

# Correlation-consistent configuration interaction: Accurate bond dissociation energies from simple wave functions

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We have developed a general method employing relatively small but well-defined CI expansions for calculating accurate bond energies [e.g., errors of 1.4 kcal/mol (1.3%) for the C–H bond energy in CH<sub>4</sub> and 4.9 kcal/mol (2.7%) for the C=C bond energy in ethylene]. The approach includes in a systematic way all correlations involving orbitals that change significantly during bond breakage. The CI expansion truncates rapidly, enabling the application of this technique to polyatomic molecules for which normal correlation approaches would be prohibitively expensive. Thus the bond energy for BH is calculated to within 0.3 kcal/mol of the full CI value but incorporating less than 0.1% of the spin eigenfunctions. Smooth dissociation to the correct adiabatic limit by the CCCI method is demonstrated for the C=C bond of ethylene. The advantage of CCCI is illustrated for C<sub>2</sub>F<sub>4</sub>, where a full CI would involve  $\sim 7 \times 10^{22}$  spatial configurations, but only 1719 are used in CCCI. Here we predict a C=C bond energy for C<sub>2</sub>F<sub>4</sub> of  $D_e(\text{F}_2\text{C}=\text{CF}_2) = 68.3 \pm 2.5$  ( $D_{298} = 64.6 \pm 2.5$ ) kcal/mol. Experimental values range from 53 to 76 kcal/mol.

## I. INTRODUCTION

Accurate bond dissociation energies are essential for assessing chemical reaction mechanisms. Unfortunately, current experimental thermochemical data (especially for organic radicals and inorganic complexes) often have error bars of 5–10 kcal/mol or more.<sup>1</sup> We propose an approach for obtaining greater accuracy with practical *ab initio* calculations for systems of experimental mechanistic interest. Our goal is to develop methods equally applicable (and accurate) for molecules containing heavy atoms or transition metals as for first row molecules. In order to be useful, it is important to obtain accuracies better than 5–7 kcal/mol. Thus our efforts are directed at achieving quantitative accuracy within a small CI expansion so that the technique can be applied to a wide variety of large molecules.

Our method involves a systematic approach for treating both the molecule and the fragments after bond rupture with consistent levels of electron correlation. Thus we focus on the dominant correlations important in bond breakage. This *correlation-consistent CI* (CCCI) method<sup>2(a),2(b)</sup> is also applicable to excitation energies (e.g., singlet–triplet splittings in substituted carbenes<sup>3</sup>) and is applied below to the doublet–quartet splitting in CH.

CCCI is similar in objective to the optimized valence configurations (OVC) method of Das and Wahl which was also designed to account self-consistently for the extra correlation energy associated with bond formation.<sup>2(c)-2(e)</sup> OVC led to excellent bond energies for single-bonded first row diatomic molecules, however it has not been applied to bond energies for polyatomics or multiply bonded systems. The difficulty in extending the OVC method is that the choice of configurations included is somewhat arbitrary (beyond the dominant bond–antibond or GVB-PP-like correlations) and quite specific to the particular molecule under study. The

CCCI method focuses on the dominant electron correlations involved in bond formation, but is a completely general, well-defined prescription for obtaining accurate bond energies, with no special considerations of the particular molecule of interest. This method applies equally well to polyatomics and multiple bonds, whereas the OVC method has not been extended to bond energies for such systems.<sup>2(g)</sup>

In the next section, we outline correlation consistency in the calculation of bond energies. To compare the accuracy of the method to a full CI result, we find that for BH, the CCCI leads to a bond energy within 0.3 kcal/mol of the full CI,<sup>4</sup> although the CCCI has only one-thousandth of the configurations of the full CI. Section III reports CCCI results for the four C–H bond energies of methane, the C=C bond energy in ethylene, and the C≡C bond energy in acetylene. An illustration of the power of this CCCI approach is given for the C=C bond energy of C<sub>2</sub>F<sub>4</sub>, a molecule for which the experimental data vary over a range of 23 kcal/mol and for which a full CI is currently out of the question ( $\sim 7 \times 10^{22}$  spatial configurations for full CI, but only 1719 spatial configurations for CCCI).

## II. THEORETICAL METHOD

### A. Generalized valence bond wave functions

For bond breaking/making processes, the many-electron wave function must dissociate smoothly to fragment wave functions. This dictates an approach based on the valence bond wave function ( $\Psi^{\text{VB}}$ ), which unlike the molecular orbital wave function ( $\Psi^{\text{MO}}$ ), has the correct form for proper dissociation<sup>5</sup> to fragment atomic orbitals for  $R_{\text{bond}} = \infty$ . The variational counterparts to VB and MO wave functions are the self-consistent field generalized valence bond (GVB) and Hartree–Fock (HF) wave functions, in which the orbitals are expanded in a basis set and optimized self-consistently. Our starting point, then, for the CCCI calculations is the GVB wave function,<sup>6,7</sup> since it has

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the correct functional form for proper dissociation (while HF often dissociates to an ionic limit).

For the GVB calculations, only the orbitals comprising the breaking bond are treated as GVB pairs,

$$\Psi^{GVB} = [\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)](\alpha\beta - \beta\alpha), \quad (1)$$

where  $\phi_a$  and  $\phi_b$  are variationally optimized, overlapping, one-electron GVB orbitals. All other electrons in the molecule are treated at the HF level.

Since the number of overlapping terms in the full GVB wave function increases as  $N!$ , where  $N$  is the number of (overlapping) orbitals,<sup>6</sup> it is more effective to do the calculations in terms of orthogonal orbitals. This is accomplished by rewriting each GVB pair in Eq. (1) in the natural orbital representation:

$$\Psi^{NO} = [C_g\phi_g^2 + C_u\phi_u^2](\alpha\beta - \beta\alpha), \quad (2)$$

where  $\phi_g$  and  $\phi_u$  are the (orthogonal) bonding and antibonding natural orbitals of a GVB pair. For a multipair system, the GVB-PP wave function has the form

$$\Psi^{PP} = A [\Psi^{NO}(1,2)\Psi^{NO}(3,4)\cdots]. \quad (2')$$

This is a special case of the full GVB wave function, since the full GVB wave function allows all possible spin couplings of the various orbitals, whereas Eq. (2') has just a single valence bond [or perfect pairing (PP)] coupling of the spins. The GVB-PP wave function builds in "static correlation" between the electrons in each GVB pair, by allowing them to each occupy their own orbital [as in Eq. (1)], on average staying farther apart from one another than if they were restricted to occupy the same spatial orbital (as in restricted HF theory). Rewriting the GVB-PP wave function (2') in terms of a configuration interaction expansion leads to a total of  $2^M N$ -electron configurations where  $M$  is the number of GVB pairs.

### B. Restricted CI calculations (RCI)

A close approximation to the full GVB wave function can be obtained by a configuration interaction expansion using GVB-PP orbitals, in which each GVB pair is allowed to have all three possible occupations for two electrons distributed among that pair of orbitals. This gives rise to  $3^M$  configurations and is denoted as GVB-RCI (restricted CI). The RCI lifts the spin-coupling restriction and also allows interpair correlation (ionic configurations) in which movement of charge in one bond pair is correlated with simultaneous movement of charge in an adjacent bond pair. The RCI wave function generally provides a reasonable description of most molecules by allowing for optimization of spin coupling and by including the dominant interpair and intrapair correlations.

### C. Correlation-consistent CI (CCCI)

In CCCI, we allow full correlation (within the basis) of the two electrons involved in the breaking bond (using the RCI configurations as reference states). Thus we allow all single and double excitations from each (breaking) bond pair to all other orbitals. This is denoted RCI\*SD<sub>bond</sub>. Since bond dissociation generally leads to geometric and hybridization changes in the resultant fragments, the shapes of the other orbitals adjacent to the breaking bond will also be al-

tered. In order to allow for such orbital shape changes among the valence orbitals not involved in the breaking bond, we add, from each RCI configuration, all single excitations from the valence space to all orbitals (RCI\*S<sub>val</sub>).<sup>8</sup> Thus the CCCI can be denoted as RCI\*[SD<sub>bond</sub> + S<sub>val</sub>]. When the orbitals are calculated self-consistently for the RCI\*SD<sub>bond</sub> wave function (e.g., using the GVB3<sup>7(b)</sup> program), the RCI\*S<sub>val</sub> configurations are not added.

### D. Dissociation-consistent CI

The philosophy behind CCCI is modeled on the dissociation-consistent CI (DCCI) developed by Bair and Goddard for closed shell systems.<sup>2</sup> The DCCI involved higher level correlations and procedures to restrict the virtual space. Thus for  $D_e(\text{CH}_3\text{-H})$ , DCCI includes 886 spin eigenfunctions leading to a bond energy of 108.8 kcal/mol, while CCCI includes 273 spin eigenfunctions and leads to a bond energy of 110.5 kcal/mol (experiment is  $111.9 \pm 0.3$  kcal/mol).

### E. BH test

As a rigorous test of how well CCCI performs relative to a full CI,<sup>4</sup> we considered the BH molecule. The experimental  $D_e(\text{B-H}) = 82.3$  kcal/mol,<sup>9</sup> while the six-electron full CI within a DZP basis (132 686 spin eigenfunctions) yields 78.9 kcal/mol.<sup>4</sup> The CCCI method applied to the same basis (110 spin eigenfunctions) yields  $D_e(\text{B-H}) = 79.2$  kcal/mol, in excellent agreement with the full CI (and experimental) value.<sup>10</sup> This indicates that CCCI, with only one-thousandth of the configurations, accounts for most of the differential correlation present in the breaking bond. This suggests CCCI as a practical method for larger systems, where full CI calculations would be impractical.

### F. Multiple bonds

The simplest extension of the CCCI method to double and triple bonds is to include the configurations corresponding to all single and double excitations out of each bond separately. These RCI\*[SD<sub>bond 1</sub> + SD<sub>bond 2</sub> + ... + S<sub>val</sub>] calculations dissociate to fragments at the HF\*S<sub>val</sub> level. That is, the correlations included at the equilibrium molecular geometry for the CCCI reduce to HF\*S<sub>val</sub> in the limit of  $R_{\text{bond}} = \infty$ . Note that we do *not* allow single and double excitations from more than one bond at the same time because that calculation is *not* correlation consistent. It would include some double excitations on fragments, which require triple and quadruple excitations on the molecule in order to be consistent.

### G. Basis sets

In all calculations, the carbon atom was described by the Dunning valence double- $\zeta$  contraction<sup>11</sup> of the Huzinaga (9s5p) basis set,<sup>12</sup> augmented by one set of Cartesian 3d polarization functions with the 3s combination removed ( $\zeta^d = 0.64$ ).<sup>13</sup> The hydrogen atoms were described with the Dunning double- $\zeta$  contraction<sup>11</sup> (scaled by 1.2) of the Huzinaga<sup>12</sup> (4s) basis set, with one set of 2p polarization functions ( $\zeta^p = 1.0$ ) added only to the H atom involved in the

breaking bond. For fluorine, the Dunning valence double- $\zeta$  contraction<sup>11</sup> of the Huzinaga (9s5p) basis set<sup>12</sup> was used.

## H. Geometries

Experimental geometries were used for CH<sub>4</sub>, CH<sub>3</sub>, the <sup>2</sup>Π and <sup>4</sup>Σ<sup>-</sup> states of CH, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>F<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>.<sup>14</sup> The equilibrium geometries of CH<sub>2</sub> (<sup>1</sup>A<sub>1</sub>) and CH<sub>2</sub> (<sup>3</sup>B<sub>1</sub>) were taken from the GVB-POL-CI calculations of Harding and Goddard<sup>15</sup> and the geometries of CF<sub>2</sub> (<sup>1</sup>A<sub>1</sub>) and CF<sub>2</sub> (<sup>3</sup>B<sub>1</sub>) were taken from the GVB(1/2) calculations (within the largest basis) of Bauschlicher *et al.*<sup>16</sup>

## III. RESULTS

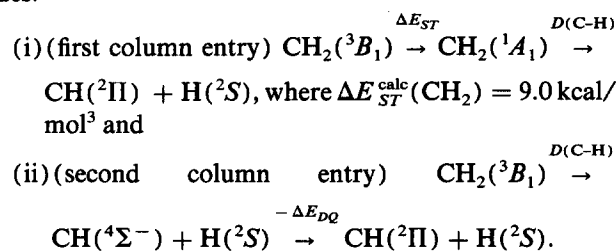
### A. CH bonds

The total energies for CH<sub>X</sub> (X = 0–4) calculated at levels ranging from HF to HF\*SD (CI–SD) to CCCI are listed in Table I and the corresponding successive C–H bond energies are shown in Table II. The CCCI method gives excellent results (within 1–3 kcal/mol) for the first two bond energies in methane, with the agreement less good (within 5–7 kcal/mol) for the last two bond energies in CH<sub>4</sub>. The values obtained with the present method are considerably better than the much larger calculations of conventional CI methodology (e.g., HF\*SD). Thus for the four C–H bonds, CCCI leads to an average error of 4.6 kcal/mol, whereas HF\*SD engenders an average error of 6.6 kcal/mol despite including four times as many configurations (820 vs 3300 for the five states). The basic problem with HF\*SD is the lack of triple and quadruple excitations needed at R<sub>e</sub>.

Three multireference CI calculations of the first C–H bond energy in CH<sub>4</sub> have been reported previously: (i) a

CASSCF/MRD-CI<sup>17</sup> with 63 608 configurations yielded D<sub>e</sub>(H<sub>3</sub>C–H) = 104.3 kcal/mol; (ii) a CASSCF/CCI<sup>18</sup> with 613 941 configurations afforded D<sub>e</sub>(H<sub>3</sub>C–H) = 109.7 kcal/mol; and (iii) a DCCI<sup>2</sup> with 886 spin eigenfunctions resulted in D<sub>e</sub>(H<sub>3</sub>C–H) = 108.8 kcal/mol. Our CCCI result, with only 241 (correlation-consistent) configurations, leads to D<sub>e</sub>(H<sub>3</sub>C–H) = 110.5 kcal/mol (experimental value = 111.9 ± 0.3 kcal/mol).

Since the CCCI method requires treatment of correlation equivalently at both endpoints (infinity and R<sub>e</sub>), two sets of bond energies are listed for CH<sub>2</sub>. The C–H bond in ground state CH<sub>2</sub> (<sup>3</sup>B<sub>1</sub>) is formed from the excited state of CH (<sup>4</sup>Σ<sup>-</sup>). However, the C–H bond in the <sup>1</sup>A<sub>1</sub> excited state of CH<sub>2</sub> is formed from the ground state of CH (<sup>2</sup>Π). The thermodynamic cycle to calculate the adiabatic bond energy [the energy to go from CH<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) to CH(<sup>2</sup>Π) + H(<sup>2</sup>S)] includes:



The <sup>4</sup>Σ<sup>-</sup>–<sup>2</sup>Π state splittings of CH shown in Table III were calculated correlation consistently using the same CI method which accurately predicts singlet–triplet gaps in substituted carbenes.<sup>3</sup> This is accomplished by allowing all single and double excitations to all virtuals from the electron pair involved in the excitation from doublet to quartet. These excitations are taken from RCI reference configurations

TABLE I. Total energies (hartrees) for CH<sub>X</sub>, X = 0–4.<sup>a</sup>

Calculation <sup>b</sup>	CH <sub>4</sub> ( <sup>1</sup> A <sub>1</sub> )		CH <sub>3</sub> ( <sup>2</sup> A <sub>2</sub> <sup>+</sup> )		CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )		CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )		CH			C( <sup>3</sup> P)
	(VDZDP) <sup>c</sup>	(VDZD) <sup>d</sup>	(VDZDP)	(VDZD)	(VDZDP)	(VDZD)	(VDZDP)	<sup>4</sup> Σ <sup>-</sup> (VDZD)	<sup>2</sup> Π(VDZDP)	<sup>2</sup> Π(VDZP)	(VDZD)	
HF	-40.201 27 (1/1)	-39.560 32 (1/1)	-39.562 82 (1/1)	-38.922 54 (1/1)	-38.925 00 (1/1)	-38.883 82 (1/1)	-38.281 18 (1/1)	-38.272 15 (1/1)	-38.269 97 (1/1)	-37.684 52 (1/1)		
GVB(1/2)PP	-40.216 50 (2/2)	-39.560 32 (1/1)	-39.577 50 (2/2)	-38.922 54 (1/1)	-38.938 34 (2/2)	-38.900 32 (2/2)	-38.281 18 (1/1)	-38.289 18 (2/2)	-38.269 97 (1/1)	-37.684 52 (1/1)		
RCI(1/2)	-40.216 50 (3/3)	-39.560 32 (1/1)	-39.578 74 (3/4)	-38.922 54 (1/1)	-38.940 41 (3/5)	-38.900 32 (3/3)	-38.281 18 (1/1)	-38.290 17 (3/4)	-38.269 97 (1/1)	-37.684 52 (1/1)		
SD <sub>C-H</sub>	-40.231 07 (141/141)	-39.560 32 (1/1)	-39.594 98 (134/245)	-38.922 54 (1/1)	-38.958 69 (118/286)	-38.914 73 (106/106)	-38.281 18 (1/1)	-38.304 27 (92/164)	-38.269 97 (1/1)	-37.684 52 (1/1)		
CCCI <sup>e</sup>	-40.244 97 (241/273)	-39.569 66 <sup>f</sup> (44/86)	-39.613 40 (228/503)	-38.934 25 <sup>f</sup> (36/76)	-38.976 40 (203/539)	-38.926 46 (176/198)	-38.292 41 <sup>f</sup> (30/54)	-38.321 92 (136/274)	-38.279 08 <sup>f</sup> (22/40)	-37.699 04 <sup>f</sup> (19/33)		
HF*SD	-40.357 55 (1183/1753)	-39.688 94 (670/1903)	-39.697 45 (929/2660)	-39.024 54 (482/1462)	-39.032 92 (691/2147)	...	-38.351 40 (306/681)	-38.376 86 (355/850)	-38.368 23 (144/314)	-37.759 31 (283/573)		

<sup>a</sup> The total energy for the hydrogen atom within the (unscaled) double- $\zeta$  basis used here is -0.499 28 hartree. 1 hartree = 627.5096 kcal/mol = 27.211 62 eV = 219 474.8 cm<sup>-1</sup>.

<sup>b</sup> Computational details are provided in Sec. II of the text. The corresponding number of spatial configurations/spin eigenfunctions for each wave function is given beneath each total energy.

<sup>c</sup> VDZDP basis: Huzinaga–Dunning (9s5p/3s2p) valence double- $\zeta$  basis plus one set of Cartesian 3d functions ( $\zeta^d = 0.64$ ; the 3s combination was removed) on carbon and the Huzinaga–Dunning scaled (4s/2s) double- $\zeta$  basis for hydrogen, with one set of 2p functions ( $\zeta^p = 1.0$ ) on the hydrogen involved in the C–H bond being broken.

<sup>d</sup> VDZD basis: the same basis as in footnote c) but with no augmenting 2p functions for hydrogen. [Total energies for calculations using VDZD basis refer to the appropriate limit at R(C–H) = ∞, i.e., HF, HF\*S<sub>val</sub>, or HF\*SD (Sec. II)].

<sup>e</sup> RCI(1/2)\*[SD<sub>C-H</sub> + S<sub>val</sub>].

<sup>f</sup> HF\*S<sub>val</sub> total energy.

TABLE II. Adiabatic bond energies ( $D_e$ ) in kcal/mol for  $\text{CH}_X\text{-H}$  ( $X = 0\text{-}3$ ).<sup>a</sup>

Calculation	$\text{CH}_3\text{-H}$	$\text{CH}_2\text{-H}$	$\text{CH-H}^b$	$\text{C-H}$	Error <sup>b</sup>
HF	88.9	88.5	80.9,74.3	55.4	27.8
HF*SD	106.3	109.0	103.8 <sup>c</sup>	74.2	6.6
GVB(1/2)PP	98.5	97.7	91.2,82.7	66.1	18.2
RCI(1/2)	98.5	98.5	91.2,84.0	66.7	17.6
$\text{SD}_{\text{C-H}}$	107.3	108.7	100.3,95.4	75.6	7.9
CCCI <sup>d</sup>	110.5	112.9	101.9,99.5	77.6	4.6
Experiment <sup>e</sup>	$111.9 \pm 0.3$	$115.8 \pm 1.4$	$107.4 \pm 1.3$	$84.5 \pm 0.2$	
$\Delta_{\text{corr}}^f$	$1.4 \pm 0.3$	$2.9 \pm 1.4$	$5.5, 7.9 \pm 1.3$	$6.9 \pm 0.2$	
ZPE <sup>g</sup>	27.10	18.41	$10.88 \pm 0.22$	4.09	

<sup>a</sup> Computational details are provided in Sec. II of the text.

<sup>b</sup> Values of  $D_e$  (CH-H) were calculated via two thermodynamic cycles in order to treat  $\text{CH}_2$  and CH consistently; (i)  $\text{CH}_2$  ( $^3B_1$ )  $\xrightarrow{\Delta E_{ST}}$   $\text{CH}_2$  ( $^1A_1$ )  $\xrightarrow{D(\text{C-H})}$   $\text{CH}$  ( $^2\Pi$ ) +  $\text{H}$  ( $^2S$ ) (first column entry) and (ii)  $\text{CH}_2$  ( $^3B_1$ )  $\xrightarrow{D(\text{C-H})}$   $\text{CH}$  ( $^4\Sigma^-$ ) +  $\text{H}$  ( $^2S$ )  $\xrightarrow{-\Delta E_{DQ}}$   $\text{CH}$  ( $^2\Pi$ ) +  $\text{H}$  ( $^2S$ ) (second column entry). [ $\Delta E_{ST}(\text{CH}_2) = 9.0$  and  $\Delta E_{DQ}(\text{CH}) = 16.4$  kcal/mol, from Ref. 3 and from Table III of this work.

<sup>c</sup> The value of  $D_e$  (CH-H) for HF\*SD is obtained directly from  $\text{CH}_2$  ( $^3B_1$ )  $\rightarrow$   $\text{CH}$  ( $^2\Pi$ ) +  $\text{H}$  ( $^2S$ ).

<sup>d</sup>  $\text{RCI}(1/2) * [\text{SD}_{\text{C-H}} + S_{\text{val}}]$ .

<sup>e</sup> Experimental  $D_e$ 's are derived from  $\Delta H_{70}^0$  [taken from Ref. 24(b) and JANAF supplements in J. Phys. Chem. Ref. Data 4, 1 (1975) and 11, 695 (1982)], with zero point energy corrections from: Ref. 24(a) for  $\text{CH}_4$ ; M. E. Jacox, J. Phys. Chem. Ref. Data 13, 945 (1984) for  $\text{CH}_3$ ; P. R. Bunker, P. Jensen, W. P. Kraemer, and R. Beardsworth, J. Chem. Phys. 85, 3724 (1986) for  $\text{CH}_2$ ; and Ref. 9 for CH.

<sup>f</sup>  $\Delta_{\text{corr}} = D^{\text{expt}}(\text{C-H}) - D^{\text{calc}}(\text{C-H})$ , where  $D^{\text{calc}}$  is from CCCI.

<sup>g</sup> ZPE = zero point energy; see footnote e.

<sup>h</sup> Average absolute value of error.

where the RCI involves correlation of the C-H bond pair [GVB(1/2)]. This correlation-consistent treatment results in a  $\Delta E_{DQ} = 16.4$  kcal/mol, in excellent agreement with experiment ( $\Delta E_{DQ}^{\text{expt}} = 16.7$  kcal/mol).<sup>9</sup>

## B. $\text{H}_2\text{C}=\text{CH}_2$

The adiabatic C-C bond energy of ethylene is shown in Table IV for various levels of calculation. Both HF and

TABLE III. Doublet-quartet splittings ( $\Delta E_{DQ} = E_{^4\Sigma^-} - E_{^2\Pi}$ ) and total energies for CH.<sup>a</sup>

Calculation	Total energies (hartrees)		$\Delta E_{DQ}$ (kcal/mol)
	$^4\Sigma^-$	$^2\Pi$	
HF	-38.281 18 (1/1)	-38.269 96 (1/1)	-7.0
HF*SD	-38.351 40 (160/364)	-38.368 23 (144/314)	+10.6
GVB-PP	-38.291 50 (2/2)	-38.307 99 (4/4)	+10.3
GVB-RCI(PP) <sup>b</sup>	-38.294 84 (3/6)	-38.309 26 (6/8)	+9.0
GVB-RCI(opt) <sup>c</sup>	-38.295 99 (3/6)	-38.309 38 (6/8)	8.4
CCCI <sup>d</sup>	-38.307 42 (67/127)	-38.333 56 (112/252)	+16.4
Experiment			+16.7 <sup>e</sup>

<sup>a</sup> VDZD basis. Computational details are provided in Sec. II. The corresponding number of spatial configurations/spin eigenfunctions for each wave function is given beneath each total energy.

<sup>b</sup> GVB-RCI using the GVB-PP orbitals.

<sup>c</sup> Self-consistent GVB-RCI.

<sup>d</sup> RCI\*SD<sub>opt</sub>(PP).

<sup>e</sup> Reference 9.

HF\*SD fall considerably short (by 57 and 25 kcal/mol, respectively) of the final CCCI value (174.1 kcal/mol), which is in excellent agreement with experiment ( $179.0 \pm 2.5$ ). A strenuous test of correlation consistency is shown in Figs. 1(a) and 1(b), where we have calculated full potential curves (for the seven calculational levels listed in Table IV) for the dissociation of the C=C double bond. These curves were computed constraining the H-C-H bond angle and the C-H bond length to be constant [fixed at the experimental values for  $\text{C}_2\text{H}_4$  ( $\theta_e = 117.6^\circ$  and  $R_e = 1.086 \text{ \AA}$ )<sup>14(a)</sup>], resulting in  $D_e$ 's larger than adiabatic  $D_e$ 's by, e.g., 2.6 kcal/mol at the SCF level. Table V displays the characteristics of each potential curve [ $R_e(\text{C}=\text{C})$ ,  $k_e(\text{C}=\text{C})$ , and  $D_e(\text{C}=\text{C})$ ] and the correlation error incurred at long  $R(\text{C}=\text{C})$  (9.939  $\text{\AA}$ ) relative to the corresponding calculation performed on the separated fragments (e.g., HF, HF\*SD, or HF\*S<sub>val</sub>). From Fig. 1 and Table V we see that both HF and HF\*SD dissociate far above the dissociated fragments (by 326.1 and 153.3 kcal/mol, respectively) with the HF curve still increasing in energy at 9.939  $\text{\AA}$ . The ionic character in the HF wave function leads to interactions which fall off as  $R^{-1}$ , and thus are felt at extremely long  $R$ . The GVB-PP curve levels off much quicker (by 3.0  $\text{\AA}$ ) than the HF-based wave functions, due to the covalent functional form of GVB. The correlation error incurred by GVB-PP (26.7 kcal/mol) at long  $R$  is due primarily to the spin restrictions in which the sigma and pi electrons for the two  $\text{CH}_2$  groups are still restricted to be singlet coupled (as preferred for  $R_e$ ), with a spin coupling between the sigma and pi electrons on each  $\text{CH}_2$  of  $\frac{3}{4}$  triplet and  $\frac{1}{4}$  singlet. Since free  $\text{CH}_2$  has these two electrons triplet coupled, the GVB-PP restriction destabilizes the limit by one carbon  $p$ - $p$  exchange term ( $K_{pp} \sim 18.4$  kcal/mol). The limit is further destabilized

TABLE IV. Adiabatic C–C bond energies ( $D_e$ ) in kcal/mol for  $H_2C=CH_2$  and  $HC\equiv CH$ .<sup>a</sup>

Calculation	Total energies (hartrees)				$D_e(H_2C=CH_2)$	$D_e(HC\equiv CH)$	
	$H_2C=CH_2$	$CH_2(^3B_1)^b$	$HC\equiv CH$	$CH(^4\Sigma^-)^b$		Direct <sup>c</sup>	Using $\Delta E_{DQ}$ <sup>d</sup>
HF	– 78.039 55 (1/1)	– 38.922 41 (1/1)	– 76.824 38 (1/1)	– 38.281 18 (1/1)	122.2	178.5	131.6
HF*SD	– 78.293 99 (1315/2092)	– 39.024 54 (250/732)	– 77.063 40 (800/1206)	– 38.351 40 (160/364)	153.7	205.2	193.5
GVB-PP	– 78.077 57 (4/4)	– 38.922 41 (1/1)	– 76.878 00 (8/8)	– 38.281 18 (1/1)	146.1		165.3
GVB-RCI	– 78.091 18 (5/6)	– 38.922 41 (1/1)	– 76.920 14 (14/20)	– 38.281 18 (1/1)	154.6		191.7
RCI*S <sub>val</sub>	– 78.128 64 (239/418)	– 38.934 15 (20/40)	– 76.954 63 (536/1306)	– 38.292 41 (18/36)	163.4		199.3
RCI*[SD <sub>σ</sub> + SD <sub>π</sub> ]	– 78.113 43 (465/596)	– 38.922 41 (1/1)	– 76.954 28 (1706/2926)	– 38.281 18 (1/1)	168.6		213.1
CCCI <sup>e</sup>	– 78.145 74 (651/944)	– 38.934 15 (20/40)	– 76.978 58 (2048/3872)	– 38.292 41 (18/36)	174.1		214.3
Experiment <sup>f</sup>					179.0 ± 2.5		236 ± 0.7
$\Delta_{corr} = D_e^{expt} - D_e^{CCCI}$					4.9 ± 2.5		21.8 ± 0.7

<sup>a</sup> VDZD basis. Computational details are provided in Sec. II of the text. The corresponding number of spatial configurations/spin eigenfunctions for each wave function are given beneath each total energy.

<sup>b</sup> Total energies for  $CH_2$  and  $CH$  are for the appropriate limit at  $R(C-C) = \infty$ , i.e., HF, HF\*S<sub>val</sub>, or HF\*SD.

<sup>c</sup> Direct  $D_e(HC\equiv CH)$  from  $D_e(HC\equiv CH) = 2 \times E(^2\Pi CH) - E(HC\equiv CH)$ .

<sup>d</sup>  $D_e(HC\equiv CH) = 2 \times E(^4\Sigma^- CH) - E(HC\equiv CH) - 2 \times \Delta E_{DQ}$ , where  $\Delta E_{DQ} = 16.4$  kcal/mol (see Table III).

<sup>e</sup> RCI\*[SD<sub>σ</sub> + SD<sub>π</sub> + S<sub>val</sub>] for  $C_2H_4$  and RCI\*[SD<sub>σ</sub> + SD<sub>π<sub>x</sub></sub> + SD<sub>π<sub>y</sub></sub> + S<sub>val</sub>] for  $HC\equiv CH$ .

<sup>f</sup> Experimental  $D_e$ 's are derived from  $\Delta H_{f0}^0$  [taken from Ref. 24(b) and J. Phys. Chem. Ref. Data 4, 1 (1975)] with zero point energy corrections for  $C_2H_4 = 30.89$  kcal/mol and  $C_2H_2 = 16.18$  kcal/mole from Ref. 24(a).

by having orbitals which reflect this nonoptimum spin coupling, leading to an overall destabilization of 26.7 kcal/mol. The CI wave functions which use the GVB-PP orbitals as the basis dissociate with little or no correlation error, since the spin-coupling constraint has been removed. Thus the RCI and RCI\*[SD<sub>σ</sub> + SD<sub>π</sub>] wave functions engender errors of only 1.8 and 0.8 kcal/mol, respectively, with these residual errors due to the nonoptimum shapes of the GVB-PP orbitals. The CI's which allow valence orbital shape changes (RCI\*S<sub>val</sub> and CCCI) eradicate the error due to improper orbital shapes, leading to correlation errors of only 0.3 kcal/mol (this is due to the overcorrelation of the limit where simultaneous single excitations are allowed on both  $CH_2$ 's).

Table V also reports equilibrium C=C bond distances and stretching force constants obtained from the curves shown in Fig. 1. We see that HF yields too short a bond distance and a very large force constant, while all of the correlated wave functions yield bond distances which are long by 0.007–0.025 Å. The force constants for the GVB-based potential curves are all very similar, ~1300 kcal mol<sup>-1</sup> Å<sup>-2</sup>, while the HF-based potential curves are considerably higher. This may be understood in terms of the distorted nature of the HF-based curves, with high force constants and short bond distances the result of the destabilized limits.

### C. $HC\equiv CH$

Table IV also displays results for the C≡C triple bond energy in acetylene. Dissociating the triple bond smoothly to CH fragments leads to the  $^4\Sigma^-$  excited state of CH. The

adiabatic C≡C bond energy of acetylene was calculated by a CCCI on both HCCH and  $CH(^4\Sigma^-)$ , followed by a CCCI deexcitation (Table III) to the ground state of  $CH(^2\Pi)$  for each fragment, similar to the method used to calculate the C–H bond energy in  $CH_2$  (*vide supra*). The results of Table IV (residual correlation error of  $21.8 \pm 0.7$  kcal/mol for CCCI) clearly indicate that for triple bonds, simultaneous correlations (up through quadruple or even sextuple excitations to virtuals) must be necessary to approach the experimental value, while for double bonds, such simultaneous excitations appear to be much less important (residual correlation error of  $4.9 \pm 2.5$  kcal/mol). The possibility of symmetric bent or “banana” bonds in  $C_2H_2$  was explored to see if such a description could account for the correlation error. We find the CCCI bond energies with a bent bond description to be the same to within 0.3 kcal/mol as with one  $\sigma$  and two  $\pi$  bonds.<sup>19</sup>

### D. $F_2C=CF_2$

The objective in developing CCCI was to address systems impossible with normal approaches. As an example of this, we applied the CCCI method to the bond energy of  $C_2F_4$ . The size of this system precludes full CI treatment (~10<sup>23</sup> spatial configurations) but requires only 1719 spatial configurations for CCCI. The experimental value for  $D_{298}(F_2C=CF_2)$  is quite uncertain, with values ranging from  $53.4 \pm 0.7$  to  $76.3 \pm 3$  kcal/mol.<sup>20–22</sup> Dissociating the  $\sigma$  and  $\pi$  bonds of  $C_2F_4$ <sup>23</sup> smoothly produces excited  $CF_2(^3B_1)$  fragments. Thus, C=C bond cleavage can be most

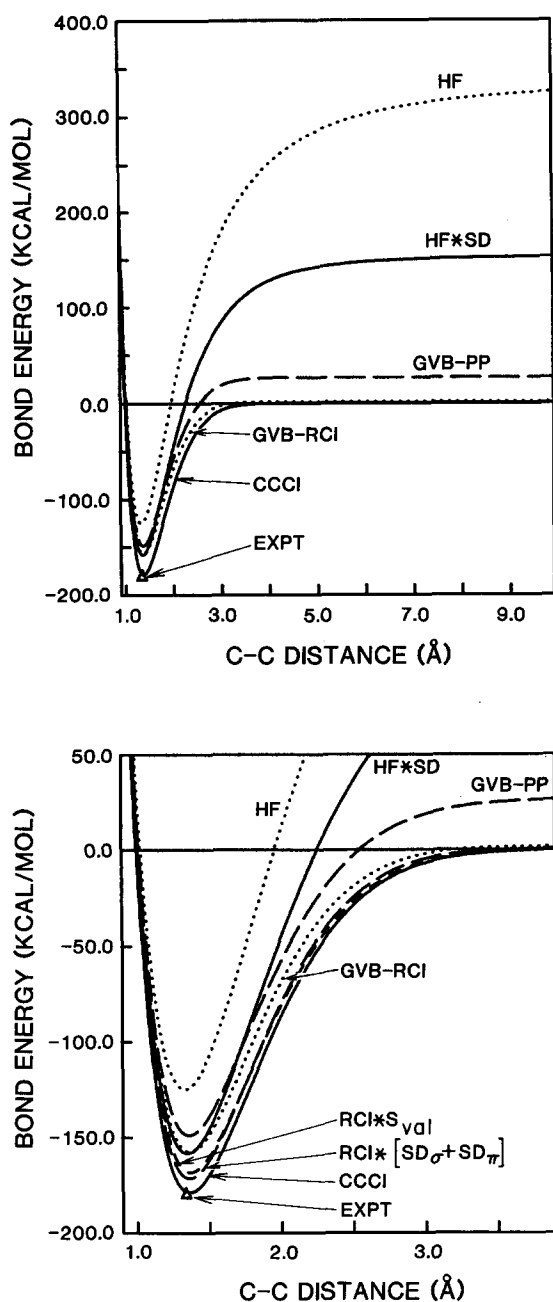


FIG. 1 (a). Potential curves for the dissociation of the C=C bond in  $C_2H_4$  over the range 0.9 to 9.9 Å. HF and HF\*SD dissociate far above the covalent limit (326.1 and 153.3 kcal/mol, respectively) due to ionic character in the wave functions, GVB-PP dissociates above the covalent limit (by 26.7 kcal/mol) due to spin-coupling restrictions, while all GVB-based CIs (RCI and CCCI shown here) dissociate properly, with little residual error at the covalent limit (see Table V). (b) Magnification of (a) over the range of 0.9 to 3.9 Å, with two other GVB-based CIs also shown (RCI\*S<sub>val</sub> and RCI\*[SD<sub>σ</sub> + SD<sub>π</sub>]).

simply described by a CCCI of  $C_2F_4$  dissociating to two  $CF_2$  ( $^3B_1$ ) fragments, followed by a CCCI deexcitation of each  $CF_2$  ( $^3B_1$ ) to the ground state of  $CF_2$  ( $^1A_1$ ). The CCCI result for  $D_e(F_2C=CF_2)$  is 63.4 kcal/mol (Table V). Assuming the same residual correlation error occurs in  $C_2F_4$  as in  $C_2H_4$  ( $\Delta_{corr} = D_e^{expt} - D_e^{CCCI} = 4.9 \pm 2.5$  kcal/mol) leads to

(Table V) an estimated adiabatic bond energy of  $D_e(F_2C=CF_2) = 68.3 \pm 2.5$ , a zero temperature value (including zero-point energy) of  $D_0 = 63.6 \pm 2.5$ , and a room temperature value of  $D_{298} = 64.6 \pm 2.5$  kcal/mol.<sup>24</sup> Using  $\Delta H_{f,298}^0(C_2F_4) = -157.4 \pm 0.7$  kcal/mol,<sup>24(b)</sup> our calculations lead to  $\Delta H_{f,298}^0(CF_2) = -46.5 \pm 1.6$  kcal/mol, supporting the experimental value of  $\Delta H_{f,298}^0(CF_2) = -44.2 \pm 1^{(c)}$  rather than  $-52$  kcal/mol.<sup>20</sup>

The CCCI bond energy may be compared with three experimental values of  $53.4 \pm 0.7$ ,<sup>20</sup>  $69.0 \pm 2.7$ ,<sup>21</sup> and  $76.3 \pm 3$  kcal/mol.<sup>22</sup> The theory rules out the lowest value and agrees rather well with the intermediate value. In contrast, the ubiquitous theoretical approach, HF\*SD, includes an order of magnitude more configurations (and requires 3 h 35 min on a DEC VAX 8650) than CCCI (which only requires 4 min on the 8650), but yields a bond energy low by 30–40 kcal/mol!

Recently, we reported a simple relationship between bond energies [ $D(C=C)$ ] in substituted olefins or methanes and singlet–triplet excitation energies ( $\Delta E_{ST}$ ) in substituted carbenes.<sup>25</sup> We showed that trends in C=C bond strengths in halogenated olefins could be explained by considering only whether the CXY fragments comprising the olefin have singlet or triplet ground states. Diabatically breaking the  $\sigma$  and  $\pi$  bonds in an olefin results in triplet fragments, but if the ground state of CXY is a singlet, the adiabatic bond energy is weaker by the electronic relaxation energy,  $\Delta E_{ST}$ . Assuming that the diabatic C=C bond energy (to dissociate to triplet fragments) is independent of substitution, we used experimental adiabatic olefin bond energies to estimate the singlet–triplet splittings of substituted carbenes.<sup>25</sup> Later, we used CCCI calculations of  $\Delta E_{ST}$  to obtain new estimates of the adiabatic bond energies,  $D_{298}(C=C)$ .<sup>3(b)</sup>

Since ethylene dissociates to triplet fragments adiabatically, these estimates were based on the assumption that the intrinsic olefin C=C bond strength is  $D_{298}(H_2C=CH_2) = 172.2 \pm 2.1$  kcal/mol.<sup>24(b),24(d)</sup> The intrinsic bond energies in ethylene (Table IV) and tetrafluoroethylene (Table VI) provide a quantitative test of this premise, with the CCCI calculations yielding intrinsic bond energies [to  $CX_2$  ( $^3B_1$ ) fragments] of  $D_e = 178.4$  kcal/mol for  $C_2F_4$  and  $D_e = 174.1$  kcal/mol for  $C_2H_4$ . Thus the assumption that the diabatic bond energy is independent of substitution is correct to 4.3 kcal/mol (2%). When zero point energy and heat capacity corrections are included<sup>24,26</sup> to arrive at  $D_{298}$  for each olefin, the intrinsic bond energy for  $C_2F_4$  is larger than for  $C_2H_4$  by 6.9 kcal/mol. Thus the error in using the relationship between  $D(C=C)$  and  $\Delta E_{ST}$  as presented in Ref. 25 is 6.9 kcal/mol. Considering that the observed adiabatic bond strengths differ by more than 100 kcal/mol, this validates the use of the simple approach of Ref. 25.

#### IV. CONCLUSIONS

We present the simplest wave function emphasizing correlation consistency while including the dominant electron correlations dictated by the physics of bond dissociation.

TABLE V. Equilibrium properties for the C=C bond in ethylene (see Fig. 1).

Calculation	$R_e(\text{C}=\text{C})$ (Å)	$k_e(\text{C}=\text{C})$ (kcal mol <sup>-1</sup> Å <sup>-2</sup> )	$D_e(\text{C}=\text{C})^a$ (kcal/mol)	Correlation error <sup>b</sup> (kcal/mol)
HF	1.327	1603.3	124.8	326.1
HF*SD	1.346	1440.2	158.2	153.3
GVB(2/4)-PP	1.358	1307.3	148.8	26.7
GVB-RCI	1.363	1276.6	157.5	1.8
RCI*S <sub>val</sub>	1.369	1248.7	168.3	0.3
RCI*[SD <sub>σ</sub> + SD <sub>π</sub> ]	1.363	1294.5	171.4	0.8
CCCI	1.364	1292.7	178.9	0.3
Experiment	1.339 <sup>c</sup>	...	179.0 ± 2.5 <sup>d</sup>	...

<sup>a</sup> Energy ( $D_e$ ) to dissociate to two CH<sub>2</sub> (<sup>3</sup>B<sub>1</sub>) fragments with  $\theta(\text{H}-\text{C}-\text{H})$  and  $R(\text{C}-\text{H})$  fixed at 117.6° and 1.086 Å, [experimental equilibrium values in C<sub>2</sub>H<sub>4</sub>; Ref. 14(a)] respectively, along the entire potential curve (Fig. 1).

<sup>b</sup> Correlation error at  $R(\text{C}-\text{C}) = 9.939$  Å relative to the separated fragments (with the same geometry as in footnote a).

<sup>c</sup> The experimental value for  $R_e(\text{C}=\text{C})$  is taken from Ref. 14(a).

<sup>d</sup> Experimental adiabatic  $D_e(\text{H}_2\text{C}=\text{CH}_2)$ ; see Table IV.

This avoids the biases plaguing conventional CI-SD approaches, while retaining a minimum number of configurations. For single and double bonds, the method predicts bond energies in good agreement (errors of 1–7 kcal/mol) with experiment. However, for triple bonds the errors are much larger (~22 kcal/mol). The CCCI wave function dissociates continuously to the correct adiabatic limit at

$R = \infty$ , as is demonstrated by the smooth dissociation of the C=C bond in ethylene. An indication of the power of this approach is given for C<sub>2</sub>F<sub>4</sub> where CCCI leads to an expected accuracy of 5 kcal/mol for 1719 configurations, while HF\*SD CI utilizes 18 772 configurations, engendering an error of 30 kcal/mol, and full CI would require ~10<sup>23</sup> configurations. Thus the error of CCCI is considerably less than

TABLE VI. Bond energies ( $D_e$ ) in kcal/mol for F<sub>2</sub>C=CF<sub>2</sub>.<sup>a</sup>

Calculation	Total energies (hartrees)		$D_e^{\text{diab}}(\text{F}_2\text{C}=\text{CF}_2)^c$	$D_e^{\text{adiab}}(\text{F}_2\text{C}=\text{CF}_2)$	
	F <sub>2</sub> C=CF <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	CF <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> ) <sup>b</sup>		Direct <sup>d</sup>	Using $\Delta E_{\text{ST}}$ <sup>e</sup>
HF	-473.492 55 (1/1)	-236.647 24 (1/1)	124.3	59.4	9.3
HF*SD	-474.076 13 (18772/34184)	-236.929 80 (3155/16053)	135.9	39.1	20.9
GVB-PP	-473.532 19 (4/4)	-236.647 24 (1/1)	149.2		34.2
GVB-RCI	-473.548 68 (5/6)	-236.647 24 (1/1)	159.5		44.5
RCI*S <sub>val</sub>	-473.580 45 (941/1724)	-236.657 39 (63/157)	166.7		51.7
RCI*[SD <sub>σ</sub> + SD <sub>π</sub> ]	-473.572 45 (849/1098)	-236.647 24 (1/1)	174.4		59.4
CCCI <sup>f</sup>	-473.599 09 (1719/2728)	-236.657 39 (63/157)	178.4		63.4
$D_e^{\text{adiab}} + \Delta_{\text{corr}}^g$					68.3 ± 2.5
Experiment <sup>h</sup>					57.2 ± 0.7, <sup>i</sup> 72.8 ± 2.7 <sup>j</sup> , 80.1 ± 3 <sup>k</sup>

<sup>a</sup> VDZD basis. Computational details are provided in Sec. II of the text. The corresponding number of spatial configurations/spin eigenfunctions for each wave function are given beneath each total energy.

<sup>b</sup> Total energies for CF<sub>2</sub> are for the appropriate limit at  $R(\text{C}-\text{C}) = \infty$ , i.e., HF or HF\*S<sub>val</sub>.

<sup>c</sup>  $D_e^{\text{diab}}(\text{F}_2\text{C}=\text{CF}_2) = 2 \times E(^3B_1, \text{CF}_2) - E(\text{C}_2\text{F}_4)$ .

<sup>d</sup> Direct  $D_e(\text{F}_2\text{C}=\text{CF}_2)$  from  $2 \times E(^1A_1, \text{CF}_2) - E(\text{C}_2\text{F}_4)$ , where the HF and HF\*SD total energies of <sup>1</sup>A<sub>1</sub> CF<sub>2</sub> are -236.698 98 and -237.006 93 hartrees (2633 spatial configurations/4399 spin eigenfunctions).

<sup>e</sup>  $D_e^{\text{adiab}}(\text{F}_2\text{C}=\text{CF}_2) = D_e^{\text{diab}}(\text{F}_2\text{C}=\text{CF}_2) - 2 \times \Delta E_{\text{ST}}$ , where  $E_{\text{ST}} = 57.5$  kcal/mol [Refs. 3(b) and 3(c)].

<sup>f</sup> RCI\*[SD<sub>σ</sub> + SD<sub>π</sub> + S<sub>val</sub>].

<sup>g</sup>  $\Delta_{\text{corr}}$  for C=C is taken from Table IV.

<sup>h</sup> Experimental  $D_e$ 's are derived from  $D_{298}^{\text{expt}}$ 's by correcting for finite temperature (subtract 1.0 kcal/mol) to obtain  $D_0^{\text{expt}}$ 's and then correcting for differential zero point energy (add 4.8 kcal/mol) to obtain  $D_e^{\text{expt}}$ 's, based on the zero point energies of 13.4 kcal/mol for C<sub>2</sub>F<sub>4</sub> and 4.3 kcal/mol for CF<sub>2</sub> [Ref. 24(a)].

<sup>i</sup> Reference 20.

<sup>j</sup> Reference 21.

<sup>k</sup> Reference 22.

TABLE VII. Explanation of acronyms for various calculational levels.

Acronym	Meaning
HF	Hartree-Fock
HF*S <sub>val</sub>	HF with all single excitations from valence orbitals
HF*SD	HF with all single and double excitations from valence orbitals
GVB-PP	Generalized valence bond with perfect pairing restriction
GVB-RCI	GVB-restricted configuration interaction
RCI*SD <sub>bond</sub>	GVB-RCI with single and double excitations from each breaking bond
RCI*S <sub>val</sub>	GVB-RCI with all single excitations from valence orbitals
CCCI	Correlation-consistent CI: RCI*SD <sub>bond</sub> + RCI*S <sub>val</sub>
DCCI	Dissociation-consistent CI (Ref. 2)
GVB-POL-CI	GVB polarization CI (Ref. 15)
CASSCF	Complete active space self-consistent field (Ref. 17)
MRD-CI	Multireference doubles CI (Ref. 17)
CCI	Contracted CI (Ref. 18)

the dispersion in experimental values. The CCCI approach has also been successfully applied to transition metal ligand systems, resulting in bond energies within 2–5 kcal/mol of experiment.<sup>27</sup> Furthermore, *intrinsic* C=C bond energies are found to be nearly constant (within 7 kcal/mol), even though the observed bond strengths differ by up to ~100 kcal/mol, supporting the previously proposed approach for estimating  $\Delta E_{ST}$  (CXY) based on C=C bond weakening.<sup>25</sup>

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<sup>8</sup>Since SCF wave functions are stable to first-order changes (Brillouin theorem), single excitations (first-order changes) within a CI wave function correspond physically to orbital shape changes.

<sup>9</sup>K.-P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).

<sup>10</sup>The CCCI calculations for BH were carried out with exactly the same basis set and geometry as used in the full CI (Ref. 4). We used  $C_{2v}$  symmetry with the experimental bond distance of 2.329 bohr. The basis set for BH was the Dunning (Ref. 11) double- $\zeta$  contraction of the Huzinaga (Ref. 12) (9s5p) basis for boron augmented by one set of 3d polarization functions ( $\zeta^d = 0.5$ , with the 3s combination included) and the Dunning (4s/2s) basis for hydrogen (scaled by  $\zeta^s = 1.2$ ) augmented by one set of 2p polarization functions ( $\zeta^p = 1.0$ ). For BH, the total energy for RCI\*[SD<sub>bond</sub> + S<sub>val</sub>] (with 110 spin eigenfunctions) is  $-25.15929$  hartrees, while the full CI (with 132 686 spin eigenfunctions) yields  $-25.22763$  hartrees (Ref. 4). The CCCI method dissociates to HF\*S<sub>val</sub> fragments, yielding a total energy for the B atom of  $-24.53376$  hartrees, while the full CI value for B is  $-24.60264$  hartrees (Ref. 4). The total energy for the H atom is  $-0.49928$  with the (4s/2s) basis.

<sup>11</sup>T. H. Dunning, Jr., *J. Chem. Phys.* **53**, 2823 (1970).

<sup>12</sup>S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

<sup>13</sup>The carbon *d* exponent was optimized for the GVB wave function of CH<sub>4</sub> by R. A. Bair and W. A. Goddard III (unpublished) [Refs. 2(a) and 2(b)].

<sup>14</sup>(a) M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, and A. G. Maki, *J. Phys. Chem. Ref. Data* **8**, 619 (1979); (b) *Landolt-Börnstein Tables* (Springer, Berlin, 1976), Vol. 7.

<sup>15</sup>L. B. Harding and W. A. Goddard III, *Chem. Phys. Lett.* **55**, 217 (1978).

<sup>16</sup>C. W. Bauschlicher, Jr., H. F. Schaefer III, and P. S. Bagus, *J. Am. Chem. Soc.* **99**, 7106 (1977).

<sup>17</sup>F. B. Brown and D. G. Truhlar, *Chem. Phys. Lett.* **113**, 441 (1985).

<sup>18</sup>P. E. M. Siegbahn, *Chem. Phys. Lett.* **119**, 515 (1985).

<sup>19</sup>The CCCI total energy [using the symmetric bent bond GVB(3/6)PP wave function] for C<sub>2</sub>H<sub>2</sub> is  $-76.97901$  hartrees, with 5138 spatial configurations and 9780 spin eigenfunctions. At the GVB-PP level, bent bonds are higher in energy than  $\sigma/\pi$  bonds for C<sub>2</sub>H<sub>2</sub> by 0.7 kcal/mol, increasing to 1.8 kcal/mol for a six-electron full CI within the six orbitals of the triple bond [ $E_{GVB-CI(3/6)}(\sigma/\pi)$  bonds] =  $-76.92150$  hartrees and  $E_{GVB-CI(3/6)}$  (symmetric bent bonds) =  $-76.91857$  hartrees. This is in



contrast to GVB-PP results for  $C_2F_2$  by R. P. Messmer and P. A. Schultz, Phys. Rev. Lett. **57**, 2653 (1986), who found bent bonds  $\sim 2$  kcal/mol lower than  $\sigma$  and  $\pi$  bonds.

<sup>20</sup>This bond energy was obtained indirectly from the heat of formation of  $C_2F_4$  ( $\Delta H_{f,298}^0 = -157.4 \pm 0.7$  kcal/mol) [Ref. 24(b)] and one experimental value for  $\Delta H_{f,298}^0(CF_2) = -52$  kcal/mol from S. G. Lias, J. F. Liebman, and R. D. Levin, J. Phys. Chem. Ref. Data **13**, 695 (1984).

<sup>21</sup>This bond energy was also obtained indirectly from  $\Delta H_{f,298}^0(C_2F_4) = -157.4$  kcal/mol and another experimental value for  $\Delta H_{f,298}^0(CF_2) = -44.2 \pm 1$  kcal/mol from Ref. 1(i).

<sup>22</sup>K. F. Zmbov, O. M. Uy, and J. L. Margrave, J. Am. Chem. Soc. **90**, 5090 (1968). This study using Knudsen cell equilibrium at high temperature ( $\sim 1200$  K) constitutes the only directly determined bond energy for  $C_2F_4$ .

<sup>23</sup>We explored the possibility of bent bonds being lower in energy than  $\sigma$  and  $\pi$  bonds for  $C_2F_4$ . We find energies equal (within 0.1 kcal/mol) at the GVB-PP level. For the four-electron full CI within the four orbitals of the double bond, the  $\sigma$  and  $\pi$  bonds are favored by 0.1 kcal/mol over symmetric bent bonds [ $E_{GVB-CI(2/4)}(\sigma/\pi \text{ bonds}) = -473.54944$  hartrees and  $E_{GVB-CI(2/4)}(\text{symmetric bent bonds}) = -473.54924$  hartrees]; E. A. Carter and W. A. Goddard III, J. Am. Chem. Soc. (submitted).

<sup>24</sup>Zero point energy and temperature corrections to  $D_e$  were obtained from (a) T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, Natl.

Stand. Ref. Data Ser., Natl. Bur. Stand. **39** (1972); (b) JANAF Thermochemical Tables, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. **37** (1971); (c) M. E. Jacox, J. Phys. Chem. Ref. Data **13**, 945 (1984); (d) JANAF Thermochemical Tables, 1982 Supplement, J. Phys. Chem. Ref. Data **11**, 695 (1982).

<sup>25</sup>E. A. Carter and W. A. Goddard III, J. Phys. Chem. **90**, 998 (1986).

<sup>26</sup>Zero point energies for  $CF_2$  were taken from Ref. 24(c) (4.3 kcal/mol) for the  $^1A_1$  state, while the zero point motion of the  $^3B_1$  state was estimated ( $4.1 \pm 0.1$  kcal/mol) from the frequency shifts in  $C_2D_4$  [Ref. 24(a)] going to  $CD_2$  [P. R. Bunker, P. Jensen, W. P. Kraemer, and R. J. Beardsworth, J. Chem. Phys. **85**, 3724 (1986)] and the frequencies in  $C_2F_4$  [Ref. 24(a)]. This leads to  $T_0(CF_2) = 57.3 \pm 0.1$  kcal/mol [ $\Delta E_{ST} = T_0(CF_2) = 57.5$  kcal/mol].

<sup>27</sup> $D_e^{\text{calc}}(Cr^+ \equiv CH_2) = 49.6$  kcal/mol [E. A. Carter and W. A. Goddard III, J. Phys. Chem. **88**, 1485 (1984)] vs  $D_e^{\text{expt}}(Cr^+ \equiv CH_2) = 52 \pm 3$  kcal/mol [N. Aristov and P. B. Armentrout, J. Am. Chem. Soc. **108**, 1806 (1986)];  $D_e^{\text{calc}}(\overset{+}{V} \equiv O) = 128.3$  kcal/mol [E. A. Carter and W. A. Goddard III, J. Phys. Chem. (in press)] vs  $D_e^{\text{expt}}(\overset{+}{V} \equiv O) = 131 \pm 5$  kcal/mol [N. Aristov and P. B. Armentrout, J. Am. Chem. Soc. **106**, 4065 (1984)]; many  $M^+ - H$  and  $M^+ - CH_3$  bond energies may be compared in: J. B. Schilling, W. A. Goddard III, and J. L. Beauchamp, J. Am. Chem. Soc. **108**, 582 (1986); J. Phys. Chem. **91**, 5616 (1987); J. Am. Chem. Soc. **109**, 5565, 5573 (1987).