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Reappraisal of *cis* effect in 1,2-dihaloethenes: An improved virtual orbital multireference approach

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Computed relative stabilities for isomers of 1,2-difluoroethene and 1,2-dichloroethene isomers are compared with predictions based on chemical hardness (η) and electrophilicity (ω) using the principles of maximum hardness and minimum electrophilicity. The chemical hardness and electrophilicity deduced either from improved virtual orbital (IVO) energies or from correlated treatments correctly predict that *cis* 1,2-difluoroethene and 1,2-dichloroethene are energetically more stable than the corresponding *trans* isomers, and the ground state energies from multireference perturbation theory with IVO orbitals agree with these predictions. However, when the same quantities are computed using Hartree–Fock orbitals, serious inconsistencies between the two approaches emerge in predicting the stability of the isomers of the 1,2-dihaloethenes. The present study clearly demonstrates that the IVO energies are appropriate for the computation of hardness related parameters, notably the chemical hardness and electrophilicity. Moreover, the IVO methods also provide smooth potential energy curves for the *cis-trans* isomerization of the two 1,2-dihaloethenes. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2958284]

I. INTRODUCTION

The structures of the 1,2-dihaloethenes are quite interesting because the relative energies of their geometrical isomers appear to conflict with expectations emerging from well-known chemical models. For example, the valence shell electron pair repulsion (VSEPR) model[1] predicts that the 1,2-dihaloethenes preferentially adopt an *anti* conformation so as to minimize the repulsions between C–X (X=F, Cl, Br) bond dipoles and to reduce steric hindrances. However, both experimental[2] and theoretical[3] studies demonstrate that *cis*-1,2-dihaloethene isomers are more stable than the *trans* isomers and thus disagree with the VSEPR model. This situation is called the *cis effect* or *cis* preference for geometrical isomerization and is also observed for other double bonded halogenated species as well as for 1,2-methoxyethene.[4] According to Wiberg *et al.*,[5] the *cis* effect arises due to destabilization of the *trans* isomer rather than the stabilization of the *cis* species. The most recent proposal for explaining the *cis* effect by Yamamoto *et al.*[6] uses high level *ab initio* and density functional theory (DFT) calculations to suggest that the *cis* effect emerges because lone pair electron delocalization reduces intramolecular interactions. In particular, the repulsion between the lone pair electrons of fluorine with the nearby bonding electron pairs overrides the VSEPR model propensities and stabilizes the *cis* conformer.

The chemical hardness[7] (η) and chemical potential[8] (μ) are widely used in conjunction with DFT calculations to provide measures of molecular stability. According to the *principle of maximum hardness*[9] (PMH), "molecules tend to arrange themselves to be as hard as possible." Thus, molecule A is predicted by the PMH as being more stable than molecule B if $\eta(A) > \eta(B)$. The concept of PMH has been applied by Kanakaraju *et al.*[10] to analyze the anomalous *cis* effect quantitatively for 1,2-difluoroethene and 1,2-dichloroethene using the PMH, but their theoretical results are inconclusive. The relative Hartree–Fock (HF) energies computed with a 6-31G* (Ref. 11) basis set find the *trans* conformer to be energetically more stable than the *cis*, whereas, in contrast, the chemical hardness of the *cis* isomer is greater than that of the *trans* isomer. HF/6-31+G* (Ref. 11) basis set calculations, on the other hand, correctly find the *cis* structure to be lower in energy and of greater hardness than the *trans* structure. Earlier MP2/6-31G* and MP2/6-31+G* (Ref. 10) calculations incorrectly predict the most stable structures for 1,2-difluoroethene and 1,2-dichloroethene, although the MP2/6-31+G* calculations presented here give the correct ordering by a small margin. These results demonstrate that the basis set required to explain the anomalous *cis* effect should contain *at least* one diffuse and one polarization function.

In the present communication, we study the relative stabilities of the 1,2-difluoroethene and 1,2-dichloroethene isomers using multireference Möller-Plesset (MRMP) (Ref. 12)

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perturbation theory calculations with a first order function derived from the improved virtual orbital (IVO)–complete active space configuration interaction (CASCI) method (which is now in the GAMESS package).[13] Unlike the more traditional (HF) treatments in which the orbitals and orbital energies are determined from a *single* Fock operator, the IVO-CASCI method uses *multiple* Fock operators to define the valence orbitals[13,14] and orbital energies from $V^{(N-1)}$ potentials, where N is the number of electrons present in the reference HF function. Therefore, the IVOs treat all valence orbitals on an equal footing, a situation contrasting the unbalanced use in HF methods of a $V^{(N-1)}$ potential for the orbitals occupied in the reference HF state and a HF V^N potential for the valence orbitals that are unoccupied in the reference state.

The IVO orbital energies provide approximations to the chemical hardness and chemical potentials, as well as to the hardness related quantity called the electrophilicity.[15,16] According to the *principle of minimum electrophilicity*[15,16] (PME), molecules arrange themselves with minimum electrophilicity. Hence, the electrophilicity is also compared to the computed relative stabilities of the *cis* and *trans* isomers in order to test the PME for the dihaloethenes.

The chemical hardness and electrophilicity evaluated from the IVO orbital energies with 6-31G*, 6-31+G*,[11] cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ (Ref. 17) basis sets are found here to be consistent (except for the smallest 6-31G* basis) with the relative stability predicted by second order Möller-Plesset perturbation theory[18] (MP2) and the IVO orbital formulation of MRMP perturbation theory.[19] The latter is a modified (and faster) version of traditional MRMP perturbation theory[12] in which the first order multiconfigurational reference space functions are generated using the IVO-CASCI scheme.

The present study clearly demonstrates the benefits of choosing IVO energies for computing the chemical hardness (η), chemical potential (μ), and electrophilicity (ω). Our calculations further indicate that multireference perturbation theory (MRPT) calculations with IVO-CASCI wavefunctions generate smooth and accurate torsional potential energy curves (PECs) and the *cis-trans* reaction pathways. In contrast, coupled cluster singles and doubles (CCSD) (Ref. 20) and the renormalized coupled cluster method CR-CC(2,3),[21] which includes an approximate treatment of triples, are unable to reproduce the transition state corresponding to a 90° twist between the =CHF groups. The single reference coupled cluster methods also require a larger basis set to properly assign the *cis* structure as lower in energy. The CCSD, CCSD(T) (Ref. 22) and third order effective valence shell Hamiltonian approaches[14,23–31] (H_v^{3rd}) using the IVOs all fail to predict the most stable structure for 1,2-difluoroethene at the cc-pVDZ geometry, requiring aug-cc-pVDZ or cc-pVTZ to properly order the *cis* and *trans* structures, where the IVO-MRMP method is correct in this respect for all but the smallest basis considered.

Since the IVOs represent an essential component in the determination of the chemical hardness and parameters related to the stability of 1,2-dihaloethene isomers, we begin with a brief description of the IVO scheme (Sec. II) followed by the theoretical background of IVO-MRMP method (Sec. III). The calculated results are presented and compared with other methods in Sec. IV.

II. GENERATION OF IMPROVED VIRTUAL ORBITALS

Because the basic philosophy of generating the IVOs applies equally for restricted and unrestricted HF orbitals, the approach is illustrated for a closed shell restricted HF reference function as used in the present calculations.

When the ground state of the system is a closed shell, the HF approximation to the ground state wave function is expressed in terms of HF molecular orbitals (MOs) as $\Phi_0=\mathcal{A}[\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_n\bar{\phi}_n]$ where $\mathcal{A}$ is the antisymmetrizer. Let the indices $i,j,k,\cdots$ refer to the HF MOs $\{\phi_i\}$ that are occupied in the ground state and $u,v,w,\cdots$ to the remaining unoccupied HF MOs. All the HF MOs are eigenfunctions of the one-electron HF operator ${}^1F$,

$$ {}^1F_{lm}=\left\langle \phi_l \middle| H_1+\sum_{k=1}^{\mathrm{occ}}(2J_k-K_k) \middle| \phi_m \right\rangle=\delta_{lm}\epsilon_l, \tag{1}$$

where l and m designate any (occupied or unoccupied) HF MO and ϵ_l is the HF orbital energy. The operator H_1 is the one-electron portion of the Hamiltonian, and J_k and K_k are Coulomb and exchange operators, respectively, for the occupied orbital ϕ_k.

An excited state HF computation would provide a new set $\{\chi\}$ of MOs that produces the lowest possible energies for the low lying singly excited $\Psi_{\alpha\to\mu}$ state,

$$\Psi(\alpha\to\mu)=\mathcal{A}[\chi_1\bar{\chi}_1\chi_2\bar{\chi}_2\cdots(\chi_\alpha\bar{\chi}_\mu\pm\chi_\mu\bar{\chi}_\alpha)\cdots\chi_n\bar{\chi}_n], \tag{2}$$

corresponding to the excitation of an electron from the orbital χ_α to χ_μ where the + and − signs correspond to triplet and singlet states, respectively. The new MOs $\{\chi_\alpha\}$ and $\{\chi_\mu\}$ may be expressed as a linear combination of the ground state MOs $\{\phi_i,\phi_u\}$. If, however, the orbitals are further restricted such that the $\{\chi_\alpha\}$ are linear combinations of only the occupied ground state MOs $\{\phi_\alpha\}$ and the $\{\chi_\mu\}$ are expanded only in terms of the unoccupied $\{\phi_u\}$,

$$\chi_\alpha=\sum_{i=1}^{\mathrm{occ}}a_{\alpha i}\phi_i,\quad \chi_\mu=\sum_{u=1}^{\mathrm{unocc}}c_{\mu u}\phi_u, \tag{3}$$

then the new orbital set $\{\chi_\alpha,\chi_\mu\}$ not only leaves the ground state wave function unchanged but also ensures the orthogonality and applicability of Brillouin's theorem between the HF ground state and the $\Psi_{\alpha\to\mu}$ excited states. In addition, this choice also benefits from using a common set of MOs for the ground and excited states, a choice that simplifies the computation of oscillator strengths, etc. However, we avoid the computationally laborious reoptimization of the occupied orbitals by setting $\{\chi_\alpha\}\equiv\{\phi_\alpha\}$, i.e., by choosing $a_{\alpha j}=\delta_{\alpha j}$, thereby simplifying enormously the procedure for generating the IVOs. Hence, the coupled equations determining the coefficients $a_{\alpha j}$ and $c_{\mu\nu}$ reduce to a single eigenvalue equation of the form $F'C=C\Gamma$, where the one-electron operator F' is given by

$$F'_{vw} = {}^{1}F_{vw} + A^{\alpha}_{vw}, \tag{4}$$

where ${}^{1}F$ is the ground state Fock operator, and the additional term A^{α}_{vw} accounts for excitation of an electron out of orbital ϕ_α,

$$A^{\alpha}_{vw} = \langle \chi_v | - J_\alpha + K_\alpha \pm K_\alpha | \chi_w \rangle. \tag{5}$$

The minus sign in Eq. (5) applies when ${}^{3}\Psi_{\alpha\to\mu}$ is a triplet state, while the plus sign is for the singlet ${}^{1}\Psi_{\alpha\to\mu}$ state.[14,32] The corresponding transition energy is

$${}^{1,3}\Delta E(\alpha \to \mu) = E_0 + \gamma_\mu - {}^{1}F_{\alpha\alpha}, \tag{6}$$

where E_0 is the HF ground state energy and γ_μ is the eigenvalue of $F'C = C\Gamma$ for the μth orbital.

III. THEORETICAL BACKGROUND FOR IVO-MRPT METHOD

The IVO-modification of MRMP theory (recently introduced into the GAMESS package[33]) is formally identical to the *single state* MCSCF formulation of MRMP perturbation theory by Hirao[12] except that those reference space orbitals that are unoccupied in the SCF reference function are generated in the IVO-MRMP approach using the IVO-CASCI procedure. The MRMP model of Hirao[12] is also equivalent to the *single state* version of Nakano's MCQDPT theory.[34] Since the basic formalism for the IVO-MRMP approach is identical to that for the MCQDPT/MRMP method, we briefly outline this theoretical background.

As in conventional many-body perturbation theory, the IVO-MRMP/MCQDPT method begins with the decomposition of the total Hamiltonian H as

$$H = H_0 + V, \tag{7}$$

where H_0 is the unperturbed Hamiltonian and V is the perturbation. The Schrödinger equation for the unperturbed system,

$$H_0 |\Phi_i\rangle = E_i^0 |\Phi_i\rangle \tag{8}$$

provides a complete set of eigenfunctions $\{|\Phi_i\rangle\}$ with corresponding eigenvalues $\{E_i^0\}$. The eigenfunctions of H_0 is then partitioned into two subspaces defined by two complementary projectors P and Q, where

$$P = \sum_{r=1}^{d} |\Phi_r\rangle\langle\Phi_r| \tag{9}$$

and

$$Q = 1 - P. \tag{10}$$

In quasidegenerate perturbation theory, the Hamiltonian is block diagonalized by a similarity transformation

$$\mathcal{H} = \Omega^{-1} H \Omega. \tag{11}$$

Using the definitions of P and Q and separating H into H_0 and V, Eq. (11) becomes

$$[\Omega_{PP}, H_0] = V_{QQ}\Omega_{QP} + V_{PP}\Omega_{PP} - \Omega_{QP}(\mathcal{H}_{\text{eff}} - H_{0,PP}), \tag{12}$$

$$\Omega_{PP}\mathcal{H}_{\text{eff}} = H_{PP}\Omega_{PP} + V_{PQ}\Omega_{QP}. \tag{13}$$

Since no equation exists for Ω_{PP}, the transformation matrix Ω is nonunique and thus requires an additional condition. Thus, Ω_{PP} is chosen to be unitary, and, hence, the transition dipole matrix is symmetric.

The perturbation approximation is completely determined by the choice of reference (P) space, orbitals, orbital energies, and the definition of the zeroth order Hamiltonian H_0. Generally, the zeroth order Hamiltonian is defined as a sum of one-electron operators,

$$H_0 = \sum_{pq} f_{pq} a_p^\dagger a_q, \tag{14}$$

to obtain the zeroth order energies as a sum of orbital energies ϵ_p. The matrix f_{pq} in Eq. (14) is defined as

$$f_{pq} = h_{pq} + \frac{1}{2}\sum_{rs} D^{\text{avg}}_{rs}\left[\langle pr \| qs\rangle - \tfrac{1}{2}\langle pr \| sq\rangle\right], \tag{15}$$

where h_{pq} and $\langle ij||kl\rangle$ represent one- and two-electron integrals and D^{avg}_{pq} denotes the average of the one-particle density matrix over all the IVO-CASCI states in the CAS. The one- and two-electron integrals appearing in f_{pq} (and in subsequent MRMP/MCQDPT calculations) are computed using the improved virtual orbitals. (Hunt and Goddard[35] and Bair and Goddard[36] also use a similar approach in their IVO based CI calculations.)

The IVO-CASCI eigenfunctions $\{|\alpha\rangle\}$ are linear combinations of configuration state functions (CSFs) $|A\rangle$,

$$|\alpha| = \sum_{\text{A}} C_{\alpha A} |A\rangle. \tag{16}$$

The effective Hamiltonian within the CAS/MCSCF reference space through first order is the diagonal matrix,

$$\langle\alpha|\mathcal{H}^{(0-1)}|\beta\rangle = E_\alpha^{\text{CASCI/MCSCF}}\delta_{\alpha\beta}, \tag{17}$$

where $E_\alpha^{\text{CASCI/MCSCF}}$ denotes the CASCI/MCSCF energy. Finally, the second order contribution to the effective Hamiltonian in the reference space is the nondiagonal matrix,

$$\langle\alpha|\mathcal{H}^{(2)}|\beta\rangle = \frac{1}{2}\sum_I \langle\alpha|V|I\rangle \frac{1}{E_\beta^0 - E_I^0}\langle I|V|\beta\rangle + \frac{1}{2}(\text{hc}), \tag{18}$$

where $|I\rangle$ denotes a CSF from the orthogonal space, E_β^0 and E_I^0 are the zeroth order energies for states β and I, respectively, and (hc) is the Hermitian conjugate of the preceding term.

The present calculations employ the CAS generated by two orbitals, the highest occupied HO molecular orbital (MO) from the HF ground state and the lowest IVO. Computations with an added second IVO yield very similar results and are not presented.

The IVO-MRMP approach and the IVO modification of the MCQDPT scheme retain all the advantages of MCSCF formulations of MRMP/MCQDPT theory. In addition, the

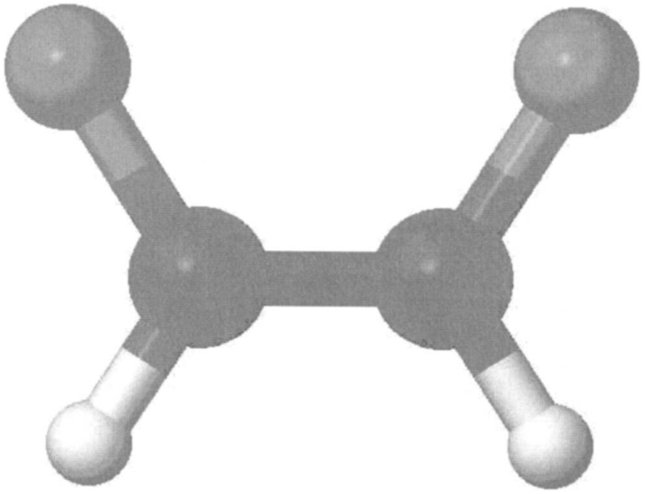

FIG. 1. Geometrical structure of *cis*-1,2-dihaloethene.

IVO-MRMP/MCQDPT method does not require tedious and costly MCSCF iterations beyond those in an initial SCF calculation.

IV. RESULTS AND DISCUSSION

The calculated structures for the ground states of *cis* and *trans* 1,2-dihaloethenes are depicted in Figs. 1 and 2, respectively.

A. Structures and relative energies of *cis*- and *trans* 1,2-difluoroethenes

The geometrical parameters for *cis*- and *trans*-1,2-difluoroethenes are optimized, employing MP2 perturbation theory. Table I summarizes the optimized ground state geometries for the 6-31G*, 6-31+G*, cc-pVDZ, and aug-cc-pVDZ basis sets. The present calculations clearly demonstrate that during the *cis*→*trans* isomerization of 1,2-difluoroethene, (a) the C–F bond length increases by ∼0.005 Å, (b) the ∠HCH increases roughly by 2.5°, (c) the ∠CCF decreases almost by the same (2.5°) amount, and (d) no significant change in the C═C and C–H bond lengths emerges between the *cis* and *trans* isomers. Table I also indicates that for a given conformer, the use of a split valence basis yields estimates of the C═C and C–H bond lengths that are shorter than those from the correlation consistent polarized valence (cc-pVDZ, cc-PVTZ) basis sets. Moreover, Table I shows that inclusion of diffuse and polarization functions increases the computed C–H and C–F bond length by 0.003 and 0.004 Å, respectively. However, the variation of the C–F bond length with basis set is most dramatic for the transition to the aug-cc-pVDZ basis where the C–F bond length increases by 0.017 Å. The bond angles, on the other hand, vary by ∼0.5°–1° when the basis sets are augmented with diffuse *s*, *p*, and *d* functions.

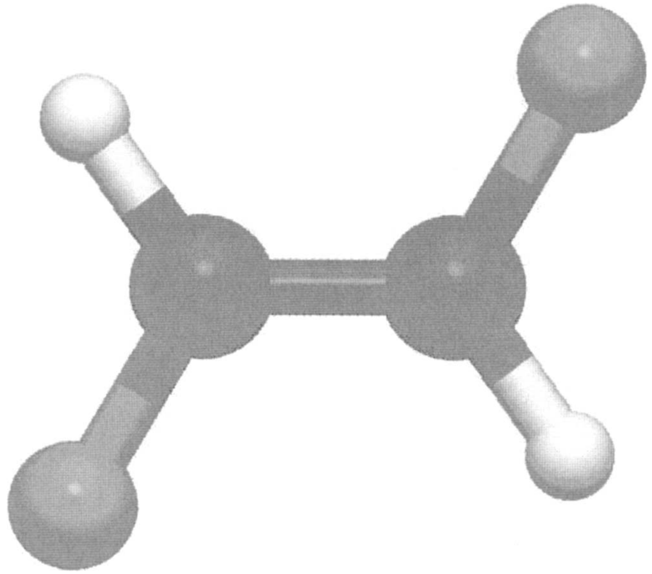

FIG. 2. Geometrical structure of *trans*-1,2-dihaloethene.

TABLE I. The MP2 optimized geometry for 1.2-difluoroethene equilibrium bond lengths and bond angles.

	6-31G*	6-31+G*	cc-pVDZ	aug-cc-pVDZ
		cis		
R(C-O)/Å	1.331	1.332	1.339	1.341
R(C-H)/Å	1.082	1.082	1.091	1.089
R(C-F)/Å	1.351	1.356	1.343	1.356
∠CCH	123.1	123.6	121.7	122.8
∠CCF	122.1	122.0	123.1	122.3
		trans		
R(C-C)/Å	1.331	1.332	1.339	1.340
R(C-H)/Å	1.082	1.082	1.092	1.089
R(C-F)/Å	1.355	1.363	1.346	1.363
∠CCH	125.3	126.4	124.2	125.0
∠CCF	119.8	119.3	120.5	119.5

Table II presents the ground state energies of the 1,2-difluoroethenes computed using the HF, MP2, IVO-MRMP, H_v^{3rd}, CCSD, and CCSD(T) methods with 6-31G*, 6-31+G*, cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, and aug-cc-pVTZ basis sets. When the smallest 6-31G* basis is used, all six levels of theory predict the *trans* isomer to be more stable than the *cis* one, while computations with the four largest basis sets considered exhibit the completely opposite (correct) trend. The energetic favorability of the *cis* structure increases with the size of the basis set, suggesting that even larger basis sets only increase the margin by which all methods predict the correct minimum energy conformer. An adequate description of electron correlation in these systems clearly requires a nonminimal basis set, such as those provided by the correlation-consistent series. The IVO-MRMP method predicts the *cis* structure to be more favorable by a larger margin than other methods, and for all but the smallest basis set. This suggests that using IVOs instead of HF orbitals results in more rapid convergence to the physical answer with respect to the basis set, which is consistent with their design.

B. Stability and chemical hardness

In this section, we analyze the relative stability of the isomers of the 1,2-difluoroethenes that are inferred from their chemical hardness (η) and electrophilicity (ω). The

TABLE II. The calculated state energy E (in a.u.) and relative energy $\Delta E=E(trans)-E(cis)$ (in kcal/mol) for 1,2-difluoroethene. CCSD and CCSD(T) results were obtained using NWChem (Ref. 37) $[E(cis/trans)=E+275.0$ a.u.$]$.

Method	$E(cis)$	$E(trans)$	ΔE	$E(cis)$	$E(trans)$	ΔE
	6-31G*			6-31+G*		
HF	−0.7163	−0.7168	−0.31	−0.7311	−0.7302	0.56
MP2	−1.3106	−1.3108	−0.13	−1.3386	−1.3379	0.44
IVO-MRMP	−1.3183	−1.3187	−0.25	−1.3479	−1.3452	1.69
H_v^{3rd}	−1.3098	−1.3102	−0.25	−1.3348	−1.3339	0.56
CCSD	−1.3310	−1.3315	−0.31	−1.3576	−1.3572	0.25
CCSD(T)	−1.3477	−1.3482	−0.31	−1.3759	−1.3755	0.25
	cc-pVDZ			aug-cc-pVDZ		
HF	−0.7383	−0.7386	−0.19	−0.7601	−0.7585	1.04
MP2	−1.3791	−1.3789	0.13	−1.4470	−1.4453	1.07
IVO-MRMP	−1.3870	−1.3866	0.25	−1.4563	−1.4525	2.38
H_v^{3rd}	−1.3835	−1.3836	−0.06	−1.4486	−1.4467	1.19
CCSD	−1.4022	−1.4023	−0.06	−1.4680	−1.4666	0.88
CCSD(T)	−1.4190	−1.4192	−0.13	−1.4900	−1.4886	0.88
	cc-pVTZ			aug-cc-pVTZ		
HF	−0.8307	−0.8298	0.56	−0.8358	−0.8325	2.07
MP2	−1.7027	−1.7016	0.69	−1.7336	−1.7317	1.19
IVO-MRMP	−1.7099	−1.7082	1.07	−1.7419	−1.7378	2.57
H_v^{3rd}	−1.7000	−1.6986	0.88	−1.7145	−1.7122	1.44
CCSD	−1.7175	−1.7168	0.44	−1.7473	−1.7458	0.94
CCSD(T)	−1.7486	−1.7479	0.44	−1.7808	−1.7793	0.94

chemical potential[8] (μ) and the chemical hardness[7] (η) of an N-electron system with total energy E are defined as

$$\mu=\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \quad \text{and} \quad \eta=\frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})}, \tag{19}$$

where $v(\vec{r})$ is the external potential. The PMH predicts that molecule A is more stable than molecule B if $\eta(A)>\eta(B)$. The other hardness related quantity called electrophilicity (ω) is defined as

$$\omega=\frac{\mu^2}{2\eta}, \tag{20}$$

and according to the PME, A is more stable than B if $\omega(A)<\omega(B)$.

The chemical potential and hardness of a molecule can be expressed in terms of its ionization potential (IP) and electron affinity (EA) as

$$\eta=\frac{\mathrm{IP}-\mathrm{EA}}{2} \qquad \mu=-\frac{\mathrm{IP}+\mathrm{EA}}{2}, \tag{21}$$

where the finite difference approximation is the only physically sensible formulation for use with *ab initio* calculations. Using Koopman's theorem to provide the approximations $\mathrm{IP}\approx-\epsilon_{\mathrm{HOMO}}$ and $\mathrm{EA}\approx-\epsilon_{\mathrm{LUMO}}$, the expressions for η and μ can be simplified to

$$\eta=\frac{\epsilon_{\mathrm{LUMO}}-\epsilon_{\mathrm{HOMO}}}{2} \qquad \mu=\frac{\epsilon_{\mathrm{LUMO}}+\epsilon_{\mathrm{HOMO}}}{2}, \tag{22}$$

where ϵ_{HOMO} and ϵ_{LUMO} represent the HOMO and lowest unoccupied (LUMO) energies, respectively, in the reference state HF approximation. Koopman's theorem provides a more accurate estimate for the IP than for the EA because electron correlation and relaxation effects tend largely to cancel each other for the ionization of a neutral molecule. The shortcomings of Koopman's EA can be partly circumvented by replacing the HF unoccupied orbital energy by the corresponding IVO orbital energy for the EA in Eq. (22). Koopman's theorem approximation for the IP remains unchanged because the IVO scheme only alters the HF unoccupied orbitals.

Table III presents the chemical hardness, chemical potential, and electrophilicity of the 1,2-difluoroethenes that are evaluated from Koopman's theorem approximation for the IP and EA. As evident from Table III, the IVO-CASCI calculations yield η (ω) for the *cis* isomer as higher (lower) than the corresponding quantities for the *trans* isomer. These findings also accord with the relative energies ($E_{\mathrm{trans}}-E_{\mathrm{cis}}$) computed using the MP2 and IVO-MRMP methods (see Table II). The similar trend also emerges for the 1,2-dichloroethenes (see Tables V and VI) and, thus, unequivocally suggests that the *cis* conformers are energetically more stable than the *trans* isomers for both the 1,2-difluoroethenes and 1,2-dichloroethenes. (CCSD computations for the relative stability of 1,2-difluroethylene at the CCSD optimized geometry also exhibit a similar inconsistency.) The chemical hardness

TABLE III. The chemical hardness η (in eV), chemical potential μ (in eV), and electrophilicity ω (in eV) of 1,2-difluoroethene calculated from the Koopman's theorem IP and EA.

		η		μ		ω	
Basis set	Orbital[a]	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
6-31G*	HF	7.66	7.62	−2.75	−2.79	0.018	0.019
	HF/MRMP	7.43	7.38	−2.77	−2.80	0.019	0.020
	IVO	2.10	2.06	−8.31	−8.35	0.602	0.621
	IVO/MRMP	7.56	7.47	−2.59	−2.63	0.016	0.017
6-31+G*	HF	6.36	6.48	−4.38	−4.26	0.056	0.051
	HF/MRMP	6.36	6.48	−4.38	−4.26	0.056	0.051
	IVO	2.09	2.01	−8.65	−8.72	0.657	0.696
	IVO/MRMP	7.28	6.65	−3.17	−3.79	0.025	0.040
cc-pVDZ	HF	7.54	7.49	−2.91	−2.95	0.021	0.021
	HF/MRMP	7.32	7.27	−2.92	−2.97	0.021	0.022
	IVO	2.07	2.02	−8.38	−8.41	0.622	0.642
	IVO/MRMP	7.43	7.37	−2.73	−2.77	0.018	0.019
aug-cc-pVDZ	HF	5.77	5.87	−4.91	−4.79	0.077	0.072
	HF/MRMP	5.77	5.87	−4.91	−4.79	0.077	0.072
	IVO	2.05	1.96	−8.63	−8.70	0.665	0.709
	IVO/MRMP	7.11	6.19	−3.28	−4.18	0.028	0.052

[a] HF, orbital energies computed from HF orbitals with HF (V^n) potenital; HF/MRMP, orbital energies computed from HF orbitals with state-average density; IVO, orbital energies computed from IVO orbitals with V^{N-1} potential; and IVO/MRMP, orbital energies computed from IVO orbitals with state-average density.

TABLE IV. The chemical hardness η (in eV), chemical potential μ, (in eV), and electrophilicity ω (in eV) of 1,2-difluoroethene calculated from correlated IP and EA calculations. CCSDT results were obtained using NWChem (Ref. 37) [$E(cis/trans)=E+275.0$ a.u.].

		η		μ		ω	
Basis set	Method	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
6-31G*	IVO-MRMP	3.39	3.37	−6.54	−6.44	0.23	0.23
	FSCCSD	3.00	3.05	−7.03	−7.00	0.30	0.30
	CCSDT	3.06	3.11	−7.13	−7.11	0.31	0.30
6-31+G*	IVO-MRMP	4.75	4.32	−5.74	−5.73	0.13	0.14
	FSCCSD	4.39	4.25	−5.99	−6.15	0.15	0.16
	CCSDT	2.93	2.98	−7.06	−7.02	0.31	0.30
cc-pVDZ	IVO-MRMP	4.04	3.96	−5.82	−5.88	0.15	0.16
	FSCCSD	3.22	3.26	−6.88	−6.83	0.27	0.26
aug-cc-pVDZ	IVO-MRMP	2.80	2.44	−7.89	−8.74	0.41	0.58
	FSCCSD	4.88	4.75	−5.56	−5.66	0.12	0.12

TABLE V. Calculated state energies E (in a.u.) and relative energy $\Delta E=E(trans)-E(cis)$ (in kcal/mol) for 1,2-dichloroethene. CCSD results were obtained using GAMESS (Ref. 33) [$E(cis/trans)=E+995.0$].

Method	$E(cis)$	$E(trans)$	ΔE	$E(cis)$	$E(trans)$	ΔE
	cc-pVDZ			aug-cc-pVDZ		
HF	−0.8825	−0.8829	−0.25	−0.8897	−0.8902	−0.31
MP2	−1.5485	−1.5478	0.44	−1.5484	−1.5477	0.44
IVO-MRMP	−1.5541	−1.5536	0.31	−1.5984	−1.5977	0.44
CCSD	−1.5827	−1.5826	0.06	−1.5826	−1.5826	0.00

TABLE VI. The calculated chemical hardness η (in eV), chemical potential μ (in eV), and electrophilicity ω (in eV) of 1,2-dichloroethene.

		η		μ		ω	
Basis set	Orbital[a]	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
cc-pVDZ	HF	6.69	6.63	−3.17	−3.22	0.03	0.03
	IVO	2.17	2.15	−7.68	−7.71	0.50	0.51
aug-cc-pVDZ	HF	5.42	5.53	−4.52	−4.42	0.07	0.06
	IVO	2.15	2.12	−7.79	−7.82	0.52	0.53

[a] HF, orbital energies computed from HF orbital with HF (V^N) potential and IVO, orbital energies computed from IVO orbital with V^{N-1} potential.

and electrophilicity evaluated using IVO energies are consistent with the relative stability predicted by the MP2 and IVO-MRMP methods, except for calculations with the 6-31G* basis set. Thus, the choice of the IVO energy for ϵ_{LUMO} is appropriate for the computation of chemical hardness, chemical potential, and, hence, electrophilicity.

Table IV presents the computed chemical hardness and chemical potential the IP and EA generated with the correlated IVO-MRMP approach[19] and the Fock space coupled cluster method with singles and double excitations (FSCCSD),[38–43] exhibiting the same trends as from the IVO and IVO-MRMP methods. For example, the chemical hardness (electrophilicity) of *cis* 1,2-difluoroethene deduced from the IVO and IVO-MRMP methods is higher (lower) than the corresponding *trans* isomer. Table IV further shows that the η (also ω) emerging from FSCCSD/IP and EA calculations are in excellent agreement with the CCSD and CCSD(T) predicted state energies (see Table II).

C. Torsional PEC for 1,2-difluoroethene

This section describes IVO-MRMP calculations for the torsional PEC of 1,2-difluoroethene. The IVO-MRMP calculations for 1,2-difluoroethene are performed with the aug-cc-pVDZ basis set for variable dihedral angles from 0° to 180° with fixed values of $R_{\mathrm{C-C}}=1.341$ Å, $R_{\mathrm{C-H}}=1.089$ Å, $R_{\mathrm{C-H}}=1.356$ Å, $\angle\mathrm{HCC}=122.8°$ and $\angle\mathrm{FCC}=122.3°$ (i.e., using the MP2/aug-cc-PVdZ optimized ground state geometry for all variables other than the torsional angle).

Figure 3 compares the PECs calculated from the IVO-MRMP and state-of-the-art CCSD methods and variants thereof. For clarity of comparison, the IVO-MRMP and CCSD ground state energies are shifted so that they are all equal to the CR-CC(2,3) energy at the *cis* geometry. The comparison of the curves in Fig. 3 is facilitated by considering the behavior of the wavefunctions upon isomerization.

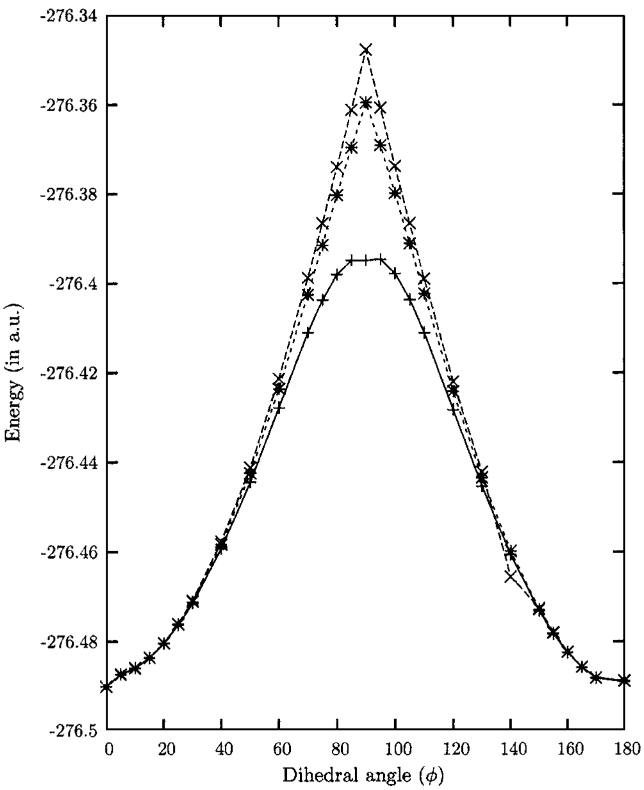

FIG. 3. The IVO-MRMP (+), CCSD(×), and CR-CC(2,3)(*) ground state energies of 1,2-difluoroethene as a function of HFC═CHF dihedral angle. CCSD and CCSD(T) results were obtained using GAMESS (Ref. 33).

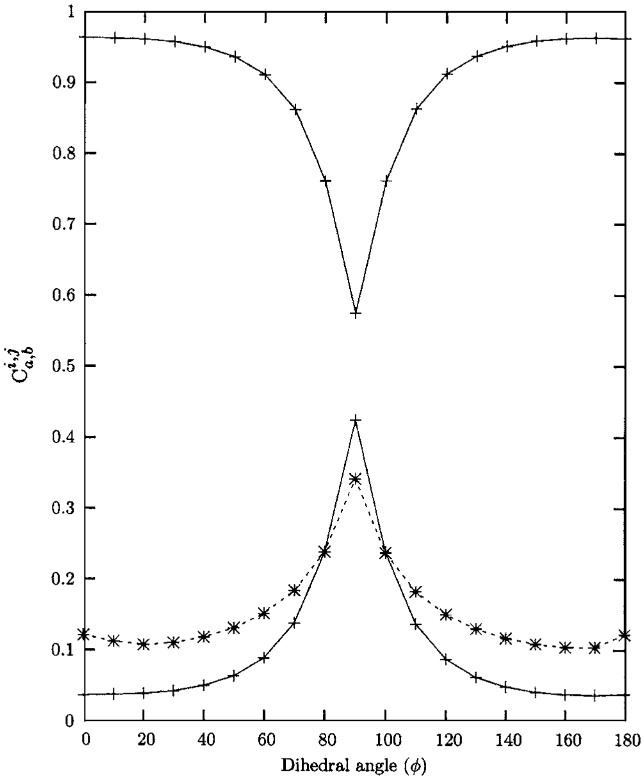

FIG. 4. Contribution of IVO-CASCI doubly excited state (+) to the ground state of 1,2-difluoroethene as a function of HFC═CHF dihedral angle. The contribution of the most important doubly excited cluster amplitude is indicated by an asterisk (*).

The ground state wavefunctions of 1,2-difluoroethene for the *cis* and *trans* geometries (and nearby geometries) are predominantly single reference in character. However, as the dihedral angle increases, the contribution of doubly excited configurations grows and reaches a maximum at the transition state geometry (see Fig. 4). The magnitude of doubly excited cluster amplitudes is depicted in Fig. 4 as also exhibiting the same pattern. Since the CCSD and CR-CC(2,3) approaches are single reference formulations, the generation of PECs for the *cis* to *trans* conversion is expected to fail with these methods near the transition state geometry. The IVO-MRMP approach, on the other hand, is not only capable of representing nondynamical electron correlation but also very effectively treats states of mixed parentage, thereby explaining why only the IVO-MRMP calculation yields a smooth curve for the *cis* to *trans* conversion, while the curves from the CCSD and CR-CC(2,3) methods exhibit a *cusp* near the transition state.

V. CONCLUDING REMARKS

Extensive calculations using the IVO-CASCI modification of the MCQDPT method produce the following important conclusions:

(a) The approximate chemical hardness and electrophilicity evaluated from IVO orbital energies suggest that *cis* 1,2-difluoroethene and 1,2-dichloroethene are energetically more stable than the corresponding *trans* isomers.
(b) The ground state energies computed using the IVO-MRMP method accord with predictions based on the chemical hardness and electrophilicity.
(c) The choice of IVO orbital energies is appropriate for estimating the chemical hardness (η) and chemical potential (μ), and hence, the electrophilicity (ω).
(d) The IVO-MRPT calculations yield smooth potentials for the computationally challenging *cis*-*trans* isomerization.
(e) An important computationally efficient feature of the IVO-MRPT method is the fact that no tedious and costly iterations are required beyond those in the initial SCF calculation.

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