The nature of the SO bond of chlorinated sulfur–oxygen compounds

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Abstract Sulfur–oxygen chemistry encompasses a rich variety of chemical species and reactions. Sulfur–oxygen bonds can be quite short and strong, and historically, there has been disagreement as to the nature of the SO bond in sulfinyl groups. Early work invoked participation by the 3d orbitals of sulfur to explain the apparent double-bond character of sulfinyl bonds, but modern calculations have clearly established that sulfur 3d atomic orbitals do not participate as valence orbitals in hypervalent sulfur compounds. In prior work, we used generalized valence bond (GVB) theory to explain the features of the SO bond in the HSO/SOH structural isomers, and we extend that work here to the chlorinated analogs (ClSO/SOCl). We also use GVB theory to elucidate the nature of the bonding in Cl₂SO and its higher energy structural isomer ClSOCl. We find that recoupled pair bonding, which we first introduced in our study of sulfur fluorides, is integral to describing the SO bond in all of these species. We also connect our analysis to the use of hyperconjugation to explain the back-bonding in the π system in the sulfinyl halides.

Keywords Recoupled pair bonding · Thionyl chloride · Hyperconjugation · Sulfinyl group · Generalized valence bond (GVB) theory

1 Introduction

Sulfur and oxygen atoms interact to form a rich variety of molecules with varying bond lengths and strengths that contribute to the diversity of sulfur–oxygen chemistry. Of interest here are molecules containing a single sulfinyl (SO) group with two additional ligands, which have the general formula XYSO. The SO bonds in these species are typically shorter and stronger than a standard single SO covalent bond [1], and their bond dissociation energies can vary significantly depending on the identity of the substituents (X, Y) [2]. Both the electronegativity and aromaticity of X and Y affect the SO bond dissociation energy. In general, electronegative substituents tend to correlate with especially strong SO bonds [3]. In fact, the SO bond in such compounds is often drawn as a double bond in recognition of its shortness and strength, but the presence of multiple bond character is controversial, and the origin of this multiple bond character has been debated [4]. For example, some texts depict XYSO species with a dative, or hypercoordinate covalent SO bond between the S3p² orbital and the empty O2p² arising from the O(¹D)/O(¹S) states with back-bonding being invoked to explain the shortness and strength of the bond.

As is typical of sulfur-containing species, the atomic 3d orbitals of the sulfur atom were employed as a possible explanation for the variation in SO bond lengths and strengths. It was suggested that the doubly occupied O2p lone pair orbitals back-bond to the S3d orbitals of the central atom [5, 6]. However, detailed calculations of various hypervalent molecules show that S3d functions only provide polarization and correlation effects [7–9]; these functions do not participate as 3d valence orbitals in the bonding in the sulfinyls. In light of this finding, other bonding schemes have been proposed. It has been

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suggested that back-bonding in the SO bonds (and related bonds involving late *p*-block elements and oxygen) is a consequence of hyperconjugation [10]. So-called anionic hyperconjugation occurs when a bond pair and lone pair interact, and the lone pair orbital energy is stabilized by interaction with the empty anti-bonding orbital of the bond [11]. Other studies have described these types of bonds as composed of a polar covalent σ bond and a nearly ionic π bond, especially when the (X, Y) substituent is a very electronegative element (e.g., a halide), without necessarily addressing the origin of the multiple bond character [12–14]. Yet other studies concluded that there in fact is no multiple bond character, and the SO bond is strengthened by purely electrostatic interactions [4].

In this work, we focus on thionyl chloride (Cl_2SO) and its structural analog, ClSOCl , as well as their parent triatomic molecules: ClSO and SOCl . Cl_2SO is interesting from a theoretical perspective but is also an important reagent in a wide variety of chlorination reactions [15] and in electrochemistry as a component in lithium/sulfinyl chloride batteries [16]. We use generalized valence bond (GVB) theory to provide insights into the nature of the bonding in these molecules. A prior study of sulfur–oxygen compounds in our group showed that recoupled pair bonding involving the electrons in the π orbitals accounts for the strength of the SO bond in the ground $X^3\Sigma^-$ state of diatomic SO, as well as for the large differences in geometry and SO bond strength of the $\tilde{X}^2A''$ states of HSO and SOH [17]. We found that a recoupled pair π bond is formed by the interaction of the electrons in the $\text{S}3p\pi^2$ lone pair and the $\text{O}2p\pi^1$ orbital in $\text{SO}(X^3\Sigma^-)$. In the $\text{S}(^3P)$ atom, the two electrons in the $\text{S}3p_y^2$ (or $\text{S}3p_{y-}3p_{y+}$) lone pair are singlet-coupled, but in $\text{SO}(X^3\Sigma^-)$, one of the electrons in the $\text{S}3p\pi$ -like orbital ($3p_{y+}$) is singlet-coupled to the $\text{O}2p\pi^1$ -like orbital to form a recoupled pair π bond. The remaining $\text{S}3p\pi$ -like orbital ($3p_{y-}$) is mostly centered on the sulfur atom. As a result, the two singly occupied orbitals of $\text{SO}(X^3\Sigma^-)$ are largely localized on the S atom and the recoupled pair π bond is maintained in HSO but must be broken to form SOH. This is shown in GVB diagrams of the $\tilde{X}^2A''$ states of HSO and SOH in Fig. 1. Consequently, the SO bond in HSO is 0.15 Å shorter and 21.5 kcal/mol stronger than that in SOH.

Fig. 1 GVB diagrams for the ground ($\tilde{X}^2A''$) states of HSO and SOH. Valence *p* orbitals for the O and S atoms and the 1s orbital of hydrogen atom are shown. We indicate the $3p^2$ ($3p_{-}$, $3p_{+}$) lone pair on sulfur with a dashed line; this pair can be recoupled to form an SO π bond

Despite this difference, the ground states of HSO and SOH are very close in energy ($\Delta E = 1.9$ kcal/mol), which is due to a near cancellation of two effects: (1) OH bonds are stronger than SH bonds (favoring SOH), and (2) the recoupled pair bond is maintained in HSO but not SOH (favoring HSO). We expect that similar effects are present in ClSO/SOCl and $\text{Cl}_2\text{SO}/\text{ClSOCl}$ and may provide an explanation for the preference of ClSO over SOCl and of Cl_2SO over ClSOCl as well as the shortness and strength of the SO bond in the former species.

The remainder of this work is organized as follows. In Sect. 2, we describe the computational methodology, including a brief overview of GVB theory. In Sect. 3, we compare the structure, energetics, and GVB orbitals of the ClSO and SOCl structural isomers. We compare the corresponding dichlorinated species (Cl_2SO and ClSOCl) in Sect. 4. Finally, in Sect. 5, we conclude.

2 Computational methods

Prior studies in our group have utilized GVB theory to gain insights into the nature of the bonding in a variety of molecules of the second-row elements. Unlike Hartree–Fock (or molecular orbital, MO) theory, GVB theory has the advantage of being inherently multi-reference and therefore able to describe bond dissociation and formation. A subset of the GVB orbitals (n_a) are singly occupied, instead of doubly occupied, and the GVB wave function can be written as follows [18–21].

$$\Psi_{\text{GVB}} = \hat{A} \phi_{d1} \phi_{d1} \cdots \phi_{dna} \phi_{dna} \phi_{a1} \phi_{a2} \cdots \phi_{ana} \alpha \beta \cdots \alpha \beta \Theta_{SM}^{n_a} \quad (1)$$

In Eq. (1), the $\{\phi_{di}\}$ are the doubly occupied core and valence orbitals and the $\{\phi_{ai}\}$ are the active GVB orbitals. The $\{\phi_{di}\}$ orbitals can be considered as orbital pairs that are singlet-coupled and overlap perfectly with one another. The active orbitals, by contrast, are singly occupied with overlaps less than unity and can be spin-coupled in various ways as described by the spin-coupling coefficients, the sum of which is $\Theta_{SM}^{n_a} = \sum_k c_{sk} \Theta_{SM;k}^{n_a}$. Because the active spatial orbitals, $\{\phi_{ai}\}$, as well as the spin-coupling coefficients, $\{c_{sk}\}$, are optimized at each nuclear configuration, the GVB wave function provides an accurate, yet compact description of the changes in the electronic structure of the molecule with changes in the nuclear configuration. This is in contrast to traditional VB calculations that typically require several covalent and ionic structures to be included for the calculation to be sufficiently accurate. Characterizing the evolution of the spatial orbitals and the associated spin-coupling patterns as a function of internuclear distance provides a clear bridge between the electronic structure of the molecule and that of its constituent fragments.

The spin-coupling coefficients, $\{c_{sk}\}$, are related to the relative weight, w_k , of a particular spin function ($\Theta_{SM;k}^{n_a}$) in the wave function. There are various choices for the spin basis functions used in the GVB calculation. The Kotani spin basis is a popular choice because the basis is orthonormal, and the squares of the resulting coefficients $\{c_{sk}\}$ yield a direct measure of the contribution of the spin-coupling patterns to the total GVB wave function, $w_k = c_{sk}^2$ [22]. Any weights reported in this work will be computed in the Kotani spin basis. A related spin basis is the Rumer spin basis [23, 24]. The Rumer spin functions have the advantage of being interpretable in terms of singlet pairs. The Kotani spin functions (in reverse order) can be obtained by Gram–Schmidt orthogonalization of the Rumer spin functions [25]. The disadvantage of using Rumer spin functions is that, because they are not orthogonal, the contribution of each spin function to the total wave function cannot be uniquely defined (though various definitions are available [26–28]). Nonetheless, the magnitudes of the coefficients provide valuable insights into the relative importance of the various Rumer spin-coupling patterns. For species in which the bonding pattern changes as a function of geometry, the Rumer spin basis is often viewed as a natural choice to describe this transition.

Generalized valence bond (GVB) calculations are inherently more accurate than Hartree–Fock calculations because they contain the major nondynamical correlation effects in a valence CASSCF wave function, e.g., those associated with the s – p near-degeneracy in the atoms and those associated with the incorrect dissociation of the Hartree–Fock wave function in the molecule. However, GVB calculations do not include dynamic correlation and are thus not as accurate as MO-based multi-reference configuration interaction (MRCI) or coupled cluster (CC) methods. Therefore, in this work, we will use a hybrid approach: (1) we use very accurate MO-based methods, such as the MRCI and CC methods, to optimize the geometries and compute the energetics of the species of interest here, and (2) we combine these results with calculations of the GVB wave function to examine the electronic structure of the molecule.

We will make use of GVB orbital diagrams to schematically represent the GVB wave function as shown in Fig. 1 in Sect. 1. In this work, the valence p orbitals of the atoms will be represented as follows: two lobes in the plane of the paper for each of the p_x and p_z orbitals, and a small circle to represent the p_y orbital, which is the p orbital that has a node in the plane of the paper. The SO bonding axis is defined to be the z -axis. The dots in the lobes represent the electronic occupation of the orbitals, and singlet coupling between two orbitals centered on different atoms (a chemical bond) is shown as a line connecting the orbitals.

Fig. 2 MO and GVB representations of the $S3p^2$ pair

We indicate the possibility of recoupling the $S3p^2$ pair with a dotted line drawn through this doubly occupied orbital. This $S3p^2$ pair is shown in Fig. 2 in both the MO and GVB representations. In MO theory, the $3p$ orbital is doubly occupied; in GVB theory, this lone pair is represented by two lobe orbitals. The $3p$ lobe orbitals result from the inclusion of an $S3d$ orbital in the GVB wave function, which provides the GVB orbitals with angular correlation such that they have some spatial separation, though their overlap is still high [29].

All calculations were performed with the Molpro suite of quantum chemical programs [30]. The GVB calculations were performed using the CASVB program of Thorsteinsson et al. [31]. We generally computed the full GVB wave function (also called the spin-coupled VB (SCVB) wave function by Gerratt et al. [18, 19]). To compute the GVB wave function, our general strategy was to localize the Hartree–Fock orbitals in terms of atomic orbitals [32] and then perform a CASSCF calculation with a small active space if needed to further refine these orbitals, which were then used to generate a starting guess for the CASVB program. The main constraint on the wave function was orthogonality between orbitals of different symmetry.

All geometries were optimized, and bond energies were calculated with explicitly correlated coupled cluster theory including a perturbative triples correction [CCSD(T)-F12 and RCCSD(T)-F12 with the “ a ” approximation] [33–36]. For geometry optimizations, the augmented correlation consistent double-zeta basis set with tight d -functions on sulfur and chlorine [AV($D + d$)Z] was used [37–39]. Because the explicitly correlated coupled cluster methodology contains terms that depend explicitly on interelectronic distances, convergence with respect to basis size is accelerated relative to traditional approaches. A calculation including explicitly correlated terms is typically at least as accurate as a calculation using a basis set that is one zeta higher without the explicitly correlated terms [40]. So we expect that the CCSD(T)-F12/AV($D + d$)Z calculations performed here are comparable in accuracy to standard CCSD(T)/AV($T + d$)Z calculations. For calculating molecular energies, we used the AV($T + d$)Z basis set, which, using the explicitly correlated methodology, should have an accuracy between quadruple or quintuple zeta for

Fig. 3 Optimized geometries and relative energetics of the ClSO and SOCl isomer. Throughout this work, the chlorine atom is *blue*, the sulfur atom is *yellow*, and the oxygen atom is *red*

Table 1 Comparison of bond lengths (in Å) and dissociation energies (in kcal/mol) for the SCl and OCl bonds in ClSO/SOCl versus the diatomic species

	R_e	D_e
Cl–SO($\tilde{X}^2A''$)	2.054	56.1
S–Cl($X^2\Pi$)	1.985	67.6
SO–Cl($\tilde{X}^2A''$)	2.121	0.1
O–Cl($X^2\Pi$)	1.569	63.8

calculations performed without the explicitly correlated terms. For potential energy scans over a range where a single-reference method was not appropriate, a CASSCF calculation [41, 42] was performed or MRCI with the Davidson correction was employed (MRCI + Q) [43, 44]. For these calculations, the AV($T + d$)Z basis set was used and a full valence active space was used unless otherwise stated.

3 The ClSO/SOCl isomers

3.1 The structures and energetics of ClSO/SOCl

The geometries and relative energetics of the ground ($\tilde{X}^2A''$) states of the ClSO and SOCl isomers are shown in Fig. 3. The structure for ClSO($\tilde{X}^2A''$) is in good agreement with a prior study [45]. The ClSO($\tilde{X}^2A''$) isomer is substantially more stable than the SOCl($\tilde{X}^2A''$) isomer, $\Delta E = 56.0$ kcal/mol. This is in contrast to the nearly energetically degenerate HSO/SOH structural isomers shown in Fig. 1. We cannot attribute the increased stability of the ClSO isomer to any inherent difference in the strengths of the SCl and OCl bonds; the dissociation energies of these bonds in the diatomic species (Table 1) are very similar, with the SCl($X^2\Pi$) state being only 3.8 kcal/mol more strongly bound than the OCl($X^2\Pi$) state. We also compare the bond lengths and energies of the diatomic molecules to those of the ClSO/SOCl molecules in Table 1. Clearly, additional factors are at play in the ClSO/SOCl isomers compared to the HSO/SOH isomers.

The SCl bond energy in the ClSO($\tilde{X}^2A''$) isomer, 56.1 kcal/mol, is slightly weakened relative to that in the SCl($X^2\Pi$) state, 67.6 kcal/mol, but similar in magnitude. Similarly, the SCl bond is only slightly longer in the ClSO($\tilde{X}^2A''$) isomer, 2.054 Å, than that in the SCl($X^2\Pi$) state, 1.985 Å. Therefore, we consider this bond to be a typical SCl covalent bond, and attribute its lengthening and weakening relative to SCl($X^2\Pi$) to the additional electronic repulsion among the SCl bond pair, the SO bond pair, and the $O2p^2$ pair in the ClSO($\tilde{X}^2A''$) isomer. By contrast, in the SOCl($\tilde{X}^2A''$) isomer, the OCl bond is weak almost to the point of nonexistence, $D_e(\text{SO}–\text{Cl}) \approx 0.1$ kcal/mol. The OCl bond length is correspondingly much longer in the SOCl($\tilde{X}^2A''$) isomer than that in OCl($X^2\Pi$): $R_e(\text{SO}–\text{Cl}) = 2.121$ Å versus $R_e(\text{O}–\text{Cl}) = 1.569$ Å. Clearly, the interaction between the O and Cl atoms cannot be described as a covalent bond. We will discuss the nature of bonding in this species in Sect. 3.3.

The SO bonds in the triatomic molecules are quite similar in terms of length, with the SO bond length only increased by 0.04 Å in the SOCl isomer relative to the ClSO isomer. This is in distinct contrast to the hydrogen-substituted case where the SO bond in HSO was 0.15 Å shorter than in SOH. However, both the HS bond length in the HSO($\tilde{X}^2A''$) isomer and the OH bond length in the SOH($\tilde{X}^2A''$) isomer were very close to that of the $X^2\Pi$ states of the corresponding diatomic molecules, XH ($X = \text{O}, \text{S}$). Thus, the shortness of the SO bond and the extraordinary length of the OCl bond in the SOCl($\tilde{X}^2A''$) isomer are peculiar to chlorine substitution.

3.2 The GVB orbitals of ClSO

In our prior study of HSO/SOH, we found that the recoupled pair π bond in SO was maintained in HSO and was broken upon formation of SOH. In contrast, for ClSO and SOCl, based on the bond lengths alone, it seems that the recoupled pair π bond in SO is maintained in both isomers. The GVB orbitals for the $\tilde{X}^2A''$ states of the ClSO and SOCl isomers support this conclusion. The five GVB valence orbitals of a'' symmetry in ClSO, as well as the associated GVB diagram, are shown in Fig. 4. In the dominant spin-coupling pattern (95.6 %), the electrons of the $\text{Cl}3p^2$ pair (φ_1, φ_2) are singlet-coupled, which is denoted by the dotted line between the orbitals. The other singlet-coupled pair (φ_3, φ_4) is a recoupled pair π bond between the $O2p^1$ -like orbital and one of the $\text{S}3p$ -like lobe orbitals, which has delocalized onto the O atom and represents the highly polarized ($\text{S}^{\delta+}\text{O}^{\delta-}$) nature of the bond. The remaining $\text{S}3p$ -like lobe orbital has α spin, yielding an overall doublet state. This bonding scheme is depicted in the GVB orbital diagram in Fig. 4. The bonding scheme for

Fig. 4 GVB orbitals for those orbitals shaded green in the accompanying GVB diagram for $\text{ClSO}(\tilde{X}^2A'')$. A dotted line separating two orbitals indicates that they are singlet-coupled in the dominant spin-coupling pattern of the wave function

the S and the O atoms in the $\text{ClSO}(\tilde{X}^2A'')$ isomer is essentially the same as that found in HSO previously.

Note that the $\text{Cl}3p^2$ lone pair is an example of a GVB description of a $3p^2$ lone pair that is not recoupled. The lone pair consists of two lobe orbitals, ($\varphi_1 \approx \text{Cl}3p_{y-}$, $\varphi_2 \approx \text{Cl}3p_{y+}$), with high overlap ($S = 0.88$) that are singlet-coupled to each other.

3.3 The GVB orbitals of SOCl

Unlike HSO and ClSO, the features of SOCl are qualitatively different than those of SOH, indicating a different bonding pattern in the two species. In SOH, the SO bond was significantly lengthened relative to that in the HSO isomer. By contrast, in SOCl, the SO bond is still fairly short, 1.502 Å in SOCl versus 1.460 Å in ClSO. However, the OCl bond is very long and weak. The GVB orbitals for the $\text{SOCl}(\tilde{X}^2A'')$ isomer are shown in Fig. 5a. In the dominant spin-coupling pattern (87.3 %), the $\text{O}2p^1$ -like GVB orbital (φ_3) is singlet-coupled to one of the $\text{S}3p$ lobes (φ_4) and not to the $\text{Cl}3p$ GVB orbital, resulting in the same type of recoupled pair π bond that we observed in the $\text{ClSO}(\tilde{X}^2A'')$ isomer. The other singlet pair consists of the $\text{Cl}3p$ -like GVB orbital (φ_2) and the remaining $\text{S}3p$ lobe orbital (φ_5). There is a slight tail of these orbitals on the O atom, but φ_2 is largely centered on the chlorine atom and φ_5 is largely centered on the S atom. Therefore, these two orbitals do not have a large spatial overlap ($S = 0.24$) with one another and do not form a conventional chemical bond. In essence, the recoupled pair bond is maintained at the expense of forming a covalent OCl bond. The π bond delocalizes slightly onto the Cl atom, which could be the genesis of the slightly longer SO bond in SOCl relative to that in the ClSO isomer.

Ongoing work in our group has observed a similar bonding pattern in the $\tilde{A}^2A'$ state of NOF (Takeshita and Dunning, to be published). We will refer to this weakly

Fig. 5 **a** GVB orbitals for those orbitals shaded green in the accompanying GVB diagram for optimized geometry of $\text{SOCl}(\tilde{X}^2A'')$. **b** The same GVB orbitals for $R(\text{SO}) = R_e(\text{SO}) + 0.12 \text{ Å}$ with optimization of the remaining degrees of freedom. Note that the dotted line indicating singlet coupling between orbitals has switched from vertical to horizontal. **c** Magnitudes of the coefficients of the Rumer spin functions for the GVB wave function of $\text{SOCl}(\tilde{X}^2A'')$ as a function of $R(\text{SO})$ for the orbital ordering indicated in (a) and (b)

overlapping singlet-coupled pair as a *through-pair* interaction. Despite the small overlap of this singlet pair, the $\tilde{X}^2A''$ state of SOCl is 10.7 kcal/mol lower in energy than the corresponding quartet state at the equilibrium geometry for the doublet state. (The O–Cl bond dissociates on the quartet surface). A more comprehensive study of the through-pair interaction will be the subject of a future article (Takeshita and Dunning, to be published); however, we speculate that the singlet coupling is energetically favorable not because a traditional covalent bond is formed, but rather because the overlap of the singlet-coupled pair reduces the electronic repulsion between the

electrons in the recoupled pair π bond and the electrons in the weakly overlapping pair.

The electronic structure of the SOCl isomer is actually even more complex than the above analysis implies. If the SO bond is lengthened (even slightly), the recoupled pair π bond weakens and the bonding pattern switches from that of a recoupled pair π bond and a through-pair interaction to that of an $S3p^2$ lone pair and a standard covalent OCl bond. At $R_e(\text{SO}) + 0.12 \text{ \AA}$, the GVB wave function (shown in Fig. 5b) is almost entirely (99.8 %) described by the latter bonding pattern. If we perform GVB calculations from $R(\text{SO}) = R_e - 0.02 \text{ \AA}$ to $R(\text{SO}) = R_e + 0.12 \text{ \AA}$ and preserve the ordering of the orbitals by atomic character, we can directly observe the switch in character between the recoupled pair bonding pattern and the covalent bonding pattern in the spin-coupling coefficients, $\{c_{Sk}\}$, associated with the Rumer spin functions. We plot these values in Fig. 5c as a function of $R(\text{SO})$. Because the spin functions in the Rumer basis are nonorthogonal, there is no unambiguous way to relate the spin-coupling coefficient to its contribution to the GVB wave function. Nevertheless, the magnitudes of the spin function coefficients are certainly correlated with the importance of the spin-coupling patterns.

At intermediate values of $R(\text{SO})$, there is some ambiguity in the assignment of the orbitals as they exchange character through both the spin and spatial degrees of freedom, and an orbital ordering that resulted in the smoothest evolution of the Rumer spin functions was chosen. At larger values of $R(\text{SO})$, the covalent OCl bonding pattern (diamonds) totally dominates, but as $R(\text{SO})$ decreases, the recoupled pair bonding pattern (upward triangles) becomes increasingly important, and becomes dominant at $R(\text{SO})$ values below $1.56 \text{ \AA}$. A third spin-coupling pattern (circles) also becomes important as $R(\text{SO})$ decreases. This spin function corresponds to coupling φ_3 and φ_4 into a recoupled pair π bond, and then singlet coupling the out-of-plane $S3p$ GVB orbital (φ_1) to the $\text{Cl}3p$ in-plane orbital (φ_2) and high spin-coupling the other in-plane $S3p$ GVB orbital (φ_5). This spin function does not describe an OCl bond. This spin-coupling coefficient increases because the triplet-coupling of the orthogonal valence $S3p$ -like orbitals (φ_1 and φ_5 in Fig. 5a) on the $\text{SO}(\tilde{X}^3\Sigma^-)$ fragment becomes important as the Cl atom becomes increasingly weakly bound. (In the Rumer spin basis, there is no spin function that corresponds directly to triplet-coupling these two orbitals). The increasing contribution of this spin function as $R(\text{SO})$ decreases is not surprising given the weakness of the OCl bond.

The presence of two distinct bonding patterns has consequences for the potential energy curve as a function of SO bond length for SOCl. For ClSO, the analogous potential energy curve acts like a Morse oscillator around the minima as the SO bond is stretched; see Fig. 6, where the energies of the respective minima have been set to zero.

Fig. 6 Potential energy curves as a function of $R(\text{SO})$ for the $\tilde{X}^2A''$ states of ClSO (circles) and SOCl (squares) with all other degrees of freedom optimized at the MRCI + Q/AV(T + d)Z level of theory. The energy at the minima is set equal to zero for both curves

However, for SOCl, while there is only one minimum, there is an obvious change in the character of the potential energy curve around $1.65 \text{ \AA}$. We attribute this feature to the competition of the two bonding motifs, which possess two distinct equilibrium bond lengths and strengths, depending on whether the recoupled pair π bond is present or absent.

4 The $\text{Cl}_2\text{SO}/\text{ClSOCl}$ isomers

Similarly to ClSO/SOCl, we can understand the energetic differences between the Cl_2SO and ClSOCl isomers in terms of recoupled pair π bonding. Consider first $\text{ClSO}(\tilde{X}^2A'') + \text{Cl}({}^2P)$. In order to form an OCl bond to yield ClSOCl, the Cl atom must bond via a through-pair interaction or it has to break the π bond just as we observed in SOCl. However, in Cl_2SO , the second SCl bond forms with the orbital left over from the formation of the recoupled pair π bond, φ_5 in Fig. 4, and the recoupled pair π bond is maintained. These pathways are depicted in Fig. 7. By this logic, we expect the energy difference between the Cl_2SO and ClSOCl isomers to be similar in magnitude to that between the triatomic ClSO and SOCl molecules, and it is: the Cl_2SO isomer is 47.0 kcal/mol lower in energy than the ClSOCl isomer.

We can also understand the variation in SO bond strength as a function of X and Y in the XYSO molecules in terms of recoupled pair π bonding. We saw in our prior studies of recoupled pair bonding that the orbital left over from the formation of the recoupled pair bond has large

Fig. 7 GVB orbital diagrams for the addition of two chlorine atoms to $\text{SO}(X^3\Sigma^-)$ to form either Cl_2SO or ClSOCl , and optimized geometries and relative energetics for these isomers

unfavorable overlaps with the bond pair [17, 46]. For ClSO , we find that φ_5 in Fig. 4 has a large energetically unfavorable overlap with the π bond pair (φ_3 and φ_4). Therefore, bond formation with this orbital will be more favorable if the incoming ligand is strongly electronegative and can polarize this orbital away from the SO bond pair, but would be less favorable or even unfavorable if the ligand is weakly electronegative and thus augments the electronic repulsion in the π system. A more in-depth discussion of Cl_2SO will be deferred until Sect. 4.2.

4.1 The ClSOCl isomer

Given the similarity in the GVB diagrams of SOCl and ClSOCl , it should come as no surprise that the potential energy curve associated with stretching the ClS-OCl bond also has contributions from two bonding patterns: recoupled pair π bond/through-pair interaction and $\text{S}3p^2$ lone pair/covalent OCl bond. However, for ClSOCl , there is increased electron repulsion between the SCl bond and the OCl bond and π orbitals. Because lengthening the SO bond reduces this repulsion, the more stable bonding pattern is shifted from the recoupled pair π bond/through-pair interaction to the $\text{S}3p^2$ lone pair/covalent OCl bond motif. As a result, ClSOCl has a longer SO bond length ($\Delta R_e = 0.10 \text{ \AA}$) but much shorter OCl bond length ($\Delta R_e = -0.37 \text{ \AA}$) than in SOCl . In addition, the potential energy curve for stretching the ClS-OCl bond is very flat, increasing by only 0.3 kcal/mol at $R(\text{SO}) = R_e(\text{SO}) - 0.1 \text{ \AA}$, compared to 8.5 kcal/mol in ClSO over the same range. In ClSOCl , the presence of the two bonding patterns is especially obvious because the balance between the two bonding motifs yields two distinct minima at the $\text{CCSD(T)-F12/AV(D+d)Z}$ level of theory (confirmed by frequency calculations); see Fig. 8a.

The two minima for ClSOCl are shown in Fig. 8b. As anticipated, the major geometric differences between these

two isomers are the SO and OCl bond lengths; the SCl bond length and the angles are effectively the same. This pair of isomers can thus be described as bond stretch isomers, although the barrier separating the two isomers is extremely small. The OCl bond length is highly dependent on the SO bond length for this entire region of the potential energy curve: as the SO bond shortens, the recoupled pair π bond strengthens at the expense of the OCl bond. Figure 8c shows the strong inverse correlation between $R(\text{SO})$ and $R(\text{OCl})$. In contrast, the $R(\text{SCl})$ bond length is effectively independent of $R(\text{SO})$.

While the miniscule barrier between these two isomers makes distinguishing between them experimentally impossible, the unusual potential energy curve shown in Fig. 8a will lead to a distinct, if complicated, infrared spectrum that could, in principle, be observed. The atypical features of this potential energy curve are similar to what has been observed previously for the H_2PO radical, where, at lower levels of theory, there was a double well in the potential energy as a function of $R(\text{PO})$ [47]. In that case, increasing the amount of dynamic correlation in the calculation eliminated the barrier completely yielding a very flat potential energy curve. There was also a change in the character of the singly occupied orbital as the PO bond length decreased, from that consistent with a single PO σ bond (singly occupied orbital localized on oxygen) to that suggestive of a σ bond plus a recoupled pair π bond (singly occupied orbital on phosphorus).

4.2 The Cl_2SO isomer

At the start of this section, we considered the formation of Cl_2SO from ClSO and Cl , which suggested a covalent σ and a recoupled pair π bond for the SO bond and, through resonance, two predominantly covalent ClS bonds. This pathway is consistent with prior studies that showed a polar covalent σ SO bond and a nearly ionic π SO bond in related molecules [9, 12–14] (recoupled pair bonds tend to be quite polarized toward the recoupling ligand). This bonding scheme would predict Cl_2SO to have two ClS bonds similar in length to that in ClSO ($2.054 \text{ \AA}$) with a ClSCl angle near 90° . It would also predict an SO bond length close to that in ClSO ($1.460 \text{ \AA}$) with $\angle\text{ClSO}$ like that in ClSO (109.2°). This compares well with the calculated structure of Cl_2SO : $R_e(\text{ClS}) = 2.069 \text{ \AA}$, $\angle\text{ClSCl} = 95.5^\circ$, $R_e(\text{SO}) = 1.435 \text{ \AA}$, and $\angle\text{Cl}_2\text{S-SO} = 115.9^\circ$ (the latter is the angle between the bisector of the Cl_2S plane and the SO bond); see Table 2. These geometric parameters compare well with prior computational and experimental studies of Cl_2SO [48–51]. Clearly, this approach provides a compelling description of the bonding in the Cl_2SO molecule. But, there are alternative descriptions of the SO bond in the sulfinyls.

Fig. 8 **a** Potential energy for ClSOCl as a function of $R(\text{SO})$ from CCSD(T)-F12/AV($T+d$)Z calculations with all other geometric parameters optimized at the CCSD(T)-F12/AV($D+d$)Z level of theory. **b** Structures and geometric parameters of the two minima at

the same level of theory as **(a)**. Optimized SCl (*squares*) and OCl (*circles*) bond lengths as a function of $R(\text{SO})$ in ClSOCl from the geometries in **(a)**

Table 2 Optimized geometric parameters (in Å and degrees) of the $\tilde{X}^1A_1$, $\tilde{a}^3B_1$, and $\tilde{b}^3A_2$ states of Cl_2S and Cl_2SO at the minimum and the planar transition state for inversion

	$R(\text{S}-\text{Cl})$	$A(\text{Cl}-\text{S}-\text{Cl})$	$R(\text{S}-\text{O})$	$A(\text{Cl}_2\text{S}-\text{S}-\text{O})^a$
$\text{Cl}_2\text{S}(\tilde{X}^1A_1)$	2.017	100.3	—	—
$\text{Cl}_2\text{S}(\tilde{a}^3B_1)$	2.117	147.8	—	—
$\text{Cl}_2\text{S}(\tilde{b}^3A_2)$	2.146	87.6	—	—
$\text{Cl}_2\text{SO}(\text{Opt.})$	2.069	95.5	1.435	115.9
$\text{Cl}_2\text{SO}(\text{T.S.})$	2.189	161.9	1.433	180.0

^a The angle between the O atom, S atom, and the bisector of the Cl–S–Cl angle

We can, for example, consider the formation of Cl_2SO from Cl_2S and O instead of ClSO and Cl. However, the ground-state fragment, $\text{Cl}_2\text{S}(\tilde{X}^1A_1)$ and $\text{O}(^3\text{P})$, cannot yield the ground singlet state of Cl_2SO , the $\tilde{X}^1A'$ state. As a result, bonding in XYSO species is often assumed to originate from the $\text{XY}(\tilde{X}^1A) + \text{O}(^1\text{D})$ asymptote. This suggests that the SO bond is a dative bond, where the $3p^2$ pair of Cl_2S is donated to the empty $\text{O}2p_z$ orbital that results from mixing the $^1A'$ states arising from the $\text{XY}(\tilde{X}^1A) + \text{O}(^1\text{D})$ and $\text{XY}(\tilde{X}^1A) + \text{O}(^1\text{S})$ asymptotes, i.e., the $\text{O}(2p_x^2 2p_y^2)$ configuration. The optimized structure of $\text{Cl}_2\text{SO}(\tilde{X}^1A')$ is in reasonable agreement with expectations based on this bonding motif: the geometric parameters of the Cl_2S group are reasonably close to those in the $\text{Cl}_2\text{S}(\tilde{X}^1A_1)$ state (see Table 2). Further, the angle between the Cl_2S plane and the oxygen atom 115.9° is consistent with what would be anticipated from bonding with one of the lone pairs of Cl_2S , a mix of $3s^2$ and $3p^2$ orbitals.

However, the $\text{Cl}_2\text{S}(\tilde{X}^1A_1) + \text{O}(^1\text{D})$ limit is actually not the lowest energy asymptote for the dissociation of $\text{Cl}_2\text{SO}(\tilde{X}^1A')$. The lowest energy asymptote that can form a singlet state is $\text{Cl}_2\text{S}(\tilde{a}^3B_1) + \text{O}(^3\text{P})$. The energy of $\text{Cl}_2\text{S}(\tilde{a}^3B_1)$ at its optimum geometry is only 36.2 kcal/mol higher in energy than that of the $\text{Cl}_2\text{S}(\tilde{X}^1A_1)$ ground state, compared to 49.1 kcal/mol for the $\text{O}(^3\text{P})$ to $\text{O}(^1\text{D})$ excitation energy [RCCSDT-F12/AV($T+d$)Z calculations]. We have described bonding in $\text{Cl}_2\text{S}(\tilde{a}^3B_1)$ elsewhere [52]. In short, the two SCl bonds comprise a σ recoupled pair bond dyad, where both Cl atoms form bonds to the $3p^2$ pair of the $\text{S}(^3\text{P})$ atom. As we have shown, recoupled pair bond dyads are very stable, consistent with the small excitation energy observed in Cl_2S . The angle between the two ClS bonds in the $\text{Cl}_2\text{S}(\tilde{a}^3B_1)$ state is 147.8° and $R_e(\text{ClS}) = 2.117 \text{ Å}$, 0.10 Å longer than in the $\text{Cl}_2\text{S}(\tilde{X}^1A_1)$ ground state. The two singly occupied orbitals, one in the plane of the molecule and one out of the molecular plane, resemble two $3p$ orbitals, with the in-plane orbital having significant $3s$ admixture that polarizes it toward the side of the sulfur atom containing the Cl atoms; see Fig. 9a. The next lowest energy electronic state of Cl_2S , the $\tilde{b}^3A_2$ state, is bound by one recoupled pair bond and one covalent bond, yielding a strongly bent geometry, 87.6° , with $R_e(\text{ClS}) = 2.146 \text{ Å}$. The $\text{Cl}_2\text{S}(\tilde{b}^3A_2)$ state lies 57.0 kcal/mol above the ground state.

The geometric parameters listed above for the optimized Cl_2SO molecule deviate significantly from those optimal for $\text{Cl}_2\text{S}(\tilde{a}^3B_1)$; see the comparison in Table 2. However, the planar transition state for the inversion of Cl_2SO possesses structural features similar to the $\tilde{a}^3B_1$ state of Cl_2S , namely $R_e(\text{ClS}) = 2.189 \text{ Å}$ and $\angle \text{ClSCl} = 161.9^\circ$. Figure 9b shows

Fig. 9 **a** Singly occupied orbitals of $\text{Cl}_2\text{S}(\tilde{a}^3B_1)$ at its optimized geometry. **b** Select GVB orbitals for the transition state to inversion of Cl_2SO

the relevant orbitals of the planar Cl_2SO transition state. The in-plane $\text{S}3p$ -like orbital from Fig. 9a forms an extremely polar σ bond with the in-plane $\text{O}2p^1$ orbital, and the out-of-plane $\text{S}3p$ orbital forms a polar π bond (though less polar than the σ bond). The remaining $\text{O}2p^2$ pair is largely localized on the oxygen atom. While both the σ and π bonds are polarized toward the more electronegative oxygen atom, the σ bond is much more polar because polarizing toward oxygen reduces the anti-bonding character present in the $\text{S}3p$ -like in-plane orbital. Despite the polar nature of these bonds, it seems reasonable that bonding in this state should be interpreted as an SO double bond, and the strength of this bond relative to the $\text{Cl}_2\text{S}(\tilde{a}^3B_1) + \text{O}(^3\text{P})$ asymptote (100.8 kcal/mol) is consistent with this interpretation. For reference, the $a^1\Delta$ state of SO, which contains a σ and a π bond, is bound by 103.2 kcal/mol. The transition state for inversion is 40.1 kcal/mol higher in energy than the minimum—similar to many other XYSO molecules where X and Y are not bonded together via rings [2, 53–57].

The equilibrium geometry of Cl_2SO leads to two questions. (1) Why do the geometries for the minimum and transition state appear to be associated with two different

Table 3 Energy (kcal/mol) of the molecular fragments (Cl_2S and O) that are capable of forming $\text{Cl}_2\text{SO}(\tilde{X}^1A')$ relative to the optimized Cl_2SO geometry

	Fixed Cl_2S	Optimized Cl_2S
$\text{Cl}_2\text{S}(\tilde{X}^1A_1) + \text{O}(^1\text{D})$	155.8	153.8
$\text{Cl}_2\text{S}(\tilde{a}^3B_1) + \text{O}(^3\text{P})$	170.1	141.0
$\text{Cl}_2\text{S}(\tilde{b}^3A_2) + \text{O}(^3\text{P})$	165.4	161.8

The Cl_2S molecule is either at the same geometry as in the optimized Cl_2SO structure (first column) or at optimized for the given electronic state of Cl_2S (second column)

asymptotes? Further, (2) why is the calculated dissociation energy for $\text{Cl}_2\text{SO}(\tilde{X}^1A') \rightarrow \text{Cl}_2\text{S}(\tilde{X}^1A_1) + \text{O}(^1\text{D})$ so large? It is 153.8 kcal/mol—substantially larger even than that for the strong bond in the ground, $X^3\Sigma^-$, state of SO. See Table 3 for the RCCSD(T)-F12 bond dissociation energies for the various asymptotes relative to the optimized $\text{Cl}_2\text{SO}(\tilde{X}^1A')$ energy. The answers to both of these questions are related.

We can understand the variation in Cl_2S angle between the optimized geometry and the planar transition state for inversion of Cl_2SO from the orbitals of the different electronic states of Cl_2S . When the Cl_2S group is constrained to be planar with the O atom, an a_1 orbital must be present and available in Cl_2S to form a σ bond with oxygen. Figure 9a shows that $\text{Cl}_2\text{S}(\tilde{a}^3B_1) + \text{O}(^3\text{P})$ clearly meets this criterion. For the $\text{Cl}_2\text{S}(\tilde{X}^1A_1) + \text{O}(^1\text{D})$ limit, the situation is not nearly as favorable. From Fig. 10, which shows the relevant orbitals of the Cl_2S group at the optimized Cl_2SO geometry, we can see that, while there is an a_1 -symmetric lone pair (a slightly polarized $\text{S}3s^2$ -like orbital) associated with the $\tilde{X}^1A_1$ state of Cl_2S , bonding between this orbital and $\text{O}(^1\text{D})$ is likely to be disfavored. This is a result of the electronic repulsion among the $\text{O}2p^2$ pairs and the $\text{S}3p^2$ lone pair, coupled with the short SO bond length that would be required for the empty $\text{O}2p$ orbital to have a large overlap with the mostly spherical $3s$ -like lone pair. The third lowest-lying state of Cl_2S , the $\tilde{b}^3A_2$ state of Cl_2S , does not have any a_1 -symmetric singly occupied orbitals that can bond with $\text{O}(^3\text{P})$. The dominance of the $\text{Cl}_2\text{S}(\tilde{a}^3B_1) + \text{O}(^3\text{P})$ asymptote is reflected in the large (161.9°) Cl–S–Cl angle that is near optimal for the $\tilde{a}^3B_1$ state, but not the $\tilde{X}^1A_1$ or $\tilde{b}^3A_2$ states, of Cl_2S .

However, if the oxygen atom approaches from an approximately 90° angle relative to the plane of the Cl_2S group, then an SO σ bond can be formed with the highest-lying b_1 orbital of Cl_2S . For $\text{Cl}_2\text{S}(\tilde{X}^1A_1) + \text{O}(^1\text{D}) \rightarrow \text{Cl}_2\text{SO}(\tilde{X}^1A')$, because the symmetry is C_s instead of C_{2v} , the $\text{S}3s$ and $\text{S}3p$ orbitals shown in Fig. 10 can mix to minimize electronic repulsion, so dative bonding from this asymptote will be more stable than in the

Fig. 10 Orbitals of Cl_2S relevant to SO bond formation to yield Cl_2SO for the $\tilde{X}^1A_1$, $\tilde{a}^3B_1$, and $\tilde{b}^3A_2$ states. The geometry is that of the Cl_2S group in Cl_2SO

planar configuration. Moreover, the singly occupied orbitals of the $\text{Cl}_2\text{S}(\tilde{a}^3B_1)$ and $\text{Cl}_2\text{S}(\tilde{b}^3A_2)$ states are well positioned to form double bonds with $\text{O}(^3P)$, as is apparent from Fig. 10. At the optimum Cl–S–Cl angle in $\text{Cl}_2\text{SO}(\tilde{X}^1A')$, all of these asymptotes are similar in energy, see the left column in Table 3. As we saw for the transition state, bonds originating from an orbital possessing anti-bonding character are likely to be quite polar to minimize this unfavorable character. The upshot of this situation is that all three asymptotes have comparable energies and have the same symmetry and basic orbital structure, and thus they all have the potential to mix to stabilize the ground state—lowering its energy and leaving the excited states with weaker bonds.

We have investigated the impact of the higher-lying asymptotes in Fig. 11 with a 6-state CASSCF/AV($T + d$)Z potential energy scan as a function of $R(\text{SO})$, where all of the other geometric parameters are fixed at the optimized Cl_2SO geometry. We include all valence orbitals except the $\text{O}2s^2$ and $\text{Cl}3s^2$ pairs in the active space and include two a' and one a'' virtual orbitals. At large $R(\text{SO})$, the first three states collapse to the $\text{Cl}_2\text{S}(\tilde{X}^1A_1) + \text{O}(^1D)$ asymptote, the fourth and fifth asymptotes correspond to $\text{Cl}_2\text{S}(\tilde{b}^3A_2) + \text{O}(^3P)$, and the sixth state is the $\text{Cl}_2\text{S}(\tilde{a}^3B_1) + \text{O}(^3P)$ asymptote. (The next asymptote is 50.9 kcal/mol higher in energy). Figure 11a shows the results of the CAS calculation, where, for clarity, several data points from the four highest-lying states at small values of $R(\text{SO})$ have not been plotted due to their interactions with even higher-lying electronic states. The ground state is bound by 119.8 kcal/mol, recovering about 77 % of the CCSD(T)-F12/AV($T + d$)Z energy reported in the upper left cell of Table 3.

Clearly, these states are interacting and curve crossings are present that complicate the interpretation of these results. However, if we assume that all states corresponding to aligning the $\text{O}2p^2$ pair with an occupied $\text{S}3p$ -like orbital are

Fig. 11 **a** Potential energy (CASSCF/AV($T + d$)Z) for the first six electronic states of Cl_2SO as a function of $R(\text{SO})$ with all other geometric parameters fixed. For clarity, some of the data points for the four highest-lying states at small values of $R(\text{SO})$ that interact with even higher-lying electronic states have been removed. **b** Fits to the parts of the potential energy curves corresponding to “bonding” asymptotes; data points from (a) shown as “x”s

purely repulsive and smooth, we can isolate the parts of the calculation related to the asymptotes that we expect to bond. We show these data (denoted by “x”s) with corresponding fits with splines in Fig. 11b. It is clear in both Fig. 11a, b that there is a dearth of favorable bonding interactions associated with the triplet asymptotes, two of which (those in Fig. 11b) are aligned to form double bonds. The remaining favorable character is mixed into the second lowest electronic state at small $R(\text{SO})$ —squares in Fig. 11a. This state is bound by 9.9 and 18.2 kcal/mol relative to the asymptotes involving $\text{Cl}_2\text{S}(\tilde{b}^3A_2)$ and $\text{Cl}_2\text{S}(\tilde{a}^3B_1)$, respectively. For reference, with the same active space, the similarly double-bonded transition

state is bound by 82.8 kcal/mol. Therefore, the majority of the bonding character associated with the triplet asymptotes is not found in the higher-lying electronic states.

The stabilizing effects of these triplet asymptotes can form an anomalously strong SO bond in the ground state, with the ground state effectively robbing these excited states of their favorable character because the orbitals between the three asymptotes are so similar. The double bonds arising from the triplet asymptotes are similar to those of the transition state, only the σ and π orbitals have switched. In this case, it is the π bonds that are extremely polar because of the anti-bonding character present in the a_1 - and b_2 -symmetry Cl_2S orbitals of the $\tilde{a}^3\text{B}_1$ and $\tilde{b}^3\text{A}_2$ states, respectively. This is direct evidence that multi-bond character is present in the ground state, significantly lowering its energy. Based on these results, we suggest that the multi-bond character owing to the triplet asymptotes dominates SO bonding in Cl_2SO , with dative bonding being of secondary importance.

Before concluding this discussion, we will consider one other point. The polarization/delocalization of the orbitals on the oxygen atom in sulfinyl groups has been previously noted in both MO and GVB calculations [9, 10, 12–14] and had been attributed to π - $3d$ back-bonding in early work. However, consistent with more modern calculations, we find that this description does not explain the polarization of these orbitals for $\text{Cl}_2\text{SO}(\tilde{X}^1\text{A}')$. Figure 12a, b both show the π GVB orbitals of Cl_2SO but those in Fig. 12b are computed with only s and p basis functions on the sulfur atom. While the polarization toward sulfur is somewhat reduced in the latter orbitals, one of the GVB lobes in each direction remains highly delocalized. This comparison is consistent with the idea that the $3d$ functions provide additional polarization and correlation corrections but do not to act as valence orbitals for sulfur. As stated above, we attribute this polarization (and the energetic stabilization that it imparts) to the participation of the triplet asymptotes in the ground state of Cl_2SO ; furthermore, we can actually see that some of the features of the low-lying triplet states of Cl_2S are present in the orbitals of Cl_2SO . The asymmetric electron density of the a_1 -symmetric orbital of $\text{Cl}_2\text{S}(\tilde{a}^3\text{B}_1)$ in Fig. 10 with respect to reflection through the xz plane (out of the plane of the paper) explains the similar asymmetric nature of φ_1 and φ_2 in Fig. 12. This asymmetric π bond may also be connected to the bent-bond description of SO bonds observed by Cooper et al. [14] for some short sulfur–oxygen bonds.

5 Conclusion

In this work, we have explained the difference in stability between two pairs of structural isomers: ClSO/SOCl and

Fig. 12 GVB orbitals in the π space of the SO bond for Cl_2SO **a** with and **b** without d basis functions on the sulfur atom

$\text{Cl}_2\text{SO}/\text{ClSOCl}$. While the bond strengths of the SCl and OCl diatomic molecules are comparable, bonding the Cl atoms to sulfur allows the recoupled pair π bond present in $\text{SO}(\tilde{X}^3\Sigma^-)$ to be maintained, whereas forming a covalent bond with oxygen causes the recoupled pair π bond to break. (This is what occurred in our prior work on SOH). However, we saw that in SOCl , instead of breaking the recoupled pair π bond, the orbital on the Cl atom is singlet-coupled with the singly occupied orbital largely localized on sulfur. We refer to this bonding motif here as a through-pair interaction and the associated bond energy is very small (essentially 0 kcal/mol in SOCl , but see the work on NOF by Takeshita and Dunning, to be published).

In ClSOCl , competition between the two modes of bonding present in SOCl yields a very flat potential energy surface when the SO bond is stretched and contains a pair of bond stretch isomers separated by a very small barrier.

The ClSOCl molecule has many commonalities with the H_2PO radical, and we suspect that there may be other instances of this behavior in compounds involving oxygen bonded to an element in the second-row late p -block where a competition between a recoupled pair bonded scheme and traditional covalent bonding yields quite interesting and unexpected features in the potential energy surface of these compounds.

For Cl_2SO , we rationalized the short SO bond length and very strong SO dissociation energy relative to the $\text{Cl}_2\text{S}(\tilde{X}^1\text{A}_1) + \text{O}(^1\text{D})$ asymptote by showing that other (slightly) higher-energy asymptotes also contribute to the ground-state Cl_2SO molecule. The polarization of the SO π orbitals can be attributed to the importance of two triplet asymptotes in the electronic structure of Cl_2SO : $\text{Cl}_2\text{S}(\tilde{a}^3\text{B}_1) + \text{O}(^3\text{P})$ and $\text{Cl}_2\text{S}(\tilde{b}^3\text{A}_2) + \text{O}(^3\text{P})$. This is a useful application of our previous work using recoupled pair bonding to describe the energetics and bonding in the $\tilde{a}^3\text{B}_1$ and $\tilde{b}^3\text{A}_2$ states of Cl_2S . Understanding the nature of the bonding in Cl_2SO provides an important motivation for fully understanding the electronic structure of not only the ground state, but also the lower-lying excited states, of the fragments that compose a molecule.

The nature of the bonding in Cl_2SO is consistent with donation from the $\text{O}2p$ orbitals to the SCl anti-bonding orbitals—or “anionic” hyperconjugation—in the MO framework, which has been suggested for similar hypervalent molecules (F_2SO and H_3PO for instance) [10]. The low-lying triplet states of Cl_2S can be generated by excitation of one of the $\text{S}3p$ electrons into one of the SCl anti-bonding orbitals of either a_1 or b_2 symmetry to yield the $\tilde{a}^3\text{B}_1$ and $\tilde{b}^3\text{A}_2$ states of Cl_2S , respectively. The MO description of these bonds is sometimes referred to as single bonds plus hyperconjugation, but from the VB perspective, it is clear that the SO bond should be considered double bonds since they arise from the triplet asymptotes, which form true double bonds. Recoupled pair bonding explains why these triplet states are so low in energy, or said in the MO framework, why some molecules have lower energy σ^* orbitals. These results unify the MO and VB perspectives (single bond and hyperconjugation versus polar σ bond and nearly ionic π bond) reported in previous work by demonstrating that hyperconjugation in this case arises from higher-lying asymptotes that are capable of forming double bonds.

The Cl_2S orbitals that contribute to the π bonding have significant anti-bonding character, which causes these bonds to be extremely polarized toward oxygen, which may make them look like lone pairs from an electron density perspective as observed in the prior studies of similar compounds [4, 58]. But the weakness of the SO bonds in the states evolving from the higher-lying triplet

asymptotes as a function of SO internuclear distance provides direct evidence that multiple bond character is a critical feature of SO bonding in sulfinyl halides. As the electronegativity of the substituents (X and Y) decreases, the energy of triplet XY states will increase, as will the polarizability of the $\text{S}3p$ -like orbital of XY. This will both decrease the importance of multi-bond character in the SO bond and increase the strength of the dative SO bond. So for compounds such as H_2SO and organic sulfoxides, the single bond plus electrostatic stabilization view may very well be appropriate. However, for the sulfinyl halides, multiple bond character is an essential feature in the description of the SO bond.

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References

- Kuczman AK, Kapovits I (1985) Organic sulphur chemistry. Elsevier, Amsterdam
- Jenks WS, Matsunaga N, Gordon M (1996) J Org Chem 61(4):1275–1283
- Benson SW (1978) Chem Rev 78(1):23–35
- Dobado JA, Martinez-Garcia H, Molina JM, Sundberg MR (1999) J Am Chem Soc 121(13):3156–3164
- Kwart H, King K (1977) d-Orbitals in the chemistry of silicon, phosphorus and sulfur. Springer, Berlin
- Mayer I, Revesz M (1983) Inorg Chim Acta 77(6):L205–L206
- Magnusson E (1990) J Am Chem Soc 112(22):7940–7951
- Magnusson E (1993) J Am Chem Soc 115(3):1051–1061
- Cooper DL, Cunningham TP, Gerratt J, Karadakov PB, Raimondi M (1994) J Am Chem Soc 116(10):4414–4426
- Reed AE, Schleyer PV (1990) J Am Chem Soc 112(4):1434–1445
- Schleyer PV, Kos AJ (1983) Tetrahedron 39(7):1141–1150
- Cioslowski J, Mixon ST (1993) Inorg Chem 32(15):3209–3216
- Cioslowski J, Surjan PR (1992) J Mol Struct Theochem 87:9–33
- Cunningham TP, Cooper DL, Gerratt J, Karadakov PB, Raimondi M (1997) J Chem Soc Faraday Trans 93(13):2247–2254
- Page EM (2007) In: Zuckerman JJ, Hagen AP (eds) Inorganic reactions and methods. Wiley, Hoboken, NJ
- Gangadharan R, Namboodiri PNN, Prasad KV, Viswanathan R (1979) J Power Sources 4(1):1–9
- Lindquist BA, Takeshita TY, Woon DE, Dunning TH (2013) J Chem Theory Comput 9(10):4444–4452
- Cooper DL, Karadakov PB (2009) Int Rev Phys Chem 28(2):169–206
- Gerratt J, Cooper DL, Karadakov PB, Raimondi M (1997) Chem Soc Rev 26(2):87–100
- Goddard WA, Dunning TH, Hunt WJ, Hay PJ (1973) Acc Chem Res 6(11):368–376
- Hiberty PC, Shaik S (2007) J Comput Chem 28(1):137–151

22. Cooper DL, Thorsteinsson T, Gerratt J (1997) *Int J Quantum Chem* 65(5):439–451
23. Rumer G (1932) *Gottinger Nachr* 3:337
24. Simonetta M, Gianinetta E, Vandoni I (1968) *J Chem Phys* 48(4):1579
25. Karadakov PB, Gerratt J, Cooper DL, Raimondi M (1995) *Theor Chim Acta* 90(1):51–73
26. Chirgwin BH, Coulson CA (1950) *Proc R Soc A* 201(1065):196–209
27. Gallup GA, Norbeck JM (1973) *Chem Phys Lett* 21(3):495–500
28. Thorsteinsson T, Cooper DL (1998) *J Math Chem* 23(1–2):105–126
29. Dunning TH, Woon DE, Leiding J, Chen L (2013) *Acc Chem Res* 46(2):359–368
30. MOLPRO, version 2010.1, a package of ab initio programs, Werner HJ, Knowles PJ, Knizia G, Manby FR, Schutz M, Celani P, Korona T, Lindh R, Mitrushenkov A, Rauhut G, Shamasundar KR, Adler TB, Amos RD, Bernhardsson A, Berning A, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Goll E, Hampel C, Hesselmann A, Hetzer G, Hrenar T, Jansen G, Koppl C, Liu Y, Lloyd AW, Mata RA, May AJ, McNicholas SJ, Meyer W, Mura ME, Nicklass A, O'Neill DP, Palmieri P, Pfluger K, Pitzer R, Reiher M, Shiozaki T, Stoll H, Stone AJ, Tarroni R, Thorsteinsson T, Wang M, Wolf A, see <http://www.molpro.net>
31. Thorsteinsson T, Cooper DL, Gerratt J, Karadakov PB, Raimondi M (1996) *Theor Chim Acta* 93(6):343–366
32. Pipek J, Mezey PG (1989) *J Chem Phys* 90(9):4916–4926
33. Knizia G, Adler TB, Werner HJ (2009) *J Chem Phys* 130(5):054104
34. Knizia G, Werner HJ (2008) *J Chem Phys* 128(15):154103
35. Knowles PJ, Hampel C, Werner HJ (1993) *J Chem Phys* 99(7):5219–5227
36. Manby FR (2003) *J Chem Phys* 119(9):4607–4613
37. Dunning TH (1989) *J Chem Phys* 90(2):1007–1023
38. Dunning TH, Peterson KA, Wilson AK (2001) *J Chem Phys* 114(21):9244–9253
39. Woon DE, Dunning TH (1993) *J Chem Phys* 98(2):1358–1371
40. Adler TB, Knizia G, Werner HJ (2007) *J Chem Phys* 127(22):221106
41. Knowles PJ, Werner HJ (1985) *Chem Phys Lett* 115(3):259–267
42. Werner HJ, Knowles PJ (1985) *J Chem Phys* 82(11):5053–5063
43. Knowles PJ, Werner HJ (1988) *Chem Phys Lett* 145(6):514–522
44. Werner HJ, Knowles PJ (1988) *J Chem Phys* 89(9):5803–5814
45. Chu LK, Lee YP, Jiang EY (2004) *J Chem Phys* 120(7):3179–3184
46. Lindquist BA, Dunning TH (2013) *J Phys Chem Lett* 4(18):3139–3143
47. Wesolowski SS, Johnson EM, Leininger ML, Crawford TD, Schaefer HF (1998) *J Chem Phys* 109(7):2694–2699
48. Mata F, Carballo N (1983) *J Mol Struct* 101(3–4):233–238
49. Mayer PM, Baer T (1996) *Chem Phys Lett* 261(1–2):155–159
50. Meloni S, Pieretti A, Bencivenni L, Albertini VR, Sadun C, Caminiti R (2001) *Comput Mater Sci* 20(3–4):407–415
51. Mootz D, Merschenz-Quack A (1988) *Acta Crystallogr. Sect C: Cryst Struct Commun* 44:926–927
52. Leiding J, Woon DE, Dunning TH (2011) *J Phys Chem A* 115(18):4757–4764
53. Cubbage JW, Jenks WS (2001) *J Phys Chem A* 105(46):10588–10595
54. Fueno H, Ikuta S, Matsuyama H, Kamigata N (1992) *J Chem Soc. Perkin Trans 2*(11):1925–1928
55. Miller EG, Rayner DR, Thomas HT, Mislow K (1968) *J Am Chem Soc* 90(18):4861
56. Rayner DR, Gordon AJ, Mislow K (1968) *J Am Chem Soc* 90(18):4854
57. Rayner DR, Miller EG, Bickart P, Gordon AJ, Mislow K (1966) *J Am Chem Soc* 88(13):3138
58. Chesnut DB, Savin A (1999) *J Am Chem Soc* 121(10):2335–2336