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A Simplified Gaussian-2 Scheme for Determining Electron Affinities of Covalent Bonds. Application to the Disulfide Bond RS−SR′ (R, R′ = H, CH_3, C_2H_5)

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A cost-effective general procedure is proposed to calculate the electron affinities of covalent linkages, which can attach an electron to create a three-electron bond. The procedure is based on a thermodynamic cycle, of which each step is calculated by a method that is specific to it. In the present work, the first step, the dissociation of a two-electron bond, is studied at the MP4 level with a correction for basis set effects, which is calculated at the MP2 level, and an empirical correlation correction that is routinely used in the Gaussian-2 scheme. Experimental data or density functional theory can be used for the second step, while the third step, the formation of a three-electron bond, is studied at the MP2 level in large basis set. ZPE corrections are included in steps 1 and 3. The method is applied to some alkyl-substituted disulfides and yields results that are in good agreement with reference values when available. Some ways to make the procedure even more economical and applicable to large molecules are discussed.

Introduction

The properties of negative ion radicals and their stabilities relative to their neutral precursor are of great importance in many areas of chemistry, especially in biochemical processes. To mention but a few examples, radical anions are associated with electron transfer in biological systems, photosynthesis and oxidative stress,[1] electron attachment to nucleic acid bases,[2,3] etc. In this context, the disulfide linkage plays an important role in determining the biological activity of numerous proteins, enzymes, and antibiotics. Covalent disulfide bonds are important determinants of the shapes of proteins because S−S bonds between cysteines stabilize folded conformations.[4,5] In addition, protein disulfide radical anions are very stable in solution,[6,7] and disulfide redox systems control numerous important events in cellular life such as the regulation of cell growth and proliferation[8] and human cancer development.[9,10] The scission of the S−S bond in RS−SR molecules can occur through one-electron reduction, leading to a disulfide radical anion in equilibrium with the dissociated species. Radical anions of sulfur-containing compounds have been observed in the pulse radiolysis of cystine and cysteamine,[11] hydrogen sulfide, and mercaptans.[12,13] More generally, disulfide anions are involved in protection mechanisms for biological systems subject to ionizing radiations or other forms of free radical damage.[14] Such examples demonstrate the importance of measuring or calculating the electron affinities of covalent linkages in chemistry or biochemistry.

Experimentally, the most accurate methods to measure EAs use the photoelectric effect.[15,16−18] The negative ion photoelectron specctroscopy (NIPES) technique, which uses pulsed lasers to photodetach negative ions, is able to provide extremely accurate electron affinities (EAs) for atoms.[15] However, difficulties can be encountered for polyatomic molecules. When the equilibrium geometry of the anion is very different from that of the neutral molecule, the spectroscopic threshold corresponding to the (0,0) band cannot be identified and the adiabatic EA, which is defined as the energy gap between the anion and the neutral in their lowest vibrational levels, is not available. In such a case, which is typical of anions that display a three-electron bond, the NIPES experiment can only give vertical detachment energies, and the adiabatic EAs must be extracted, with considerable uncertainty, from fitting of Franck−Condon profiles. Moreover, EAs for very large molecules are often not accessible experimentally.

On the theoretical side, calculation of molecular electron affinities remains one of the most difficult problems in computational chemistry. This is because one has to compare the energies of species, the neutral molecule and its anion, that have different numbers of electrons, hence the necessity of a very accurate treatment of electron correlation. Thus, the direct calculation of the anion−neutral energy difference converges only slowly to the full CI limit for a given basis set, and very high angular momentum basis set functions are required to approach the complete basis set limit.[15] In view of these difficulties, it is clear that direct calculations of electron affinities by economical ab initio methods (e.g., MP2) cannot be considered as reliable, even if some accidental successes may be encountered.

The experimental and theoretical methods to calculate EAs have been reviewed very recently by Schaefer and Ellison and co-workers[15] with special emphasis, as far as theory is concerned, on density functional theory (DFT). This latter theory provides EA predictions with reasonable accuracy in general (within 0.2 eV or better of experiment), but an important exception must be kept in mind: those cases in which the extra electron is captured by a covalent linkage A−B, leading to an anion A∴B displaying a three-electron bond:

$$A{-}B + e^{-} \rightarrow [A\therefore B]^{-} \qquad (1)$$

In molecular orbital terms, the three-electron bond is made of

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two electrons occupying a σ bonding orbital, and a third one occupying the corresponding antibonding σ^* one, leading to a net bond order of 0.5. The bond may also be represented in the valence bond framework as a resonance between two limiting structures, as will be seen (eq 4).

Because three-electron-bonded species have been shown to be poorly described at the DFT level, having overestimated binding energies,[19,20] three-electron-bonded anions are found systematically too low in energy relative to the neutral compound, leading to much overestimated EAs with errors on the order of 1 eV in some cases.[15] Thus, DFT methods are not the solution to compute the EAs of covalent bonds.

On the side of more accurate methods, the accuracy of coupled-cluster calculations can be impressive for atoms, but it performs a little less well for molecules and is anyway restricted to small systems.[15] More applicable to medium-sized systems are the model chemistry methods such as Gaussian-*X* (G2, G3) theory[21−26] or the complete basis set (CBS) methods developed by Petersson,[27] which are able to achieve EAs often within 0.1 eV or less of experiment. Even more accurate are the Weizmann techniques (W1 and W2),[28] which have accuracies of 0.02 and 0.01 eV, respectively. All of these methods are too computationally demanding for being applicable to large systems. There is therefore still a need for cost-effective methods that would be applicable to molecules of significant size. The first aim of this paper is to provide such a method, specifically designed for the calculation of the EA of covalent linkages, that is, neutral molecules that may bind an electron to form a three-electron-bonded anion. The S−S linkage with various alkyl substituents has been taken as an applicatory example for its importance as an electron receptor in biochemistry and because some DFT and MP2 calculations have been recently done for these systems,[29] aiming at interpreting experimental data. Thus, a second aim of our paper is to provide some reliable values for the adiabatic electron affinities of alkyl-substituted disulfides, and to confirm or falsify the theoretical values proposed by Desfrançois and co-workers.[29]

Theoretical Section

All calculations have been done with the Gaussian 98 series of programs.[30] The following standard basis sets have been used: (i) 6-31G(d) is a basis set of double-ζ quality with polarization functions on the heavy atoms (other than hydrogens), which is routinely used in the G2 scheme for geometry optimization of neutral, as well as anionic, species; (ii) 6-311G(d,p) is a basis set of triple-ζ quality with exponent contractions that have been specifically devised for the MP2 method, which bears polarization functions on all atoms, including hydrogens; (iii) the 6-311+G(3df,p) basis set is of triple-ζ + diffuse quality with polarization functions on the hydrogens and an elaborated set of polarization functions on the heavy atoms. This latter basis set is appropriate for accurate calculations on anionic species.

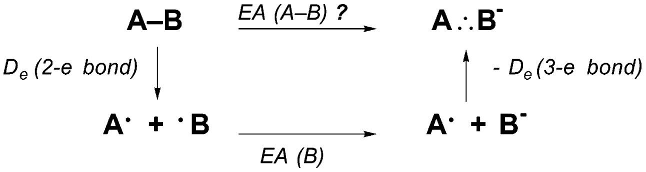
The following levels of theory have been used: (i) The vibrational frequencies have been calculated at the Hartree−Fock level and scaled by a factor of 0.893, as in the G2 scheme. These scaled frequencies are used to calculate the zero-point vibrational energies (ZPE) of the molecules. (ii) The Møller−Plesset many-body perturbation theory has been used at second order with all electrons correlated (MP2(full)). (iii) Some reference calculations have used coupled-cluster theory[31] with inclusion of all single and double excitations and perturbative treatment of triple excitations (CCSD(T)). (iv) The density functional theory (DFT) has been used with the B3LYP functional, which incorporates a mixture of the correlation functional of Lee, Yang, and Parr[32] with the three-parameter Hartree−Fock/DFT hybrid exchange functional of Becke.[33]

For radical species, all theoretical methods have been used in their spin-unrestricted forms.

Strategy and Methods

For the reasons expressed above, a direct calculation of the EA as the energy gap between a molecule and its anion is out of the question for the method to be applicable to significant molecular sizes, at least when the anion is of the three-electron-bonded type. A much less demanding strategy consists of using a thermodynamic cycle and computing the energetic balance of each step of the cycle. The advantage of this strategy is that the computational method that is used throughout the cycle need not be a unique universal method. The only thing that matters is that a realistic reaction energy be obtained for each step of the cycle. This allows one to use for each cycle the method that is best adapted to it, and not necessarily an expansive one. As we will see, the use of easily accessible experimental data will also be part of our strategy.

The thermodynamic cycle that we use to get the electronegativity of the covalent linkage A−B, referred to as EA(A−B), is shown here:



The cycle involves three steps. The first step, which is the calculation of a two-electron single-bond energy, is well documented in computational chemistry and there are many methods available, ranging from fairly accurate to very accurate. The G2 and G3 methods are accurate but expansive; however, some good results are also obtained with cheaper methods such as CASPT2, fourth-order Møller−Plesset (MP4), or DFT.[34] The second step consists of estimating the electron affinity of a radical. This is a rather simple task that can be done by a DFT calculation, for example, with the popular B3LYP or other hybrid functionals, because it is known that this theory can yield accurate EAs provided the anion is not an open-shell species.[15] Besides, the EAs of many radicals are known experimentally and tabulated, and this is information that will be used in our procedure as often as possible. Last, the third step involves the estimation of a three-electron bonding energy. This last step is much less documented than the first one, and it is now known that DFT performs very poorly in that case,[19,20] which by the way explains why DFT also performs poorly in calculating the EAs of covalent linkages. The G2 technique is accurate; however, it is even more expansive in step 3 than in step 1 (actually twice as much) because the radical nature of the anion requires using spin-unrestricted methods. Now our group has accumulated enough experience in the study of three-electron bonds to be able to evaluate the various theoretical methods for calculating the dissociation energies of such bonds, and we can now propose some economical methods with a reasonable degree of confidence. Thus, our past experience can be summarized as follows: (i) Møller−Plesset perturbation theory is ideally suited for the study of three-electron-bonded systems with good convergence properties, so an MP2 performs very well and yields dissociation energies in very good agreement with higher levels (e.g., MP4). These conclusions hold for symmetric systems.[35,36] (ii) In disymmetric systems, MP2 and MP4 calculations can be in error; however, a very simple reliability index can be calculated to verify the MP2 calculation a posteriori.[35] (iii) multiconfiguration self-consistent field (MC-SCF) methods are not accurate for these systems, if not followed by a perturbative treatment, unless a very large active space is employed. (iv) DFT methods overestimate three-electron bonding energies by variable quantities, which can be very large.[19,20]

It follows from the preceding that, if there is no universal and economical methods for all of the steps of the thermodynamic cycle, there exists for each step an optimal method that can be reasonably accurate and economical. In accord, the principle of our method will be to use different methods for different steps, the only requirement being that, for each step, the calculated energy be close or expected to be close to the experimental value. In that spirit, we will allow ourselves to use different theories, different basis set, or even experimental quantities when available to estimate the energetics of each step of the cycle. In this framework, the method that we have used in the present work decomposes as follows.

Step 1. Dissociation of the A−B Molecule. The calculation of the dissociation energy of A−B into its constituting radical fragments $A^\bullet$ and $B^\bullet$ is based on a simplified G2 scheme (the basic principles of the standard G2 method are recalled in the Appendix). Our procedure involves the following series of elementary calculations: (i) Geometry optimization of A−B, $A^\bullet$, and $B^\bullet$ at the MP2(full) level in 6-31G(d) basis set is performed. (ii) Single-point calculations of the same species at the MP4 level in 6-311G(d,p) basis set are performed. (iii) Correction for basis set effects is made. This correction, which is assumed to be independent of the level of correlation, is estimated at the MP2 level and takes care of the effect of adding diffuse and high-rank polarization functions to the former 6-311G(d,p) basis set. Thus, for each species, an MP2 calculation is done in 6-311+G(3df,p) basis set, and the correction C to be added to the former MP4 energy is estimated as follows:

$$C = E(\mathrm{MP2/6\text{-}311{+}G(3df,p)}) - E(\mathrm{MP2/6\text{-}311G(d,p)}) \quad (2)$$

(iv) The vibrational frequencies are calculated at the Hartree−Fock/6-31G(d) level and scaled to estimate the zero-point-vibration energy (ZPE). (v) The higher-level empirical correction, ΔHLC, for the correlation energy, which is routinely applied in the G2 method, is kept in our procedure and calculated by using the standard simple formula (eq A1 in the Appendix). The final energy of each species, neutral A−B molecule or radical fragment $A^\bullet$ and $B^\bullet$, is given by the following expression:

$$E = E(\mathrm{MP4}) + C + \mathrm{ZPE} + \Delta\mathrm{HLC} \quad (3)$$

Step 2. Electron Attachment to Radical Fragments. This step is relatively easy to deal with, owing to the small size of the species to be calculated, the availability of experimental data, and the good performance of DFT. Indeed, it has been shown by Schaefer and co-workers that DFT performs well in general for calculating electron affinity, provided that the anion is not an open-shell species.[15] Thus, DFT and in particular the popular B3LYP or other hybrid functionals can be used for computing the EA of the radical fragment $A^\bullet$ or $B^\bullet$. However, if one of the fragments is sufficiently small, the standard G2 method may also be employed. It should be noted that the choice of the fragment, $A^\bullet$ or $B^\bullet$, that is ionized in our thermodynamic cycle is free. Because the cycle is imaginary and not connected to any real experiment, it is not necessary to choose the fragment that has the largest electron affinity.

In the present work, experimental EAs for all of the radical fragments involved in our study have been used throughout.

Step 3. Formation of a Three-Electron Bond. Basis set effects are important for three-electron bonding energies to be accurately calculated. The reason is that a three-electron-bonded anion, $A\therefore B^-$, can be described as a resonance between two limiting structures, as in eq 4:

$$A\therefore B^- = A\!:^{-}{}^{\bullet}B \leftrightarrow A^{\bullet}\!:\!B^- \quad (4)$$

Each limiting structures represents a neutral fragment in the vicinity of an anion and is stabilized by a charge-induced-dipole interaction, which requires basis sets including high-rank polarization functions. On the other hand, as recalled above, the Møller−Plesset series converges very well and can be limited to the MP2 level, an economical computational level that can be used directly in large basis set for single-point energy calculations. In accord, our procedure for step 3 consists of the following series of elementary calculations: (i) geometry optimization of $A\therefore B$ at the MP2(full) level in 6-31G(d) basis set; (ii) single-point calculations of $A\therefore B$ at the MP2(full) level in 6-311+G(3df,2p) basis set; (iii) the vibrational frequencies are calculated at the Hartree−Fock/6-31G(d) level and scaled to estimate the ZPE. Note that this latter theoretical level, albeit very poor for calculating three-electron bonding energies, is on the contrary adequate for geometry optimization and frequency calculation purposes because the potential surface calculated at this level has locally the right shape in the vicinity of the minimum, while being greatly upshifted relative to the dissociated fragments.[37]

4. Results and Discussion

The above method has been applied to calculate the EAs of some alkyl-substituted disulfides. Recent Rydberg electron transfer and negative ion photoelectron measurements have been performed by Desfrançois and co-workers on these compounds.[29] However, the adiabatic EAs could not be experimentally obtained because of poor Franck−Condon overlaps between the neutral and anion ground states. The experiments were completed by DFT and MP2 calculations, which were found to strongly disagree with each other. As has been seen above, these two computational levels are too crude to provide reference values for the EAs, even if the authors made the right choice (as we will see) by rather trusting the MP2 values. Therefore, one of the objectives of this paper is to calculate reliable reference EAs for some alkyl-substituted disulfides and to confirm the MP2 values of Desfrançois and co-workers.[29]

For this purpose, we have applied our method to the three disulfides that have been studied by Desfrançois and co-workers, namely, HS−SH, $H_3CS{-}SCH_3$, and $H_5C_2S{-}SC_2H_5$, to which we have added the asymmetrical species $HS{-}SCH_3$ and $H_5C_2S{-}SCH_3$.

Geometry Optimizations. The geometries of the five neutral disulfides and their anions have been optimized at the MP2 level in 6-31G(d) basis set to remain faithful to the geometry optimization procedure of the G2 scheme. The resulting geometries are represented in Figure 1, along with the numerical values of some critical parameters (S−S bond lengths, R−S−S angles, and R−S−S−R dihedral angles). As regards the remaining geometrical parameters, it is clear that, for molecules involving methyl or ethyl groups each having small rotational barriers, many secondary minima exist on the potential surfaces within a small energy range, so it is difficult to claim that the

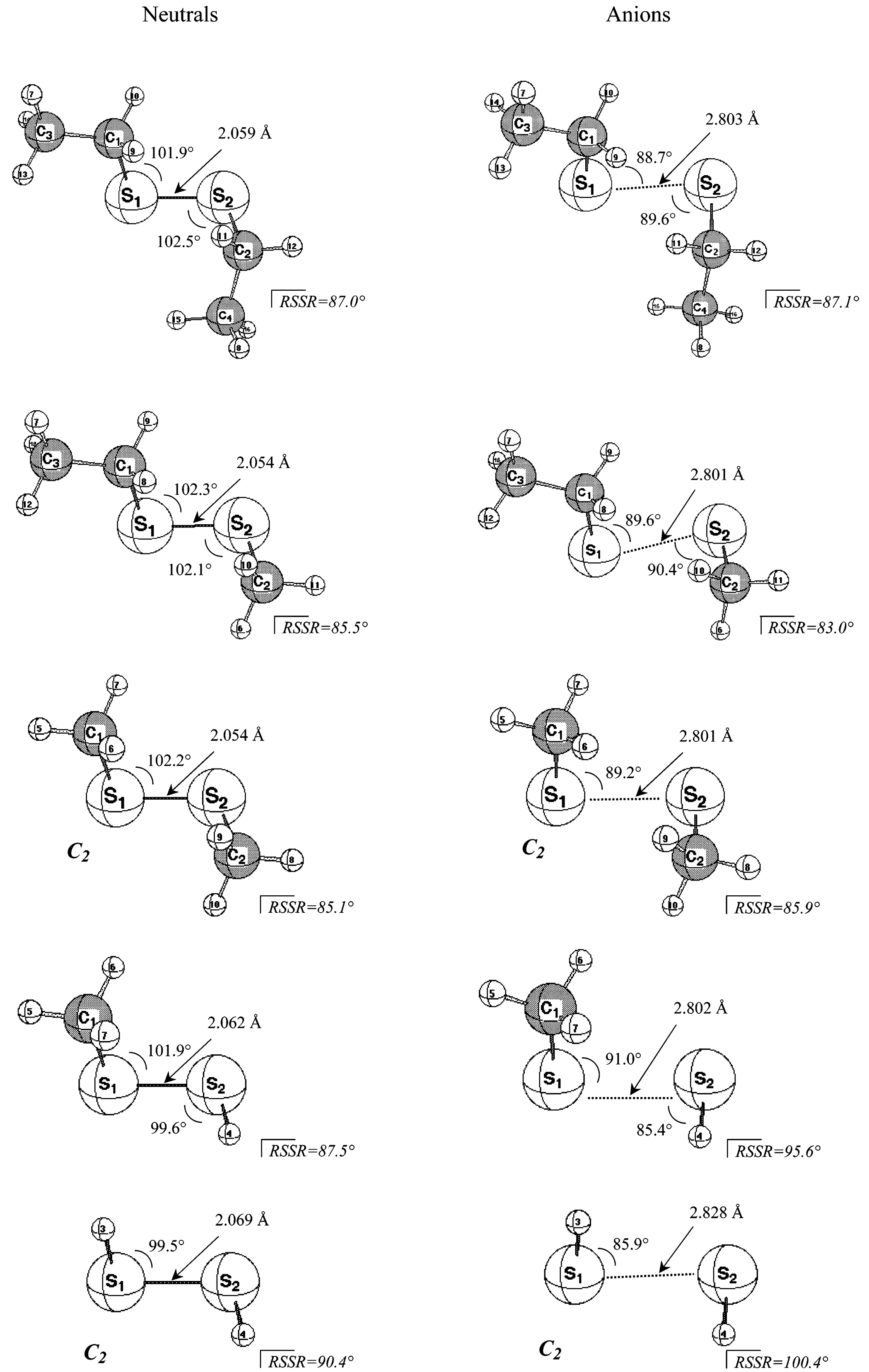


Figure 1. Geometries of the neutral disulfides and the corresponding anions as optimized at the MP2(full) level in 6-31G(d) basis set.

geometries arising from our study are absolute minima. However, the energy shift relative to the absolute minimum, if any, is expected to be small and, more importantly, to carry over to the whole dissociation energy curves and therefore to lead to negligible errors in the calculated dissociation energies, which are the quantities that we eventually need in our thermodynamic cycle.

Examination of the geometries displayed in Figure 1 reveals important differences between the anions and the corresponding neutral systems. While the S−S bond lengths in the neutral systems, irrespective of substituents, are all close to 2.06 Å, they are some 0.75 Å longer in the anions, an elongation that is explained by the different natures of the two-electron (2-e) and three-electron (3-e) bonds. Indeed, a simple MO model[38]

TABLE 1: Dissociation Energies (kcal/mol) of Some Neutral and Anionic Disulfides

	HSSH	HSSMe	MeSSMe	EtSSMe	EtSSEt
			Neutral		
G2	62.8	63.7	64.6		
our method	63.7	65.2	66.8	66.3	67.9
			Anion		
CCSD(T)[a]	23.6	18.3	23.2		
G2	24.1	18.6	23.0		
our method	24.3	19.3	24.7	23.5	25.2

[a] Single-point energy in 6-311+G(3df,2p) basis set. Geometries were optimized at the MP2/6-311+G(d,p) level, and ZPE correction was calculated at the scaled Hartree−Fock/6-31G(d) level.

TABLE 2: Electroaffinity of the RS Fragments at the B3LYP and G2 Levels Compared with Experiments

	HS	CH_3S	C_2H_5S
B3LYP[a]	2.32	1.82	1,89
G2	2.30	1.87	1.97
expt	2.32[b]	1.87[c]	1.95[d]

[a] Single points using the 6-311+G(3df,2p) basis set on geometries optimized using the 6-311+G(d,p) basis set. [b] Reference 46. [c] Reference 47. [d] Reference 48.

shows that the three-electron interaction gets its maximum stabilization for a small optimal value (0.17) of the overlap between the highest occupied values of each fragments. This optimal overlap, which has been confirmed by ab initio calculations,[39] is much smaller than the orbital overlaps that are typical of two-electron bonds (close to 0.5 in general), hence the large bond length difference. Another parameter that varies significantly, although to a lesser extent, from the neutral to the anion is the R−S−S angle, typically smaller by 12°−14° in the anion. This angle is generally close to 90° in the anions, showing that the orbitals that are involved in the three-electron bond are not hybridized, a further consequence of the weakness of the bond and the small value of the corresponding overlap. Be it as it may, the large geometry difference between any molecule before and after electron attachment to a covalent linkage is expected to be general and explains why adiabatic electron affinities are difficult to measure experimentally in such cases. Indeed, owing to very large geometry changes from the anion to the neutral molecule, the photodetachment process cannot access the ground-state rovibrational level of the neutral and reaches a vibrationally excited state. It follows that the EAs that are measured as threshold photodetachment energies by NIPES techniques are vertical rather than adiabatic, as concluded by Desfrançois and co-workers[29] in the disulfide case.

Dissociation Energies. The dissociation energies for the disulfides and their anions have been calculated by means of the computational methods described in section II and are displayed in Table 1, along with some values calculated at high theoretical levels (G2 or CCSD(T) in large basis sets) for the smallest molecules.

Let us consider the neutral molecules first. Our dissociation energies are in good agreement with the reference G2 values that have been calculated for the parent molecule and the mono- and dimethyl-substituted ones. For these three molecules, the error is in the range 1−2 kcal/mol and is positive, a slight overestimation that is expected for dissociation energies calculated at low Møller−Plesset orders. The substituent effect is weak, showing a maximum bond strengthening of ca. 4 kcal/mol.

Our computational procedure also yields some bonding energies for the anions that are very close to the much more expansive G2 values (Table 1). They are also in good agreement with some reference calculations that we have done for the three smallest molecules with the notoriously accurate CCSD(T) method in large basis set. Interestingly, our values are once again slightly overestimated relative to the accurate calculations, so the errors in steps 1 and 3 of our thermodynamic cycle nearly compensate for each other.

Some comments are in order to explain the generally good performances of the MP2 method to compute bonding energies for three-electron bonds. In this type of bond, the electron correlation is entirely dynamical in nature and consists of an instantaneous adaptation of the orbitals of each fragment to the electron fluctuation that characterizes the $A^{\bullet}B^{-} \rightarrow A^{-}B^{\bullet}$ exchange. This adaptation can be retrieved through a CI involving all of the monoexcitations from an active space made of the ground and first excited configurations, as has been demonstrated elsewhere.[37] Such excitations are very numerous and each has a small coefficient in the correlated wave function, and ideal situation for a perturbation method to be at its best. It follows that Møller−Plesset perturbation theory converges well for three-electron-bonded systems, so that an MP2 calculation is expected to yield dissociation energies in very good agreement with higher levels (e.g., MP4) and accurate methods. This prediction, which is based on qualitative theoretical considerations, has always, to our knowledge, been confirmed by accurate ab initio calculations.[20,36,38,40−42] Some rare exceptions, which concern asymmetrical systems, are related to the artifact of symmetry-breaking and are easily detected.[35]

The basis set effects for the three-electron bonding energies are very weak so far as symmetrically susbtituted molecules are concerned, that is, $HS\therefore SH^-$, $MeS\therefore SMe^-$, and $EtS\therefore SEt^-$, in agreement with a previous study that shows that alkyl substituent effects are weak on three-electron bonds involving atoms of the third row of the periodic table.[39] On the other hand, the dissymmetrically substituted $HS\therefore SMe^-$ anion undergoes a nonnegligible bond weakening relative to the parent anion, which reflects the necessity for a three-electron interaction to be effective that the two fragments have similar electronegativities.[43,44]

Electron Affinities of the RS Fragments. The EAs of numerous radicals are available experimentally and can be found on the Internet as part of the NIST Chemistry Webbook.[45] Thus, the experimental EAs of the $HS^{\bullet}$, $H_3CS^{\bullet}$, and $H_5C_2S^{\bullet}$ radicals have been used in this study as the energy data corresponding to step 2 of our thermodynamic cycle. For the sake of comparison, these quantities have also been calculated at the G2 level and at the DFT level using the B3LYP functional (see Table 2). The G2 level is, as expected, in excellent agreement with experiment. The B3LYP calculations are more approximate, having an error of about $^1/_2$ eV relative to experiment, which is however better than the average accuracy of B3LYP in this respect, 0.1−0.2 eV according to Schaefer and coworkers.[15] This somewhat good performance of the DFT method in the present application might be due to our choice of a large basis set for this calculation, a choice that is allowed by the low cost of the computational method and should be recommended in general for step 2 of our proposed procedure.

Electron Affinities of the RS−SR′ Dimers. Summing up the energy balance of the three steps of our thermodynamic cycle, as calculated by our procedure, yields the adiabatic EAs of the disulfides dimers, displayed in Table 3. The EAs have also been calculated directly by the G2 method for comparison for the three smallest species.

It appears that, unlike bonding energies, the electron affinities of disulfides are much substituent-dependent and significantly

TABLE 3: Calculated Adiabatic Electron Affinities (eV) for Some Substituted Disulfides

	HSSH	HSSMe	MeSSMe	EtSSMe	EtSSEt
G2	0.62	0.35	0.07		
our method	0.60	0.32	0.04	0.10	0.10

lowered by alkyl substitution. Although we do not have enough examples to draw general tendencies, the substituent effect seems to be linear, two alkyl substituents lowering the EA about twice as much as a single one, and the effects of methyl and ethyl substituents are about the same. The adiabatic EAs remain positive in all cases, albeit very small (0.04 eV) for the dimethyl disulfide.

Whenever the comparison is possible, the EAs that have been obtained by our procedure are in excellent agreement with the reference values calculated at the G2 level, the discrepancy being no larger than 0.03 eV. This agreement, which is better than expected owing to the relatively modest level of theory that we have employed, is partly because, as noted above, the errors on the dissociation energies computed in steps 1 and 3 tend to compensate.

Our values for MeS∴SMe and EtS∴SEt, respectively, 0.04 and 0.10 eV, are also in good agreement with the estimations (0.12 and 0.10 eV, respectively) of Desfrançois and co-workers.[29]

Summary and Conclusion

The procedure that we propose to calculate electron affinities of covalent linkages is based on a thermodynamic cycle of which each step is calculated by a method that is specific to it. In the present work, the first step, the dissociation of a two-electron bond, is studied at the MP4 level with a correction for basis set effects that is calculated at the MP2 level and an empirical correlation correction that is routinely used in the G2 scheme. Experimental data have been used for the second step, while the third step, the formation of a three-electron bond, is studied at the MP2 level in large basis set. ZPE corrections are included in steps 1 and 3.

Our procedure is obviously more economical than the standard G2 scheme; however, it could be made even cheaper by calculating the 2-e dissociation energy at the DFT level, using, for example, the popular B3LYP functional, which is known to perform well for this purpose. Still better performances can be obtained by using the recently developed 10-parameter functional of Schmider and Becke,[49] of which the accuracy in terms of enthalpies of formation seems to be comparable to the G2 method. In case EAs of the free radicals involved in step 2 are not available, once again the DFT method might be used. Thus, using DFT for steps 1 and 2 and keeping the MP2 method for step 3 should allow the calculation of EAs for molecules of quite significant sizes, the bottleneck being the MP2 calculation, which is by itself among the cheapest available methods.

Although our procedure has still not been applied to a large set of molecules, we can put trust in its reliability as a mean to calculate electron affinities of covalent linkages for the following reasons: (i) the theoretical methods that are appropriate for steps 1 and 2 of our thermochemical cycle are well documented and have long been critically evaluated; (ii) the reliability of the MP2 method for step 3, the formation of a three-electron bond, has been shown to be general on the basis of well-defined theoretical reasons.[35−37]

It is hoped that the present method will be used to better understand the radical reactions, electron transfers, and electron attachment processes in chemistry and biochemical applications.

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Appendix

The Gaussian-2 theory[21] is a general composite procedure based on ab initio molecular orbital theory for computing very accurate enthalpies of formation, leading to accurate dissociation energies, ionization energies, electron affinities, and proton affinities. Treatment of electron correlation is by Møller−Plesset (MP) and quadratic configuration interaction methods (QCI). The 6-311G(d,p) basis set is used, and several basis set extension corrections are computed, making certain assumptions about additivity of correlation and basis set effects.

The procedure can be summarized as follows: (i) Geometry optimizations are carried out at the HF/6-31G(d) level, and harmonic frequencies are calculated, which are then scaled by a factor of 0.893 to take account of known deficiencies at this level. (ii) Geometries are then refined at the MP2(full)/6-31G-(d) level using HF/6-31(d) geometry and Cartesian frequencies as an initial input. (iii) Single-point calculations at the MP4/6-311G(d,p) level are carried out. (iv) A correction, Δ(QCI), for higher correlation effects is evaluated as

$$\Delta(\mathrm{QCI}) = E[\mathrm{QCI/6\text{-}311G(d,p)}] - E[\mathrm{MP4/6\text{-}311G(d,p)}]$$

(v) A correction Δ(+) for diffuse functions is estimated as

$$\Delta(+) = E[\mathrm{MP4/6\text{-}311{+}G(d,p)}] - E[\mathrm{MP4/6\text{-}311G(d,p)}]$$

(vi) A correction Δ(2df) for higher polarization functions is estimated as

$$\Delta(\mathrm{2df}) = E[\mathrm{MP4/6\text{-}311G(2df,p)}] - E[\mathrm{MP4/6\text{-}311G(d,p)}]$$

(vii) A second correction Δ(ExtraBasis) for basis set incompleteness is estimated as

$$\Delta(\mathrm{ExtraBasis}) = E[\mathrm{MP2/6\text{-}311{+}G(3df,2p)}] - E[\mathrm{MP2/6\text{-}311G(2df,p)}] - E[\mathrm{MP2/6\text{-}311{+}G(d,p)}] + E[\mathrm{MP2/6\text{-}311G(d,p)}]$$

(viii) A final small higher-level empirical correction (HLC) is appended to the energy to accommodate remaining deficiencies,

$$\Delta(\mathrm{HLC}) = -5n_{\mathrm{pairs}} - 0.19n_{\mathrm{unpaired}}$$

where n_{pairs} is the number of valence electron pairs and n_{unpaired} is the number of unpaired electrons in the system. Δ(HLC) is expressed in millihartrees. (ix) Then, the scaled vibrational frequencies calculated at the HF/6-31G(d) are used to estimate the zero-point-vibration energy (ZPE). The G2 (0 K) E_0 energy is then given by the following expression:

$$E_0 = \mathrm{MP4/6\text{-}311G(d,p)} + \Delta(\mathrm{QCI}) + \Delta(+) + \Delta(\mathrm{2df}) + \Delta(\mathrm{ExtraBasis}) + \Delta(\mathrm{HLC}) + \mathrm{ZPE}$$

References and Notes

(1) Halliwell, B.; Gutteridge, J. M. C. *Free Radicals in Medicine and Biology*, 3rd ed.; Oxford University Press: New York, 1999.

(2) Desfrançois, C.; Abdoul-Carime, H.; Carles, S.; Périquet, V.; Scherman, J. P.; Smith, D. M. A.; Adamowicz, L. *J. Chem. Phys.* **1999**, *110*, 11876.

(3) Chen, E. C. M.; Chen, E. S. *J. Phys. Chem. B* **2000**, *104*, 7835.

(4) Valentine, S. J.; Anderson, J. G.; Ellington, A. D.; Clemmer, D. E. *J. Phys. Chem. B* **1997**, *101*, 3891.

(5) Velazquez, I.; Reimann, C. T.; Tapia, O. *J. Phys. Chem. B* **2000**, *104*, 2546.

(6) Favaudon, V.; Tourbez, H.; Houée-Levin, C.; Lhoste, J. M. *Biochemistry* **1990**, *29*, 10978.

(7) Lmoumene, C. E.; Conte, D.; Jacquot, J. P.; Houée-Levin, C. *Biochemistry* **2000**, *39*, 9295.

(8) Nakamura, H.; Nakamura, K.; Yodoi, J. *Annu. Rev. Immunol.* **1997**, *15*, 351.

(9) Baker, A.; Payne, C. M.; Briehl, M. M.; Powis, G. *Cancer Res.* **1997**, *57*, 5162.

(10) Gallegos, A.; Berggren, M.; Gasdaska, J. R.; Powis, G. *Cancer Res.* **1997**, *57*, 4965.

(11) Mezyk, S. P. *Chem. Phys. Lett.* **1995**, *235*, 89.

(12) Karmann, W.; Meissner, G.; Henglein, A. *Z. Naturforsch.* **1967**, *B22*, 273.

(13) Karmann, W.; Granzow, A.; Meissner, G.; Henglein, A. *Int. J. Radiat. Phys. Chem.* **1969**, *1*, 395.

(14) (a) Schöneich, C.; Aced, A.; Asmus, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 375. (b) Schöneich, C.; Aced, A.; Asmus, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 11376. (c)Schöneich, C.; Bobrowski, K. *J. Phys. Chem.* **1994**, *98*, 12613. (d) Kishore, K.; Anklam, E.; Aced, A.; Asmus, K.-D. *J. Phys. Chem. A* **2000**, *104*, 9646.

(15) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F., III; Nandi, S.; Ellison, G. B. *Chem. Rev.* **2002**, *102*, 231.

(16) Lineberger, W. C. In *Chemical and Biochemical Applications of Lasers*; Moore, C. B., Ed.; Academic Press: New York, 1974; Vol. 1, pp 71−101.

(17) Lineberger, W. C. *Laser Spectroscopy*; Plenum Publishing: New York, 1975.

(18) Mead, R. D.; Stevens, A. E.; Lineberger, W. C. *Ions and Light*; Academic Press: Orlando, FL, 1984.

(19) (a) Bally, T.; Narahari, S. *J. Phys. Chem. A* **1997**, *101*, 7923. (b) Zhang, Y.; Yang, W. *J. Chem. Phys.* **1998**, *109*, 2604. (c) Sodupe, M.; Bertran, J.; Rodriguez-Santiago, L.; Baerends, E. J. *J. Phys. Chem. A* **1999**, *103*, 166.

(20) Braïda, B.; Savin, A.; Hiberty, P. C. *J. Phys. Chem. A* **1998**, *102*, 7872.

(21) (a) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. (b) Curtiss, L. A.; Raghavachari, K. In *Computational Thermochemistry*; Irikura, K. K., Frurip, D. J., Eds.; ACS Symposium Series 677; American Chemical Society: Washington, DC, 1998; Chapter 10, p 176.

(22) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 42.

(23) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(24) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.

(25) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Baboul, A. G.; Pople, J. A. *Chem. Phys. Lett.* **1999**, *314*, 101.

(26) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 7374.

(27) Petersson, G. A. In *Computational Thermochemistry*; Irikura, K. K., Frurip, D. J., Eds.; ACS Symposium Series 677; American Chemical Society: Washington, DC, 1998; Chapter 13, p 237.

(28) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843.

(29) Carles, S.; Lecomte, F.; Schermann, J. P.; Desfrançois, C.; Xu, S.; Nilles, J. M.; Bowen, K. H.; Bergès, J.; Houée-Levin, C. *J. Phys. Chem. A* **2001**, *105*, 5622.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(31) (a) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (b) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. (c) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513.

(32) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(33) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(34) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(35) Braïda, B.; Lauvergnat, D.; Hiberty, P. C. *J. Chem. Phys*. **2001**, *115*, 90.

(36) Braïda, B.; Hiberty, P. C. *J. Phys. Chem. A* **2000**, *104*, 4618.

(37) Hiberty, P. C.; Humbel, S.; Danovitch, D.; Shaik, S. *J. Am. Chem. Soc.* **1995**, *117*, 9003.

(38) Gill, P. M. W.; Radom, L. *J. Am. Chem. Soc.* **1988**, *110*, 4931.

(39) Braïda, B.; Hazebroucq, S.; Hiberty, P. C. *J. Am. Chem. Soc*. **2002**, *124*, 2371.

(40) Illies, A. J.; Livant, P.; McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 7980.

(41) Deng, Y.; Illies, A. J.; James, M. A.;. McKee, M. L; Peschke, M. *J. Am. Chem. Soc.* **1995**, *117*, 420.

(42) McKee, M. L. *Chem. Phys. Lett.* **1990**, *165*, 265.

(43) Clark, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672.

(44) Hiberty, P. C.; Humbel, S.; Archirel, P. *J. Phys. Chem.* **1994**, *98*, 11697.

(45) Mallard, W. G., Linstrom, P. J., Eds. *NIST Chemistry Webbook*; NIST Standard Reference Database Number 69; National Institute of Standards and Technology: Gaithersburg, MD, February 2000 (http://webbook.nist.gov/chemistry/form-ser.html).

(46) Breyer, F.; Frey, P. Hotop, H. *Z. Phys. A* **1981**, *300*, 7.

(47) Schwartz, R. L.; Davico, G. E.; Lineberger, W. C. *J. Electron Spectrosc. Relat. Phenom.* **2000**, *108*, 163.

(48) Janousek, B. K.; Reed, K. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 3125.

(49) Schmider, H. L.; Becke, A. D. *J. Chem. Phys.* **1998**, *109*, 8188.