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A new way of calculating bond dissociation energies

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INTRODUCTION

Knowledge of accurate values of homolytic bond dissociation energies (BDEs) is one of the prerequisites for the understanding of free radical reactions and reaction mechanism in general. BDEs lead to atomization and bond energies, which are used to characterize and to rationalize the nature of the chemical bond and molecular structure [1]. Therefore, considerable efforts have been devoted to the determination of BDEs for many molecules. However, even nowadays, with improved and refined techniques, experimentally determined BDEs rarely have an accuracy of ± 1 kcal/mol or better. Since BDEs are mostly based on experimental heats of formation and since these are extremely difficult to measure for dissociation products which are short-lived free radicals, errors as large as 5 kcal/mol are to be expected. This is reflected by the existing compilations of heats of formation and BDE values [2-13].

Theory does not have to cope with the difficulties of experiment, and, therefore, it has become a primary source for accurate molecular data. As a matter of fact, highly accurate BDE values have been obtained from *ab initio* calculations [14, 15]. But also in the case of theoretical BDEs, one has to pay a considerable price to get this accuracy. As is well known, simple restricted Hartree-Fock (RHF) theory fails to describe homolytic bond dissociation correctly. Unrestricted HF (UHF) theory describes homolytic bond dissociation qualitatively correctly but does not lead to reasonable BDE values. Therefore, one has to go beyond the HF level in order to get a better calculational description of bond dissociation. Highly accurate BDE values are obtained when multi-configuration SCF (MCSCF) is combined with CI in order to describe static and dynamic correlation in reactant and products adequately [15-20]. This, of course, requires considerable computational effort, and sufficiently accurate BDE values can only be obtained for relatively small molecules. Therefore, simpler

methods have been looked for, which may lead to reasonable BDE values. For example, single-determinant-based correlation methods such as Møller-Plesset perturbation theory [21] or configuration interaction (CI) have been tested [22]. Although calculated BDE values are better than HF results, differences as large as 50 kcal/mol from experimental values are not very encouraging. Recently, these investigations have been improved by including bond functions in the basis set used [23-26]. An additional improvement has been found by using coupled cluster (CC) theory rather than MP or CI methods [27].

An alternative way has been used by Pople and co-workers [28-30]. These authors considered combinations of bond dissociation reactions that lead to formal (isogyric) reactions with a constant number of unpaired electron spins. By using exact experimental data together with the computed BDE values, they were able to calculate BDEs for AH_n molecules with an accuracy of 1 kcal/mol or better.

While these more recent approaches for calculating BDEs are quite promising, it remains to be seen whether they can be applied in a routine way. For example, the use of bond functions leads to excellent results in the case of AH_n molecules [24-26], but extension of the calculations to heavy atom bond dissociation seems to increase the rms error in calculated BDE values to 10 and more kcal/mol [23]. Also, the use of isogyric reactions strongly depends on the availability of accurate heats of reaction for an appropriate reference reaction. This is the case for AH bond dissociation (reference reaction: $H_2 \rightarrow 2H$), but not necessarily for homolytic dissociation of an arbitrary bond AB.

In order to calculate BDE values for a variety of homolytic bond dissociation reactions including both AH and heavy atom bonds AA and AB at relatively low costs, it will be necessary to stick to methods that are similar in their cost requirements to HF and that can be run with basis sets of moderate size, for example split valence basis sets such as 6-31G(d) or 6-31G(d,p) [31]. Such a method, of course, should start from a wavefunction that describes dissociation correctly. This implies that the method in question has to be based on a small MCSCF approach which covers the most important static (non-dynamic) correlation effects needed for proper description of dissociation at the *ab initio* level. We have chosen GVB for this purpose since GVB can be considered as a simple systematic MCSCF description.

As for the assessment of dynamic correlation effects, we have used local spin density (LSD) functional theory [32]. LSD functionals offer a way of predicting correlation effects at a cost level which is essentially that of HF. It has been shown that LSD functionals can lead to useful predictions of molecular properties [32, 33]. In this chapter we will investigate what level of accuracy is achieved if BDE values of a variety of molecules are determined by a method that combines the calculational advantages of both GVB and LSD. A clear assessment of this new GVB-LSD method can only be made if results are compared with BDE values from HF, HF-LSD and GVB calculations obtained with the same basis set at the same geometry. Thus, we will present here for the first time a thorough comparative investigation of BDE values obtained at the four levels of theory described above.

Our investigation has been stimulated by earlier research carried out along similar lines and with similar intentions. In 1974, Lie and Clementi investigated local density functionals (LDF) designed to yield proper dissociation potential curves for simple diatomic molecules [34, 35]. These authors stressed the necessity of using density

functionals in connection with a proper reference function that describes homolytic dissociation correctly. For this purpose, they added to the HF function a few configurations that guaranteed proper dissociation on at least a qualitative basis. This approach may be termed a MCSCF-LDF description of homolytic dissociation. Unfortunately, a routine implementation of the MCSCF-LDF approach requires for each molecule considered a decision on how many and which configurations have to be included. For example, for Li_2 , just one additional configuration ($1\sigma_g^2, 1\sigma_u^2, 2\sigma_u^2$) turned out to be necessary, while for N_2 nine additional singlet- or triplet-coupled configurations were needed [35]. Also, the density functional used by Lie and Clementi was a preliminary one and subject to further improvements. Because of this and the limited number of test examples, a positive assessment of the utility of the MCSCF-LDF approach could not be made.

USE OF LOCAL SPIN DENSITY FUNCTIONAL THEORY

In this work, LSD is used to calculate the correlation energy E_c as a corrective term for the HF energy, as was suggested by Stoll and co-workers [36-38]. Within this LSDC (C for correlation) approach the total energy is given by

$$E = E(\text{HF}) + E_c(\text{LSDC}) \quad (1)$$

with

$$E_c(\text{LSDC}) = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_c[\rho_+(\mathbf{r}), \rho_-(\mathbf{r})] - \int d\mathbf{r} \rho_+(\mathbf{r}) \varepsilon_c[\rho_+(\mathbf{r}), 0] - \int d\mathbf{r} \rho_-(\mathbf{r}) \varepsilon_c[0, \rho_-(\mathbf{r})] \quad (2)$$

where $\rho(\mathbf{r})$, $\rho_+(\mathbf{r})$, and $\rho_-(\mathbf{r})$ denote total electron density as well as α - and β -spin density distribution:

$$\rho(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r}) \quad (3)$$

We use for ε_c the Vosko-Wilk-Nusair (VWN) functional [39] that is based on accurate Monte Carlo data for the homogeneous electron gas calculated by Ceperley and Alder [40]. Kemister and Nordholm [41, 42] have extended the VWN parametrization to arbitrary polarization according to the method of von Barth and Hedin [43]. In addition, Kemister and Nordholm have used Gaussian basis functions to evaluate ε_c , which significantly facilitates the inclusion of the LSDC algorithm into standard *ab initio* packages. We have taken the LSDC programs from the Ph.D. thesis of Kemister [44], rewritten them for routine use in multipurpose *ab initio* programs and adapted them to our program package COLOGNE90 [45]. The modified LSDC programs can be used at the restricted and the unrestricted HF level in an iterative and non-iterative way (see below). They allow the use of electron density distributions resulting from HF, MP, CI, CC, QCI, GVB, MCSCF and CASSCF calculations [46].

At the HF level of theory, there are two ways of including the LSDC functional [41]. For example, the LSD correlation energy E_c can be calculated at the end of the SCF iterations by using the converged density distributions $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$. Alternatively, the LSDC functional can be included directly in the SCF iterations in order to minimize the sum $E(\text{HF}) + E_c$ rather than the HF energy alone. This can be

done by extending the Fock operator according to

$$F = F_{\text{HF}} + F_c \quad (4)$$

with

$$F_c^+ = \varepsilon_c[\rho_+(\mathbf{r}), \rho_-(\mathbf{r})] - \varepsilon_c[\rho_+(\mathbf{r}), 0] + \rho_+(\mathbf{r})\varepsilon'_c[\rho_+(\mathbf{r}), \rho_-(\mathbf{r})] - \rho_+(\mathbf{r})\varepsilon'_c[\rho_+(\mathbf{r}), 0] \quad (5)$$

where

$$\varepsilon'_c = \delta\varepsilon'_c/\delta\rho_+ \quad (6)$$

and similar equations for β spin electrons.

Both the fixed and the iterative HF-LSDC procedures have been applied at the HF level of theory throughout this chapter. As was found in earlier work [41], the correlation energies obtained by the two procedures are very similar, differing in most cases by less than 3 mHartree. Since the calculation of BDE values leads to partial cancellation of these differences, final BDEs differed by less than 1 kcal/mol in all cases considered. Therefore, only those LSDC correlation energies that are calculated after the SCF iteration (fixed HF-LSDC energies) will be discussed in the following.

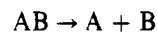
The fact that the two ways of calculating HF-LSDC energies lead to similar values suggests that the VWN functional depends only little on changes in the HF electron density distribution. We have checked the dependence of ε_c on $\rho(\mathbf{r})$ further by feeding into the VWN functional various types of correlation corrected density distribution, resulting from MP, CI, CC, QCI and GVB calculations [46]. In all cases, the dependence of the calculated LSDC energy on corrections in $\rho(\mathbf{r})$ turned out to be small. These observations led us to couple the LSDC functional to GVB in the simplest way possible: First the GVB calculation is carried out, and upon reaching convergence, $\rho(\mathbf{r})$, $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$ are calculated at the GVB level and used to calculate the LSDC energy. This leads to the GVB-LSDC energy according to

$$E(\text{GVB-LSDC}) = E(\text{GVB}) + E_c(\text{LSDC}) \quad (7)$$

The energies obtained in this way were used to determine the BDEs.

CALCULATION OF BOND DISSOCIATION ENERGIES D_e

The BDE of a molecule AB is defined as the difference of the energy of AB and those of the dissociation products A and B, where AB and the dissociation products are all at their equilibrium geometry.



One has to distinguish between D_e , D_0 and D_T values which refer to energy differences taken at the bottom of the potential well, at the zero vibrational level or some averaged vibrational level corresponding to temperature T K. Theory leads to D_e values, which with the help of calculated or experimental frequencies can be transformed to D_0 or D_T values. Alternatively, experimental D_0 values can be transformed to D_e values for reasons of comparison. We have used the latter approach using experimental frequencies in order to eliminate error sources that stem from inaccurate *ab initio* frequencies.

While in all cases investigated in this work AB is a closed-shell system, the dissociation products A and B are open-shell molecules or atoms. Accordingly, we have calculated AB at the restricted HF (RHF) level, while A and B have been calculated at the unrestricted HF (UHF) level. This is an economic way of calculating BDEs, but it is not without ambiguity. Comparison of RHF and UHF energies is problematic owing to the increased flexibility of the UHF wavefunction. A consistent description of the dissociation process can only be achieved by calculating the potential energy surface of the system AB along the dissociation coordinate by one and the same method. Since RHF leads to heterolytic dissociation, with BDE values being far too high, a reasonable description can only be obtained by using the UHF approach for the calculation of the dissociation energy. In many cases, UHF and RHF possess the same solution at or close to the equilibrium of AB. For these cases, our approach of calculating AB at RHF and the dissociation products at UHF is justified. There are, however, other molecules for which a unique UHF solution exists throughout the dissociation process. Then, BDE values are obtained which are larger than those reported here. But even the UHF values are considerably smaller than the true BDE values.

Since we are primarily concerned with correlation-corrected BDE values and since the differences between RHF and UHF energies are largely annihilated by correlation corrections, we are justified in comparing RHF- and UHF-based energy values in the following.

USE OF GVB FOR THE CALCULATION OF DISSOCIATION ENERGIES

The generalized valence bond (GVB) method is a variational version of the valence bond (VB) approach [47, 48]. The method allows one to correlate individual electron pairs that are associated with specific bonds via localized MOs. In the case of homolytic bond dissociation, only the orbitals describing the breaking bond form GVB pairs.

$$[\text{pair}] = [\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (8)$$

while all other occupied orbitals are considered to form an HF core.

$$[\text{core}] = [\phi_{c_1}(1)\phi_{c_1}(2)\alpha\beta\phi_{c_2}(1)\phi_{c_2}(2)\alpha\beta \dots] \quad (9)$$

Pair orbitals ϕ_a and ϕ_b are variationally optimized (as are core orbitals ϕ_c) overlapping one-electron GVB orbitals. While HF orbitals are orthogonal, GVB orbitals in general are not. But for computational reasons the GVB pair can be rewritten in terms of natural orbitals χ .

$$[\text{pair}]^{\text{NO}} = [c_g\chi_g^2 + c_u\chi_u^2][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (10)$$

with

$$c_g^2 + c_u^2 = 1 \quad (11)$$

where χ_g and χ_u correspond to the orthogonal bonding and antibonding natural orbitals of the GVB pair. In the perfect pairing (PP) version of GVB, electrons are always singlet coupled and the GVB-PP wavefunction for a closed-shell molecule

with several pairs takes the form:

$$\Psi^{\text{GVB-PP}} = A[[\text{core}][\text{pair}(1,2)][\text{pair}(3,4)] \dots].$$

The GVB-PP approach can be considered as a simple MCSCF method [48]. It recovers static correlation effects and gives the correct functional form for proper bond dissociation.

In this work, the GVB-PP approach has been used to account for static correlation effects influencing BDEs. Thus if the bond A—B is broken in the dissociation, only the electron pair associated with the corresponding localized AB bond orbital has been correlated. None of the other electron pairs that are responsible for bonding within A or B has been considered in the dissociation process. For example, static correlation effects in the dissociation of the CC bond in H_3CCH_3 , H_2CCH_2 and HCCH have been described by correlating 1, 2, and 3 CC bond electron pairs, respectively, but none of the CH bond electron pairs.

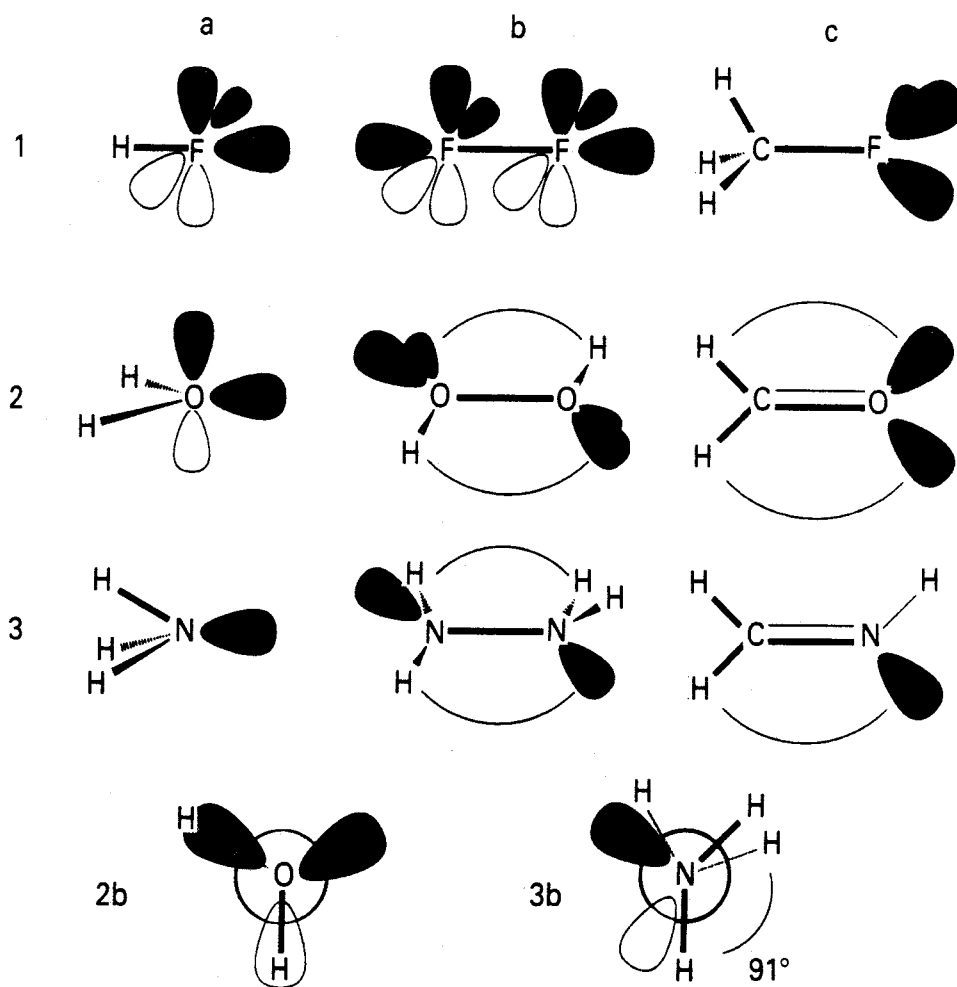
While this approach seems to be straightforward at first sight, it leads to unreasonable results if hetero atoms with electron lone pairs are involved in the dissociation process. For example, there is just an OO single bond in hydrogen peroxide, H_2O_2 , but from experimentally as well as theoretically determined properties of H_2O_2 it becomes clear that the lone pairs at the two O atoms participate to some extent in bonding [49, 50]. In the equilibrium geometry of H_2O_2 , one lone pair at each O atom is collinear with the neighbouring OH bond (see Schemes 1, 2b). It delocalizes into the $\sigma^*(\text{OH})$ orbital (anomeric effect) thus leading to partial π -character of the OO bond and thereby increasing its stability. At the same time, lone pair-lone pair repulsion leads to some weakening of the OO bond, but the net effect of the O electron lone pairs is still stabilizing [49, 50].

It is clear that electron lone pairs have to be considered in the dissociation process. But using the same reasoning one has also to consider interactions of vicinal bonds, e.g. the CH bonds in H_3CCH_3 , H_2CCH_2 and HCCH , in the dissociation process. Repulsive interactions will decrease, and attractive interactions will increase the BDE. We have tested this and have found that contrary to the effects of electron lone pairs, the effects of vicinal CH bond electron pairs on the static correlation energy of the dissociation process are negligibly small. Therefore, only the electron lone pairs of hetero atoms have been considered in the GVB calculations.

Even though it is not difficult to identify the impact of a lone pair on the BDE, a consistent treatment of lone pair effects at the GVB level is very difficult. In the example given above, the participation of two electron lone pairs in the OO bond is obvious. What is not obvious is the role of the two remaining lone pairs with regard to OO bonding. Inclusion of all four electron lone pairs in the GVB calculation leads to static correlation effects and dissociation energies which are far too large. This indicates that not all electron lone pairs participate in OO bonding. According to the anomeric interaction of O electron lone pairs, there are just two of the four lone pairs that participate in OO bonding while the two other lone pairs may not affect in any way bonding in H_2O_2 . This, however, is difficult to assess on a quantitative basis, in particular if molecules such as CH_3OH , CH_3NH_2 , etc. are considered.

Since the question of lone pair participation in bonding cannot be satisfactorily answered in any case, we have adopted the following approach. For molecules AH_n we have not considered those electron lone pairs which are directed away from the AH

bonds, since their influence on AH bonding is negligible. This applies to the σ lone pair of FH, H₂O and NH₃ (see Schemes 1, 1a, 2a, 3a). However, the impact of the $p\pi$ electron lone pairs at F and O (Scheme 1) cannot be neglected. Calculations show that the distribution of the $p\pi$ lone pairs directly affects the electronic charge along the AH bond and at H. For example, augmentation of the H basis set by polarization functions leads to AH bond strengthening owing to pseudo- π character of the AH bond introduced by the polarization functions. This, of course, does not mean that the AH bond gets any double-bond character, but the distribution of the $p\pi$ lone pairs has to be taken into account for an accurate *ab initio* description of AH bonding. In this chapter we have used polarization functions only for the heavy atoms. However, in view of a correct and consistent treatment of lone pair effects we include the $p\pi$ lone pairs of F and O in the GVB treatment of AH bonding and indicate this by lone pair participation numbers q of 2 and 1, respectively.



Once the lone pair participation numbers q of molecules AH_n have been fixed, these numbers are used to determine q for bonds AB in molecules H_aABH_b . Thus, $q(OO)$ for H_2O_2 is calculated to be $4 - 2q(OH) = 2$ in accordance with the description of the anomeric effect for H_2O_2 given above (see also Schemes 1, 2b). Nevertheless, there are several cases that need special consideration. In the equilibrium conformation of N_2H_4 (Schemes 1, 3b) the electron lone pairs are almost collinear with the vicinal NH bonds although this also implies some NH eclipsing. This indicates anomeric participation of the electron lone pairs in NN bonding. Accordingly, we have set $q(N_2H_4)$ to 2 as in the case of H_2O_2 .

For F_2 (Schemes 1, 1b), ClF and Cl_2 , $q = 4$ leads to better BDEs than $q = 6$. This adds support to exclude those lone pairs that are directed away from the AA or AB bond. However, for CH_3F it is no longer possible to distinguish between σ and π electron lone pairs at F (Schemes 1, 1c) since the three lone pairs are equivalent owing to symmetry. Their spatial distribution is best described by sp^3 hybrid orbitals. Therefore, we have included all three electron lone pairs in the GVB calculation ($q = 3$).

For all molecules with multiple bonds, electron lone pairs have been fully included into the GVB calculation. The reason for this is given in Scheme 1, which shows that the electron lone pairs in CH_2O or CH_2NH are collinear with the vicinal CH bonds and, therefore, can undergo anomeric delocalization into the AB bond. In the case of N_2 , HCN and CO the electron lone pairs also prove to be necessary to get accurate BDEs. This can be rationalized by interactions between σ -bond and lone pair orbitals. Electron lone pair participation numbers q are listed together with the calculated BDE values in Table 2.

In order to obtain a consistent description of all compounds, experimental geometries have been used at all levels of theory employed. It is well known that calculated geometries may differ considerably from experimental ones, thus causing a geometry error in computed BDEs. In some cases we have tested changes in BDEs upon geometry optimization. It turned out that these changes only led to minor improvements of calculated BDE values for the molecules considered in this chapter.

EXPERIMENTAL DISSOCIATION ENERGIES

In the literature, there are several compilations of experimental BDEs [2-7]. Unfortunately, these compilations often comprise just D_o or D_T values intermingled with unspecified estimates and outdated values of uncertain origin. Therefore, we have refrained from using any of these compilations. Instead we have taken the most recent update of the JANAF tables as a source for heats of formation $\Delta H_f^0(298)$ and $\Delta H_f^0(0)$ [11, 12]. In two cases (BeH_2 , BH_3), we had to take ΔH_f^0 values as well as geometries and vibrational frequencies from *ab initio* calculations [28] since the latter turned out to be more reliable than experimental data. In the second step, we have collected vibrational frequencies for all molecules considered in this chapter [9, 52, 53] and used them to calculate $\Delta H_f^0(0)$ (if not available), D_{298} , D_o and D_e values. Some of these data are given in Tables 1 and 2 together with the sources for heats of formation and experimental frequencies.

SELECTION OF TEST MOLECULES

Previous investigations of BDEs using density functional theory have been constrained to simple diatomic molecules [34, 35, 41]. Even though results on these molecules may provide first indication on the usefulness of a particular calculational approach, they do not allow one to draw any conclusion with regard to routine use of the method in the case of polyatomic molecules. Therefore, we have looked for a larger set of representative homolytic dissociation reactions that can be made up from molecules containing just first row atoms. We have settled on three groups of molecules and three groups of dissociation reactions: first, molecules AH_n that can lead to AH bond dissociation reactions; secondly, molecules A_2H_{2a} ($a = 0, 1, \dots$) and AA bond dissociation reactions; finally, molecules AH_aBH_b and BDEs AB, with A a carbon atom, that are representative for bond dissociation in organic compounds.

Within this set of test examples some molecules had to be excluded. These are Be_2 , B_2 and O_2 . Be_2 is a van der Waals compound with a binding energy of less than 2 kcal/mol [54] and, therefore, does not fall into the group of covalently bonded molecules investigated in this chapter. The O_2 molecule has been excluded since it is well known that GVB with perfect pairing cannot describe homolytic dissociation of the $^3\Sigma_g^+$ ground state of O_2 correctly [55]. The value of the BDE of B_2 was actually calculated in this work ($D_e(\text{GVB-LSDC}) = 61.3$; $D_e(\text{exp}) = 70$ kcal/mol), but after dropping molecular oxygen, B_2 would have been the only open-shell molecule within our set of examples and, therefore, we will include it in a forthcoming investigation of BDE values of open-shell molecules.

As discussed above, the inclusion of electron lone pairs into the GVB calculations turned out to be a stumbling block in the beginning. This was particularly true with regard to F_2 . Comparative calculations for halogen compounds such as HCl, Cl_2 and ClF indicated that reasonable results are obtained when two rather than three electron lone pairs per halogen atom are included in the GVB calculation. Even though the additional calculations involved molecules with a second period atom, they are included in the present work which is thus based on a sample set of 27 molecules and 27 different dissociation reactions.

RESULTS AND DISCUSSION

In Table 1, heats of formation ΔH_f^0 at 298 and 0 K are given for those atoms and molecules that occur in the dissociation reactions investigated. Also listed are sources for vibrational frequencies needed for the calculation of D_e values from experimental D_0 values and those for the experimental geometries used in the calculations. Table 2 gives calculated and experimental D_e values for the 27 dissociation reactions investigated. HF, HF-LSDC, GVB and GVB-LSDC values are plotted against experimental D_e values in Figs 1, 2, 3 and 4, respectively. A more detailed analysis of the calculated BDEs is given in Table 3 as well as Figs 5, 6 and 7.

BDEs calculated at the HF level of theory are always too small. Discrepancies are as large as 100 kcal/mol and more. Fig. 1 shows that computed HF BDEs do not correlate with experimental BDE values. It is noteworthy that the BDEs of both F_2 and H_2O_2 are negative (-35.2 and -1.5 kcal/mol, respectively) which means that these molecules are not stable at the HF level of theory. This has been reported several

Table 1—Heats of formation ΔH_f° and zero-point energies (ZPE) for all molecules^a.

Molecule	Sym	$\Delta H_f^\circ(298)$	$\Delta H_f^\circ(0)$	ZPE	References		
					ΔH_f°	Freq	Geom
LiH	$C_{\infty v}$	33.61	33.65	1.94	12	52	51
BeH ₂	$D_{\infty h}$	39.50	39.86	10.16	28	28	28
BH ₃	D_{3h}	74.80	74.71	10.86	28	28	28
CH ₄	T_d	-19.895	-15.992	27.11	12	52	51
NH ₃	C_{3v}	-10.97	-9.30	11.46	12	52	51
H ₂ O	C_{2v}	-57.80	-57.11	12.88	12	52	51
FH	$C_{\infty v}$	-65.14	-65.13	5.66	12	52	51
HCl	$C_{\infty v}$	-22.06	-22.02	4.12	12	9	51
Li ₂	$D_{\infty h}$	51.60	51.50	0.49	12	52	51
C ₂ H ₆	D_{3d}	-20.04	-16.27	45.46	12	52	51
C ₂ H ₄	D_{2h}	12.54	14.58	30.87	12	52	51
C ₂ H ₂	$D_{\infty h}$	54.19	56.37	16.19	12	52	51
C ₂	$D_{\infty h}$	200.22	198.20	2.61	12	9	51
N ₂ H ₄	C_2	22.79	26.22	31.82	12	52	51
N ₂ H ₂	C_{2h}	50.90	52.61	17.18	12	52	51
N ₂	$D_{\infty h}$	0	0	3.33	12	52	51
H ₂ O ₂	C_2	-32.53	-31.03	15.90	12	52	51
F ₂	$D_{\infty h}$	0	0	1.27	12	52	51
Cl ₂	$D_{\infty h}$	0	0	0.79	12	9	51
CH ₃ NH ₂	C_s	-5.49	-1.92	39.17	12	52	51
CH ₂ NH	C_s	27.60	29.49	24.22	59	52	51
HCN	$C_{\infty v}$	32.30	32.39	9.77	12	52	51
CH ₃ OH	C_s	-47.96	-45.33	31.15	12	52	51
CH ₂ O	C_{2v}	-27.70	-26.78	16.14	12	52	51
CO	$C_{\infty v}$	-26.42	-27.20	3.06	12	52	51
CH ₃ F	C_{3v}	-56.00	-54.08	23.95	12	52	51
ClF	$C_{\infty v}$	-12.02	-12.00	1.11	12	9	51
Dissociation products							
H(² S)		52.10	51.63		12		
Li(² S)		38.07	37.70		12		
BeH	$C_{\infty v}$	81.70	81.10	2.84	12	9	51
BH ₂	C_{2v}	74.80	74.71	10.86	12	12	51
CH ₃	D_{3h}	34.80	35.62	18.25	12	53	51
CH ₂ (³ B ₁)	$C_{\infty v}$	92.35	92.23	10.45	12	^b	51
CH	$C_{\infty v}$	142.00	141.18	3.91	12	9	51
C(³ P)		171.29	169.98		12		
NH ₂	C_{2v}	45.50	46.19	11.46	12	53	51
NH	$C_{\infty v}$	81.4	81.2	4.47	12	9	51
N(⁴ S)		112.97	112.53		12		
OH	$C_{\infty v}$	9.32	9.17	5.10	12	9	51
O(³ P)		59.55	58.98		12		
F(² P)		18.97	18.47		12		
Cl(² P)		28.99	28.59		12		

^a All values in kcal/mol.

^b *Chem. Phys. Lett.* **123**, 187 (1988).

Table 2—Calculated and experimental bond dissociation energies^a.

Molecule	Bond	q^b	$D_e(\text{HF})$	$D_e(\text{HF-LSDC})$	$D_e(\text{GVB})$	$D_e(\text{GVB-LSDC})$	$D_e(\text{Exp})$
LiH	LiH		31.11	49.54	41.33	59.76	57.62
BeH ₂	BeH		74.46	100.09	82.08	107.71	100.19
BH ₃	BH		88.70	112.72	96.88	120.90	112.81
CH ₄	CH		85.84	109.75	95.51	119.43	112.10
NH ₃	NH	0	79.93	103.80	91.24	115.11	116.28
H ₂ O	OH	1	80.99	105.60	100.82	125.43	125.69
HF	FH	2	86.99	111.22	115.37	139.60	140.89
HCl	ClH	2	70.71	92.97	82.17	104.43	106.37
Li ₂	LiLi		1.72	14.00	8.90	21.18	24.39
C ₂ H ₆	CC		69.34	86.80	78.81	96.27	96.50
C ₂ H ₄	CC		118.50	156.87	145.13	183.50	179.67
C ₂ H ₂	CC		180.34	199.33	215.01	234.00	234.38
C ₂	CC		9.26	43.30	99.80	133.84	144.37
N ₂ H ₄	NN	2	30.18	44.29	56.37	70.34	75.11
N ₂ H ₂	NN	2	46.23	80.04	92.58	126.39	118.03
N ₂	NN	2	107.36	167.14	163.25	223.03	228.39
H ₂ O ₂	OO	2	-1.50	11.96	37.34	50.90	55.07
F ₂	FF	4	-35.16	-23.57	35.55	47.14	38.21
Cl ₂	ClCl	4	10.60	22.55	39.56	51.51	57.97
CH ₃ NH ₂	CN	0	58.17	74.70	75.82	92.34	93.18
CH ₂ NH	CN	1	92.16	128.06	126.85	162.75	153.25
HCN	CN	1	154.12	193.43	186.87	226.18	227.27
CH ₃ OH	CO	1	58.70	75.16	78.53	94.99	97.97
CH ₂ O	CO	2	99.69	135.89	144.83	180.83	183.69
CO	CO	3	169.84	205.40	226.37	261.93	259.22
CH ₃ F	CF	3	68.86	84.64	97.98	113.76	113.87
CIF	CIF	4	4.04	17.87	47.28	61.11	60.16

^a All values in kcal/mol.^b Lone pair participation number; for explanation, see text.

times for F₂ [56], but it is less known that the same is true for H₂O₂. Both Cl₂ and CIF possess positive D_e values at the HF level, but their values are 56 and 47 kcal/mol smaller than the experimental BDEs. Although the failure of HF theory seems to be particularly dramatic in the case of F₂, even larger discrepancies are calculated in the case of homolytic dissociation of multiple bonds. For example, the HF error for C₂ dissociation is 135 kcal/mol, for N₂ dissociation 121 kcal/mol and for homolytic CO dissociation 89 kcal/mol.

The inclusion of LSDC corrections leads to an improvement of homolytic dissociation energies, as has been noted before by Kemister and Nordholm [41]. Errors in calculated AH BDE values are decreased by *ca.* 20 kcal/mol, yielding for Be—H, B—H and C—H dissociation almost exactly the experimental D_e values. This is due to a 10–60 kcal/mol enlargement of HF–LSDC BDE values. On the other hand, the F₂ dissociation energy is still negative at the HF–LSDC level (–23.6 kcal/mol) and the errors for C₂, N₂ and CO are 101, 61 and 53 kcal/mol, respectively. Figs 2 and 6 clearly reveal that at the HF–LSDC level only a small, but not very significant, improvement of calculated BDEs has been achieved. A somewhat more positive assessment of the capability of LSDC to predict dissociation energies given in the literature [41] was due to the limited test examples considered. We conclude that HF–LSDC is not able to predict reasonable D_e values for homolytic dissociation reactions.

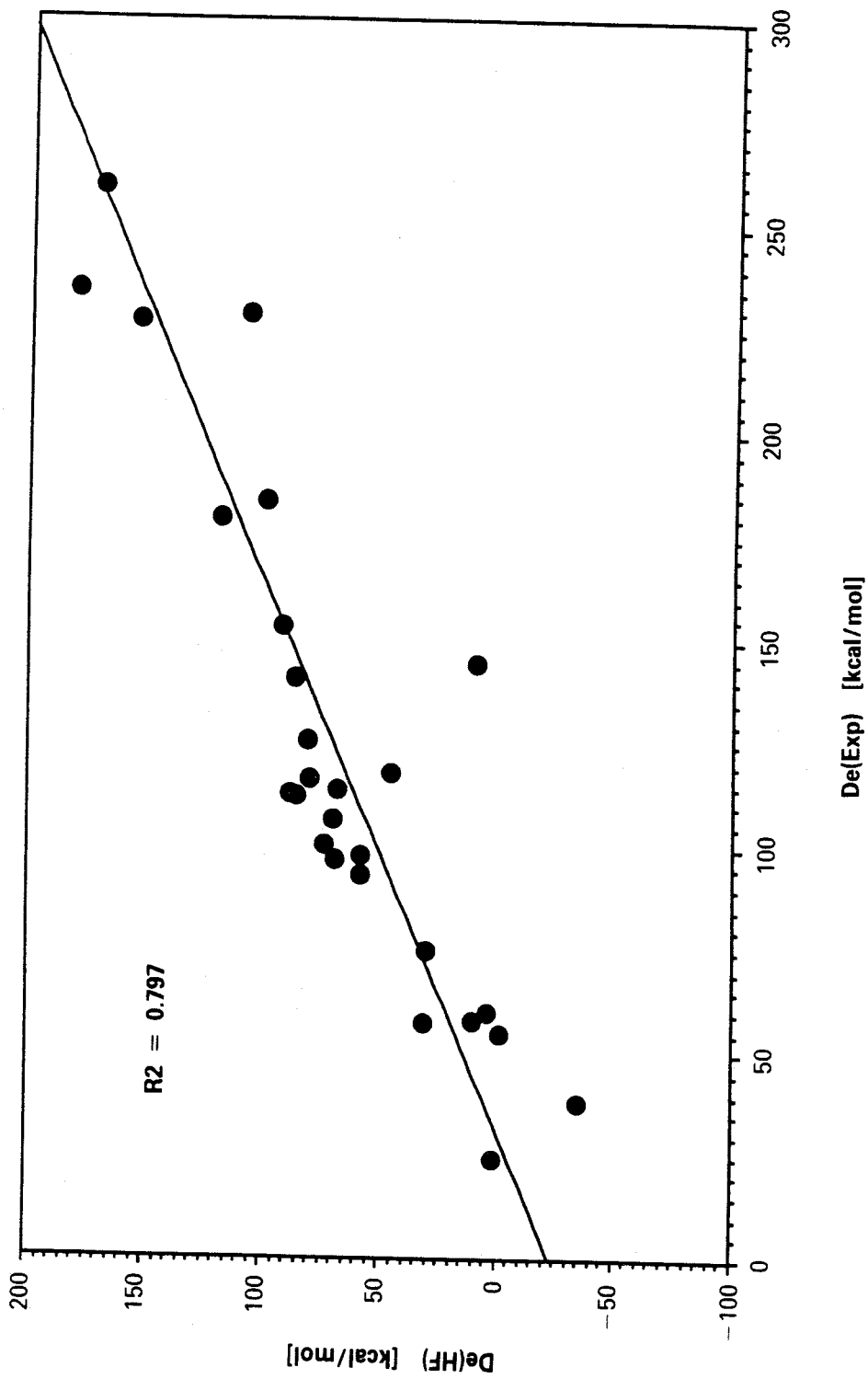


Fig. 1. Correlation of HF bond dissociation energies $D_e(\text{HF})$ with experimental dissociation energies $D_e(\text{Exp})$. R^2 is the correlation coefficient.

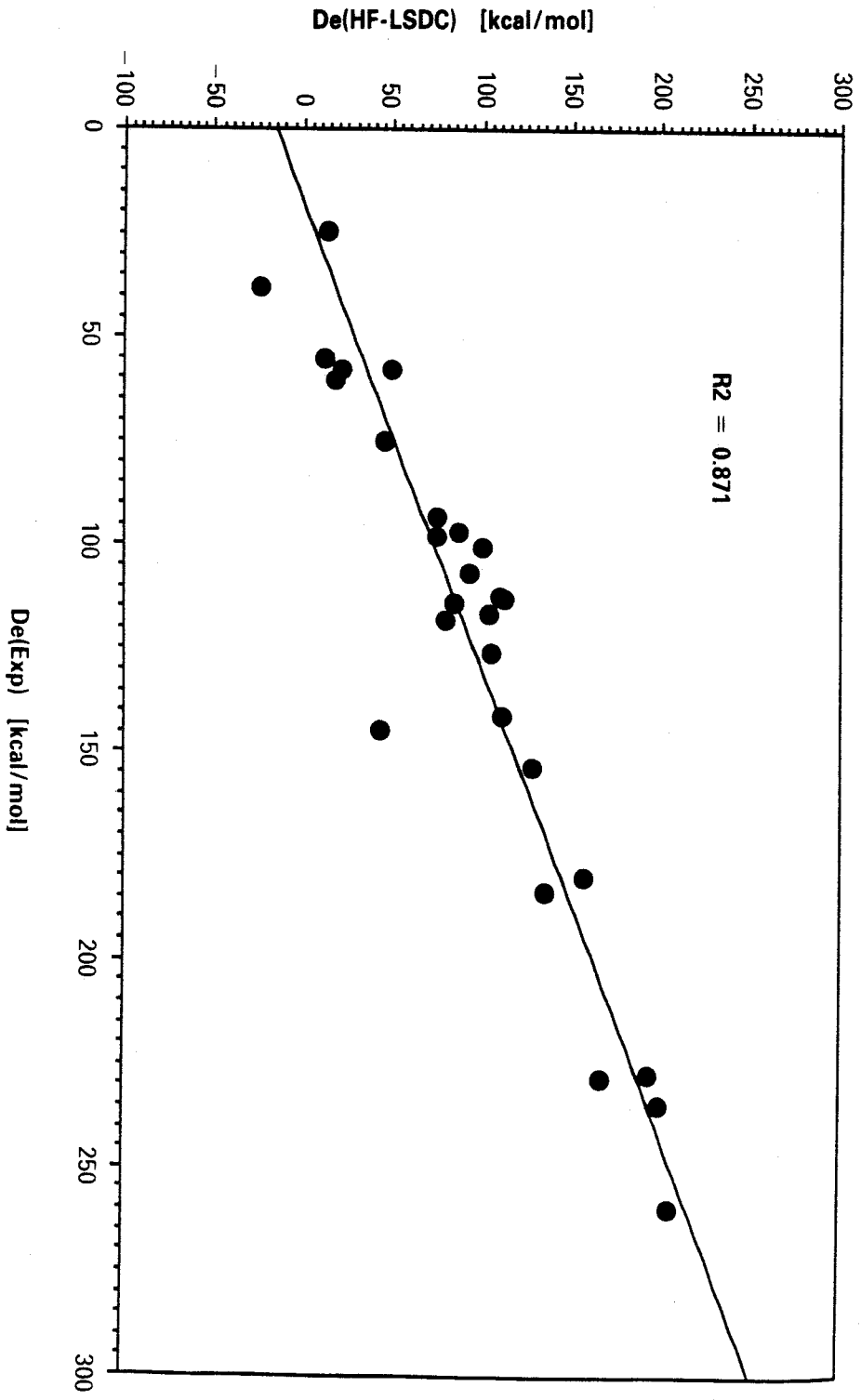


Fig. 2. Correlation of HF-LSDC bond dissociation energies $D_e(\text{HF-LSDC})$ with experimental dissociation energies $D_e(\text{Exp})$. R^2 is the correlation coefficient.

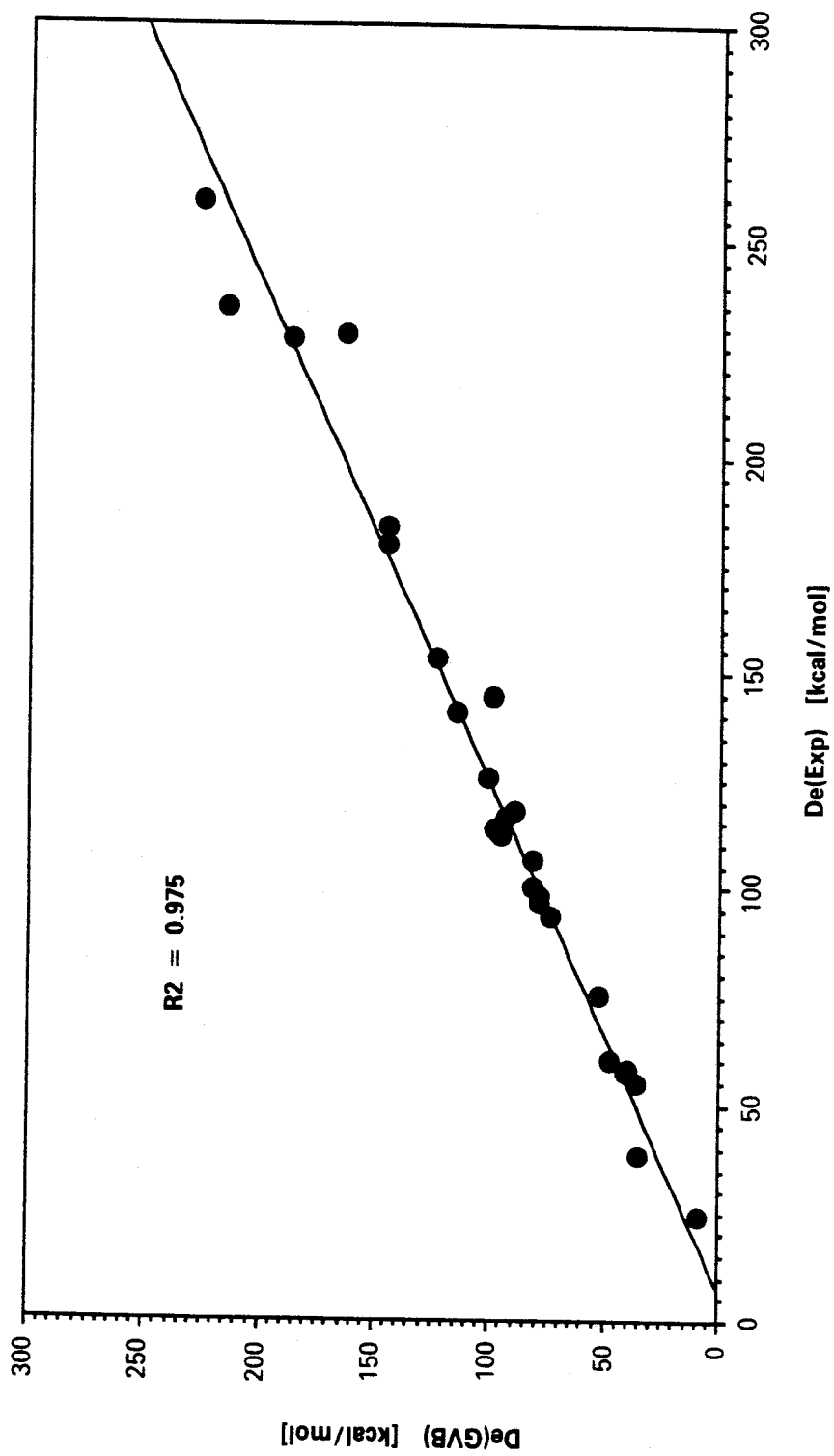


Fig. 3. --- Correlation of GVB bond dissociation energies $D_e(\text{GVB})$ with experimental dissociation energies $D_e(\text{Exp})$. R^2 is the correlation coefficient.

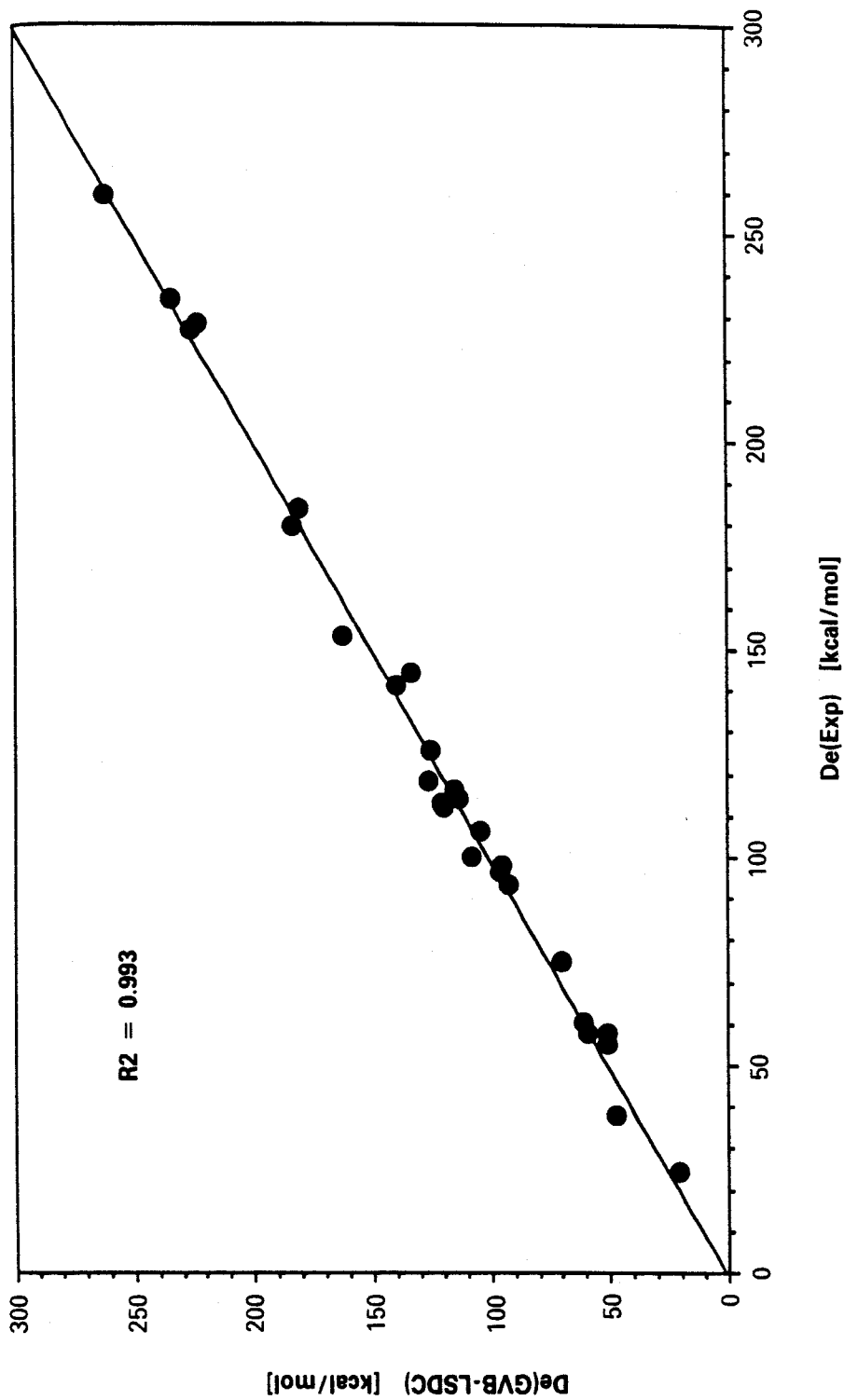


Fig. 4.—Correlation of GVB-LSDC bond dissociation energies $D_e(\text{GVB-LSDC})$ with experimental dissociation energies $D_e(\text{Exp})$. R_2 is the correlation coefficient.

Table 3—Comparison of experimental and calculated bond dissociation energies^a.

Molecule	Bond	$D_e(\text{Exp.}) - D_e(\text{HF})$	$D_e(\text{Exp.}) - D_e(\text{HF-LSDC})$	$D_e(\text{Exp.}) - D_e(\text{GVB})$	$D_e(\text{Exp.}) - D_e(\text{GVB-LSDC})$
LiH	LiH	26.51	8.08	16.29	-2.14
BeH ₂	BeH	25.73	0.10	18.11	-7.52
BH ₃	BH	24.11	0.09	15.93	-8.09
CH ₄	CH	26.26	2.35	16.59	-7.33
NH ₃	NH	36.35	12.48	25.04	1.17
H ₂ O	OH	44.70	20.09	24.87	0.26
FH	FH	53.90	29.67	25.52	1.29
HCl	ClH	35.66	13.40	24.20	1.94
Li ₂	LiLi	22.67	10.39	15.49	3.21
C ₂ H ₆	CC	27.16	9.70	17.69	0.23
C ₂ H ₄	CC	61.17	22.80	34.54	-3.83
C ₂ H ₂	CC	54.04	35.05	19.37	0.38
C ₂	CC	135.11	101.07	44.57	10.53
N ₂ H ₄	NN	44.93	30.82	18.74	4.77
N ₂ H ₂	NN	71.80	37.99	25.45	-8.36
N ₂	NN	121.03	61.25	65.14	5.36
H ₂ O ₂	OO	56.57	43.11	17.73	4.17
F ₂	FF	73.37	61.78	2.66	-8.93
Cl ₂	ClCl	47.37	35.42	18.41	6.46
CH ₃ NH ₂	CN	35.01	18.48	17.38	0.84
CH ₂ NH	CN	61.09	25.19	26.40	-9.50
HCN	CN	73.15	33.84	40.40	1.09
CH ₃ OH	CO	39.27	22.81	19.44	2.98
CH ₂ O	CO	84.00	47.80	38.86	2.86
CO	CO	89.38	53.82	32.85	-2.71
CH ₃ F	CF	45.01	29.23	15.89	0.11
CIF	CIF	56.12	42.29	12.88	-0.95
Average error		54.50	28.94	24.09	3.96

^a All values in kcal/mol.

The failure of LSDC is not astonishing in view of the fact that it predominantly accounts for dynamic electron correlation effects but not for static correlation effects. For this reason, LSDC cannot be better than any other single-determinant-based correlation method such as MP or CI. This is also suggested by the fact that LSDC correlation energies correlate to some extent with MP2, MP3 and MP4 correlation energies [46].

Contrary to HF and single-determinant correlation methods, GVB [48] leads to a qualitatively correct description of homolytic dissociation [57]. This is nicely illustrated by Fig. 3, which shows that GVB BDE values correlate with experimental BDEs ($R^2 = 0.975$). Both F₂ and H₂O₂ possess positive dissociation energies at the GVB level. However, GVB does not lead to quantitatively correct D_e values, as is reflected by Fig. 7. GVB values are still between 10 and 65 kcal/mol too small, where the largest deviations are again calculated for multiple-bonded molecules such as N₂ (-65 kcal/mol) and C₂ (-45 kcal/mol). Accordingly, the correlation line shown in Fig. 3 does not go through the origin.

Our GVB results compare well with those obtained by Hay, Hunt and Goddard [57] who computed hydrocarbon dissociation energies with a DZ and a DZ + P

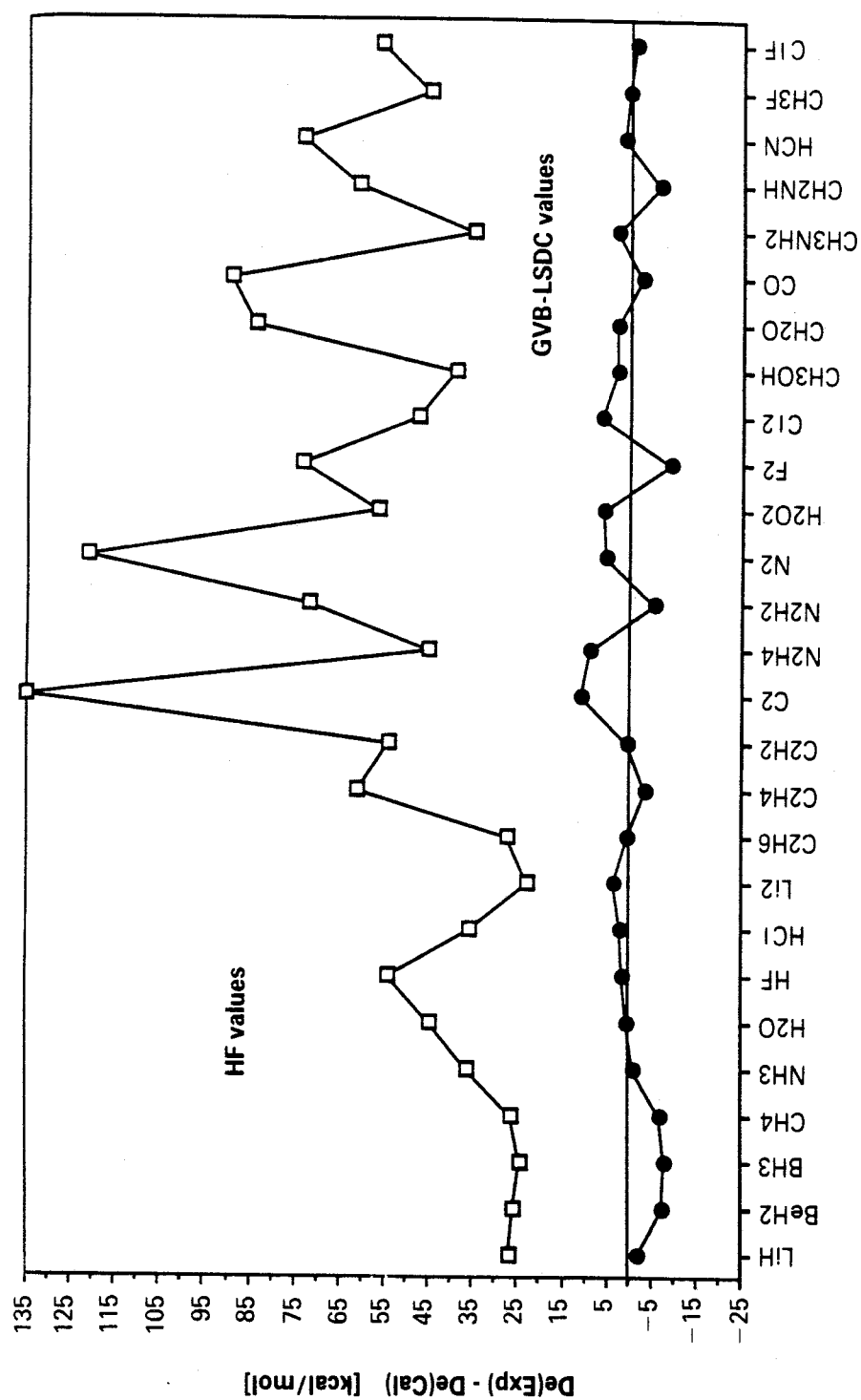


Fig. 5. — Deviation of HF bond dissociation energies $D_e(\text{HF})$ from experimental dissociation energies $D_e(\text{Exp})$. For reasons of comparison, the corresponding deviations of GVB-LSDC dissociation energies are also shown.

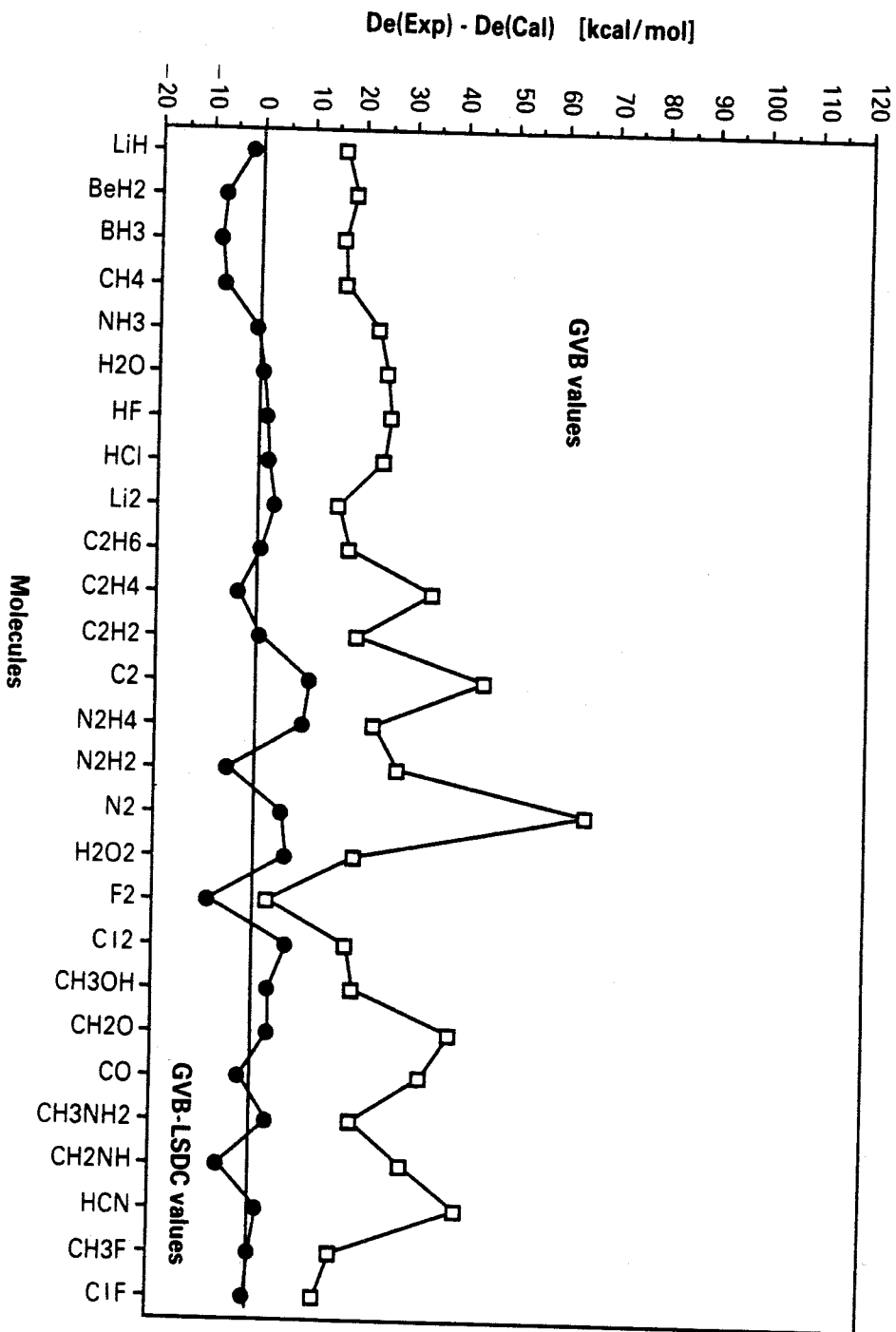
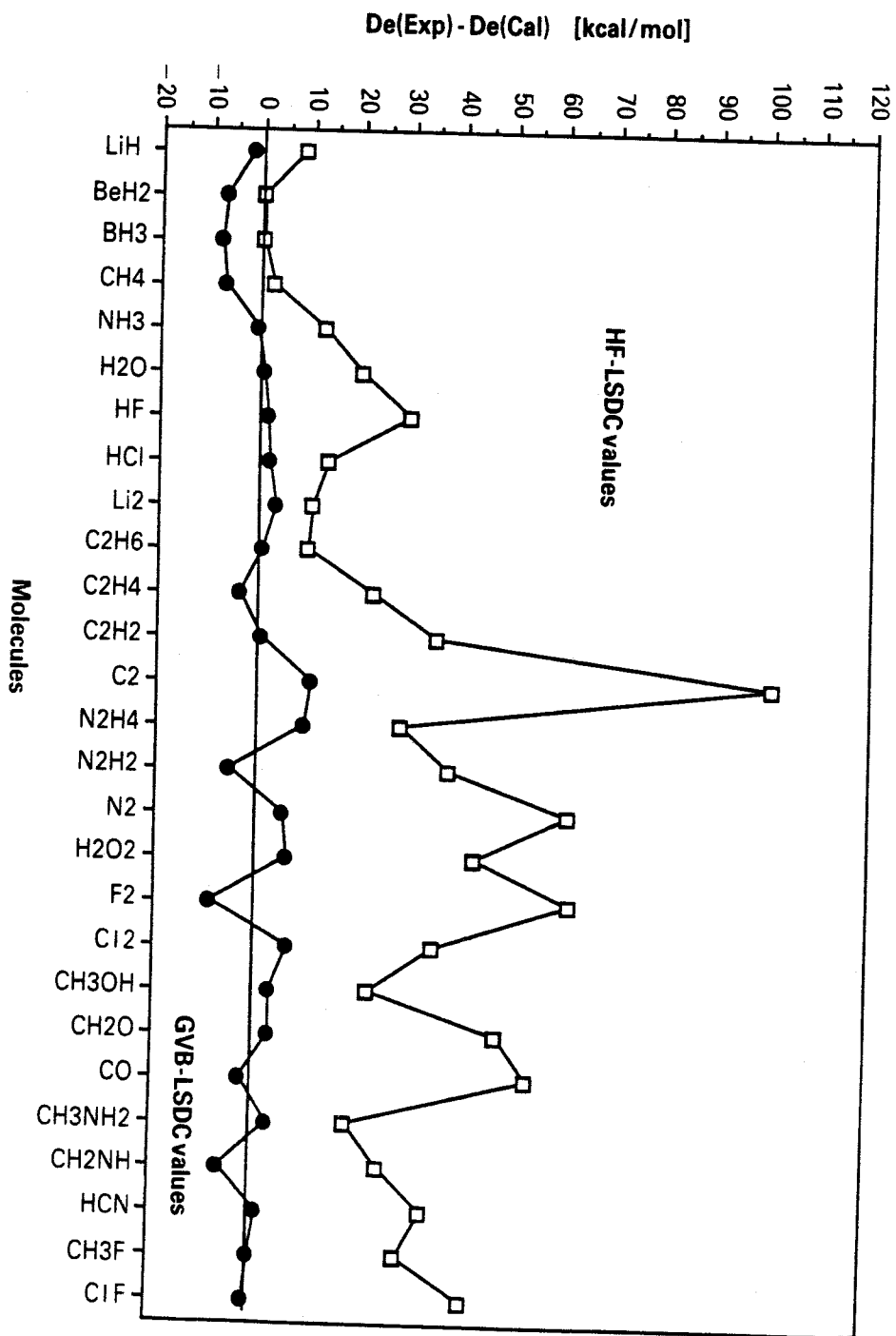


Fig. 6. Deviation of HF-LSDC bond dissociation energies $D_e(\text{HF-LSDC})$ from experimental dissociation energies $D_e(\text{Exp})$. For reasons of comparison, the corresponding deviations of GVB-LSDC dissociation energies are also shown.

Fig. 7.— Deviation of GVB bond dissociation energies D_e (GVB) from experimental dissociation energies D_e (Exp). For reasons of comparison, the corresponding deviations of GVB-LSDC dissociation energies are also shown.



basis set. For example, these authors obtained for homolytic CC dissociation of C_2H_6 , C_2H_4 and C_2H_2 BDE values of 76, 147 and 180 kcal/mol at the GVB/DZ + P level to be compared with our values of 78, 145 and 215 kcal/mol (Table 2). Hay and co-workers also showed that GVB dissociation energies can be improved at the GVB-CI level owing to the inclusion of dynamic correlation effects. Unfortunately, the computational demands of GVB-CI prevented the authors from carrying out a thorough investigation of a large number of homolytic dissociation reactions [57].

In Fig. 4, GVB-LSDC results on homolytic BDEs are shown. Obviously, at this level of theory, calculated BDEs correlate satisfactorily with experimental D_e values ($R^2 = 0.993$). Also, the correlation line is going through the origin thus indicating that the calculated BDEs are no longer too small. The average error is 4 kcal/mol (see Table 3), which is comparable to the error in experimental heats of formation. Clearly, results are much better than both HF-LSDC and GVB BDEs. This is also suggested by Figs 6 and 7, where HF-LSDC and GVB errors in calculated BDE values are compared with the corresponding GVB-LSDC errors for each homolytic dissociation reaction investigated.

Calculated GVB-LSDC BDEs can be both smaller and larger than experimental D_e values (compare with Table 3 and Fig. 7). It is particularly interesting to analyse those cases that lead to an overestimate of D_e at the GVB-LSDC level. These comprise AH_n molecules with a relatively electropositive central atom A and, therefore, a relatively high electronic charge at the H atom(s). In such a situation, the 6-31G(d) basis is certainly not sufficient for an adequate description of the charge distribution. For example, if one considers the ionic resonance structure Li^+H^- to make a large contribution to the LiH wavefunction, then both atoms Li and H possess two electrons in the LiH molecule. With the 6-31G(d) basis, 15 basis functions are used to describe the electron distribution at Li while only two basis functions describe that at H. Clearly, this leads to an unbalanced description of LiH and its homolytic dissociation reaction. Use of the 6-31G(d,p) basis would lead to a better description of the electronic structure of LiH, and this would also be true for the other AH_n systems.

However, it is easy to see that the 6-31G(d,p) basis causes a lowering of the LiH (AH_n) energy while leaving that of Li and H unaltered. Accordingly, HF and GVB dissociation energies become larger rather than lower. As noted above, LSDC correlation energies show little dependence on small changes in the electron density distribution caused either by method or basis set improvements. Test calculations carried out in this work reveal that in most cases E_c (LSDC) decreases by some mHartrees upon improvement of the basis set from minimal to DZ or better quality. Therefore, an improvement of the basis from 6-31G(d) to 6-31G(d,p) quality leads to larger rather than smaller GVB-LSDC BDE values for the AH_n molecules. Hence, overestimation of calculated D_e values for AH_n molecules such as LiH, BeH₂, BH₃, etc. must be of different origin.

An insufficient basis set will also lead to a large basis set superposition error (BSSE) in calculated BDEs. Correcting for the BSSE error by the counterpoise method [58] leads to a decrease in the calculated D_e values. We have done this for some of the AH_n molecules and, indeed, have obtained improved values for the BDEs.

Another possible reason for overestimating D_e values at the GVB-LSDC level of theory has to do with electron lone pair participation at the GVB level. For example, in the case of F_2 , the inclusion of the 4 $p\pi$ electron lone pairs leads to an increase in the

D_e value from 23 to 47 kcal/mol. This, of course, is a simplification of lone pair participation since it may not only be stabilizing but also destabilizing owing to electron pair-electron pair repulsion. At the GVB level, the pairs are correlated independently of each other, thus exaggerating the stabilizing effect. On the other hand, destabilizing repulsion of electron pairs at vicinal atoms will decrease with the distance. Hence, it is not surprising that $p\pi$ lone pair inclusion at the GVB-LSDC level does not lead to the same exaggeration in D_e in the case of CIF and Cl₂ (see Tables 2 and 3).

Finally, there are multiply bonded molecules such as CH₂CH₂, CH₂NH, HNNH and CO with GVB-LSDC BDEs that are too large. This may be partially due to inaccurate or missing experimental BDEs in the case of CH₂NH and HNNH. The heat of formation of CH₂NH is not known and, therefore, it had to be estimated from experimental group additivity increments and calculated *ab initio* energies [59]. For HNNH, it is unclear whether the measured heat of formation corresponds to the *trans* configuration or to the less stable *cis* form [60]. If the latter were the case, the experimental D_e value for the *trans* form, which has been considered in this work, would be close to the calculated BDE given in Table 2. Other reasons for an overestimation of calculated D_e values may again be the number of lone pairs correlated at the GVB level (HNNH, CH₂NH, CO) or an inadequate description of the dissociation products at the LSDC level (CH₂ and NH).

The largest underestimation of D_e at the GVB-LSDC level is found for C₂ (-10.5 kcal/mol, Table 2). This is not surprising since the correct description of homolytic C₂ dissociation requires a larger MCSCF expansion than that provided by GVB. Lie and Clementi used nine configurations in their MCSCF-LDF approach, but obtained a BDE for C₂ that was 26 kcal/mol too small [35]. Future work has to show whether improvement of MCSCF, LSD or basis set will lead to a more accurate BDE.

CONCLUSIONS AND OUTLOOK

We have found that the GVB-LSDC approach provides an economic and reasonable description of the energies of homolytic dissociation reactions. This is due to an adequate treatment of static and dynamic correlation effects which are important in order to obtain a proper description of bond dissociation. GVB-LSDC results are better than both GVB and HF-LSDC BDEs. For 27 dissociation reactions investigated we obtained an average error for calculated D_e values of 4 kcal/mol.

It is obvious that future investigations have to add further proof for the usefulness of the GVB-LSDC approach. Test examples have to be extended to the dissociation of open-shell compounds and to second-row molecules. Also, it will be interesting to see whether calculated atomization and bond energies are as satisfactory as GVB-LSDC BDE values. Work is in progress to investigate this question.

The method presented is intriguing owing to its modest computational requirements. Because of this, calculations with larger basis sets than the one used in this work will be feasible. Future work has to reveal whether the use of larger basis sets will lead to a significant improvement of calculated BDEs. In this connection, it will be necessary to test the usefulness of bond functions and the impact of the BSSE on

calculated values. Yet another problem to be investigated is the question of whether the fact that GVB is not size-consistent has an impact on the accuracy of D_e . Finally, it will be interesting to see whether more recent density functionals than the VWN functional [39] will lead to an improvement in theoretical BDE values.

The GVB-LSDC method presented here may be considered to be in the mainstream of theoretical approaches that attempt to cover adequately both static and dynamic correlation effects. One has early realized that even large MCSCF treatments lack an appropriate coverage of dynamic correlation effects. Therefore, MRD-CI or CASSCF-CI methods have been designed to obtain highly accurate values of reaction energies and molecular properties. As pointed out above, these methods are often too costly. Therefore, alternatives have been developed such as the GVB-MP2 method [61] or the CASSCF-MP2 approach [62]. These or similar methods will prove their calculational usefulness in the future. Owing to the physical nature of the approximations used in the application of the LSDC functional, the method proposed here cannot, with respect to the possibility of systematic improvement, compete with the *ab initio* methods just mentioned. However, its range of applicability will be much larger owing to its low computational cost.

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