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IMOMO-G2MS Approaches to Accurate Calculations of Bond Dissociation Energies of Large Molecules

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Accurate calculations were performed for single bond dissociation energies using the IMOMO (integrated MO + MO) method, a version of the ONIOM method, with a variety of molecular orbital (MO) combinations and were compared with the experimental values. The dissociation energies studied are for the C−H bond of benzene (with ethylene and butadiene as a model system), the C−F bond of fluorobenzene (model CH_2═CHF), the C−CH_3 bond of toluene (model CH_2═CH−CH_3), the Si−H bond of phenylsilane $C_6H_5SiH_2$−H (models of CH_2═$CHSiH_2$−H and SiH_3−H), the O−H bond of *n*-propanol, isopropanol, *n*-butanol, and *t*-butanol (model H_2O), the C−S bond of $PhCH_2$−SCH_3 (model CH_3−SH), and the O−O bond of SF_5O−OSF_3 (model HO−OH). The IMOMO(G2MS(R):ROMP2/6-31G(d)) calculation, which uses G2MS(R) for the model dissociation and ROMP2/6-31G(d) for the substituent effect, at the B3LYP/6-31G(d) (or sometimes /6-31G) optimized geometries (and zero-point corrections) using two non-hydrogen-atom model systems, A−B for the A−B bond or AB−H for the B−H bond, is found to consistently give an accurate bond dissociation energy within a few kcal/mol of the experimental value. This recommended scheme provides estimates of accurate bond energies for very large molecules, for which experimental values are rarely known, with a small additional cost beyond B3LYP/6-31G(d) geometry optimizations and MP2/6-31G(d) single-point energies.

I. Introduction

Quantum chemistry has made great strides toward the quantitative prediction of chemical properties. High-level ab initio methods, such as the coupled cluster method with single and double excitations with perturbation correction for triples, CCSD(T)[1] with a very large basis set, reach chemical accuracy. Various extrapolation schemes toward such limits, such as G2,[2] CBS,[3] G2M,[4] and G2MS,[5] have been proposed. However, the largest problem of these accurate methods is the high-order dependency of the computational efforts on the size of the system, which limits their applicability to rather small molecules consisting of up to seven or eight non-hydrogen atoms. On the other hand, some quantum chemical methods, including the local correlation technique within the ab initio molecular orbital (MO) method[6] and density functional theory,[7] in particular with linear scaling methods,[8] can handle large molecular systems.

Over the years, a number of hybrid quantum mechanics/molecular mechanics (QM/MM) methods have been suggested to circumvent the problems of larger systems.[9] Recently, we have introduced a new integrated approach ONIOM,[10−13] which can combine different levels of theoretical methods (various levels of MO methods as well as MM methods) within a large molecular system (real system), using multiple layers of model systems. This method can be considered as an extrapolation scheme for the size of the system and gives an estimate of the energy at the highest level of theory for the real system.[12b] The integrated MO + MO method (IMOMO) method, a two-layer version of ONIOM, has been shown to be invaluable for accurate energy calculations of medium-sized systems.[12] The generalized multilayered ONIOM approach has been tested for more than two layers and shown to be valuable in certain instances.[13]

The prediction of bond dissociation energies[14] has long been a task of quantum chemistry. It is well recognized that highly accurate procedures including high levels of electron correlation, such as CCSD(T) or G2-type methods, are required to predict dissociation energies accurately. It is therefore rather difficult to accurately calculate bond dissociation energies for molecular systems that are too large for direct application of G2-type methods. One can recognize, however, that the bond dissociation is a rather local phenomenon. While very high levels of electron correlation are required for the local region of the bond to be broken, often the effects of the nearby substituent atoms can be handled with a lower level of electron correlation treatment. Therefore, the IMOMO method, which can exactly do this, may be an ideal method for accurate prediction of bond dissociation energies of large molecular systems.

Our goal in the present work is to examine whether the IMOMO method can be used to accurately determine bond dissociation energies of a variety of molecular systems. We chose several systems, containing 6−14 non-H atoms, for which experimental values of the bond dissociation energy are available and can be compared with the calculation for validation of the computational method. Geometries will be determined with a standard density functional theory, which is known to provide excellent optimized geometries in many cases, and the IMOMO method will be used for energetics. We will adopt relatively small models for which high-level methods such as MP4, CCSD(T), and G2MS can be used. By use of the G2MS procedure, up to seven or eight heavy atoms can easily be included in the model, but our preference is to use a maximum of three or four to make the procedure computationally more attractive. In fact, for many systems, we would like to test only the two atoms (with attached hydrogens) directly involved in the bond-breaking procedure as the model. Different low-level

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methods will be studied with the focus being on SCF and MP2. We note two recent papers in which the IMOMO procedure was used to predict accurate bond energies on a series of simple saturated hydrocarbon systems.[15]

II. Computational Methods

All calculations were carried out with the Gaussian94 program.[16] Geometries were optimized using the gradient-corrected hybrid B3LYP method.[17] The 6-31G,[18] 6-31G(d), and 6-311G(d,p)[19] basis sets were used for the optimizations. All the zero-point corrections (ZPC) were taken from analytical frequency calculations for these optimized structures. The spin contamination in the B3LYP calculations for radical species is rather small; the worst case is the $PhCH_2$ radical as part of $PhCH_2-SCH_3$, which had the expectation value of the $\mathbf{S}^2$ operator ($\langle \mathbf{S}^2 \rangle$) of 0.784, with most others within the 0.75−0.77 range. Single-point energy predictions were made at various nonintegrated (normal) MO methods and also by use of the IMOMO method with a variety of combinations of levels of MO methods. In the IMOMO method, the total energy E(IMOMO) is defined as[10,12]

$$E(\text{IMOMO}) = E(\text{high,model}) + E(\text{low,real}) - E(\text{low,model})$$

where “high” and “low” refer to the levels of theory and “model” and “real” refer to the size of the system. E(IMOMO) is an extrapolated estimate for E(high,real), the energy of the real system at the high level, which is too expensive to calculate. The model systems are defined from the real system by breaking certain bonds and mending the broken bonds with hydrogens. These hydrogens possess the same angle and torsion values as the atoms of the real system and are assumed to have standard X−H bond lengths, for example, 1.085 Å for C−H, 0.98 Å for O−H in both alcohols and SF_5OOSF_5, and 1.38 Å for S−H.

While we have tested many combination of various MO methods in IMOMO, the IMOMO(G2MS(R):MP2/6-31G(d)) is the highest level of theory we adopted. G2MS is a simplified version of the G2-type extrapolation method,[5] with the definition

$$E[\text{G2MS}] = E[\text{CCSD(T)/6-31G(d)}] + E[\text{MP2/6-311+G(2df,2p)}] - E[\text{MP2/6-31G(d)}]$$

Here, the MP2/6-31G(d) energy is the starting point. The higher correlation effect is evaluated at the CCSD(T) level with the 6-31G(d) basis set, and the effect of a larger basis set is evaluated with the 6-311+G(2df,2p) basis set at the MP2 level to estimate the results at the CCSD(T)/6-311+G(2df,2p) level. Thus, the IMOMO(G2MS:MP2/6-31G(d)) method can be considered to be a triple extrapolation scheme for the basis set, the correlation, and the substituent effects.[12b] The difference between the G2MS(R) and G2MS(U) is whether the basis set correction is calculated at the second-order restricted open shell (ROMP2) or unrestricted (UMP2) perturbation theory level in the dissociation limit (for the undissociated closed-shell molecule, the restricted MP2 is always used). For CCSD(T) we always used the UCCSD(T) method available in Gaussian. The HLC term in the original G2MS method is neglected.

III. Aromatic Systems

At first, we tested the dissociation energies of C−X single bonds in aromatic systems, including benzene (C−H), fluorobenzene (C−F), toluene ($C-CH_3$), and $PhSiH_3$ (Si−H). These systems may be more difficult to treat using the IMOMO method, as the bond to be broken is next to or a part of a conjugated system. Care has to be taken for spin contamination problems, which can lead to spurious results.

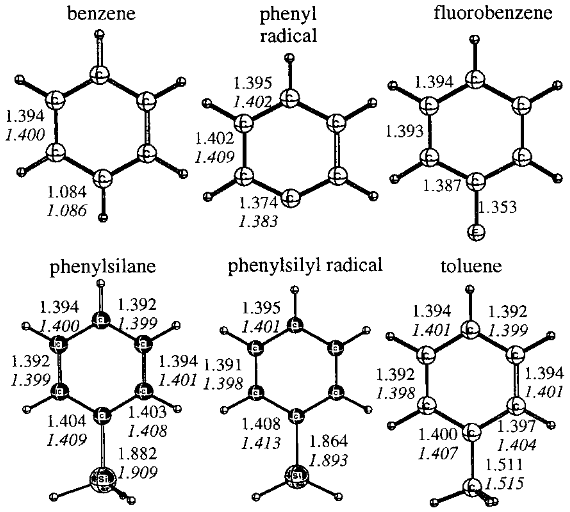


Figure 1. Important optimized bond distances (in Å) of benzene, the phenyl radical, fluorobenzene, toluene, phenylsilane, and the phenylsilyl radical using the B3LYP method with the 6-311G(d,p) and 6-31G (in italic) basis sets.

A. C−H Bond Dissociation Energy in Benzene. In this section, we will at first examine the C−H bond dissociation energy of benzene using the nonintegrated G2MS method. We will then examine benzene using the IMOMO method with models of ethylene (2C model) and butadiene (4C model) and compare these with our benchmark G2MS results. Figure 1 shows some of the important geometrical features of benzene and the phenyl radical optimized at the B3LYP level using the 6-311G(d,p) and 6-31G basis sets. There is no major difference in the geometries despite the more than twice as large basis set utilized (144−66 basis functions).

Table 1 shows the C−H bond dissociation energy of benzene calculated at various levels of theory using both nonintegrated (normal) MO and IMOMO approaches. For the nonintegrated calculations, it can be seen that the G2MS methods give 111.2 (U) or 111.5 (R) kcal/mol, in excellent agreement with experimental results and within the experimental error bars.[14] The only other method that agrees with the experiment for this compound is B3LYP with either 6-311G(d,p) or 6-31G. Of the other nonintegrated methods, ROMP2/6-31G(d) gives the best value at 102.8 kcal/mol, while UMP2/6-31G(d) is poor because of the spin contamination in the phenyl radical. CCSD(T)/6-31G(d) still has an error of 6 kcal/mol due to the small basis set.

In the IMOMO approach, we have examined the two different model systems depicted in Figure 2, the butadiene (4-C) model and the ethylene (2-C) model. It should be reminded that the geometrical parameters of these models are taken from those of benzene and thus are different from those of free ethylene or butadiene. The results of the IMOMO calculations in Table 1 clearly show that of the low-level methods to be used in conjunction with the high-level G2MS methods, the Hartree−Fock (HF) approach is inappropriate and the use of MP2 is required to attain accuracy. We have previously recognized that G2MS:HF is a poor combination, as HF is unable to take care of the substituent effect with the same accuracy as the high-precision G2MS does for the bond breaking.[12b]

As mentioned earlier, spin contamination is a serious problem in the bond dissociation. For instance, $\langle \mathbf{S}^2 \rangle$ is 1.13 (UHF/6-31G-

TABLE 1: Calculated Bond Dissociation Energies (in kcal/mol) for the Breaking of C−H, C−F, C−CH$_3$, and Si−H Bonds in Benzene, Fluorobenzene, Toluene, and Phenylsilane, Respectively, with Various Nonintegrated MO and IMOMO Methods, Using Either 2C (CH$_2$=CH$_2$, CH$_2$=CHF, CH$_2$=CHCH$_3$, CH$_2$=CHSiH$_3$, Respectively) or 4C (Butadiene in Benzene) Models for the IMOMO Method[a]

geometry	benzene: C−H /6-311G(d,p)		benzene: C−H /6-31G	C$_6$H$_5$F: C−F /6-311G(d,p)	toluene: C−C /6-311G(d,p)	C$_6$H$_5$SiH$_3$: Si−H /6-311G(d,p)	
nonintegrated							
B3LYP/6-311G(d,p)	109.1		122.2	95.5	86.5		
B3LYP/6-31G			110.2				
UHF	79.5		78.9	75.3	66.0	70.5	
ROHF	88.4		88.4	86.1	77.7	70.6	
UMP2	126.2		126.1	150.0	126.9	82.4	
ROMP2	102.8		102.9	126.6	104.5	77.5	
UMP4	114.6						
CCSD	104.2						
CCSD(T)	104.4						
G2MS(R)	111.5						
G2MS(U)	111.2						
IMOMO model	4-C	2-C	2-C	2-C	2-C	2-C	0-C
UMP2:UHF	131.6	110.5	110.7	135.2	109.9	91.2	79.0
G2MS(U):UHF	125.3	109.8	109.7	126.1	100.5	92.2	88.0
UMP4:UMP2	120.3	124.3	124.2	140.2	120.1	81.1	84.2
CCSD:UMP2	109.8	117.8	117.5	132.6	112.9	76.2	84.2
CCSD(T):UMP2	111.2	118.4	118.2	135.0	115.0	76.5	84.3
G2MS(U):UMP2	119.9	125.4	125.2	140.8	117.5	83.4	91.4
G2MS(R):UMP2	117.8	124.9	124.6	140.2	115.8	83.3	91.4
G2MS(U):ROMP2	114.0	109.8	109.9	125.2	101.9	86.2	86.3
G2MS(R):ROMP2	112.0	109.3	109.3	124.6	100.3	86.2	86.3
experiment[b]	(110.9−111.3) ± 2			125.7 ± 2	101.8 ± 2	88.2	

[a] The 6-31G(d) basis set is used in all MO and IMOMO calculations, excluding G2MS or if not specified. All the calculations use optimized geometries and zero-point corrections at the B3LYP level with either the 6-31G or 6-311G(d,p) basis set. [b] Experimental values from ref 14.

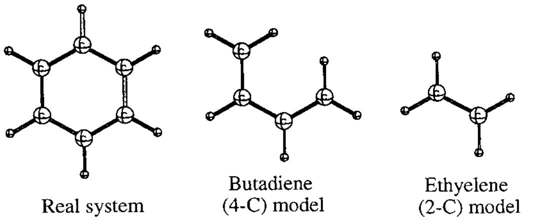


Figure 2. For benzene, an illustration of the real system (benzene), the butadiene (4-C) model system, and the ethylene (2-C) model system as used for the IMOMO calculations.

(d)) and 1.09 (UHF/6-311+G(2df,2p)) for the C$_2$H$_3$ radical in the C-2 model, 1.63 (UHF/6-31G(d)) and 1.61 (UHF/6-311+G-(2df,2p)) for the C$_4$H$_5$ radical in the C-4 model, and 1.39 (UHF/6-31G(d)) and 1.35 (UHF/6-311+G(2df,2p)) for the phenyl radical in the benzene real system. In the IMOMO(G2MS:low) scheme, there are two terms where spin contamination can play an important role. The first is the G2MS basis set correction [MP2/6-311+G(2df,2p) − MP2/6-31G(d)]. In this correction, the two $\langle \mathbf{S}^2 \rangle$ values are nearly the same regardless of the C-2 or C-4 models; thus, the errors are expected to cancel out to a certain extent. Thus, if we compare the G2MS(U):ROMP2 and G2MS(R):ROMP2, we find that this is true, although there is a difference of as much as 2.0 kcal/mol. The second effect should be significantly more important. As in the previous case, the IMOMO substituent correction [MP2/6-31G(d)$_{\text{real}}$ − MP2/6-31G(d)$_{\text{model}}$] also involves badly spin-contaminated wave functions, but in this case, the two wave functions are contaminated to differing degrees. For example in the 2-C model system, the correction term MP2$_{\text{real}}$ ($\langle \mathbf{S}^2 \rangle = 1.39$) − MP2$_{\text{model}}$ ($\langle \mathbf{S}^2 \rangle = 1.11$) involves wave functions with differing degrees of spin contamination. Thus, we would anticipate that the use of unrestricted open-shell methods for the substituent effects would leave some spin contamination effects uncanceled. Therefore, it is much more desirable to use a restricted open-shell method as the low level of the IMOMO method. Indeed, the difference between the G2MS(R):UMP2 and G2MS(R):ROMP2 for the 2-C model is as large as 15.6 kcal/mol. Thus, our best predictions for the C−H bond dissociation energy in benzene are at the IMOMO-(G2MS(R):ROMP2) level and are 112.0 kcal/mol for the 4-C model and 109.3 kcal/mol for the 2-C model, both in good agreement with experimental values. Apparently, for the estimation of the C−H bond dissociation energy, the effect of conjugation through the carbon atom to which the hydrogen atom is bound is not very large, as much as 3 kcal/mol.

A second test that we have undertaken is performing a much cheaper geometry optimization of benzene and the radical at the B3LYP/6-31G level as well as the vibrational frequencies and zero-point corrections (ZPC). As indicated in Figure 1, geometrical changes are not very significant. A comparison of the energies at all nonintegrated and IMOMO methods between B3LYP/6-31G and B3LYP/6-31G(d) optimized geometries showed how similar the values were and the highest level prediction, G2MS(R):ROMP2, is exactly the same for two optimized geometries. This is probably more likely for molecules without heteroatoms, like benzene. We will, nonetheless, utilize this result later when we perform optimizations at the B3LYP/6-31G level before doing higher level IMOMO single-point energy calculations.

B. C−F and C−C Bond Dissociation Energies in Fluorobenzene and Toluene. The middle columns of Table 1 also show a variety of bond dissociation energy results for two substituted benzene systems: fluorobenzene and toluene. In both of these systems, geometries were optimized at the B3LYP/6-311G(d,p) level. At this level of theory, the C−F bond dissociation energy is too low by 3.5 kcal/mol for fluorobenzene and the C−CH$_3$ bond dissociation energy in toluene is too low by 6.3 kcal/mol, not a bad performance for an inexpensive method. Among the nonintegrated ab initio methods, the

TABLE 2: Calculated Bond Dissociation Energies (in kcal/mol) for the Breaking of the O−H Bond in a Series of Alcohols, *n*-Propanol, Isopropanol, *n*-Butanol, *t*-Butanol, with Various Nonintegrated MO and IMOMO Methods (with the H−O−H Model)[a]

	n-propanol	isopropanol	*n*-butanol	*t*-butanol
nonintegrated				
B3LPY/6-31G (6-31G(d))	91.3 (94.2)	91.6 (94.7)	89.7 (92.9)	92.4 (95.2)
UHF	63.9 (65.1)	63.9 (65.1)	62.5 (63.6)	64.4 (65.5)
ROHF	66.8 (68.1)	69.2 (71.5)	65.3 (66.5)	69.6 (71.6)
UMP2	93.5 (93.9)	94.1 (94.5)	92.0 (92.5)	94.8 (95.2)
ROMP2	93.5 (93.9)	97.0 (98.7)	92.0 (92.5)	97.8 (99.2)
IMOMO				
UMP2:UHF	93.7 (94.3)	93.4 (94.3)	91.8 (92.3)	94.3 (94.9)
G2MS(U):UHF	103.1 (103.3)	102.8 (103.0)	101.1 (101.2)	103.9 (104.2)
UMP4:UMP2	89.8 (90.3)	90.3 (90.9)	88.3 (88.8)	91.0 (91.6)
CCSD:UMP2	89.2 (89.6)	89.7 (90.2)	87.6 (84.5)	90.5 (91.0)
CCSD(T):UMP2	89.5 (89.8)	89.9 (90.4)	87.8 (88.3)	90.8 (91.2)
G2MS(U):UMP2	102.9 (103.0)	103.5 (103.5)	101.3 (101.4)	104.4 (104.5)
G2MS(R):UMP2	102.6 (102.6)	103.1 (103.1)	101.0 (101.1)	104.1 (104.1)
G2MS(U):ROMP2	101.5 (100.8)	102.7 (102.8)	98.5 (97.8)	105.1 (105.4)
G2MS(R):ROMP2	101.2 (100.5)	102.3 (102.4)	98.3 (97.5)	104.7 (105.1)
experiment[b]	103.4 ± 1	104.7 ± 1	102.9 ± 1	105.1 ± 1

[a] The 6-31G(d) basis set is used in all MO and IMOMO calculations, excluding G2MS or if not specified. All use optimized geometries at the B3LYP level with the 6-31G and 6-31G(d) (in parentheses) basis sets, with zero-point corrections from the B3LYP/6-31G calculation. [b] Experimental values from ref 14.

ROMP2 values are the closest to the experimental values and are better than the B3LYP values.

For the integrated calculations, models adopted are of 2-C type, $CH_2{=}CHF$ and $CH_2{=}CHCH_3$, respectively. Again, the ROMP2 method is far superior to the UMP2 method for the IMOMO substituent effects. For fluorobenzene, our highest level calculation G2MS(R):ROMP2 leads to a calculated C−F bond energy of 124.6 kcal/mol, which is within the experimental error bars.[14] Similarly, the $C-CH_3$ bond energy in toluene of 100.3 kcal/mol is also within the error limits of the experiment.[14] It should be noted that the C−F bond energy calculated purely from the $CH_2{=}CHF$ model G2MS(R) leads to a value of 122.7 kcal/mol and the ROMP2 substituent effects ($\mathrm{ROMP2_{real}} - \mathrm{ROMP2_{model}}$) correct this value by +1.9 kcal/mol, leading to the 124.6 kcal/mol. As long as the carbon atom is of sp^2 type, the C−F dissociation energy does not seem very much affected whether the carbon is conjugated in an aromatic ring or on an isolated C═C bond. For toluene, the effects are similar, since the $CH_2{=}CHCH_3$ model gives a value of 97.5 kcal/mol for the $C-CH_3$ bond dissociation energy while the correction from the remainder for the benzene ring adjusts this value by only +2.8 kcal/mol.

While the B3LYP/6-311G(d,p) method appears to be giving good results for these calculations, it should be noted that the computer time required to perform a single-point calculation for the bond dissociation energy with the IMOMO(G2MS(R):ROMP2) method for fluorobenzene with a $CH_2{=}CHF$ model was approximately only equal to a B3LYP/6-311G(d,p) single gradient calculation. Clearly, these predictions require trustworthy geometries, but it appears that the most efficient method is the use of B3LYP/6-31G geometries and frequencies and the IMOMO(G2MS(R):ROMP2/6-31G(d)) energies.

C. Si−H Bond Dissociation Energy in Phenylsilane, $C_6H_5SiH_3$. The Si−H bond dissociation energy in phenylsilane, $C_6H_5SiH_3$, was examined with the IMOMO procedure. In this case, the geometries were optimized at the B3LYP/6-311G(d,p) and B3LYP/6-31G levels, and these are shown in Figure 1. The IMOMO calculations were only made on the larger basis set geometries. Unlike the benzene case where the lack of a polarized triple-ζ basis set still led to accurate C−H dissociation energies, this was not the case here as the B3LYP/6-31G method predicted an Si−H bond energy of 81.8 kcal/mol, too low by 6.4 kcal/mol. The B3LYP/6-311G(d,p) improved the results to within 2 kcal/mol of experimental value.

Two different models were used for the IMOMO calculations: an extremely small SiH_4 (0C) model and a $CH_2{=}CHSiH_3$ (2C) model. The small model led to less spin contamination problems of the UHF wave function compared with the other conjugated systems involved. The larger model has spin contamination problems; thus, the best comparison is still to use the G2MS(R):ROMP2 method with either model. In both of these model systems, the substituents play a small role, since the G2MS(R) values for only the model are 87.3 kcal/mol for the small model and 85.1 kcal/mol for the larger model. The substituent corrections at the ROMP2/6-31G(d) level are −1.0 and 1.1 kcal/mol, leading to almost identical results for the Si−H bond dissociation energies of 86.3 and 86.2 kcal/mol, respectively. These values are within 2 kcal/mol of experimental results.[14]

IV. O−H Bond Dissociation Energies in Alcohols

The O−H bond dissociation energies of a series of alcohols, namely, *n*-propanol, isopropanol, *n*-butanol, and *t*-butanol, were examined. The conformations of the alcohols were assumed to have the longest alkyl group anti to the OH group. Since the energy differences between different stable conformers are within 1.0 kcal/mol,[20] the error due to this assumption should be small. The results are shown in Table 2 based on the B3LYP/6-31G and /6-31G(d) (parentheses) geometries. The results indicate how insensitive the integrated calculations are to the geometries. Therefore, the discussions here will be based on the cheaper calculations, i.e., the 6-31G geometries. In all systems, the model in the IMOMO calculation was taken to be water, H−O−H. A comparison of the highest level IMOMO calculation with experiment indicates that we underestimate the dissociation energies in all cases. The calculated (G2MS(R):ROMP2)/experimental values for the four systems are the following: *n*-propanol, 101.2/103.4; isopropanol, 102.3/104.7; *n*-butanol, 98.3/102.9; *t*-butanol, 104.7/105.5 kcal/mol, with the error ranging from 1.2 to 4.6 kcal/mol.[14] In comparison with experimental results, these values are the most inaccurate of all studied in this paper. The B3LYP/6-31G energies are in error in the absolute values by 12−13 kcal/mol, and this error is corrected somewhat with additional polarization functions on oxygen, although there still is a 10% error.

The difference in the bond dissociation energies between two alcohols in the IMOMO method using the same model system can be expressed as

$$\begin{aligned}\Delta\Delta E(\text{IMOMO}) &= \Delta\Delta E(\text{high,model}) + [\Delta\Delta E(\text{low,real}) - \Delta\Delta E(\text{low,model})] \\ &= \Delta\Delta E(\text{high,model}) + \Delta\Delta S(\text{low})\end{aligned}$$

i.e., as a sum of the contribution of the strain energy of the model part (HOH), $\Delta\Delta E$(high, model), and the contribution of the effect of the substituents, $\Delta\Delta S$(low). The largest difference in bond dissociation energies among the four alcohols (*t*-butanol − *n*-butanol, 6.4 kcal/mol at the best IMOMO(G2MS:ROMP2) level) was found to consist of $\Delta\Delta E$(G2MS,HOH) = 1.1 kcal/mol and $\Delta\Delta S$(ROMP2,*t*-butanol−*n*-butanol) = 5.3 kcal/mol. The effect of the strain energy in the HOH part is small, as expected for noncyclic structures that are relatively strain-free. The 5.3 kcal/mol substituent effect contribution can further be divided into $\Delta\Delta$S(ROMP2,*t*-butanol−water) = 2.6 kcal/mol + $\Delta\Delta S$(ROMP2,*n*-butanol−water) = −2.7 kcal/mol. The bond dissociation energy is increased upon going from water to *t*-butanol by 2.6 kcal/mol, while it is decreased from water to *n*-butanol by 2.7 kcal/mol.

V. Dissociation Energies in Two Larger Molecules

The IMOMO method is suited to handle larger systems. Up to this point, we have dealt with smaller systems where experimental results are known and benchmark calculations and comparison could be made. It has been shown that a model consisting of only the two bond-breaking atoms with the remaining atoms replaced with hydrogens can be successfully applied. Hence, we can use the IMOMO(G2MS(R):ROMP2) method for accurate calculation of bond dissociation energies of any system up to a size where the B3LYP/6-31G or /6-31G-(d) optimization and ROMP2/6-31G(d) single-point calculation can be performed. Here, we applied the method to two larger systems where experimental data were available, namely, the C−S bond dissociation in $PhCH_2-SCH_3$ and O−O bond dissociation in SF_5O-OSF_5, as shown in Table 3. We have done optimizations at both the B3LYP/6-31G and B3LYP/6-31G(d) levels of theory, but once again, we found that the B3LYP energies change but the IMOMO energies do not change very much. We have used the B3LYP/6-31G method for the zero-point corrections.

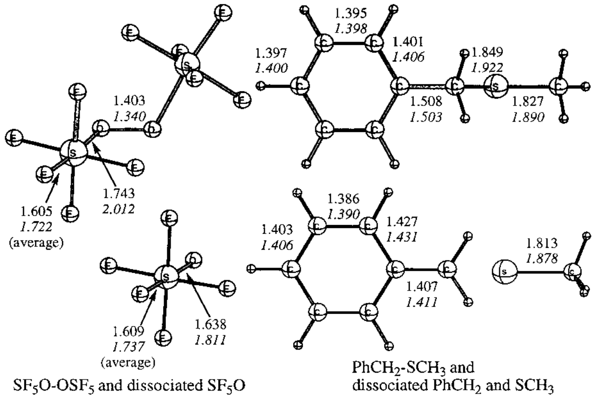
A. C−S Dissociation Energy in $PhCH_2-SCH_3$. The B3LYP/6-31G and B3LYP/6-31G(d) geometries of the full system and the two doublet radicals are shown in Figure 3. The molecule has a fully delocalized π-system on the phenyl ring. However, once the C−S is broken, the resultant benzyl radical is planar, with the odd π electron on the external CH_2 group conjugating with the π orbital of the ipso carbon of the phenyl group. Thus, the two phenyl C−C bond lengths next to the CH_2 substituent are slightly longer at 1.43 Å and the adjoining two C−C bond lengths are shorter.

The experimental value for the C−S bond dissociation energy in this molecule is 61.4 kcal/mol.[14] The density functional method with a small basis set B3LYP/6-31G leads to an underestimation of the dissociation energy by about 30%. The larger basis set B3LYP/6-31G(d) improves this value substantially, but it is still too low by 10 kcal/mol. The ROMP2/6-31G(d) method happens to be quite good in this case, differing from experimental results by less than 1 kcal/mol, although this is not in general the case.

TABLE 3: Calculated Bond Dissociation Energies (in kcal/mol) for the Breaking of the C−S Bond in $PhCH_2-SCH_3$ and the O−O Bond in $F_5SO-OSF_5$, with Various Nonintegrated MO and IMOMO Methods, Using CH_3-SH and HO−OH as Models, Respectively, for the IMOMO Method

	$PhCH_2-SCH_3$	$F_5SO-OSF_5$
nonintegrated		
B3LYP/6-31G (6-31G(d))	43.5 (50.8)	44.3 (33.6)
UHF/6-31G(d)	16.3 (18.6)	−57.4 (−25.7)
ROHF/6-31G(d)	37.2 (39.2)	−49.5 (−11.8)
UMP2/6-31G(d)	82.4 (83.8)	46.3 (49.5)
ROMP2/6-31G(d)	60.5 (62.3)	38.2 (38.2)
IMOMO		
UMP2:UHF	44.3 (46.7)	-6.6 (27.8)
G2MS(U):UHF	46.2 (48.1)	-7.2 (26.6)
UMP4:UMP2	78.8 (79.9)	37.1 (35.0)
CCSD:UMP2	78.1 (79.2)	36.5 (34.4)
CCSD(T):UMP2	80.2 (81.2)	39.1 (37.4)
G2MS(U):UMP2	80.2 (85.3)	45.8 (43.0)
G2MS(R):UMP2	83.5 (84.5)	45.4 (42.7)
G2MS(U):ROMP2	62.4 (63.7)	37.7 (37.0)
G2MS(R):ROMP2	61.6 (62.9)	37.3 (36.7)
experiment[b]	61.4 ± 2	37.2

[a] The 6-31G(d) basis set is used in all MO and IMOMO calculations, excluding G2MS or if not specified. All the calculations use optimized geometries at the B3LYP level and the 6-31G and 6-31G(d) (in parentheses) basis sets, with zero-point corrections from the B3LYP/6-31G calculation. [b] Experimental values from ref 14.



SF_5O-OSF_5 and dissociated SF_5O

$PhCH_2-SCH_3$ and dissociated $PhCH_2$ and SCH_3

Figure 3. Important optimized bond distances (in Å) of ground singlet state and dissociated doublet radical fragments of the SF_5O-OSF_5 and $PhCH_2S-CH_3$ systems, using the B3LYP method with the 6-31G(d) and 6-31G (in italic) basis sets.

For the simple model system of CH_3-SH, the G2MS(R) dissociation energy is 69.2 kcal/mol. The substituent effect from the model to real at the ROMP2/6-31G(d) level is −7.6 kcal/mol, which reduces the bond energy to the IMOMO (G2MS-(R):ROMP2/6-31G(d)) value of 61.6 kcal/mol for the real system. The result agrees almost exactly with the experimental value of 61.4 ± 2 kcal/mol. As noted before, if UMP2/6-31G-(d) is used for the substituent effect, there is a significant error (21.9 kcal/mol). In many of the cases examined here, the substituent effect or the model → real correction was not very large relative to the total dissociation energy. It is, however, substantial in this case, with a 7.6 kcal/mol effect of the substituents.

B. O−O Bond Dissociation Energy in SF_5O-OSF_3. The final example that we examined is the O−O dissociation energy in SF_5O-OSF_3. Once again, we have optimized the geometry using both the B3LYP/6-31G and B3LYP/6-31G(d) methods, as shown in Figure 3. The SF_5O-OSF_3 molecule has very weak

S−O bonds and a relatively strong O−O bond. The O−O bond length of 1.340 Å in $SF_5O{-}OSF_3$ at the B3LYP/6-31G(d) level can be compared to the much longer 1.531 Å in HO−OH at the same level. We would not expect 6-31G to be large enough with the presence of highly electronegative atoms. The optimization of this full system with polarization functions required about 5 times the resources than without these functions; thus, this example is another good test of sensitivity of the bond dissociation energy on the geometries used. In this case, the B3LYP/6-31G method overestimated the dissociation energy by 19% or 7.1 kcal/mol while the B3LYP/6-31G(d) method overcorrected the value and is too low by 3.6 kcal/mol or about 10%. The best of the nonintegrated methods was the ROMP2/6-31G(d) method, which gives a calculated value of 38.2 kcal/mol, differing from the experimental value by only 1.0 kcal/mol.

For the integrated predictions, we decided to use the smallest model feasible, that being hydrogen peroxide, HO−OH. Many of the integrated values shown in Table 3 give qualitatively good results. However, the best results are obtained when using our highest level, IMOMO(G2MS(R):ROMP2). This method leads to a calculated bond dissociation energy of 37.3 kcal/mol, only 0.1 kcal/mol off the experimental value.[14] By use of the better B3LYP/6-31G(d) geometries, which differed in the important O−O distance by 0.063 Å or 4.5%, the IMOMO(G2MS(R):ROMP2) dissociation energies were very similar at 36.7 kcal/mol, indicating once again that the IMOMO method is not very sensitive to the geometry. The highest level model prediction, G2MS(R), for the model system HOOH (with the geometry taken from the real system) was 42.5 kcal/mol. In many of the previously studied examples, the correction for the substituent effects, *S*(real−HOOH), was very small. In this case, however, the correction for substituent effects at our most reliable ROMP2/6-31G(d) level is quite large, −5.8 kcal/mol, leading to the G2MS(R):ROMP2 BDE of 36.7 kcal/mol. This is understandable because the substituent SF_5 is electronically very different from the hydrogen atom.

VI. Conclusions

Accurate calculations on dissociation energies of various single bonds have been made using the IMOMO method with a variety of MO combinations. The bonds treated here are the following: (1) C−H bond of benzene (with ethylene and butadiene as model), C−F bond of fluorobenzene (model $CH_2{=}CF{-}H$), $C{-}CH_3$ bond of toluene (model $CH_2{=}CH{-}CH_3$); (2) Si−H bond of phenylsilane $C_6H_5SiH_2{-}H$ (model $CH_2{=}CHSiH_2{-}H$); (3) O−H bond of *n*-propanol, isopropanol, *n*-butanol, and *t*-butanol (model H_2O); (4) C−S bond of $PhCH_2{-}SCH_3$ (model $CH_3{-}SH$); (5) O−O bond of $SF_5O{-}OSF_3$ (model HO−OH). These were chosen because of the availability of experimental values for comparison and the size of the molecules where a direct application of accurate methods (such as G2-type) required for accuracy is (or is becoming for small examples) prohibitive. The overall conclusion of the present study is that the IMOMO(G2MS(R):ROMP2/6-31G(d)) level of calculation at the B3LYP/6-31G(d) (or sometimes B3LYP/6-31G) optimized geometry (and zero-point correction) with two non-hydrogen-atom model system, A−B for A−B bond or AB−H for B−H bond, consistently gives accurate bond dissociation energy within a few kcal/mol.

A high level of electron correlation, such as CCSD(T), and a very large basis set are required for the model system in which the relevant bond is actually broken. Extrapolation schemes such as G2-type or CBS methods are suited for this purpose, and in particular, the relatively inexpensive and simple G2MS method is found to work very well. There is little difference between G2MS(R) and G2MS(U) methods, i.e., whether one used ROMP2 or UMP2 for the basis set correction for the model system. As to the low-level method whose role is to evaluate the substituent effect accurately, we found that ROMP2/6-31G(d) is the best choice for accuracy and cost. The HF method is not good enough for this purpose. The UMP2 for the dissociation product suffers seriously from the spin contamination, in particular, from the imbalance of the amount of spin contamination between the large real system and the small model system.

Concerning the choice of the model system for bond dissociation of a single bond, a model that includes only the two bond-breaking atoms and the attached hydrogens seems to be satisfactory, regardless of the size of the real molecule. Therefore, as the size of the real molecule grows, the cost of the *E*(high,model) calculation remains constant and the expense of doing the IMOMO(G2MS(R):ROMP2/6-31G(d)) calculation becomes determined only by the ability to calculate the MP2/6-31G(d) calculation for the real system, since the additional cost for improving from the MP2/6-31G(d) results, which are only qualitatively correct, to the IMOMO(G2MS(R):ROMP2/6-31G(d)) results, which are nearly quantitative, is such a small fraction of the cost for B3LYP/6-31G(d) (or B3LYP/6-31G) geometry optimization plus ROMP2/6-31G(d) single-point energy calculation. Therefore, this IMOMO(G2MS(R):ROMP2/6-31G(d))//B3LYP/6-31G(d) procedure is strongly recommended for any bond dissociation calculations and maybe for any other energy calculation. It should be noted that in this procedure no geometry optimization is performed with the ONIOM method, and therefore, one does not require any ONIOM optimization program such as that implemented in Gaussian 98.[21]

The largest errors relative to experiment in the present study were found for the O−H bond dissociation energies in a series of four alcohols: *n*-propanol, isopropanol, *n*-butanol, and *t*-butanol. It appears that a basis set larger than 6-31G(d) including a polarization function on H and a triple-ζ function may be required for MP2 calculations for the real system and possibly for CCSD(T) calculations for the model system. The HLC term, which was neglected in the present paper, may also be important for this example.

Encouraged with the success of the IMOMO(G2MS(R):ROMP2/6-31G(d)) method presented here, we recently applied a similar scheme to the breaking of the CC π bond and the full CC double bond in C_{60}.[22] We used a three-layered ONIOM method, with ethylene (2-C) as the "model" system to be treated by G2MS, with the "intermediate" system of naphthalene (10-C) by ROMP2/6-31G(d), and with the "real" system C_{60} by ROHF/6-31G. This scheme gave the CC π bond energy with an error of 1 kcal/mol compared with the experimental value.

During the present research, we have searched for experimental values of bond dissociation energies for large molecules but could not find many, especially systematic, results.[14] While the heat of formation is related to the breaking of all the bonds in a molecule and is "measured" directly in calorimetric measurements, the dissociation energy of a particular bond in a molecule is usually "derived" from thermal measurements and thermodynamic cycles involving energies of intermediate radical species, especially for large molecules.[14] Therefore, the bond dissociation energy is harder to obtain experimentally, despite the fact that often one is interested in the energy to break a particular bond in large molecules. Therefore, if one can calculate the bond dissociation energy accurately for large molecules and molecular systems, the merit would be tremendous. Further development of the ONIOM-based methods are highly desired.

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