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Nature of the Three-Electron Bond in $H_2S \therefore SH_2^{+}$ [†]

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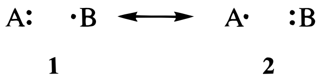
We have investigated the model system $H_2S \therefore SH_2^+$, i.e., the sulfur−sulfur bound dimer radical cation of H_2S, using both density functional theory (LDA, BP86, PW91) and traditional ab initio theory (up to CCSD-(T)). Our purpose is to better understand the nature of the three-electron bond. The S−S bond length is 2.886 Å and the bond enthalpy (for 298.15 K) amounts to −40.7 kcal/mol at the BP86/TZ2P level. The best ab initio estimates for the S−S bond strength (our CCSD(T)/6-311++G(2df,2pd)//MP2(full) and literature values) are some 10 kcal/mol weaker than those from nonlocal DFT. It is shown, using an energy decomposition scheme for open-shell systems, that the sulfur−sulfur bond ($\Delta E = \Delta E_{2c-3e} + \Delta E_{elst}$) is nearly 60% provided by the three-electron bond (ΔE_{2c-3e}) between the unpaired sulfur $3p_x$ electron on $H_2S^{+\bullet}$ and the sulfur $3p_x$ lone pair on H_2S; electrostatic attraction (ΔE_{elst}) is important, too, with a contribution of somewhat more than 40%. We show furthermore that the three-electron bond ($\Delta E_{2c-3e} = \Delta E_{2c-1e} + \Delta E_{Pauli}$) can be conceived as and quantitatively analyzed in terms of a one-electron bond (ΔE_{2c-1e}), arising from the β-electron of the H_2S lone pair interacting with the corresponding empty β-spin orbital of $H_2S^{+\bullet}$, opposed by the Pauli repulsion (ΔE_{Pauli}) between the α-electrons of the H_2S lone pair and $H_2S^{+\bullet}$ SOMO.

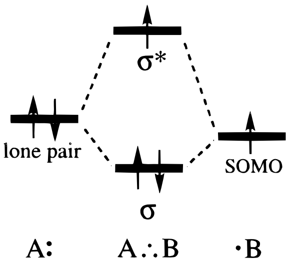
1. Introduction

The idea of the three-electron bond was introduced in the early 1930s by Pauling in the context of the valence bond model of the chemical bond.[1] Since, it has been further developed both in valence bond (VB) and in molecular orbital (MO) theory and has become a standard concept in chemistry.[2−4] The equivalence between the VB and MO description has recently been analyzed in detail by Harcourt.[2a] In VB theory,[1,2] the two-center three-electron (2c-3e) bond between two fragments A and B is viewed as arising from a stabilizing resonance between two valence bond structures in which an electron pair is on fragment A and an unpaired electron on B (**1**), or the other way around (**2**), as shown below:



1 **2**

A sizable resonance stabilization is only achieved if configurations **1** and **2** have "similar" energies. The picture in MO theory[2,3] is that of a closed-shell orbital, typically a lone pair, of one fragment A interacting with the singly occupied molecular orbital (SOMO) of the other fragment B, resulting in a doubly occupied bonding MO (σ) and a singly occupied antibonding MO (σ*) of the composite molecule A∴B; see **3**:



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It follows from **3** that the 2c-3e bond may be viewed as composed of an electron-pair bond $(\sigma)^2$ counteracted by a destabilizing component owing to the antibonding electron $(\sigma^*)^1$ leading formally to a bond order of $^1/_2$ or less. In order to arrive at a stable 2c-3e bond, the interacting fragment molecular orbitals (FMOs) must be close in energy—similar to the requirement for **1** and **2** in the VB model—and they should have sufficient overlap S as both these factors stabilize the electron-pair bonding configuration $(\sigma)^2$. Note, however, that the antibonding σ^* MO is generally more destabilized than the bonding σ MO is stabilized, and that this excess destabilization aggravates with increasing overlap. Thus, when S exceeds a certain critical value, the net 3c-2e interaction becomes nonbonding or even repulsive. In the simple Hückel model with overlap, for example, the net 2c-3e interaction associated with two initially degenerate FMOs on fragments A and B, respectively, is optimal for $S = 0.17$ and becomes antibonding for $S > 0.33$.[2c,g]

The above MO analysis of the 2c-3e bond, in terms of electron-pair bonding through $(\sigma)^2$ opposed by an electron in the antibonding σ^*, is done so-to-say from the point of view of the composite molecule A∴B and the properties of its MOs.

[†] Dedicated to Professor R. D. Levine on the occasion of his 60th birthday.

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In the present paper, we follow a different—although equivalent—approach to the 2c-3e bond, namely, from the perspective of the fragments and their mutual interaction. In particular, we analyze the sulfur−sulfur three-electron bond in $H_2S\therefore SH_2^+$ using local as well as nonlocal density functional theory (DFT)[5] in conjunction with a quantitative energy decomposition scheme for open-shell fragments.[6,7] The $H_2S\therefore SH_2^+$ structure has been found by Gill and Radom[2c] to be the only minimum on the MP2/6-31G* potential energy surface of $(H_2S)_2^{+\bullet}$. Our main purpose is to better understand the nature of the 2c-3e bond and to evaluate and probe this concept more quantitatively within modern Kohn−Sham MO theory.[5,8] For example, to what extent is this bond really provided by orbital interactions? Are electrostatic forces also important in our cationic model system $H_2S\therefore SH_2^+$? Of more general interest is our attempt to identify both qualitatively and quantitatively the repulsive component in the 2c-3e bond that causes the bond order to be *less* than $^1/_2$. Furthermore, we have performed traditional ab initio computations, up to the CCSD(T)/6-311++G(2df,2pd) level of theory, which serve to provide accurate benchmarks for the geometry and the sulfur−sulfur bond energy.[9,10]

We have chosen $H_2S\therefore SH_2^+$ as our model system for two reasons: (i) it is a simple representative of 2c-3e bound species, allowing us to concentrate on the main features of the bonding mechanism; (ii) it is the archetype $R_2S\therefore SR_2^+$ system and its theoretical analysis provides insights complementary to those from our recent FT-ICR mass spectrometric study of dialkylsulfide dimer radical cations ($R_2S\therefore SR_2^+$),[4a] leading to a more complete picture of cationic sulfur−sulfur three-electron bonding.

2. Methods

2.A. DFT Computations: General Procedure. All DFT calculations were performed using the Amsterdam density functional (ADF) program developed by Baerends and others.[6,7] The MOs were expanded in a large uncontracted set of Slater type orbitals (STOs) containing diffuse functions: TZ2P (no Gaussian basis functions are involved).[6c] The basis set is of triple-ζ quality, augmented with two sets of polarization functions: 3d and 4f on S, and 2p and 3d on H. The 1s2s2p core shells of S were treated by the frozen-core approximation.[6a,b] An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular density and to represent the Coulomb and exchange-correlation potentials accurately in each self-consistent field (SCF) cycle.[6a] The numerical integration was performed using the procedure developed by Boerrigter et al.[6d]

Geometries were optimized using analytical gradient techniques.[6e] Frequencies[6f] were calculated by numerical differentiation of the analytical energy gradients. Energies, geometries and frequencies were computed at three different levels of theory: (i) the local density approximation (LDA), where exchange is described by Slater's Xα potential[5e] and correlation is treated in the Vosko−Wilk−Nusair (VWN) parametrization;[6g] (ii) with nonlocal corrections to exchange due to Becke[6h,i] and correlation due to Perdew[6j] added self-consistently[6k] (BP86); (iii) with nonlocal corrections to exchange and correlation due to Perdew and Wang[6l,m] also added self-consistently (PW91).

Energies are calculated directly *with respect to atoms* in *one* numerical integration of the difference energy density $\epsilon[\rho, \mathbf{r}] - \sum_A \epsilon_A[\rho, \mathbf{r}]$ between the overall molecule and the constituting atoms (eq 1).

$$\Delta E[\rho] \int (\epsilon[\rho, \mathbf{r}] - \sum_{A} \epsilon_A[\rho, \mathbf{r}])\, d\mathbf{r} \qquad (1)$$

In other words, we evaluate the energy of the overall molecule, $E[\rho] = \int \epsilon[\rho,\mathbf{r}]\, d\mathbf{r}$, and the energies of each of the composing atoms, $E_A = \int \epsilon_A[\rho, \mathbf{r}]\, d\mathbf{r}$, in *the same* numerical integration grid. This provides more accurate relative energies than subtracting total energies from separate calculations because the same relative numerical integration error applies to a much smaller quantity, yielding in turn a much smaller absolute error.

2.B. DFT Computations: Bond Analysis. The 2-center-3-electron bonding mechanism in $H_2S\therefore SH_2^+$ was analyzed using the extended transition state (ETS) method developed by Ziegler and Rauk.[7] The overall bond energy ΔE is divided in two major components (eq 2):

$$\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}} \qquad (2)$$

The preparation energy ΔE_{prep} is the amount of energy required to deform the separated fragments from their equilibrium structure to the geometry, which they acquire in the composite molecule. The actual interaction energy ΔE_{int} between the prepared fragments can be further split up into three physically meaningful terms (eq 3):

$$\Delta E_{\text{int}} = \Delta E_{\text{elst}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} \qquad (3)$$

Here, ΔE_{elst} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments and is usually attractive. The Pauli repulsion ΔE_{Pauli} comprises the four-electron destabilizing interactions between occupied orbitals and is responsible for any steric repulsion. The orbital interaction ΔE_{oi} accounts for electron-pair bonding,[7a] charge transfer (e.g., HOMO−LUMO interactions), and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment).

2.C. Ab Initio Computations. The ab initio calculations were performed using the Gaussian program package.[10] Geometries were optimized at the MP2(full) level (i.e., with all electrons included in the correlation treatment) with the 6-311++G(2df,2pd) basis set, using the spin-unrestricted formalism for the open-shell species, $H_2S^{+\bullet}$ and $H_2S\therefore SH_2^+$.[9] At the geometries thus obtained we have carried out single-point energy calculations with the 6-311++G(2df,2pd) basis set at the following levels: HF, PMP2 (where the effect of spin contamination is corrected for by projection techniques), CCSD, and CCSD(T).

3. Results and Discussion

3.A. Geometry and Bond Strength. The formation of $H_2S\therefore SH_2^+$ from H_2S and H_2S^+ has been studied at the LDA/TZ2P, BP86/TZ2P, and PW91/TZ2P levels of DFT. In Table 1, the results are summarized and compared with our ab initio values and with data from literature.

The local density approximation (LDA) leads, in line with general experience,[5c,d] to strong overbinding. This shows up in far too high values for the electronic bond energy, $\Delta E = -50.8$ kcal/mol, and 298.15 K bond enthalpy, $\Delta H_{298} = -48.7$ kcal/mol. For comparison, the corresponding ab initio values are $\Delta E = -32.6$ kcal/mol (PMP4/6-31+G(2df,p)//MP2/6-31G*) and $\Delta H_{298} = -28.6$ kcal/mol (G2 level). The rather short LDA sulfur−sulfur bond distance ($d_{SS} = 1.778$ Å) is indicative for overbinding, too, as follows from the bond elongation on introduction of gradient corrections for exchange and correlation

TABLE 1: Analysis of the Sulfur−Sulfur Three-Electron Bond in C_{2h} Symmetric $H_2S\therefore SH_2^+$ Using Local and Nonlocal Density Functionals and the TZ2P Basis Set[a]

	LDA[a]	BP86[a]	PW91[a]	ab initio and lit.[b,c]
		Bond Distance (Å)		
d_{SS}	2.778	2.886	2.859	2.729 (MP2/6-311++G(2df,2pd))[a] 2.835 (MP2/6-31G*)[b]
		Thermochemistry (kcal/mol or cal/mol K)[d]		
ΔH_{298}	−48.7	−40.7	−42.1	−28.6 (G2)[b]
ΔS_{298}	−29.6	−29.5	−31.2	−28.7 (MP2/6-31G*)[b]
ΔG_{298}	−39.9	−31.9	−32.8	−20.0[e]
		Bond Energy Decomposition (kcal/mol)		
ΔE_{elst}	−23.8	−18.4	−19.4	
ΔE_{Pauli}	30.2	25.4	26.0	
ΔE_{oi}	−58.1	−51.3	−52.5	
ΔE_{int}	−51.7	−44.3	−45.9	
ΔE_{prep}	0.9	1.5	1.5	
ΔE^f	−50.8	−42.8	−44.4	−19.5 (HF/6-311++G(2df,2pd)),[a] −33.5 (PMP2/6-311++G(2df,2pd)),[a] −30.0 (CCSD/6-311++G(2df,2pd)),[a] −31.9 (CCSD(T)/6-311++G(2df,2pd)),[a] −19.9 (HF/6-31G*),[b] −33.4 (PMP2/6-31+G(2df,p)),[b] −32.6 (PMP4/6-31+G(2df,p))[b]
		Fragment Orbital Overlaps $\langle H_2S \mid H_2S^{+\bullet}\rangle$		
$\langle 1b_1 \mid 1b_1\rangle$	0.20	0.18	0.18	0.13 (STO-3G),[c] 0.17 (EH)[c]
$\langle 1b_1 \mid 2a_1\rangle$	0.04	0.04	0.04	
$\langle 2a_1 \mid 2a_1\rangle$	0.04	0.03	0.03	

[a] This work, see section 2. All our ab initio single-point computations are done in the MP2(full)/6-311++G(2df,2pd) geometries. [b] Deng et al., ref 3b. [c] Gill and Radom, ref 2c. [d] Calculated bond enthalpy, bond entropy, and bond Gibbs free energy at 298.15 K. [e] Calculated using G2 ΔH and MP2/6-31G* ΔS values from ref 3b. [f] Electronic energy without zero-point vibrational energy correction.

(vide infra). The longer bond distance obtained by Deng et al.[3b] at MP2/6-31G* ($d_{SS} = 2.835$ Å) seems to be in line with this. Note, however, that the MP2 value is substantially reduced ($d_{SS} = 2.729$ Å) and, in fact, ends up even below the LDA one, when our more flexible 6-311++G(2df,2pd) basis is used.

The introduction of gradient corrections in the nonlocal BP86 and PW91 density functionals significantly improves the results and reduces the overbinding. The sulfur−sulfur bond elongates by ca. 0.1 Å, and, more importantly, the electronic bond energy ΔE decreases by some 8 kcal/mol and amounts to −42.8 and −44.4 kcal/mol at BP86 and PW91 (Table 1). Note that this is still 10−12 kcal/mol stronger than the PMP4 value of −32.6 kcal/mol[3b] and our CCSD(T) value of −31.9 kcal/mol, which in turn is 13 kcal/mol stronger than the HF result. Similarly, the BP86 and PW91 bond enthalpies ΔH_{298} of −40.7 and −42.1 kcal/mol are 12−14 kcal/mol stronger than the G2 value. This is a rather large error for the nonlocal functionals. It has been attributed recently[11a] to a well-known deficiency[11b] of the existing exchange functionals to properly cancel the self-interaction part of the Coulomb energy in case of delocalized ionization out of symmetry equivalent weakly overlapping (or nonoverlapping) orbitals (i.e., the $3p_x$ lone pairs of the two H_2S units;[11c] see Figure 1). While this particular deficiency of the exchange functionals should be kept in mind, it does not hamper our qualitative analysis of the bonding mechanism (see section 3B).

Bond entropies ΔS_{298} obtained at LDA (−29.6 cal/mol K), BP86 (−29.5 cal/mol K), and PW91 (−31.2 cal/mol K) are all in reasonable agreement with the MP2 value (Table 1). The gradient-corrected bond Gibbs free energies ΔG_{298} are with −31.9 (BP86) and −32.8 kcal/mol (PW91) again ca. 12 kcal/mol stronger than the best ab initio estimate.

3.B. Nature of the Three-Electron Bond. The sulfur-sulfur bond in $H_2S\therefore SH_2^+$ has been analyzed at various levels of DFT, local (LDA) as well as nonlocal (BP86 and PW91), to assess possible effects of varying the computational level on our physical model of the 2c-3e bond. The results in Table 1 show that, although numerically different, the relative proportions of the different physical terms (ΔE_{elst}, ΔE_{Pauli}, ΔE_{oi}) in the S-S interaction are very similar for all three levels, thus yielding the same physical picture. In the following, we discuss the results of the analysis at the BP86/TZ2P level, which gives the least overbinding.

The sulfur−sulfur bond in $H_2S\therefore SH_2^+$ is mainly provided (vide infra) by the three-electron orbital interactions between the $1b_1$ (essentially sulfur $3p_x$) orbitals of the two fragments, i.e., the lone pair $3p_x$ of H_2S and the $3p_x$ SOMO of $H_2S^{+\bullet}$ (see Figure 1). Taking the repulsive and bonding orbital interactions together (eq 4), i.e.

$$\Delta E_{2c-3e} = \Delta E_{Pauli} + \Delta E_{oi} \tag{4}$$

one arrives at a three-electron interaction $\Delta E_{2c-3e} = -25.9$ kcal/mol or ca. 60% of the net interaction ΔE_{int} (Table 1). However, the electrostatic interaction ΔE_{elst} of −18.4 kcal/mol still contributes about 40% to the net sulfur−sulfur interaction. Thus, although clearly smaller than ΔE_{2c-3e}, it is an important component. The deformation energy ΔE_{prep} is very small, about 1 kcal/mol, because the two H_2S moieties in $H_2S\therefore SH_2^+$ are hardly deformed with respect to free H_2S and $H_2S^{+\bullet}$.

The two $3p_x$ orbitals participating in the three-electron bond are pointing toward each other, leading to a sizable (for this type of bond) overlap[11c] of 0.18 at a relatively large equilibrium bond distance of 2.886 Å as shown in Table 1. This shows up in a large splitting of 2.4 eV between the bonding and the antibonding combinations (Figure 1). The overlap and interaction between other H_2S and $H_2S^{+\bullet}$ fragment MOs, e.g., the weakly S−H bonding $2a_1$ lone pairs with $S = 0.03$ and a splitting of 0.2 eV between bonding and antibonding combinations, is much smaller (see Figure 1). Also note the very close agreement, which is probably fortuitous, between our (0.18) and the optimal Hückel 2c-3e bond overlap (0.17, see Table 1).

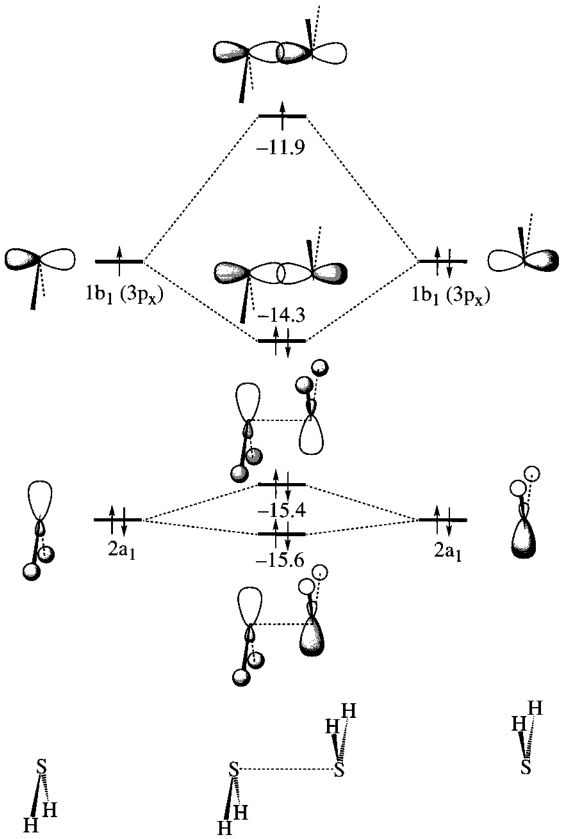

Figure 1. Schematic orbital interaction diagram for $H_2S \therefore SH_2^+$ (MO energies in eV).

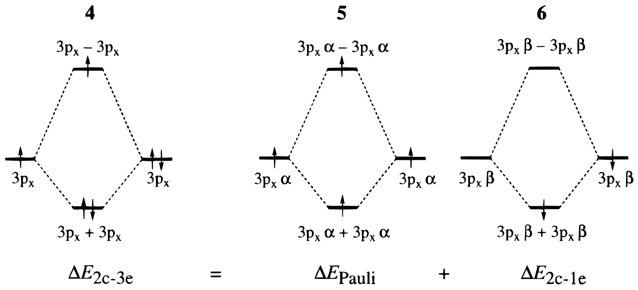

Figure 2. Qualitative and quantitative decomposition of the three-electron bond (**4**) into a Pauli repulsive component (**5**) plus a one-electron bond (**6**) between the interacting fragments.

As pointed out in the introduction, the three-electron bond is associated with a formal bond order of $^1/_2$ (or less), similar to the one-electron bond. Taking the overall complex $H_2S \therefore SH_2^+$ as the starting point, this may be viewed as resulting from the $3p_x + 3p_x$ *electron-pair* bond being counteracted by *one antibonding* $3p_x - 3p_x$ electron. A different, although completely equivalent, perspective arises if one takes the two fragments as the starting point, as we are doing in the present analysis of the bonding mechanism.

The three-electron bond **4** contains a repulsive term $\Delta E_{\mathrm{Pauli}}$, which is mainly due to the destabilizing interaction **5** between the unpaired $3p_x\alpha$ electron on $H_2S^{+\bullet}$ and the same-spin $3p_x\alpha$ electron of the lone pair on H_2S (the excess spin is arbitrarily chosen α; see Figure 2). The repulsion between the same-spin electrons in the 2c-3e bond has also been recognized by Linnett and others from a valence bond (VB) point of view.[2e,h,i] Note that the two-electron two-*spin* orbital repulsion for α spin, **5**, is entirely analogous to the well-known four-electron two-orbital destabilizing interaction between closed shells. The latter is less important in $H_2S \therefore SH_2^+$ owing to the small overlaps, e.g., between the H_2S and $H_2S^{+\bullet}$ $2a_1$ lone pairs (vide supra). Results of recent mass spectrometric experiments do, however, show that in the related dialkyl sulfide dimer radical cations $R_2S \therefore SR_2^+$, Pauli repulsion between closed shells, i.e., steric repulsion between substituents R, may become important when R is propyl or a larger alkyl group.[4a] The bonding orbital interaction ΔE_{oi} is simply provided by a one-electron bond **6** between the $3p_x\beta$ electron of the lone pair on H_2S and the empty $3p_x\beta$ orbital on $H_2S^{+\bullet}$, i.e., $\Delta E_{\mathrm{oi}} = \Delta E_{\mathrm{2c-1e}}$ (see Figure 2). In this way, the three-electron bond is naturally linked to the one-electron bond plus a characteristic Pauli repulsive term. Important is also that we are able to compute the different terms in the overall bond energy. This places the physical model on a more quantitative basis. In particular, it becomes clear that the three-electron bond is in principal weaker than the corresponding one-electron bonding component. In our $H_2S \therefore SH_2^+$ model system, for example, the three-electron bond ($\Delta E_{\mathrm{2c-3e}} = -25.9$ kcal/mol) is about two times weaker than the corresponding one-electron bonding component ($\Delta E_{\mathrm{2c-1e}} = \Delta E_{\mathrm{oi}} = -51.3$ kcal/mol) owing to the Pauli repulsive term ($\Delta E_{\mathrm{Pauli}} = 25.4$ kcal/mol).

4. Conclusions

The sulfur−sulfur bond in $H_2S \therefore SH_2^+$ is mainly, i.e., for ca. 60%, provided by the three-electron bond between the unpaired sulfur $3p_x$ electron on $H_2S^{+\bullet}$ and the corresponding sulfur $3p_x$ lone pair on H_2S. However, electrostatic attraction is an important factor, too, contributing ca. 40% to the net interaction energy.

Furthermore, we have shown that the three-electron bond may be thought of as consisting of two components: (i) a repulsive term, arising from the unpaired electron on $H_2S^{+\bullet}$ interacting with a same-spin electron of the lone pair on H_2S, and (ii) a one-electron bonding term. And we have also quantified the different physical terms: $\Delta E_{\mathrm{2c-3e}} = \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{2c-1e}}$. Thus, it is easily seen that the three-electron bond must in principle always be weaker than the associated one-electron bonding component (twice as weak in case of $H_2S \therefore SH_2^+$).

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