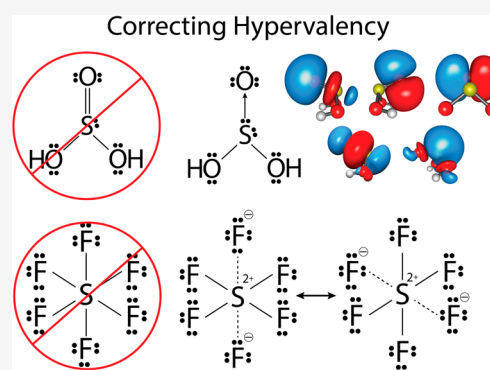
ABSTRACT: The concept of an atom with an expanded octet, known as hypervalency, has persisted in the general chemistry curriculum, despite abundant theoretical work disputing its veracity. Here, the electronic structure of traditionally hypervalent molecules (H_2SO_3 , H_2SO_4 , PF_5 , and SF_6) is explored through quantum chemical calculations to illustrate the inaccuracies of hypervalency. Through the framing of ionic and dative bonding, an alternative way to conceptualize bonding in such molecules is introduced based on the octet rule already canonized in the general chemistry curriculum. These results are used to construct new Lewis structures that more accurately describe their chemical nature while simultaneously reducing the complexity of drawing Lewis structures. Teaching applications and heuristics are discussed with the hope that these models may eventually supplant hypervalency in the curriculum.

KEYWORDS: Covalent Bonding, First-Year Undergraduate/General Chemistry, VSEPR Theory, Valence Bond Theory

INTRODUCTION

Chemical bonding is one of the core concepts of the general chemistry curriculum.¹ Lewis theory, valence shell electron pair repulsion (VSEPR), valence bond theory (hybridization), and molecular orbital theory are the common models introduced in the first semester of general chemistry. Each approach has its strengths and limitations, and students are asked to know which one should be applied to explain molecular features, such as molecular geometry, electronic structure, dipole moment, and intermolecular forces. In introducing Lewis theory, the common “octet rule” is described to represent the most stable configurations for many Lewis structures. Inevitably, the concept of expanded octets (hypervalency) is used to “explain” the bonding in compounds such as H_2SO_3 , H_2SO_4 , PF_5 , SF_6 , and XeF_4 , where the central atoms appear to have more than eight electrons in their valence space. However, this concept generates more questions than answers. For example, why can sulfur but not oxygen accommodate more than eight electrons in its valence space? What is the best way to conceptualize the double bond between sulfur and the terminal oxygen atoms?

The concept of expanded octets has been referred to in the literature by various names, from the “exceptions to the rule of eight” of Gilbert N. Lewis,² to the “transargononic structures” of Linus Pauling,³ and to the hypervalency term of Jeremy L. Musher.⁴ A more detailed account on the origin and history of this topic can be found elsewhere.^{5,6} For mainly historic reasons, the idea that an atom can accommodate more than eight electrons in its valence space has persisted in chemical education, and it is included in many older and modern general

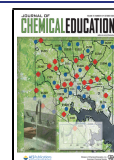


chemistry textbooks. Hypervalency was first introduced by Musher as an initial classification for these unusual systems; but Musher himself rejected octet expansion, believing alternative bonding schemes were necessary to describe these systems.⁵ Since its inception, the concept of hypervalency has been widely disputed within the theoretical chemistry community.^{5,7} Over time, however, this classification became the accepted explanation for these systems within the general chemistry course. It became a form of circular reasoning: “Sulfur in H_2SO_4 exhibits hypervalency because it is hypervalent” (see, for example, refs 8 and 9). Ample theoretical work is available that disputes the veracity of hypervalency as a description of the electronic structure, but despite this, the concept has persisted as the default explanation for both historical reasons and its perceived ease of explanation. Hypervalency has become a convenient “hand-wave” explanation for systems which seemingly defy traditional Lewis bonding schemes. Nevertheless, this “explanation” provides no chemical insight and necessitates the introduction of problematic descriptions such as sp^3d and sp^3d^2 hybridization.¹⁰ However, quantum chemical calculations have shown that this concept of expanded octets is problematic.^{6,9–17} In light of this

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theoretical work, some textbooks use careful wording and offer alternative descriptions. For example, the second edition of "Chemistry, an atoms-focused approach" states, "Others [chemists] have proposed that hypervalency is really an illusion and that atoms can form five or six bonds using only eight valence electrons".¹⁸ While a promising direction, further efforts are necessary to correct the inaccuracies that the teaching of hypervalency introduces in the classroom.

Problems with the hypervalent description can be exemplified in the Lewis structures of H_2SO_3 , PCl_5 , and SF_6 . According to the conventional rules, the two possible Lewis structures for H_2SO_3 are shown in Figure 1. Structure 1B is

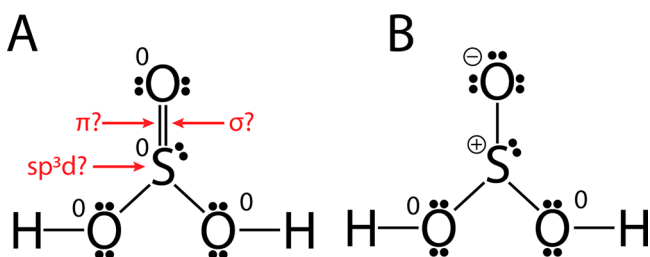


Figure 1. Two Lewis structures of H_2SO_3 , with formal charges shown.

characterized by a full octet for all p-block elements, a single bond between sulfur and oxygen, and formal charges of +1 and -1 on these respective atoms. On the other hand, in structure 1A there is a double sulfur–oxygen bond and zero formal charges on all atoms, but the central sulfur atom appears to have ten valence electrons. In presenting these structures to students, it is taught that structure 1A is more stable since it minimizes formal charges. However, this representation is problematic and introduces two main questions: How can the sulfur atom host more than eight electrons in its $3s3p$ valence space? What is the character of this double bond: is it one σ and one π bond?

For PCl_5 and SF_6 , students are taught that some atoms tend to have expanded valence shells when they bond to strongly electronegative atoms such as F and Cl and/or when the expanded shell produces a Lewis structure in which the atoms' formal charges are close to zero.¹⁸ The commonly presented Lewis structures for SF_6 and PF_5 are shown in Figure 2 with

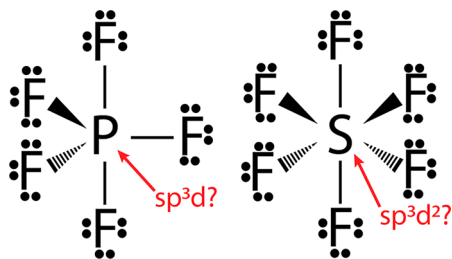


Figure 2. Conventional Lewis structures of PF_5 and SF_6 indicating the "hypervalency" of S and P.

single bonds between the central atoms and fluorine atoms. However, these structures introduce problems similar to those discussed above, including that of sp^3d and sp^3d^2 hybridization and how they can violate the octet rule.

Presently, we propose an alternative, simple (and more accurate) way to conceptualize bonding in molecules traditionally described as hypervalent. We report easily reproduc-

ible quantum calculations using one of the most popular electronic structure software (Gaussian16)¹⁹ to demonstrate the misleading description provided by the concept of hypervalency for typical hypervalent molecules. These calculations point to more accurate dative-type and ionic-type models that are arguably easier to understand and more accurately represent the nature of bonding than the hypervalent explanation. It should be stressed that the computational evidence is not intended as a teaching tool in a regular general chemistry course but is the basis for revising the models we use to teach. Similar attempts in the near past show the importance of this topic.²⁰

It is our hope that the evidence presented here will convince instructors to adopt a model different from the traditional hypervalent "explanation". For ease of reading, we have split this paper into two sections. The first section details our computational methodology, which provides the evidence to support the dative and ionic conceptualizations of bonding in traditionally hypervalent molecules (Computational Evidence). The second section describes an alternative way to teach bonding in traditionally hypervalent molecules for a general chemistry audience that incorporates this evidence (Teaching Applications). In addition, included in the Supporting Information is an example of a textbook passage, which explains these concepts and how they may be applied by students.

COMPUTATIONAL EVIDENCE

Methodologies

The general practice of generating molecular orbitals proceeds by writing them as linear combination of functions, called the basis functions, which resemble (but are not necessarily identical to) the atomic orbitals. These basis functions include s -, p -, d -, etc. type functions. In the discussion of molecular orbital (MO) theory, this is generally described as a linear combination of atomic orbitals (LCAO), but this terminology is misleading in the sense that molecular orbitals are linear combinations of basis functions rather than actual atomic orbitals. During chemical bonding, the initial atomic orbitals are highly distorted. In order to properly describe the distortion, it is necessary to include more functions, called polarization functions. For example, to describe the molecular orbitals of sulfuric acid we need to add not only s - and p -type basis functions of sulfur but also d -, f -, etc. type functions. This is not to be confused with the inclusion of d -atomic orbitals of sulfur.^{10,14–17} These additional functions are necessary to describe the distortions atomic orbitals experience in a molecular environment. For example, the σ bond in H_2 is a result of interactions between only two $1s$ atomic orbitals of each hydrogen. However, additional p -type basis functions are necessary to accurately describe how these atomic orbitals are distorted in the formation of the σ bond, despite p atomic orbitals playing no role in this formation.

To solve the Schrödinger equation for the considered molecules, we applied both density- and wave function-based methodologies. All optimized structures were obtained with density functional theory (DFT) combined with the B3LYP functional.^{21–24} Energetics discussed in Ionic-Type Hypervalent Molecules are estimated with second-order Møller–Plesset perturbation theory (MP2).^{25–27} The potential energy curves shown in Dative-Type Hypervalent Molecules are constructed at the Davidson corrected multireference config-

uration interaction (MRCI+Q) level.^{28–30} The active space at the reference complete active space self-consistent field (CASSCF) wave functions is composed of 8 and 6 electrons in 7 and 5 orbitals representing the two sulfur lone pairs and the terminal oxygen $2p_x$, $2p_y$, and $2p_z$ electrons and orbitals of H_2SO_3 and H_2SO_4 , respectively. The hydrogen atoms are equipped with s -, p -, and d -type functions of the cc-pVTZ basis, and the remaining atoms are equipped with s -, p -, d -, and f -type functions of the cc-pVTZ (for S, P, and O) and aug-cc-pVTZ (F) bases.^{31–33} All valence electrons are correlated at the MRCI level.

To interpret our wave functions, calculate atomic charges, and obtain orbital populations, we implemented the natural bond orbital (NBO) analysis.³⁴ The NBO analysis provides a thorough account and clear representation of the bonding, antibonding, and nonbonding orbitals offering chemically intuitive bonding schemes. Finally, we invoked the NRT keyword of the NBO code to get resonance structures for PF_5 , SF_6 , and XeF_2 .^{35–37} These results are mentioned briefly in the text and discussed further in the Supporting Information.

Dative-Type Hypervalent Molecules: H_2SO_3 and H_2SO_4

Our first example of an alternative description of a hypervalent system is that of H_2SO_3 and H_2SO_4 , two molecules that are commonly discussed in a general chemistry course and are excellent examples of what we will refer to here as the dative-type hypervalent molecule. These molecules are not truly hypervalent but are more accurately described in the context of dative bonds, which involve the partial donation of an electron pair to an empty orbital.

To examine the bonding character between sulfur and the terminal oxygen of H_2SO_3 , we first inspect how Lewis structures of the two individual fragments H_2SO_2 and O compare to their calculated NBOs (see Figure 3). The Lewis

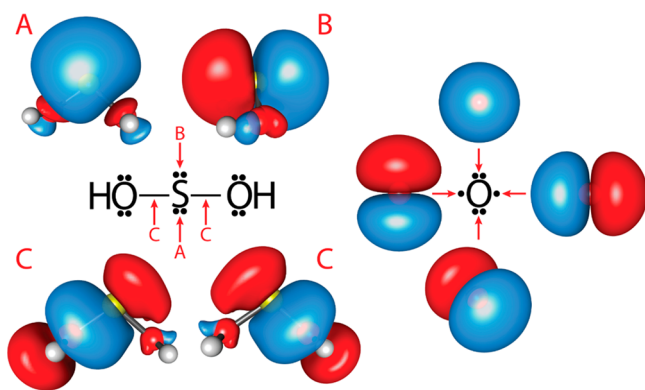


Figure 3. Select NBOs for H_2SO_2 and atomic oxygen.

structure for H_2SO_2 accurately describes the electronic structure of the molecule with two σ bonds between sulfur and the oxygen of each OH group and two lone electron pairs localized on sulfur, as evidenced by our NBO analysis. The Lewis structure of oxygen, shown also in Figure 3, correctly predicts two unpaired electrons in two $2p$ orbitals and two electron pairs in one $2p$ and $2s$ atomic orbitals.

With this in mind, we can examine how the system will change through the binding of the two fragments H_2SO_2 and O to form H_2SO_3 . The conventional Lewis structure for this system is seen in Figure 1A, where its construction would initially involve a single bond between sulfur and the additional oxygen, and then, an oxygen lone pair would be used to make a

double bond in order to reduce the formal charge of all atoms. To investigate the accuracy of this model, we monitored the morphology of NBOs and calculated the energy of the system at different S–O distances. The resulting potential energy curves are depicted in Figure 4; the NBOs shown are that of the interaction between an oxygen $2p_z$ orbital and a sulfur lone pair.

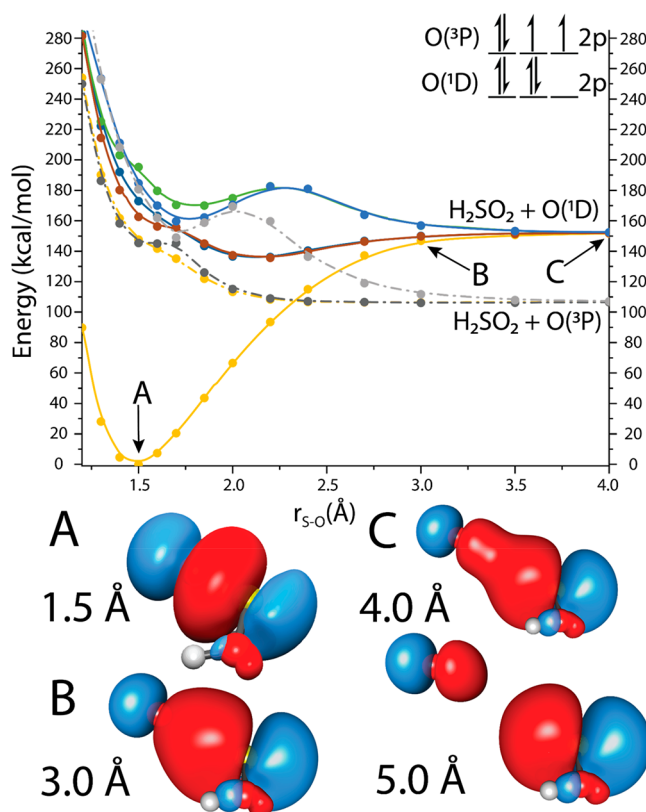


Figure 4. MRCI+Q potential energy curves of H_2SO_3 with respect to the $(\text{OH})_2\text{S}-\text{O}$ distance. The NBOs of the S–O σ bond along the yellow solid curve are shown at different distances: 1.5 (point A of the plot), 3.0 (point B), 4.0 (point C), and 5.0 Å (beyond the scale of the plot). Solid lines depict the interactions between H_2SO_2 and the 5 degenerate ^1D states of oxygen, and the dashed lines depict that of the 3 degenerate ^3P states. Also shown are the electron configurations for one component of the ^3P and ^1D electronic states.

The ground state of oxygen (^3P) is triply degenerate and adopts one of the three electronic configurations: $2s^2 2p_x^2 2p_y^1 2p_z^1$, $2s^2 2p_x^1 2p_y^2 2p_z^1$, or $2s^2 2p_x^1 2p_y^1 2p_z^2$ (see Figure 4). The interaction of these three different states with sulfur produces the three dashed potentially energy curves. The approach of any of these states with the closed-shell H_2SO_2 fragments results initially in a weak attraction at around 2.5 Å, but finally, the energy rapidly increases, signaling an overall repulsive interaction. The first excited state of oxygen is 5-fold degenerate (^1D), and one of its electronic configurations is $2s^2 2p_x^2 2p_y^2 2p_z^0$ (see Figure 4). When H_2SO_2 approaches an oxygen atom with this configuration, the energy decreases, producing a bonding interaction and the ground state of H_2SO_3 (see yellow solid curve of Figure 4). As oxygen approaches H_2SO_2 an electron pair on sulfur is attracted to the oxygen atom until it begins to populate the empty $2p_z$ orbital and eventually forms the S–O bond. The NBO at 5.0 Å shows a pure sulfur lone electron pair. At shorter distances (4.0 and

3.0 Å), the NBO represents the partial population of the $2p_z$ orbital of oxygen, which finally leads to the σ -bonding orbital at 1.5 Å. Therefore, this σ bond is best described as a dative bond from sulfur to oxygen.

Figure 5 sheds light on whether the oxygen lone pair is used in a double bond. This shows three orbitals localized on the

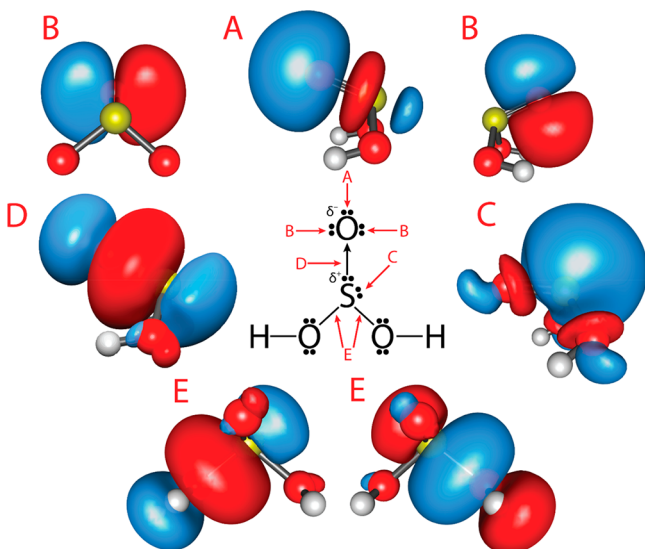


Figure 5. Select NBOs of H_2SO_3 , representing the lone and bonding electron pairs.

terminal oxygen; A represents a predominantly 2s orbital, and B depicts clean $2p_x$ and $2p_y$ orbitals. The remaining orbitals are shown in Figure 5D, the dative σ bond; C, the sulfur lone pair; and E, the two S–OH sigma bonds. From this, one can see there is no S–O double bond, and the terminal oxygen has three lone pairs. Therefore, a more accurate Lewis structure would be drawn as in Figure 6.

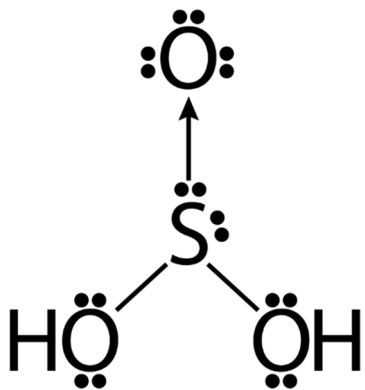


Figure 6. Adjusted Lewis structure of H_2SO_3 , illustrating the dative bond between sulfur and the terminal oxygen.

The formation of H_2SO_4 from H_2SO_3 and O occurs through a similar mechanism. The remaining electron pair of sulfur in H_2SO_3 imitates the lone pair of H_2SO_2 and binds to a second oxygen atom. The same dative bond from sulfur to an excited state oxygen takes place as revealed by the potential energy curves of Figure 7. The potential energy curves have the exact same morphology as those of H_2SO_3 (Figure 4), and the lowest energy structure comes from $\text{H}_2\text{SO}_3 + \text{O}({}^1\text{D}; 2s^2 2p_x^2 2p_y^2 2p_z^0)$. Also, the oxygen atom possesses three lone

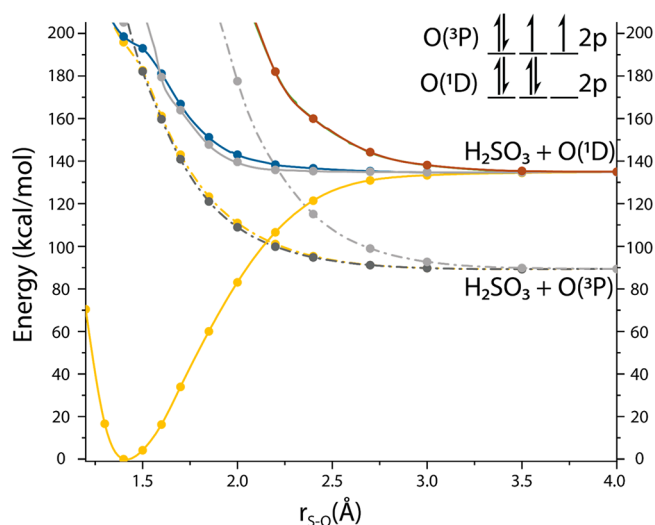


Figure 7. MRCI+Q potential energy curves of H_2SO_4 with respect to the S–O distance ($\text{H}_2\text{SO}_3 + \text{O} \rightarrow \text{H}_2\text{SO}_4$). Also shown are the electron configurations for one component of the ${}^3\text{P}$ and ${}^1\text{D}$ electronic states. Solid lines depict the interactions between H_2SO_3 and the five degenerate ${}^1\text{D}$ states of oxygen, and the dashed lines depict those of the 3 degenerate ${}^3\text{P}$ states.

pairs in orbitals similar to those seen in Figure 5A and B. The more accurate Lewis structure then is shown in Figure 8, which depicts two dative bonds from sulfur to the two oxygen atoms.

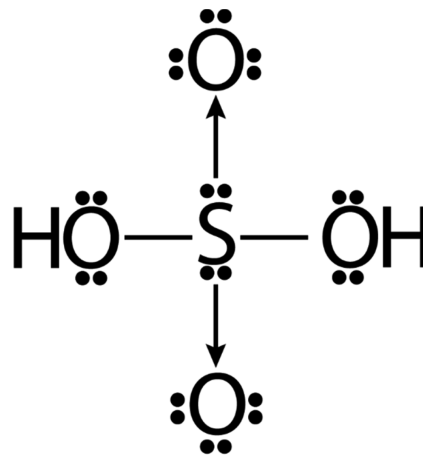


Figure 8. Adjusted Lewis structure of H_2SO_4 , illustrating a dative bond between sulfur and the two terminal oxygen.

The proposed bonding scheme shows that the octet rule is not violated for sulfur in either H_2SO_3 or H_2SO_4 . An additional source of evidence is obtained from an electron population analysis (Figure 9). The occupation of the 3s, 3p, and 3d orbitals of sulfur are $3s^{1.53} 3p^{2.57} 4s^{0.03} 3d^{0.10} 4p^{0.01}$ for H_2SO_3 and $3s^{0.96} 3p^{2.29} 3d^{0.18} 4p^{0.03}$ for H_2SO_4 . The occupations of the 3s and 3p orbitals account for the +1.74 and +2.5 charge of sulfur in H_2SO_3 and H_2SO_4 , while 3d orbitals (or more accurately 3d functions) facilitate the polarization of the electronic density in the interatomic region.^{10,14–17} As such, a description of sp^3d^1 and sp^3d^2 hybridization for sulfur is inaccurate. According to NBO charges, the donation of electrons from sulfur to oxygen is rather substantial, with approximately 0.9 electrons transferred to oxygen (see δ_b and δ_d values in Figure 9). The picture of a single (strongly) polar bond between sulfur and oxygen

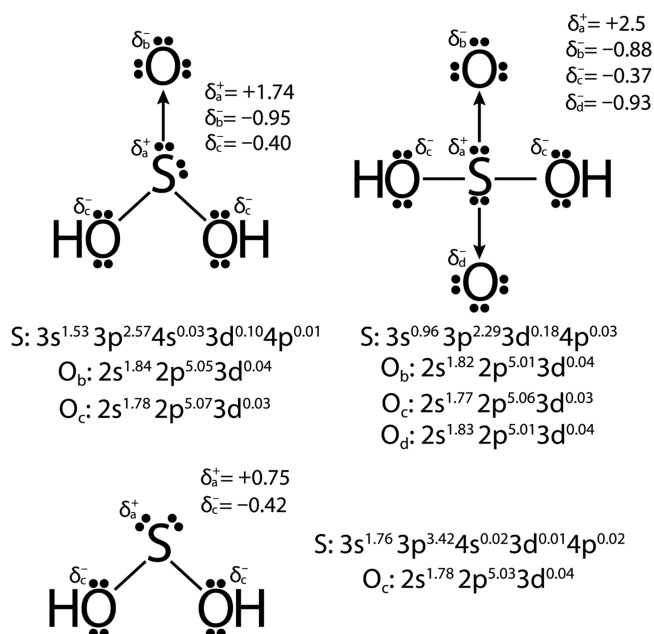


Figure 9. Atomic occupations and charges for H_2SO_2 , H_2SO_3 , and H_2SO_4 . The charges on the hydroxyl groups, shown as δ_o , are the sum of the oxygen and hydrogen partial charges.

explains also the strong oxidative properties of H_2SO_3 , H_2SO_4 , and other similar oxo-terminated hypervalent species, such as $\text{C}_6\text{H}_5\text{I}^{\delta+} \rightarrow \text{O}^{\delta-}$.¹¹

Our picture of highly polarized dative bonds agrees with an earlier, more detailed NBO analysis³⁸ and the definition of a dative (or coordination) bond by the IUPAC Gold Book, which distinguishes dative and covalent bonds by the significant polarity of the former.³⁹

Overall, based on our orbital analysis and atomic charges of sulfurous and sulfuric acid, we propose the bonding schemes of Figures 6 and 8. The commonly drawn double sulfur–oxygen bonds should be replaced with single polar dative bonds from sulfur to oxygen. This picture is more accurate and provides a more meaningful picture without introducing the problematic concepts of sp^3d or sp^3d^2 hybridization and superficial π bonds. From our occupation analysis, there is no clear contribution of the d orbitals to the formation of the bonds in these molecules. Therefore, for these types of molecules, sp^3d and sp^3d^2 hybridization cannot occur. Similarly, Figure 5 shows that the valence electrons around oxygen remain in orbitals resembling the atomic 2s and 2p orbitals, eliminating the possibility of π -bond formation.

Ionic-Type Hypervalent Molecules: SF_6 and PF_5

Two molecules commonly depicted as hypervalent are SF_6 and PF_5 , which provide a convenient example of another alternative description of hypervalence, which we refer to here as the ionic-type hypervalent molecules. Like H_2SO_3 and H_2SO_4 , these molecules are not actually hypervalent despite being commonly described as such. Instead, they are better described in the context of the formation of fully ionic bonds rather than the electron pair donation of dative bonds or conventional sigma bonds.

The commonly drawn Lewis structure of SF_6 is shown in Figure 2, which depicts a central sulfur atom that forms six sigma bonds with the 6 peripheral fluorine atoms, and the sulfur atom has a total of 12 valence electrons, but this is

inaccurate. To describe the electronic structure of SF_6 , we can imagine its stepwise formation starting at SF_2 (see Figure 10).

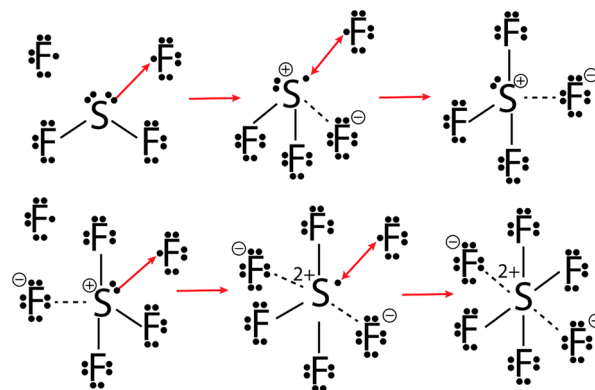


Figure 10. Mechanism for the formation of SF_6 , starting from SF_2 .

The structure of SF_2 is analogous to water and is accurately described by its Lewis structure. The two fluorine atoms are bound by two σ bonds to a sulfur atom that has two lone pairs. The addition of two more fluorine atoms proceeds through the following mechanism: first, one sulfur electron transfers to fluorine to form SF_2^+ and F^- , and the remaining unpaired electron forms a σ bond with the other fluorine to make SF_4 . Starting from SF_4 , the formation of SF_6 proceeds through a similar mechanism: the transfer of one electron to a fluorine atom and subsequent σ -bond formation with the remaining valence electron of sulfur. This proposed mechanism is in agreement with a previous theoretical work.⁴⁰ This story clearly illustrates the ionic character of this system with a S^{2+} center and two F^- atoms electrostatically bound.

The NBO analysis of SF_6 presents a similar picture. The NBOs are depicted in Figure 11; from these, it is shown that each fluorine atom has six valence electrons, which are in “clean” atomic 2s and two 2p orbitals. The fourth electron pair

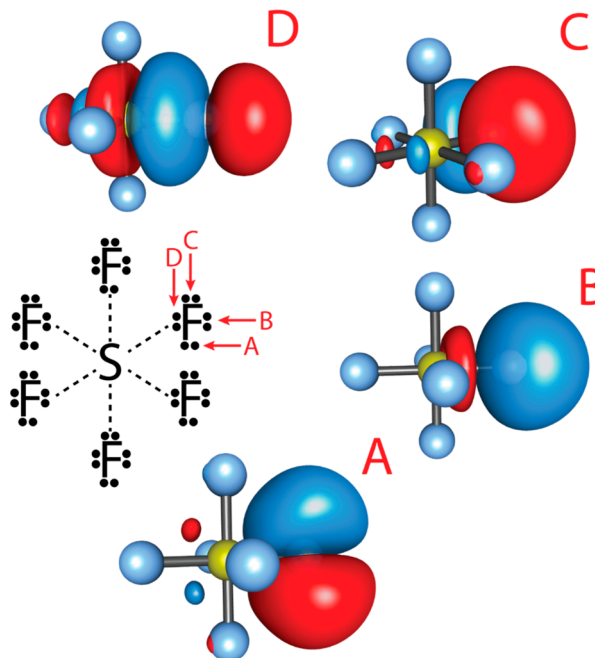


Figure 11. Select NBOs of one fluorine atom in SF_6 .

(Figure 11D) occupies a molecular orbital, which initially appears to be the Lewis-predicted S–F covalent bond. However, the population analysis indicates a highly polarized ionic-type bond (see Figure 12). The natural ionicity, i_{AB} ,

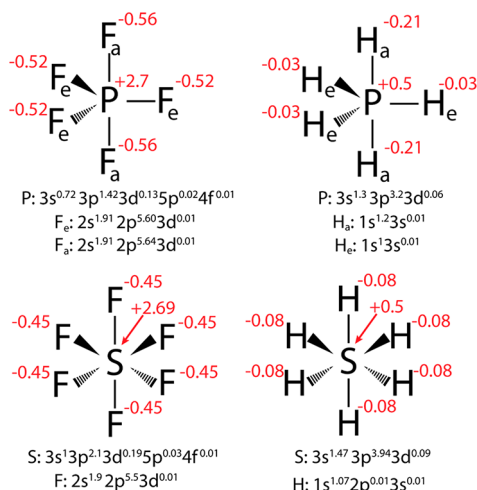


Figure 12. Atomic occupations and charges for PF_5 , PH_5 , SF_6 , and SH_6 .

describes the degree to which the σ bond between two atoms A and B is ionic; natural ionicities of $i_{AB} > |0.95|$ describe traditional Lewis ionic bonds.⁴¹ The natural ionicity, i_{SF} , of each S–F bond is 0.86, indicating a rather ionic σ bond. Each fluorine has an average charge of -0.45 , resulting in a sulfur center of charge $+2.69$ (Figure 12).

In summary, the electronic structure of this system is best described as a sulfur center with a charge somewhere between $2+$ and $3+$; the corresponding negative charge is distributed among the equivalent fluorine atoms. Shown in Figure 12 is the orbital occupation of the sulfur center, $3s^1 3p^2 1.3d^0.19 5p^0.03 4f^0.01$. The minimal occupation of d-type orbitals eliminates the possibility of $sp^3 d^2$ hybridization. As above, this small occupation is necessary for the polarization of the atomic orbitals.

The exact same bonding scheme is seen for PF_5 . Its formation begins with PF_3 , and the addition of the next F atom results in the removal of one electron from P and σ -bond formation with the last F. The net charge on phosphorus is the same seen on sulfur, despite the fewer number of fluorine bonds (see Figure 12). This can be explained by the lower electronegativity of phosphorus and the resulting formation of more polar bonds. The natural ionicity, i_{PF} , of the equatorial and axial P–F bonds is 0.91 and 0.93, respectively. Given these results, we propose that the more accurate Lewis diagrams of SF_6 and PF_5 are those shown in Figure 13, where dashed lines have been used to show ionic bonds. Resonance structures are used here to illustrate the equivalency of the fluorine atoms. For reasons of brevity and clarity, the resonance structures obtained using the NRT keyword of the NBO code agree with the presented mixed ionic/covalent character and are reported and discussed in the Supporting Information.

At this point, it is pertinent to refer to three center–four electron bonds ($3c/4e$), which can be thought of a mix of ionic and covalent bonds within a molecule. As an example, we focus on XeF_2 . One electron from each fluorine and two 5p electrons from xenon form two bonds along the F–Xe–F interatomic axis. According to our NRT calculations, this bond can clearly

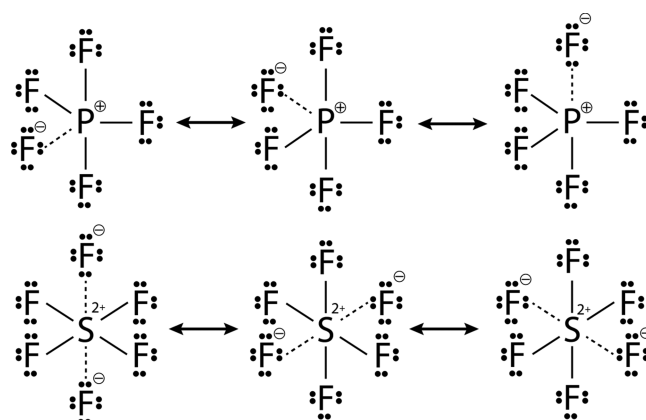


Figure 13. Adjusted Lewis structures of SF_6 and PF_5 , with dashed lines to indicate ionic bonds and resonance structures to show fluorine equivalency. Note that not all the resonance structures are shown.

be represented as $\text{F}^-\text{Xe}^+-\text{F} \leftrightarrow \text{F}-\text{Xe}^+\text{F}^-$, where there is one ionic and one covalent bond between the unpaired electron of Xe^+ and F. As a result, each bond is half ionic and half covalent, giving a bond ionicity of 54%. These $3c/4e$ bonds are analogous to the bonding character of the ionic-type hypervalent molecules. This representation agrees with the σ molecular orbital picture, which clearly indicates that only valence orbitals of Xe and F are involved (see ref 42 for a discussion on the similar I_3^- anion). Two doubly occupied σ molecular orbitals (one bonding and one nonbonding) point to Xe–F bonds being a mix of a single and an ionic bond (see Supporting Information).

Note, PF_5 is depicted as $\text{PF}_4^+ + \text{F}^-$ despite these calculations predicting a similar charge of P and S (Figure 12). As discussed, the charge equivalency is a result of the more polar P–F bond. In an effort to strictly follow the octet rule, some accuracy is lost in its representation. However, this Lewis structure remains a far more accurate description of the ionic nature of PF_5 while avoiding the erroneous hypervalency and is readily obtainable from the simple heuristics discussed in the Supporting Information.

The highly ionic bonding scheme of these two molecules can explain why strongly electronegative atoms are prerequisites for the formation and thermodynamic stability of these systems. For example, similar structures would be expected from SH_6 and PH_5 ; however, the low electron-affinity of hydrogen produces less stable structures. Resonance structures similar to those of Figure 13 can also be used to describe the bonding, but the present ionic bonds are weaker in these systems. Specifically, the total binding energy of SH_6 and PH_5 is nearly half that of SF_6 and PF_5 , as seen in Figure 14. Another reason for the instability of these systems is the stability of the H_2 bond favoring dissociation to $\text{SH}_2 + 2\text{H}_2$ and $\text{PH}_3 + \text{H}_2$. The binding energy of H_2 and F_2 is 104 and 39 kcal/mol, respectively.⁴³ The electronegativity of the bonding atoms alone is necessary but not sufficient. The weak binding energy of F_2 disfavors the dimer formation, making it unique in this regard. For the same exact reasons, $\text{Te}(\text{CH}_3)_6$ (studied in the past)⁴⁴ is thermodynamically unstable with respect to $\text{Te}(\text{CH}_3)_2 + 2\text{C}_2\text{H}_6$ by 88.2 kcal/mol (present calculations; see Supporting Information).

In short, through an orbital and population analysis, we have shown that the electronic structures of SF_6 and PF_5 are

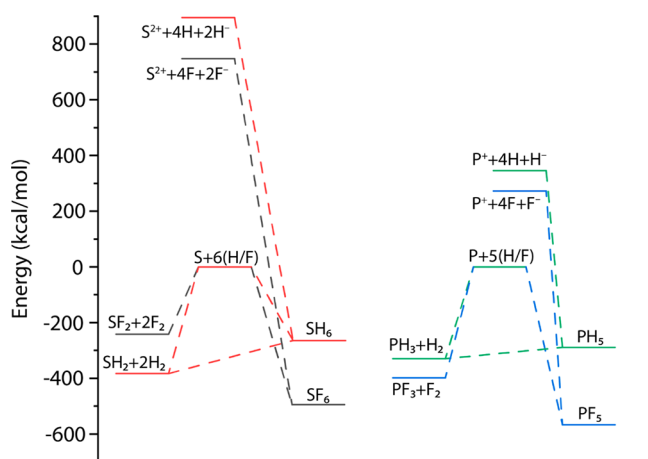


Figure 14. Relative MP2 energetics for the formation and fragments of PF_5 , PH_5 , SF_6 , and SH_6 . Each plot is zeroed at the energy of the neutral fragments, i.e., $\text{S}+6(\text{H}/\text{F})$ and $\text{P}+5(\text{H}/\text{F})$.

described more accurately in terms of ionic bonds, avoiding any need for the erroneous description of hypervalency. The population analysis of Figure 12 proves that sp^3d^1 or sp^3d^2 hybridization is not involved in the formation of these molecules. Instead, they are best described as involving a mixture of ionic and covalent bonding. Given this, a more accurate Lewis structure would be that presented in Figure 13.

TEACHING APPLICATIONS

While these descriptions have more computational depth, they do not introduce any new concepts than what students have already learned. First and foremost, to account for a more accurate depiction of traditionally hypervalent molecules, the octet rule is the only rule that needs to be satisfied. For this reason, increased formal charges are acceptable in some cases. In the molecules exhibiting dative-type bonds, every atom follows the octet rule, as the lone pair of the dative bond can be conceptualized as in the valence sphere for each atom in the bond. In molecules exhibiting ionic-type bonds, the central atom can be thought to have a full octet, with any excess bonds being ionic. Second, the explanation of *why* this is the case is readily explained in terms of electronic excitation, a concept familiar from the introduction of the Bohr model and hybridization. Students are expected to understand that C sp^3 hybridization (forming CH_4) involves the promotion of a $2s$ electron to an empty $2p$ orbital. This is directly mirrored here in the explanation of bonding in the dative-type molecules of ^3P to ^1D to free up a $2p$ orbital for the dative bond. Both involve an electron excitation rearrangement of the valence space to allow bonding. Moreover, the energy cost for this rearrangement in the case of oxygen is smaller than carbon ($33,735$ vs $15,868$ cm^{-1}),⁴⁵ consistent with the explanation that lower energy equates to more stability inundated throughout bonding chapters in textbooks. Third, students are frequently taught that orbitals can mix and that delocalized/hybrid structures exist for molecules with at least one multiple bond. It is therefore not a stretch to introduce a “mixing” of ionic and covalent bonding schemes to explain the structure of PF_5 .

In short, the application to teaching of this simple computational study is that there exists a clear alternative to the traditional hypervalent “explanation” of a molecule that relies on principles that would naturally be taught anyway. This

enhanced explanation comes at the cost of needing to introduce dative-type bonding in addition to ionic and covalent and relying on the student’s ability to conceptualize hybrid/resonance structures. However, it is relatively simple to predict whether a molecule will exhibit ionic- or dative-type interactions (depending largely on the electronegativity of the atoms involved) and produce a more accurate Lewis structure than the one predicted by hypervalency. Also important to teaching is the use some simple heuristics, making it possible to quickly determine hard rules to determine if a structure is correct or incorrect.

To ease the burden of implementation of this computational study into the classroom, we have provided the reader with a few sections of sample text that we feel could explain the concepts discussed here (see Supporting Information). First, in the chapter that typically introduces ionic and covalent bonding, we propose additionally introducing students to the notion of dative bonds. To achieve maximum success, bonding will need to be approached as a model to conceptualize the electron location between atoms as opposed to strict definitions based on surface features (i.e., ionic bonding is metal–metal; covalent is metal–nonmetal). Then, in the chapter traditionally dedicated to molecular shapes (Lewis structure and VSEPR), we suggest replacing any text that introduces expanded octets or hypervalency with the text provided. Our sample text walks the student through the conceptual formation of dative- and ionic-type bonds within a molecule and then provides heuristics to apply them to novel molecules.

CONCLUSIONS

On the basis of the NBO analysis, we conclude that the traditionally hypervalent/expanded octet “explanation” is inaccurate. Additionally, it is unsatisfactory for learning as it relies on circular reasoning without a chemical conceptual foundation. On the basis of our calculations, we divide these systems into two alternative categorizations that accurately depict bonding: dative-type and ionic-type hypervalency. The former is characterized by dative bonds formed by the donation of the lone-pair electrons of the central atom to the unoccupied orbitals of the peripheral atoms (see Figures 6 and 8). The latter type is distinguished by highly ionic σ bonds between the central and peripheral atoms (see Figure 13). Dative- and ionic-type bonding models were shown to better represent the types of bonding that occurs in traditionally hypervalent molecules, and these concepts should not pose more of a cognitive burden to students than do the frequently used hypervalent explanations. These categories of bonding can be readily applied to explain the structure of other systems. For example, HIO_4 , HIO_3 , HNO_3 , and HClO_4 ;⁸ XeO_4 ;⁴⁶ and OSCl_2 and POCl_3 ⁹ all fit our dative-type description, while SiF_5^- , ClF_3 , XeF_4 , and I_3^- fit the ionic type. These two categories are not mutually exclusive; for example, the experimentally observed OXeF_4 molecule⁴⁷ exhibits dative-type bonding between oxygen and xenon, while the xenon–fluorine bonds are ionic-type.

These descriptions build on topics which are already discussed within the general chemistry curriculum and do not require the introduction of any new concepts. It is our hope that the presented ionic- and dative-type bonding schemes may gradually replace hypervalency within general chemistry courses.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available at <https://pubs.acs.org/doi/10.1021/acs.jchemed.0c00368>.

A sample textbook section and resonance structures for the XeF₂, PF₅, SF₆, and H₂SO₃ molecules are provided in the Supporting Information (PDF)

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Notes

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