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A multireference coupled-cluster study of the ground state and lowest excited states of cyclobutadiene

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The electronic structure of the ground state and several low-lying excited states of cyclobutadiene are studied using the new state-universal multireference coupled-cluster method with single and double excitations (MR-CCSD) augmented by a noniterative inclusion of the triple excitations [MR-CCSD(T)]. Two possible ground state configurations are examined, namely the square and the distorted rectangular geometries, and the multireference coupled-cluster energy barrier for the interconversion between the two rectangular ground state structures is estimated to be 6.6 kcal mol^{-1} compared with the best theoretical value, 6.4 kcal mol^{-1} obtained using the highly accurate coupled-cluster method with full inclusion of the triple excitations (CCSDT). The ordering of electronic states for the square geometry is determined, with the ground state singlet being located 6.9 kcal mol^{-1} below the lowest triplet electronic state. We also examine the potential energy surface for the interconversion between the two equivalent second-order Jahn–Teller rhombic structures for the first excited singlet state. When comparing the MRCC energies with the results provided by various single- and multireference correlation methods, the critical importance of including both the *dynamic* and *nondynamic* correlation for a qualitatively correct description of the electronic structure of cyclobutadiene is emphasized. We also address the invariance properties of the present MRCC methods with respect to the alternative selections of reference orbital spaces.

I. INTRODUCTION

After two decades of controversy about its physicochemical properties, cyclobutadiene (CB) has become an illustrative example of the synergistic cooperation between experimentalists[1–5] and theorists[6–16] in the interpretation of sometimes contradictory spectroscopic evidence. Among the most intriguing problems *qualitatively* resolved by their collective efforts were, e.g., (a) the structure and relative ordering of the lowest electronic states of CB;(b) the ground state (GS) and excited singlet state potential energy surfaces (PES) for interconversion between the second-order Jahn–Teller (SOJT) distorted isomeric structures; and (c) the closely related effect of heavy atom tunneling on the rate of the ground state valence tautomerization.

As Arnold and Michl have discussed in their excellent review on the spectroscopy of CB,[1] the current status of cyclobutadiene chemistry has recently reached a more *quantitative* stage, when "the heat of the argument may not quite match that of the classical era of cyclobutadiene...," nevertheless "the possible impact on the way in which chemists think about molecular structure in their more philosophical moments may be longer lasting." The role of the theorists in this process is indisputable, as their more and more advanced computational tools may not only provide very accurate *quantitative* evidence for the various chemical properties of this elusive species[7–13,15,16] but, as a by-product, they can furnish *qualitative* predictions as well.[14,16] Admittedly, in order to achieve these ambitious goals one has to resort to state-of-the-art correlation methods which are capable of describing both the *nondynamic* and *dynamic* correlation effects in a very accurate manner. [The former effects are of a rather localized nature having their origin in the biradical-like open-shell electronic structure of square cyclobutadiene; the latter effects then represent the delocalized correlation contributions of a large set of excited configurations (usually truncated after a certain excitation level) to the energy of the pertinent electronic state.]

For over a decade the single-reference many-body perturbation theory (MBPT) and the closely related coupled-cluster method (CC) (Ref. 17) have been routinely implemented for *dynamic* correlation studies of atoms and molecules. During that period the CC approaches have gained a reputation as very efficient, reliable, and size-extensive computational tools whose applicability frequently reaches beyond situations well-represented by a single-determinant description of the reference state. For example, among the various CC correlation models the coupled-cluster method including the single and double excitations (CCSD) (Ref. 18) has earned special attention as a highly accurate approach combining the infinite-order summation of the most important *dynamic* correlation effects with a relatively modest computational cost. Nevertheless, the convergence of the standard CCSD method deteriorates rapidly when the higher (triple- and quadruple-) excitations become increasingly important, or alternatively a single-determinant vacuum does not provide an adequate description of the reference space. As suggested by several authors,[19–25] one can naturally amplify the range of applicability of the single-reference CCSD method by including some of those higher excitation effects explicitly in the expression for the approximate correlated wave function. Oftentimes, however, improving the convergence properties of the CC method by incorporating the triple[19–24] or even quadruple[25] excitations is not commensurate with the expense for such an application.

In their pioneering study on the rate of interconversion between two equivalent rectangular isomers of cyclobutadi-

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ene, Čársky *et al.*[12] have implemented several single-reference MBPT/CC models in order to establish how the computed activation barrier is affected by the level of inclusion of the *dynamic* correlation effects. As already mentioned the biradical-like character of square CB calls for using a multiconfiguration wave function to properly describe the corresponding ground state singlet state. On the other hand the equilibrium rectangular structure is a well behaved closed-shell singlet amenable to single-reference calculations, and is, therefore, favored preferentially with respect to the ground state square structure. As documented by the authors,[12] including the *dynamic* correlation corrected this shortcoming. Nevertheless, the convergence of the electron correlation contributions to the barrier height was very slow, with the best, CCSDT-1b (Ref. 21) prediction being about 9.0–9.5 kcal mol^{-1}.[12] The behavior is clearly controlled by the importance of the *nondynamic* correlation. A similar performance of the standard CCSD model was encountered when considering the location of the lowest excited states.[26] Much like the ground state CB correlation problem, discussed above, the triplet square configuration was favored with respect to the multiconfiguration square singlet in many single-reference formulations except when triple excitations were included in the corresponding CC expansion in an iterative manner [CCSDT-1b approach[26b]]. This resulted in the triplet state being the ground state for the square CB (which accidentally conforms with the qualitative Hund's rule). In return, the large-scale multiconfiguration SCF (MCSCF) application of Nakamura *et al.*[15] provided a significant lowering of the interconversion barrier of cyclobutadiene, with the corollary of a proper ordering of its lowest singlet and triplet electronic states at the square geometry. Valence tautomerization of CB thus seems to be a clear example where a proper inclusion of *nondynamic* correlation is of vital importance for fast convergence of *dynamic* correlation effects. Due to a very restricted inclusion of the *dynamic* correlation effects in the MCSCF approach, the question, however, remains as to the importance of their net contribution to the correlation energy of cyclobutadiene.

As recently well established by several methodological and computational developments, the state-universal (SU) or Hilbert space multireference coupled-cluster (MRCC) formalism[27–37] with all possible external single and double excitations considered for each reference function,[33] offers an alternative and more efficient way to account for the effect of higher excitations and still profit from the efficacy of a standard CCSD model. By a careful repartitioning of the excitations into external and internal ones the *nondynamic* correlation effects can be treated within a multiconfiguration active space, with *dynamic* correlation from single and double excitations relative to each reference included via the corresponding CC expansion. It cannot be emphasized enough that the choice of active space (which should obviously comprise those functions which are essential to describe the basic physicochemical properties we would like to study) plays a crucial role in the successful application of the multireference CC method. The larger the space, the larger amount of the *nondynamic* correlation introduced; however, by doing so we also increase the incidence of intruder states[38] present in our active space, which often results in the necessity of reducing the size of a complete active space (CAS) or even implementing an incomplete active space (IAS) option[31,34,36c,38b]. Nevertheless, in such a case adopting the single and double excitation model for the multideterminant reference is not necessarily sufficient for a quantitative estimate of the overall correlation effect.

In order to explore its range of applicability and level of performance, we apply a recently proposed MRCC method[27,33] to the correlation problem of cyclobutadiene. With a view to avoiding the intruder state problem, the minimal, two-determinant (TD) active space is employed for describing the electronic structure of several low-lying states of CB with *dynamic* correlation included in the TD CCSD (Ref. 18) manner. In general, such a formulation belongs to the class of so-called special incomplete active spaces,[34(a),34(b)] where two configurations doubly excited with respect to each other (either of a closed-shell or an open-shell structure) span the reference active space. (For instance, the recently published SU TD open-shell singlet formalism[37] is an example of the open-shell case.) To investigate the importance of the residual *nondynamic* correlation effects, neglected in our TD formulation we also examine a new TD CC approach,[39] where we introduce, noniteratively, triple excitations in the CCSD(T) (Refs. 23,24) fashion for both reference determinants. For the sake of clarity it should be emphasized, that the TD formulation implemented in our study can be extended in a straightforward manner to a general multireference case. Nevertheless, due to the increasing size of the active space and closely related difficulties with the intruder states, such a formulation is much more involved than the minimal TD active space one.

A brief synopsis of the general concepts of the MRCC method is presented in Sec. II. More than the formal structure of the working TD CC equations, the discussion focuses on the similarities and differences between the corresponding single- and multireference CC formulations. In Sec. III the results of the CC study of several low-lying electronic states of cyclobutadiene are summarized and compared to the best correlated results from the prior studies. Special attention is paid to two possible mechanisms for the second-order Jahn–Teller distortion of the ground and first excited singlet states (rectangular and rhombic deformations, respectively). We also address the relative ordering of the lowest electronic states, their equilibrium geometries and the corresponding vibrational energies. Conclusions of the study are given in Sec. IV.

II. THEORY

As the general concepts and assumptions of the Hilbert space, SU MRCC formalism have been presented,[27,30,33] here we highlight only a few important structural features which distinguish the MRCC equations from their single-reference CC counterpart.

The common denominator of various CC formulations is the exponential ansatz based expansion for the exact wave function, Ψ,

$$\Psi=\hat{\Omega}\Psi_0. \tag{1}$$

Here $\hat{\Omega}$ is the exponential wave operator which formally generates the exact wave function while operating on the single- or multiconfiguration reference Ψ_0, defined within a d-dimensional active space P,

$$\hat{P}\Psi=\Psi_0, \quad \hat{P}^2=\hat{P}, \quad \hat{P}=\sum_{I=1}^{d}|\Phi_I\rangle\langle\Phi_I|. \tag{2}$$

The concept of completeness of the active space plays a crucial role in formulating the size-extensive CC formalism. In fact, until very recently it was generally believed that only the active space spanned by all possible distributions of the active electrons among the valence orbital levels [a condition equivalent to imposing the intermediate normalization (IN) on $\hat{\Omega}$ (Ref. 40)] guaranteed the linked cluster (LC) (Ref. 41) structure of the resulting CC equations. Nevertheless, as proposed by several authors[31,34] the connectedness of the corresponding MRCC expansions can also be achieved for IAS situations. For example, the MRCC formalism for a special class of incomplete active spaces[34(a),34(b)] arrives at the LC structure by relaxing the IN, while retaining some internal excitations in the IAS CC expressions.

A. Single-reference CC approach

In the simple case of the one-dimensional, complete active space $P,\hat{P}=|\Phi_0\rangle\langle\Phi_0|$ we arrive at the single-reference CC formalism with the wave operator defined by the expression

$$\hat{\Omega}=\mathrm{e}^{\hat{T}}, \tag{3}$$

where the operator $\hat{T}$ is the usual cluster operator

$$\hat{T}=\sum_n \hat{T}_n,$$
$$\hat{T}_n=(n!)^{-2}\sum t^{a_1a_2\ldots a_n}_{i_1i_2\ldots i_n}\hat{a}_1^\dagger\hat{a}_2^\dagger\ldots\hat{a}_n^\dagger\hat{i}_n\ldots\hat{i}_2\hat{i}_1, \tag{4}$$

and $\hat{a}_k^\dagger$, $\hat{i}_k$ are the second-quantized creation and annihilation operators, respectively, defined with respect to the one-determinant reference, $\Phi_0\equiv\Psi_0$. The single-reference CC equations may be formally written as

$$\langle\Phi^{abc\ldots}_{ijk\ldots}|(\hat{H}_N\mathrm{e}^{\hat{T}})_c|\Phi_0\rangle=0, \tag{5}$$

where $\Phi^{abc\ldots}_{ijk\ldots}$ is a one-determinant configuration in which orbitals $i,j,k,\ldots$, originally occupied in Φ_0 have been replaced by virtuals $a,b,c,\ldots$, and $\hat{H}_N$ is the usual normal-ordered {} operator

$$\hat{H}_N=\sum_{pq}\hat{f}_{pq}\{\hat{a}_p^\dagger\hat{a}_q\}+\frac{1}{4}\sum_{pqrs}\langle pq\|rs\rangle\{\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\}$$
$$=\sum_p \epsilon_p\{\hat{a}_p^\dagger\hat{a}_p\}+\hat{W}_N=\hat{H}_N^0+\hat{W}_N. \tag{6}$$

In applications we truncate the infinite-order expression, Eq. (4) after the second [CCSD (Ref. 18)] or third (CCSDT) term, while further approximation can be accomplished by terminating the $\mathrm{e}^{\hat{T}}$ expansion in Eq. (5). For example we can introduce the selected contributions of the $\hat{T}_3$ clusters, as done in different iterative CCSDT-n ($n=1,3$) approaches.[21] The simplest, CCSDT-1 method thus considers only linear contributions of the $\hat{T}_2$ operators in the corresponding equations for the t^{abc}_{ijk} amplitudes, and is defined by the following expressions:

$$\langle\Phi_i^a|[\hat{H}_N(\mathrm{e}^{\hat{T}_1+\hat{T}_2}+\hat{T}_3)]_c|\Phi_0\rangle=0, \tag{7a}$$

$$\langle\Phi_{ij}^{ab}|[\hat{H}_N(\mathrm{e}^{\hat{T}_1+\hat{T}_2}+\hat{T}_3)]_c|\Phi_0\rangle=0, \tag{7b}$$

$$\langle\Phi_{ijk}^{abc}|(\hat{H}_N\hat{T}_2)_c|\Phi_0\rangle=0. \tag{7c}$$

Terminating this procedure by converging CCSD but not allowing $\hat{T}_3$ amplitudes in Eq. (7) to change, gives the computationally even less involved, noniterative CCSD+T(CCSD) (Ref. 22) and CCSD(T) (Refs. 23,24) approximations. Here the effect of the $\hat{T}_3$ clusters is evaluated from the converged CCSD, t_i^a and t_{ij}^{ab} coefficients with the total energy expressed as

$$E=E_{\mathrm{CCSD}}+E_T^{[4]}+E_{ST}^{[5]}. \tag{8}$$

(Here notation $E_X^{[n]}$ refers to nth-order-type perturbation contribution where in the corresponding nth-order MBPT expression the first-order $\hat{T}_i$ ($i=1,2$) amplitudes are replaced by their converged CC equivalents.)

In the simplest, canonical SCF case the fourth-order triple correction can be expressed according to the formula[23,24]

$$E_T^{[4]}=\sum_{abcijk}\frac{|\langle\Phi_{ijk}^{abc}|\hat{H}_N\hat{T}_2|\Phi_0\rangle_c|^2}{\epsilon_i+\epsilon_j+\epsilon_k+\epsilon_a-\epsilon_b-\epsilon_c}. \tag{9}$$

The fifth-order triple correction, $E_{ST}^{[5]}$ which distinguishes CCSD(T) from CCSD+T(CCSD) is then obtained by inserting the first-order, t_{ijk}^{abc} amplitudes (estimated from the converged CCSD, t_{ij}^{ab} coefficients) into the $\hat{T}_1$ equations and by noniteratively evaluating the corresponding energy contributions.

B. Multireference CC approach

As already discussed in the Introduction the multireference CC formalism adopts a philosophically different approach to evaluate the effect of higher rank clusters. Instead of computing some important but many mostly negligible contributions, as done in the single-reference CC method, the corresponding MRCC procedure attempts to include the most important *nondynamic* correlations in the multidimensional reference space; the *dynamic* correlation effects are then evaluated for each reference configuration using the corresponding truncated CC approximations.

In our MRCC formulation[33,36,37] we implemented the state universal (or Hilbert space) *exponential* ansatz of Jeziorski and Monkhorst,[27]

$$\hat{\Omega}=\sum_L \mathrm{e}^{\hat{T}(L)}\hat{P}_L \tag{10}$$

in which the hole ($\hat{i}_1,\hat{i}_2,\ldots,\hat{i}_n$) and particle ($\hat{a}_1^\dagger,\hat{a}_2^\dagger,\ldots,\hat{a}_n^\dagger$) operators [Eq. (4)] as well as the range of summations over occupied and virtual indices are defined relative to each reference configuration, $|\Phi_L\rangle$ playing, by turns, the role of a vacuum.[38(b),42]

The corresponding MR CCSD equations for the single and double excitation amplitudes with respect to the reference vector $|\Phi_K\rangle$ can be formally expressed as

$$D_i^a t_i^a(K) = \langle \Phi_i^a(K) | \hat{W}_N e^{\hat{T}(K)} | \Phi_K \rangle_c - \sum_{L \neq K} [\langle \Phi_i^a(K) | e^{\hat{T}(L)} | \Phi_L \rangle \langle \Phi_L | \hat{W}_N e^{\hat{T}(K)} | \Phi_K \rangle]_c \tag{11}$$

and

$$\begin{aligned} D_{ij}^{ab} t_{ij}^{ab}(K) = {} & \langle \Phi_{ij}^{ab}(K) | \hat{W}_N e^{\hat{T}(K)} | \Phi_K \rangle_c \\ & - \sum_{L \neq K} [\langle \Phi_{ij}^{ab}(K) | e^{\hat{T}(L)} | \Phi_L \rangle \\ & \times \langle \Phi_L | \hat{W}_N e^{\hat{T}(K)} | \Phi_K \rangle]_c - \sum_{L \neq K} [t_i^a(K) - t_i^a(L)] \\ & \times [\langle \Phi_j^b(K) | e^{\hat{T}(L)} | \Phi_L \rangle \langle \Phi_L | \hat{W}_N e^{\hat{T}(K)} | \Phi_K \rangle]_c , \end{aligned} \tag{12}$$

respectively, where the summation runs over all reference configurations, $|\Phi_L\rangle$, $(L \neq K)$, and only connected terms are considered in the resulting diagrammatic expressions (see Ref. 33 for details).

Conceptually, this MRCC approach is closely related to the single-reference CC theory; in fact, if we suppress all but the first (*direct*) terms on the rhs of Eqs. (11), (12), subject to the particular vacuum $|\Phi_K\rangle$, we arrive at the standard CCSD equations[18] with the only exception that now all internal excitation amplitudes are eliminated from the corresponding CC expansions. Consequently, it is fairly straightforward to exploit the existing single-reference CC program[43] in order to evaluate the *direct term* CCSD energy contributions and, if desired, also the corresponding, noniterative CCSD(T) perturbation corrections, Eq. (8).

The rest of the rhs terms of Eqs. (11), (12) constitutes the so-called *renormalization* part of the MRCC equations, which has no counterpart in the single-reference CC formulation.[27,30,33] A new operator, termed the effective Hamiltonian is introduced in the $\hat{T}_1$ and $\hat{T}_2$ *renormalization* terms

$$\hat{H}_{KL}^{\text{eff}} = \langle \Phi_L | \hat{W}_N e^{\hat{T}(K)} | \Phi_K \rangle \tag{13}$$

which operates entirely within the d-dimensional reference space P, while furnishing the part of the energy spectrum of the exact Hamiltonian, $\hat{H}$,

$$\hat{H}^{\text{eff}} \Psi_0 \equiv \hat{P} \hat{H} \hat{\Omega} \Psi_0 = E \Psi_0 . \tag{14}$$

Given the definition of the new amplitudes which exclusively generate the excitations within the active space, $w_{pq\ldots}^{rs\ldots}(K) = \langle \Phi_{pq\ldots}^{rs\ldots}(K) | \hat{W}_N e^{\hat{T}(K)} | \Phi_K \rangle \equiv \langle \Phi_{pq\ldots}^{rs\ldots}(K) | \hat{H}^{\text{eff}} | \Phi_K \rangle$ we can arrive at the working expressions for the MR CCSD, w_p^r and w_{pq}^{rs} internal excitation coefficients. Analogous to the equations for the external t_i^a and t_{ij}^{ab} amplitudes, the corresponding $\hat{H}^{\text{eff}}$ formulas are represented by *direct* and *renormalization* terms and can be formally derived from Eqs. (11), (12) (except that we do not attach denominators and that the summation over hole and particle indices is limited to the active orbital levels) (see Ref. 33 for details).

In order to evaluate the MR CCSD(T) perturbation energy correction[39] we have to (a) implement the multireference analogue of the SR, CCSDT-1 formula for the t_{ijk}^{abc} coefficients, Eq. (7c),

$$D_{ijk}^{abc} t_{ijk}^{abc}(K) = \langle \Phi_{ijk}^{abc}(K) | \hat{W}_N \hat{T}_2(K) | \Phi_K \rangle_c - \sum_{L \neq K} [\langle \Phi_{ijk}^{abc}(K) | \hat{T}_2(L) | \Phi_L \rangle \hat{H}_{KL}^{\text{eff}}]_c ; \tag{15}$$

(b) perform one iteration of Eq. (15) with the converged MR CCSD, t_{ij}^{ab} coefficients; (c) evaluate the fourth-order triple contribution [Eq. (9)] according to the modified, $E_{T(MR)}^{[4]}$ formula,

$$E_{T(MR)}^{[4]}(K) = \sum_{abcijk} \frac{\{\langle \Phi_K | [-\Sigma_{L \neq K} \hat{T}_2(K) \hat{W}_N | \Phi_L \rangle \langle \Phi_L | \hat{T}_2(L) + \hat{T}_2(K) \hat{W}_N] | \Phi_{ijk}^{abc}(K) \rangle \}_c [\langle \Phi_{ijk}^{abc}(K) | \hat{W}_N \hat{T}_2(K) | \Phi_K \rangle]_c}{\epsilon_i + \epsilon_j + \epsilon_j - \epsilon_a - \epsilon_b - \epsilon_c} ; \tag{16}$$

and (d) estimate the MR CCSD, $E_{ST}^{[5]}$ energy correction. [It is interesting to note the absence of the disconnected term on the rhs of Eq. (15) as the consequence of the linear approximation for the cluster operator in the CCSD(T) approach (see Ref. 39 for details).]

Compared to the canonical single-reference CCSD(T) (Refs. 23,24) energy expression, Eq. (8) there are several modifications adopted in its noncanonical MR CCSD(T) analog.

First, contrary to the symmetric, fourth-order expression, Eq. (9) the modified, $E_{T(MR)}^{[4]}$ correction [Eq. (16)] is evaluated in a nonsymmetric manner, with the *renormalization* contributions to the T_3 equations included only in one of the two resulting T_3 terms (as the w_{pq}^{rs} interactions already include certain excitation terms via diagonalization of the $\hat{H}^{\text{eff}}$ matrix).

Second, although the $E_{ST}^{[5]}$ contributions are evaluated in an analogous fashion as in the single-reference case (by inserting the first-order, t_{ijk}^{abc} coefficients into the corresponding T_1 CC expression), for the non-Hartree–Fock (HF) orbitals adopted in our MR formulation, the canonical fifth-order correction, $E_{ST}^{[5]}$ formally represents the noncanonical fourth-order energy contribution, $E_{ST}^{[4]}$. As a consequence, the additional, sixth-order HF terms have to be considered in the T_1 expression, Eq. (7a) for obtaining the pertinent non-HF, $E_{ST}^{[5]}$ perturbation correction [see Ref. 24(a) for details].

Third, concerning the off-diagonal $\hat{H}^{\text{eff}}$ elements, we have to evaluate the noniterative contribution of the modified first-order, t_{ijk}^{abc} amplitudes to the w_p^r and w_{pq}^{rs} internal coefficients. The corresponding perturbation expressions can be formally derived from the CCSDT-1 equations for the T_1 and T_2 amplitudes, Eqs. (7a), (7b); once again, no denominators are attached to the resulting $\hat{H}^{\text{eff}}$ formulas and the summation over occupied and virtual indexes is limited to the active orbital levels.

Compared to their single-reference counterparts, however, there are several complications connected with the invariance of the resulting energies, obtained by diagonalization of the MR CCSD(T) effective Hamiltonian. The first problem concerns using the semicanonical transformation,[44] which is adopted in the single-reference, noncanonical case to eliminate the off-diagonal elements of the occupied–occupied, $\hat{F}_{\text{oo}}^{nd}$ and virtual–virtual, $\hat{F}_{\text{vv}}^{nd}$ blocks of the non-HF matrix representation.[24(a)] In our MR approach those terms are, in part included through the diagonalization of the effective Hamiltonian matrix and therefore we choose to avoid the semicanonical transformation to obviate counting the corresponding contributions twice. In such a case, however, the resulting, noniterative MR CCSD(T) energy corrections, corresponding to the $\hat{F}_{\text{oo}}^{nd}$ and $\hat{F}_{\text{vv}}^{nd}$ terms will not be invariant with respect to different orbital choices. Considering the fact that those terms will be of different magnitude for different determinants (for one vacuum those terms can be identically equal zero, while for the other one they can be quite significant), this can create a potential imbalance in treating the overall correlation effect. The second potential problem is the noninvariance of our MR CCSD(T) approach with respect to shifting the orbital energies (introduced in our method in order to improve convergence properties). We shall address both issues in the presentation of our results.

To finish discussion on the structure of the MRCC equations, we briefly mention methodological and computational simplifications implemented in our application.

As already discussed the cluster operator, Eq. (4) is truncated after the $\hat{T}_2$ term $[\hat{T}=\hat{T}_1+\hat{T}_2$ (CCSD approximation)] and all possible products (up to quartic contributions) are included in the corresponding *direct* and *renormalization* terms, Eqs. (11), (12).[33,45] Consequently, the $\hat{H}^{\text{eff}}$ energy expression is formally truncated after the single and double excitation terms, which represents in the case of two active electrons, the exact solution of the effective Hamiltonian[33] within the CCSD approximation. In fact, for the minimal, TD IAS option,[34(a),34(b),37] adopted in our study, the off-diagonal part of the effective Hamiltonian reduces to only one term, w_{pq}^{rs}, representing the internal double excitation. This simplifies both the *renormalization* part of the CCSD equations, Eqs. (11), (12) and the expansion for $\hat{H}^{\text{eff}}$ since there are no summations over either internal lines or reference determinants in the resulting CC expressions (for additional simplifications in the open-shell TD IAS situation see Ref. 37). As a lesser point, but in the interest of accuracy; for a special case of the TD incomplete active space, characterized by different spatial symmetries of the active orbitals, the further modifications of the *renormalization* formula for w_{pq}^{rs} are possible, which formally lead to the corresponding CAS expression.

To increase the efficiency of our MR CCSD calculations, Abelian molecular symmetry was considered explicitly in solving the corresponding expansions, Eqs. (11), (12), based on a direct product decomposition of T amplitudes and the terms with which they are contracted.[46] All calculations were performed using the MRCC code, which is a part of the advanced concepts in electronic structure (ACES) II correlation program package developed in our group.[43]

III. DISCUSSION

A. General outline

The MRCC method is implemented to study the structure and selected properties of cyclobutadiene. Among the challenges are (a) the mechanism of the second-order Jahn–Teller distortion for the ground state of CB, closely related to the tunneling rate of the carbon atoms; (b) the relative ordering of lowest electronic states of CB, including the singlet–triplet splitting (S–T) at the square geometry; and (c) the equilibrium structure and harmonic vibrational spectrum of several low-lying states of CB, embracing the distorted (rectangular and rhombic) SOJT geometries.

A variety of problems outlined above suggests why cyclobutadiene, despite its small size and rather unremarkable electronic structure, has such an appeal to both theorists and experimentalists. Compared to the past two decades of fundamental *qualitative* findings on its structure and properties, however, the present research in cyclobutadiene chemistry is aimed more at the *quantitative* aspects of its spectroscopy. This fact, along with the difficulties connected with the experimental detection of most of the CB electronic states necessitates that the theoretical investigation be an integral, critical component of the collective research effort.

To provide an explanation for most of the intriguing features of CB we focus on the electronic structure of this simplest cyclic four-electron π system at the square geometry. Here, two electrons have to be accommodated in a pair of frontier, degenerate π (e_g) orbitals, which gives rise to four possible configurations, representing the minimal, four-dimensional (FD) active space. (Due to the D_{2h} symmetry constraints implemented for all structures of CB considered, the resulting FD space can be further reduced to two, two-dimensional, orthogonal subspaces, each of them spanned by two configurations of closed-shell and open-shell electronic structures, respectively.) As the resulting three singlet states $({}^1B_{1g}$, ${}^1A_{1g}$, and ${}^1B_{2g})$ and one triplet state $({}^3A_{2g})$ are expected to be located closely to each other at the square geometry, one can naturally assume that some of them will stabilize through the SOJT vibronic coupling effect. Unlike in cases with $(2n+1)$-fold symmetry axes where stabiliza-

TABLE I. The [$3s2p1d/1s$] optimal geometries (8 dropped orbitals) for cyclobutadiene (in a.u.).

	GS structures, $^1A_g(D_{2h})$[a]							
	Rectangular				Square			
	SR[b]		MR[c]		SR[b]		MR[c]	
	x	z	x	z	x	z	x	z
C	1.493 894 70	1.283 458 69	1.483 192 74	1.291 544 93	1.380 290 53	1.380 290 53	1.386 320 38	1.386 320 38
H	2.960 784 94	2.764 589 24	2.949 895 97	2.772 064 71	2.852 776 12	2.852 776 12	2.861 398 00	2.861 398 00

	Excited state structures (D_{2h})[a,c]							
	Square						Rhombic	
	$2\ ^1A_g^d$		$1\ ^3B_{1g}^e$		$1\ ^1B_{1g}$		$2\ ^1A_g$	
	x	z	x	z	x	z	x	z
C	1.376 491 23	1.376 491 23	1.375 536 92	1.375 536 92	1.367 968 56	1.367 968 56		
H	2.848 209 83	2.848 209 83	2.847 967 73	2.847 967 73	2.840 076 00	2.840 076 00		
C	0.000 000 00	1.948 814 49	1.374 817 62	1.374 817 62			0.000 000 00	1.848 590 95
H	1.948 814 49	0.000 000 00	2.847 324 31	2.847 324 31			2.032 621 97	0.000 000 00
C	0.000 000 00	4.030 421 95					0.000 000 00	3.948 485 30
H	4.030 421 95	0.000 000 00					4.100 698 99	0.000 000 00

[a] The geometry to which the positions of nuclei have been constrained in CCSD optimization.

[b] The SR CCSD minimum geometry [CCSD(T) minimum geometry for square singlet, Ref. 26(a)].

[c] The TD CCSD optimal geometry using HF reference.

[d] The TD CCSD optimal geometries using delocalized and localized HF orbitals (first and second input, respectively) (see text for explanation).

[e] The TD and SR CCSD optimal geometries (first and second input, respectively).

tion occurs only along one (degenerate) normal mode, two different (nondegenerate) modes actually effect SOJT distortion in fourfold symmetry. These two modes correspond to the rectangular and rhombic, D_{4h} distortions, respectively, both of which necessarily induce a finite lowering of the total energy. The magnitude of the stabilization energy together with a knowledge of the shape of the corresponding potential barrier can then provide insight into the mechanism and the rate of the corresponding deformation process and ultimately give an explanation for the phenomenon of heavy atom tunneling in CB.[1–5,10,12,13]

To determine the relative ordering of the lowest electronic states of square CB as well as to describe the potential energy surfaces for the aforementioned SOJT distortions, represents a real challenge for a method capable of *quantitatively* treating both the *nondynamic* and *dynamic* correlation effects. As already mentioned, the proximity of several electronic singlet states of CB at the square geometry calls for using the multireference method, incorporating in the active configuration space at least those four determinants mentioned above. [In fact, the qualitative, 3×3 configuration interaction (CI) description of the two-electron two-orbital model for biradicals, which has been routinely used in organic chemistry for nearly two decades,[16(b),47] proves to be fairly successful in treating the correlation problem of these open-shell species.] At the same time, the residual correlation effects associated with the configurations, limited to the excited space should also be considered at some computationally reasonable level.

In our study we would like to present the results obtained using our recently proposed MR CCSD method,[33] which we believe possesses both aforementioned attributes. In addition, the *linked cluster*[41] structure of its approximate wave function guarantees a qualitatively correct, extensive description of the resulting energy quantities (a fact which does not apply to the frequently used multireference CI analog of our formalism[48–51]).

B. Computational details

In order to compare our MRCC results with the previous, single-reference *ab initio* CC studies on CB, we employ the same basis set and, at the initial stage of our application, also the same geometries for the square and rectangular ground state singlet structures as in the Čársky *et al.* paper.[12] As the aforementioned study of the ground state potential energy surface of cyclobutadiene[12] recommends a rather moderate, split-valence-shell ($3s2p1d/1s$) basis set,[52] this certainly imposes limitations, as well as does the minimal TD description of the reference space. Nevertheless, experience collected in the previous MR CCSD applications demonstrated that the *qualitative* outcome of the minimal CAS, DZP study should not be affected by extending the orbital and/or active configuration spaces.

To determine the effect of geometry relaxation on the computed energy quantities we also perform the full geometry optimization of all structures of CB studied in the paper. The numerical procedure used is based on successive interpolation of the corresponding TD CC energies,[53] calculated at various grid points; and the numerical errors in reported bond lengths and angles (Table I) are believed to be smaller than 0.000 01 a.u. and 0.001°, respectively. In general, including the CCSD electron correlation provides an increase in the corresponding bond lengths relative to the reference, Čársky values.[12] When comparing the single- and two-determinant CC results, however, the distinct behavior of the corresponding correlation expansions for the geometry parameters is observed, including (a) a relatively larger increase of the single-reference CC geometries for the square ground state configuration [compare, e.g., the corresponding single- and two-determinant values for the C–C bond length (1.467 and 1.461 Å, respectively) with its TD CISD counterpart (1.448 Å) (Ref. 12)], and (b) a *less distorted* rectangular ground state structure within the TD CCSD optimization as documented by the corresponding SR and TD long (short) C–C bond lengths [1.581 Å (1.358 Å) and 1.570 Å (1.367 Å), respectively]. In fact, the phenomenon of lesser distortion, when the multiconfiguration description of the rectangular interconversion is applied, was already reported in several prior studies (see, e.g., Table I in Ref. 1). Considering the remaining square structures in study ($^1A_{1g}$, $^1B_{2g}$, and $^3A_{2g}$) the resulting TD CCSD geometry parameters are fairly similar to the corresponding ground state values. In accord with the best theoretical results from the previous applications,[15] the shortest bond distances are found for the lowest singlet of B_{2g} symmetry. The distorted rhombic SOJT (D_{2h}) structure for the first excited singlet state, $^1A_{1g}$ is also optimized and reported in Table I.

To explore in depth the potential energy surfaces of the rectangular and rhombic isomerization processes, harmonic force constants in terms of symmetry coordinates are obtained numerically using double-sided numerical differentiation (a procedure implemented in the ACES II program system[43]). Fourty four (twenty four) calculations of the energy at rectangular (square) geometries displaced from the corresponding minimum energy structures are sufficient to determine the entire harmonic field (and the error between analytic and numerical force constants is believed to be well below 1%).

To complete our information on the computational details, the lowest, 1*s* orbitals on the carbon atoms are not correlated in our application and correspondingly, the highest four virtual orbitals are also not considered in the post-HF calculations, thus reducing the number of correlated MO's to 60 orbitals. We are fully aware of the limitations of such an approximation for the split-valence shell basis set implemented in our study. In fact, we have tested the effect of neglecting the contribution of the highest virtuals to the correlation energy of valence electrons, and, in particular, to the studied energy barriers. As expected, the former energy contributions are quite significant, while the latter ones remain practically unaffected by including the four highest orbitals into the correlation energy expression (the maximum difference between the corresponding 60 and 64 MO's CCSD energy gaps being smaller than 0.1 kcal mol^{-1}).

C. Rectangular interconversion for the ground state of CB

It is well known that the lowest square singlet geometry actually represents the transition state for the isomerization reaction yielding two equivalent rectangular structures of D_{2h} symmetry. Therefore, the first problem we would like to discuss is the height of the interconversion barrier for the ground state of CB, the parameter which is closely connected with the rate and the mechanism of the SOJT distortion in consideration.

To determine how successfully the various approximate correlation expansions describe the aforementioned process, we collect the results of our TD CC study (obtained under the same constraints as applied by Čársky *et al.*[12]) in comparison with the corresponding single-reference calculations (Table II). (Although some of the present single-reference results were already published in Ref. 12, for completeness we reproduce all of them here.) To establish the convergence of *dynamic* correlation contributions to the best theoretical estimate of the computed activation barrier [represented here by the corresponding full-CCSDT (Refs. 19,20) result, 6.4 kcal mol^{-1}] the first seven lines of Table II show the results of the single-reference CC study. Two facts are immediately apparent when comparing the single-reference CC results in Table II. The first observation concerns the vital role of triple excitations in the corresponding correlation expressions for both the square and rectangular SR CC applications [compare, e.g., the relative CCSD and CCSD(T) contributions to the gross (CCSDT) correlation effect for the square (92.5% and 97.6%, respectively) and rectangular (95.8% and 99.8%, respectively) geometries of CB]. The second finding refers to the outstanding performance of the SR CC method for the rectangular, D_{2h} geometry as opposed to the much slower convergence of the triple excitation correlation contributions for the square singlet structure, when even the best among the implemented approximate triple excitation methods, CCSDT-1b provides only 99.1% of the total CCSDT correlation energy compared with the corresponding rectangular value, 99.9%. As a consequence of this behavior, which is deeply rooted in the electronic structure of the geometries, the significant overestimation of the interconversion barrier is encountered even at the quite involved, CCSDT-1b (Ref. 21) computational level (~3 kcal mol^{-1} above the reference, CCSDT value). [As already mentioned the degeneracy of π orbitals at square geometry disqualifies, to some extent the single-reference approaches from successfully treating the multiconfiguration character of the corresponding ground state singlet structure. On the other hand, due to the degeneracy breaking of π orbitals in the rectangular, D_{2h} symmetry, the equilibrium rectangular geometry is very well described even at relatively modest CCSD(T) level (and therefore too favored compared to the square singlet structure in most of the applied SR CC models).]

As suggested in previous correlation studies on CB [Refs. 8–11,14–16(a)] a remedy for the cost of accurate single-reference CC applications is furnished by treating the expensive, higher-order correlation effects as the internal excitations in the multidimensional reference space (with a possibility of including the moderate *dynamic* correlation at the single and double excitation level for each reference configuration). The results of our TD CC calculations, presented in Table II (lines 8 through 13) clearly manifest how, already, the simplest, two-determinant CCSD description of the rectangular and square singlets lowered the barrier significantly, bringing it in close agreement with the values obtained from the full-CCSDT computations. In order to examine the in-

TABLE II. Energies for the ground state of cyclobutadiene (8 dropped orbitals) (E in a.u.).[a]

	Structure				
	Rectangular	Square			
Method	^1A_g	$^1A_g^f$	ΔE^g	$^3B_{1g}^f$	ΔE^h
SCF	−153.649 369 24	−153.600 636 90	30.6	−153.658 892 20	−36.6
SDTQ(4)	−154.191 273 51	−154.160 227 67	19.5	−154.175 803 26	−9.8
CCSD[b]	−154.174 044 56	−154.142 529 11	19.8	−154.158 462 08	−10.0
CCSD[b,c]	−154.175 515 89	−154.142 991 30	20.4	−154.158 818 31	−9.9
CCSD(T)[b]	−154.195 792 57	−154.172 549 71	14.6	−154.178 257 96	−3.6
CCSDT-1b[b]	−154.196 491 44	−154.181 589 56	9.4	−154.178 773 55	1.8
CCSDT[b]	−154.196 882 66	−154.186 769 75	6.4	−154.179 009 61	4.9
MRCCSD[b,d]	−154.177 667 67	−154.168 442 64	5.8	−154.160 062 53	5.3
MRCCSD(T)[b,d]	−154.197 302 73	−154.188 044 85	5.8	−154.177 550 02	6.6
MRCCSD[b,c,d]	−154.179 478 57	−154.169 144 70	6.5	−154.160 450 82	5.5
MRCCSD(T)[b,c,d]	−154.199 738 06	−154.189 254 16	6.6	−154.178 221 03	6.9
MRCCSD[b,e]	−154.177 585 13	−154.167 082 10	6.6	−154.159 396 78	4.8
MRCCSD(T)[b,e]	−154.197 334 42	−154.187 824 26	6.0	−154.177 924 27	6.2
MCSCF-1[i]	−153.650 60	−153.642 97	4.8	−154.622 76	12.7

[a] Energies calculated at the optimal geometries taken from Ref. 12.

[b] See text for explanation of the abbreviations used for various CC approaches.

[c] Energies at the corresponding CC optimal geometries (see Table I).

[d] TD CC values obtained from the N-electron HF reference.

[e] TD CC values obtained from the $(N-2)$-electron QRHF (Ref. 54) reference.

[f] In all calculations the positions of nuclei have been constrained to the D_{2h} symmetry.

[g] Activation barriers for the rectangular automerization (in kcal/mol).

[h] The S–T splitting at the square (D_{2h}) geometry (in kcal/mol).

[i] MC SCF/6-31G energies (Ref. 15).

variance of our approach with respect to different orbital choices two sets of TD CCSD values for the barrier of isomerization of CB are listed in Table II, namely the N-electron, HF reference results (lines 8 and 10) and the alternative $(N-2)$-electron, quasi-restricted HF (QRHF) (Ref. 54) reference based values (line 12). Although both sets of orbitals are of a delocalized nature[55] and, therefore, they consistently follow the rectangular interconversion potential surface, there is a visible difference in the convergence behavior of the corresponding correlation expressions for the CB structures in the study. While at rectangular geometries the choice of different orbitals does not have any profound effect on the values of the pertinent TD CCSD energies, the corresponding square structure results reflect the importance of a balanced treatment of the $\hat{F}_{\text{oo}}^{nd}$ and $\hat{F}_{\text{vv}}^{nd}$ terms in the individual correlation expressions (compare lines 8 and 12). As a result the final TD CCSD values for the interconversion barrier differ as much as 0.8 kcal mol^{-1} with the reference, CCSDT result being somewhere between the lower, HF and higher, QRHF TD CCSD values. Although the aforementioned deviations of the TD CCSD isomerization energies from the *best*, CCSDT one, are much smaller than those observed for any approximate single-reference CC model we decided to examine the importance of including the triple excitations to obtain better agreement between the HF and QRHF TD CC results. The outcome of our TD CCSD(T) study (lines 9, 11, and 13 in Table II) clearly demonstrates an excellent performance of the proposed, noniterative triple excitation CC formalism,[39] when the original value of the deviation between HF and QRHF TD CCSD total energies for the square structure (1.4 mH) is reduced to 0.2 mH for the corresponding TD CCSD(T) results. Considering the methodological differences in the formulation of the present single- and multireference CC correlation expressions, the final TD CCSD(T) isomerization energies (5.8 and 6.0 kcal mol^{-1} for HF and QRHF CC models, respectively) are in surprisingly good accord with the best single-reference, CCSDT estimate (6.4 kcal mol^{-1}). Among possible reasons for the residual discrepancies between SR and TD values are (a) a different effect of geometry relaxation on the corresponding single- and two-determinant correlation contributions; (b) the potential importance of connected quadruple excitations,[25] entirely neglected in the single-reference CC approaches applied in the study; and (c) the noninvariance of the $\hat{F}_{\text{oo}}^{nd}$ and $\hat{F}_{\text{vv}}^{nd}$ contributions in the TD CCSD(T) nonsemicanonical orbital perturbation expression.

In order to shed light on the geometry dependence of our TD CC results, we also carried out computations of the interconversion barrier using fully optimized TD CCSD rectangular and square geometries (see Table I for corresponding data). As can be seen in Table II (lines 10 and 11) the geometry relaxation contributes to lowering the final energies of both configurations considered; however, its more significant impact on the rectangular structure contributes to increasing the height of the interconversion barrier to its final, optimized TD CCSD(T) value, 6.6 kcal mol^{-1} (once again, notice an excellent agreement with the full-CCSDT value). In addition, a very good (and balanced) convergence of the TD CC correlation contributions is encountered for both rectangular and square optimized geometries of CB [compare, e.g., the negligible differences between the corresponding CCSD and CCSD(T) TD interconversion barriers in Table II (lines

10 and 11, respectively)]. This behavior is a truly remarkable feature of our TD formalism, especially in the context of the aforementioned rather poor convergence of the single-reference CC models.

To conclude our discussion, the single- and two-determinant CC results are also compared to the corresponding, large scale 20-configuration MCSCF values of Nakamura *et al.*[15] Considering the general anticipated limitation of the MCSCF approach, caused by a very restricted treatment of *dynamic* correlation, the resulting interconversion barrier seems to be in fairly good agreement with our best CC results. [Contrary to the single-reference correlation methods where the best convergence to the *exact* energies is obtained for the problems controlled by *dynamic* correlation, the MCSCF formalism performs very well in the case when *nondynamic* effects dominate the correlation expression. This explains why in the present MCSCF applications the multiconfiguration, square singlet was too favored with respect to the single-reference rectangular structure. It should be emphasized, however, that the MCSCF value for the isomerization energy of CB was lowered even more after the zero-point vibrational energy (in harmonic approximation) was added to the corresponding total energies (the final value being 2.5 kcal mol^{-1}).[15,56]]

D. Ordering of electronic states of CB

A further problem to be considered in the valence tautomerization of CB is the location of the lowest excited states at the square geometry. In fact, the energy of the lowest triplet state, $^3A_{2g}$ is fairly close to that of the ground state singlet, $^1B_{1g}$ and their relative ordering is intimately involved with the problem of the activation parameters for interconversion of CB. (If the square triplet were higher in energy than the corresponding singlet transition structure, the rectangular isomerization process would probably be adiabatic; on the other hand, the triplet state lower in energy indicates that the reaction could occur by a surface crossing.)

The values of energy splitting between the lowest triplet and singlet square structures, computed using several single- and two-determinant CC models are presented in Table II. The same geometries are initially used for both square structures considered; however, the fully optimized CCSD geometries (Table I) are also employed in order to distinguish the contribution of geometry relaxation to the final S–T energy gaps (lines 4, 10, and 11).

Let us address the single-reference CC application first. Similarly to the ground state correlation problem of CB, discussed above, the *effectively* single-reference triplet square configuration is favored with respect to the multiconfiguration square singlet in all of the applied single-reference CC methods, except for the expensive, iterative triple excitation CC applications (lines 6 and 7). This results, erroneously, in the triplet state being the ground state of CB at the square geometry for most of the applied single-reference CC models. Nevertheless, even for the iterative triple excitation approaches, which provide a qualitatively correct ordering of the lowest electronic states of CB, poor convergence of the corresponding *dynamic* correlation expressions is apparent [compare, e.g., the CCSDT-1b and CCSDT values of the S–T splitting (1.8 and 4.9 kcal mol^{-1}, respectively)]. To no surprise the relaxation of molecular geometries has a negligible effect on the resulting (negative) SR CCSD S–T energy splitting (lines 3 and 4 in Table II). This fact, along with the slow convergence of *dynamic* correlation emphasizes once again a major drawback to single-reference CC applications, caused by the lack of important higher-order excitations[25] in the approximate SR correlation expressions.

As already discussed for the interconversion of CB, the simplest TD description of the corresponding electronic states qualitatively improves the convergence of the resulting CCSD correlation expansions. The same trend is demonstrated in our TD CC application to the S–T splitting of CB, where the best SR CCSDT value (4.9 kcal mol^{-1}) is reproduced already at the TD CCSD level for a fraction of the computational cost of the full-CCSDT calculations. Compared to the isomerization study, however, the final CCSD S–T splitting manifests a higher sensitivity to orbital choice as well as to including the noniterative triple excitations. In general, the effect of triple excitation correlation contributions increases the corresponding S–T energy gaps when relatively better convergence is obtained for the HF reference orbitals (lines 8 and 9 in Table II). The geometry relaxation of the lowest singlet and triplet square structures (Table I) also has a measurable effect on the resulting S–T splitting with the *best* optimized TD CCSD(T) estimate being 6.9 kcal mol^{-1}. With respect to the MCSCF S–T splitting, 12.7 kcal mol^{-1} reported by Nakamura *et al.*[15] and the corresponding Ågren MCSCF result, 15.9 kcal mol^{-1} [Ref. 11(a)] our value seems to be rather underestimated. Nevertheless, considering the limitations inherent to the MCSCF studies of dynamic correlation, which primarily affects the triplet configuration, the agreement between the corresponding TD CC and MCSCF S–T energy gaps is fair.

Table III summarizes the optimized structures and energies for several low-lying electronic states of CB at the square geometry. Besides the already discussed ground state singlet, $^1B_{1g}$, and triplet, $^3A_{2g}$, two additional square equilibrium structures are studied, namely the lowest singlet states of A_{1g} and B_{2g} symmetry. All structures are determined at the CCSD level using the N-electron HF reference while the D_{2h} symmetry constraints are imposed on all geometry optimizations. As discussed in prior studies on excited states of CB,[15,16] the electronic structure of the lowest states of CB at the square geometry strictly depends on the reference orbital representation applied;[55] for the delocalized, HF orbitals the second lowest singlet, $^1A_{1g}$ was obtained from the TD closed-shell $(S_0,S_1)\hat{H}_{\mathrm{eff}}$ eigenvalue problem (column 5 in Table III), while the localized representation furnished the excited state in question by solving the closed-shell TD CC problem, (S_1,S_2) (column 6 in Table III, see also Table I for corresponding optimized structures). The best optimized TD CCSD(T) energy separations, S_0-S_1 (40.9 and 42.7 kcal mol^{-1} in delocalized and localized representation, respectively) compared fairly well with the MCSCF splitting, computed by Nakamura *et al.* (55.9 kcal mol^{-1}) (if taken into account that no polarization function were considered in the reported MCSCF calculations[15]). The same concerns the corresponding, $S_0(^1B_{1g})-S_2(^1B_{2g})$

TABLE III. Geometries (in Å)[a] and relative energies (eV) in low-lying states (8 dropped orbitals) (E in a.u.).

		State					
Method		$1\,^1A_g$ (sq.)	$1\,^3B_{1g}$ (sq.)	$2\,^1A_g$ (sq.)[b]	$2\,^1A_g$ (sq.)[b]	$2\,^1A_g$ (rh.)	$1\,^1B_{1g}$ (sq.)
CCSD[c]	C–C	1.467 218	1.455 044				
	C–H	1.103 903	1.101 979				
	E	−154.142 991 30	−154.158 818 28				
	ΔE^g	0.0	−0.43				
CCSD(T)[c]	E	−154.173 921 14	−154.178 916 99				
	ΔE^g	0.0	−0.14				
CCSDT-1b[c]	E	−154.182 993 57	−154.179 444 32				
	ΔE^g	0.0	0.10				
MRCCSD[d,e]	C–C	1.460 836	1.455 805	1.456 815	1.458 433	1.453 922	1.447 795
	C–H	1.101 963	1.101 922	1.101 389	1.101 538	1.111 216	1.101 680
	C–H	1.101 963	1.101 922	1.101 389	1.101 538	1.094 379	1.101 680
	<	90.0	90.0	90.0	90.0	95.429	90.0
	E	−154.169 144 70	−154.160 450 82	−154.098 416 53	−154.103 610 30	−154.106 082 72	−154.084 871 76
	ΔE^g	0.0	0.24	1.92	1.78	1.72	2.29
MRCCSD(T)[d,e]	E	−154.189 254 16	−154.178 221 03	−154.124 069 27	−154.121 179 12	−154.126 904 54	−154.105 480 44
	ΔE^g	0.0	0.30	1.77	1.85	1.70	2.28
MRCCSD[d,f]	E	−154.167 654 64	−154.159 693 85	−154.098 791 21	−154.103 717 12	−154.106 631 94	−154.085 814 46
	ΔE^g	0.0	0.22	1.87	1.74	1.66	2.23
MRCCSD(T)[d,f]	E	−154.189 104 23	−154.178 561 76	−154.124 029 21	−154.119 576 94	−154.126 602 19	−154.105 937 16
	ΔE^g	0.0	0.29	1.77	1.89	1.70	2.26
MCSCF[h]	E	−153.642 97	−153.622 76	−153.553 86		−153.559 09	−153.490 83
	ΔE^g	0.0	0.55	2.42		2.28	4.14

[a] See Table I for the exact geometries and optimization constraints.

[b] Results obtained at optimal HF TD-CCSD geometries using delocalized and localized orbitals (columns 5 and 6, respectively) (see text and Table I).

[c] Results at optimal CCSD(T) [Ref. 26(a)] and CCSD geometries of singlet and triplet, respectively (see text for explanation of the abbreviations used for various CC approaches).

[d] Results at optimal two-determinant CCSD geometries using HF orbitals.

[e] TD CC results obtained from the N-electron HF reference.

[f] TD CC results obtained from the $(N-2)$-electron HF reference.

[g] Relative energies (in eV).

[h] MCSCF/6-31G energies (Ref. 15).

energy gap (52.6 kcal mol^{-1}), which, in the delocalized orbital picture is obtained by solving two independent TD CC problems [the closed-shell (S_0,S_1) and the open-shell (T_1,S_2) ones, respectively] (column 8 in Table III). We also investigate the effect of different orbital choices, when two sets of orbitals [based on the N-electron- and $(N-2)$-electron references, respectively] are used in a TD CC application. Similar to the isomerization study for GS of CB, we find different convergence patterns for the alternative, HF and QRHF TD CCSD expressions (Table III). Nevertheless, including the noniterative triple excitations, as done in TD CCSD(T) (Ref. 39) improves the convergence behavior of the corresponding CC procedures, which results in very close agreement of the final optimized HF and QRHF CCSD(T) energy separations, S_0-S_2 (compare lines 16 and 20 in Table III).

In general, the energy splitting for excited states of CB, obtained in our TD CC study are the lowest reported in the literature so far. Nevertheless, considering the size of the basis set, and a *decent* amount of both *dynamic* and *nondynamic* correlations included in our application, we are confident that our results represent a reliable estimate of the energy separations in question.

E. Rhombic interconversion for the first excited singlet state of CB

There is another interesting problem addressed in Table III. Since the ground state of CB becomes stable at a rectangular geometry, one might naturally assume that the equilibrium structure of the corresponding excited singlet, $^1A_{1g}$, will be square. In fact, most of the prior studies on excited states of CB have suggested that the lowest excited singlet state is destabilized toward the rectangular distortion, thus maintaining square geometry. Nevertheless, the question remains whether the stability of the first excited singlet state is affected by the aforementioned rhombic destabilization mode, which would yield two isomeric rhombi of D_{2h} symmetry. In their MCSCF study on the SOJT effect in CB, Nakamura *et al.*[15] furnished the first computational evidence for the possibility of rhombic stabilization of the excited singlet state in question. Due to ill convergence of their MCSCF procedure, however, unphysically large imaginary frequencies were obtained for the corresponding vibrational mode of b_{2g} symmetry. To make their results even more controversial, prior to their applications, Ågren *et al.*[11(a)] failed to observe any stabilization of the first excited singlet state along the b_{2g} rhombic mode, although their MCSCF study employed a more extended basis set.

In our attempt to resolve this issue, we study the potential energy surface of the rhombic distortion for the first excited singlet state, $^1A_{1g}$ (Table III). The energies for the first excited singlet state of CB at square and rhombic geometries are obtained by diagonalization of the TD closed-shell effective Hamiltonian problem [(S_0,S_1) and (S_1,S_2), respectively]. To accommodate the symmetry mode of the SOJT

TABLE IV. The CC vibrational energies for the ground state of cyclobutadiene (in cm^{-1}).

	Structure						Structure	
Mode	Rectangular, ^1A_g					Mode	Square, $^1B_{1g}$	
	MRCCSD[a]	CCSD[b]	CCSD[c]	CCSD(T)[d]	MCSCF[e]		MRCCSD[a]	MCSCF[e]
a_g	1113	1120	1123	1104	1212	a_{1g}	1273	1306
a_g	3206	3205	3211	3181	3465	a_{1g}	3217	3472
a_g	1469	1572	1580	1506	1486	a_{2g}	1224[g]	1336
a_g	925	954	957	935	958	b_{1g}	803i	990i
b_{1g}	1145[g]	1153	1155	1136	1338	b_{1g}	838	1186
b_{1g}	867[g]	870	873	860	1010	b_{2g}	949	1048
b_{1g}	3157[g]	3157	3167	3133	3439	b_{2g}	3178	3445
b_{2g}	540	568	569	523	556	ϵ_g	512	554
b_{3g}	776	814	815	767	784			
b_{1u}	577	589	589	562	585	a_{2u}	539	561
a_u	509	524	524	504	549	b_{1u}	461	509
a_u	754	782	779	729	806		620	702
b_{2u}	760	750	749	733	821	ϵ_u	921	973
b_{3u}	1023	1030	1031	1016	1127			
b_{2u}	1253	1251	1254	1233	1417	ϵ_u	1326	1440
b_{3u}	1542	1593	1600	1543	1587			
b_{2u}	3178	3176	3183	3152	3449	ϵ_u	3198	3463
b_{3u}	3195	3195	3203	3171	3449			
ZPE[f]	37.15[g]	37.60	37.69	36.86	40.08		34.61[g]	37.78

[a] TD CCSD vibrational energies (8 dropped orbitals).
[b] SR CCSD vibrational energies (8 dropped orbitals).
[c] SR CCSD vibrational energies with all electrons correlated.
[d] SR CCSD(T) vibrational energies (8 dropped orbitals).
[e] MCSCF/6-31G vibrational energies (Ref. 15).
[f] Zero point correction (ZPE) (kcal mol^{-1}).
[g] Extrapolated values (see text for details).

TABLE V. The CC vibrational energies for the low-lying states of cyclobutadiene (in cm^{-1}).[a]

	Structure							
	Square						Rhombic	
Mode	$^3A_{2g}$		$^1B_{2g}$		$^1A_{1g}$	Mode	^1A_g	
	MRCCSD[b]	MCSCF[c]	MRCCSD[b]	MRCCSD[b]	MCSCF[c]		MRCCSD[b]	MCSCF[c]
a_{1g}	1292	1305	1317	1284	1240	a_g	1287	1278
a_{1g}	3217	3474	3228	3228	3484	a_g	3105	3405
a_{2g}	1232[d]	1340	1218[d]	1224[d]	1330	a_g	3274	3526
b_{1g}	878	1092	909	940	1147	b_{1g}	1083[d]	1179
b_{1g}	1284	1435	1240	1783	2125	b_{1g}	2397[d]	2609
b_{2g}	953	1048	1187	1104i	9423i	a_g	851	1055
b_{2g}	3177	3442	1959	3107	3376[d]	b_{1g}	1230[d]	1339
ϵ_g	535	611	667	627	615	b_{3g}	506i	459i
						b_{2g}	1051	1072
a_{2u}	552	602	573	421	540	b_{1u}	404i	247i
b_{1u}	476	518	493	479	520	b_{1u}	473	544
b_{1u}	615	721	695	677	701	b_{1u}	883	930
ϵ_u	885	885	954	961	1046	b_{3u}	956	1061
						b_{2u}	974	1121
ϵ_u	1294	1408	1370	1373	1492	b_{3u}	1307	1485
						b_{2u}	1462	1527
ϵ_u	3194	3474	3207	3212	3463	b_{3u}	3122	3394
						b_{2u}	3271	3570
ZPE[c]	36.44[d]	39.65	36.05[d]	36.44[d]	39.59[d]		38.21[d]	41.59

[a] TD CCSD vibrational energies (8 dropped orbitals).
[b] MCSCF/6-31G vibrational energies (8 dropped orbitals) (Ref. 15).
[c] Zero point energy (ZPE) (kcal mol^{-1}).
[d] Extrapolated values (see text for details).

distortion considered, the localized orbital representation is adopted to describe the corresponding square and rhombic structures.[55] In addition, similar to the delocalized applications two different choices of localized orbitals are employed in our isomerization study, namely the N-electron- and $(N-2)$-electron reference based choices (columns 6 and 7 in Table III).

In general, the rhombic D_{2h} structures for the first excited singlet state are below the corresponding square geometries for all the CC approaches and orbital representations studied in our applications (compare columns 5 through 7 in Table III). Depending on the orbital choice, the value of the TD CCSD stabilization energy for the interconversion process varied from 1.6 kcal mol^{-1} (localized orbitals for square structure) to 4.9 kcal mol^{-1} (delocalized description of square geometry). After introducing the triple excitations the trend of the lower values of stabilization energies within the localized representation is completely reversed, with the highest TD CCSD(T) energy gap, S_1(sq.)–S_1(rh.) obtained for the QRHF localized orbitals [compare its value, 4.4 kcal mol^{-1} with the corresponding QRHF CCSD(T) delocalized result (1.6 kcal mol^{-1})]. It is interesting to note that the corresponding TD CC energies for the square structures are fairly invariant with respect to different orbital choices within the given (localized or delocalized) orbital representation (columns 5 and 6 in Table III). On the other hand, when comparing the delocalized and localized CC correlation energies for the first excited square singlet, lesser invariance with respect to the inclusion of triple excitations can be observed for the former CC procedure [compare, e.g., the triple excitation contributions to the resulting HF CCSD(T), $^1A_{1g}$ energies, 25.7 and 17.6 mH, respectively]. The qualitative differences in the convergence of the corresponding correlation expressions can be explained, in part, by symmetry considerations, as the localized orbitals are symmetry adapted to the rhombic potential energy surface while the pertinent delocalized representation consistently follows the rectangular interconversion path. {Admittedly, if the complete configuration space were considered in the correlation expression for external excitations [as done in full CI (FCI)] or at least the full spatial (non-Abelian) symmetry of the square geometry (D_{4h}) were implemented within our truncated TD CC applications, the description of the square structures obtained by localized and delocalized orbitals, respectively would be equivalent.}

TABLE VI. Relative energies, ΔE^{a} for several low-lying states of CB (ΔE in kcal mol^{-1}).

		State						
Method		$1\,^1A_g$ (sq.)	$1\,^1A_g$ (rect.)	$1\,^3B_{1g}$ (sq.)	$2\,^1A_g^{d}$ (sq.)	$2\,^1A_g^{d}$ (sq.)	$2\,^1A_g^{e}$ (rh.)	$1\,^1B_{1g}$ (sq.)
MRCCSD[b]	ΔE^{f}	0.0	−6.5	5.5	44.4	41.1	−1.6	52.9
	ΔE^{g}	0.0	−3.9	7.3	46.2	43.0	0.2	54.3
MRCCSD(T)[b]	ΔE^{f}	0.0	−6.6	6.9	40.9	42.7	−3.6	52.6
	ΔE^{g}	0.0	−4.0	8.8	42.7	44.5	−1.8	54.0
MCSCF[c]	ΔE^{f}	0.0	−4.8	12.7	55.9	55.9	−3.3	95.5
	ΔE^{g}	0.0	−2.5	14.6	57.7	57.7	−1.3	···

[a] See Table I for the exact geometries and optimization constraints.

[b] TD CC energy differences with respect to the square ground state singlet (results obtained from the HF orbitals).

[c] MCSCF/6-31G energy differences with respect to the square ground state singlet (Ref. 15).

[d] TD CC energy differences with respect to square ground state singlet [results obtained from the delocalized and localized orbitals (columns 6 and 7, respectively)].

[e] Energy differences with respect to the first excited square singlet (column 7).

[f] Energy differences between the corresponding potential surface minima (in kcal mol^{-1}).

[g] Energy differences between the corresponding ground vibrational states (in kcal mol^{-1}) (for ZPE see Tables IV and V).

To conclude, we demonstrate that the first excited state of CB stabilizes upon the rhombic distortion with the best TD CCSD(T) estimate for the stabilization energy being 3.6 kcal mol^{-1}, the value obtained using HF localized orbitals.

F. Vibrational spectrum of several electronic states of CB

Finally, we present the results of the vibrational analysis of the harmonic force field for all the electronic states of CB considered in our TD CCSD application (Tables IV–VI) with the goal to furnish the ultimate test of their structure and stability.

Similar to the geometry optimization, the procedure for the numerical evaluation of vibrational modes implemented in our study, is constrained to the D_{2h} Abelian symmetry, and it involves calculating the specific symmetry points close to the energy minima (44 for the rhombic and rectangular structures, and 24 for square geometries). As some of these points represent the distorted geometries of a symmetry lower than D_{2h}, we have to pay special attention to the spatial symmetries of the active orbitals within the given computational point group; the problem which is ultimately involved with the completeness of our TD active space. In fact, as can be seen in Tables IV and V we are not able to obtain the corresponding CCSD vibrational energies for the IAS case, characterized by the same symmetry representation of the valence orbitals [see, e.g., the b_{1g} vibrational problem for the rectangular structure, solved in C_{2h} computational symmetry (Table IV)]. (Nevertheless, work in now in progress to determine how including the triple excitations in MRCC correlation expression will improve the convergence properties of the IAS CC vibrational problem.) To be able to evaluate the zero point energies (ZPE) for the individual electronic states of CB, we therefore have to extrapolate the pertinent TD CCSD vibrational energies from the data furnished by different correlation calculations. Except the rectangular, b_{1g} vibrational frequencies which are obtained by extrapolation from the corresponding single-reference CCSD(T) energies, all the estimated, TD CCSD values are determined from the Nakamura *et al.* MCSCF results.[15] {The extrapolation procedure includes (a) evaluating the scaling factor as a ratio of the corresponding, TD CCSD and MCSCF [CCSD(T)] zero point energies (both calculated without the contribution of the vibrational energies in question), and (b) scaling the pertinent MSCSCF [CCSD(T)] vibrational frequencies to obtain the extrapolated, TD CCSD results. In fact, this procedure is also used in a reversed order, to *correct* the unacceptably large MC SCF, b_{2g} vibrational energy for the excited singlet square structure, using the corresponding TD CCSD results (Table V).}

Let us address the ground state vibrational problem of CB first. Table IV collects the TD CCSD vibrational energies for the rectangular and square ground state singlets of CB in comparison with the single-reference CC values and the corresponding MCSCF results.[15] In order to shed light on (a) the convergence of the *dynamic* correlation, and (b) the effect of the frozen core approximation for the vibrational problem studied, three sets of the single-reference, CC vibrational frequencies for the rectangular structure are listed in Table IV (columns 3 through 5). In general, including the core, 1*s* orbitals in the CCSD correlation expression increases the final values of CCSD vibrational energies by a few wave numbers [compare data in columns 3 and 4 (Table IV)], while the triple excitations in the CCSD(T) expression have just the opposite effect (decreasing the pertinent CCSD values by few tens of wave numbers for most cases). Nevertheless, considering a rather negligible change in the resulting CC vibrational frequencies, the *frozen-core* CCSD model implemented in our application seems to be a reliable compromise between the accuracy of the correlation calculations and their computational cost. As can be seen in Table IV the TD CCSD vibrational energies for rectangular geometry (column 2) are fairly close to the values obtained by the single-reference CC approaches [with the relatively smallest deviations of the TD CC results from the corresponding SR CC ones found for the CCSD(T) approach]. On the other hand, compared to both single- and two-determinant CC results, the MCSCF vibrational energies are rather overestimated; the effect controlled by a limited amount of *dynamic* correlation included in the MCSCF computations of the rectangular structure.[15] The only exception is found for the strongly coupled vibration modes of A_g symmetry, and, in particular for the a_g mode representing the symm. CCH bend [compare the corresponding CCSD(T) and MCSCF values (1506 and 1486 cm^{-1}, respectively)]. To provide an explanation for the relative overestimation of the SR CC vibrational energies with respect to both the MCSCF and TD CC results will require a more involved study of the vibrational problem in question, including the effect of (a) polarization functions (not included in the MCSCF calculations);[15] (b) *nondynamic* correlation (not adequately described in the SR CC approaches applied in the study); and (c) *dynamic* correlation contributions from the triple excitations (not incorporated in our TD CCSD vibrational analysis). [For instance, to illustrate the importance of including both the polarization functions and *dynamic* correlation for describing the equilibrium CCH angle at the rectangular geometry, we can compare the corresponding MCSCF (Ref. 15) and SR CCSD(T) values (134.8° and 132.6°, respectively).] Compared to the rectangular vibrational spectrum, the deviations between the corresponding MCSCF and TD CCSD frequencies at square ground state geometries decreases a fair amount, with the values of the latter being systematically lower by 2.5%–12.7% (columns 8 and 9 in Table IV). The imaginary frequency for the b_{1g}, interconversion motion ($803i$ and $990i$ for TD CCSD and MCSCF applications, respectively) corroborates once again the ground state square singlet as the transition structure on the GS isomerization PES.

As a consequence of the general overestimation of the MCSCF vibrational energies, the resulting MCSCF values of ZPE were larger by $\sim 3\ \mathrm{kcal\,mol}^{-1}$ compared to the TD CCSD ones for both ground state structures in study (Table IV); however, the final zero point corrections to the interconversion barrier are fairly comparable [see the corresponding TD CCSD and MCSCF (Ref. 56) corrections (2.5 and 2.3 $\mathrm{kcal\,mol}^{-1}$, respectively)]. To conclude, the ZPE corrected TD CC barrier for the rectangular distortion process (Table VI) is estimated to be 3.9 $\mathrm{kcal\,mol}^{-1}$ and 4.0 $\mathrm{kcal\,mol}^{-1}$ [TD CCSD and TD CCSD(T) optimized calculations, respectively] compared with the ZPE corrected MCSCF interconversion barrier, 2.5 $\mathrm{kcal\,mol}^{-1}$.[56]

We present a comparison of the TD CCSD vibrational energies for selected excited electronic states of CB with the corresponding MCSCF values[15] in Table V. Similar to the results for the square ground state structure (Table IV) we observe the general overestimation of the MCSCF vibrational frequencies compared to the TD CCSD ones for all electronic states considered (see the pertinent ZPE corrections in Table V). It is interesting to note that the ZPE's for different excited electronic states of CB are very similar within both methods [compare, e.g., the identical TD CCSD value of ZPE (36.44 $\mathrm{kcal\,mol}^{-1}$) for the ground state triplet and first excited square singlet]. Concerning the stability of the individual states, no imaginary frequency is observed for the ground state triplet and second excited singlet of CB [columns 2 through 4 (Table V)], thus confirming the fact that their equilibrium is represented by the square structure. On the other hand, the first excited singlet exhibited the instability of its square equilibrium with respect to the b_{2g}, rhombic deformation mode [compare its frequency, $1104i$ with the corresponding MCSCF/6-31G vibrational energy, $9423i$ (Ref. 15)]; however, even the resulting rhombic geometry did not represent the true equilibrium when it stabilized along the two out-of-plane bending modes of b_{1u} and b_{2g} symmetry with the corresponding vibrational energies being $404i$ and $506i$, respectively (Table V). At the same time, the high frequency shift with respect to the rectangular, b_{1g} motion is detected for the first excited singlet state, a phenomenon which is closely connected with the destabilization of the state towards the rectangular deformation.

The TD CCSD zero point energies are also evaluated (Table V) with the energy differences between (a) the potential surface minima and (b) ground vibrational states, listed in Table VI. In general, we find a close agreement between the MCSCF and TD CC, ZPE corrections to the energy separations considered. The positive ZPE corrections to the values of energy barriers at square geometries result in increasing the corresponding energy differences (Table VI). On the other hand, the energy barrier for the rhombic distortion of the first excited state decreases upon the ZPE correction, which in some cases even suggests the stability of the square singlet structure [see, e.g., the positive value of the corresponding energy separation in the TD CCSD application (Table VI)]. Admittedly, a more exacting study of the interconversion process will be necessary, including (a) a more

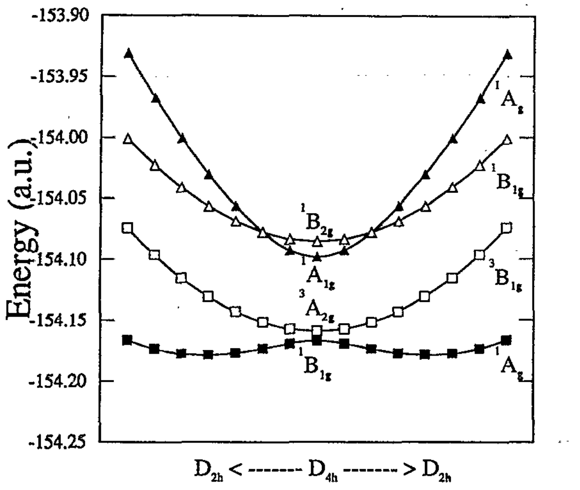

FIG. 1. MRCCSD energies of the four lowest electronic states of cyclobutadiene along a rectangular distortion path (E in a.u.). The curves are identified as follows: ground state singlet, S_0 (■); ground state triplet, T_0 (□); first excited singlet, S_1 (▲); second excited singlet, S_2 (△).

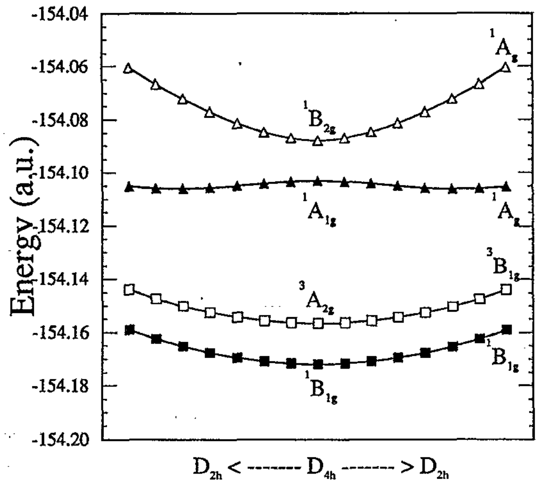

FIG. 2. MRCCSD energies of the four lowest electronic states of cyclobutadiene along a rhombic distortion path (E in a.u.). The curves are identified as follows: ground state singlet, S_0 (■); ground state triplet, T_0 (□); first excited singlet, S_1 (▲); second excited singlet, S_2 (△).

extended basis set; (b) a larger active configuration space; and last but not least (c) consideration of the anharmonic correction to the zero point vibrational level. (In fact, the third issue has been addressed in several prior studies on the ground state isomerization process in CB,[1,12,13] which were geared at the explanation of the phenomenon of heavy atom tunneling.[1–5,10,12,13] For example, Čársky suggested that due to the strong coupling of the interconversion mode with other motions of the same A_g symmetry, at least three vibrational, A_g modes should be treated nonadiabatically.[13(a)] As a result, splitting of the first and third A_g lines was observed, thus corroborating the possibility of quantum mechanical tunneling in CB.)

Finally, the findings about the structure of all electronic states of CB studied in the paper, including their stability towards the two possible SOJT distortion motions are also summarized in Figs. 1 and 2. The finite lowering of the energy for the square ground state singlet (first excited singlet) is demonstrated in Fig. 1 (Fig. 2) as a function of the rectangular (rhombic) reaction coordinate, with the three remaining electronic states of CB found to be stable with respect to the pertinent vibrational mode. It is interesting to note that the aforementioned stabilization is strongly coupled with the destabilization of the corresponding excited singlet state (Figs. 1 and 2). By contrast the energy separations between the other two electronic states [(T_1,S_2) and (S_0,T_1) for rectangular and rhombic interconversion, respectively] remain fairly constant along the whole distortion path.

IV. CONCLUSIONS

Potential energy surfaces for the ground and several excited states of cyclobutadiene were investigated by the MRCC method and the results were critically compared to the conclusions drawn from the *best* single- and multireference correlated calculations. Besides the *standard* MR CCSD approach, we also examined a new multireference CC method including the triple excitations in a noniterative, CCSD(T) fashion. Among the problems studied in the paper were (a) the ground and first excited singlet state isomerization processes of CB; (b) the ordering of its lowest electronic states at the square geometry; and (c) the harmonic vibrational spectrum for all the electronic states considered.

By comparing the convergence of the corresponding single- and two-determinant CC computations we demonstrated the higher efficacy of the TD CC treatment of the (quasi)-degenerate ground state correlation problem of cyclobutadiene including (a) a more economic, TD evaluation of the effect of higher excitations, whose inclusion is imperative for a qualitatively correct description of the square singlet geometries of CB [compare the CCSDT single-reference estimate of the ground state interconversion barrier with the pertinent TD CCSD value (6.4 and 6.6 kcal mol^{-1}, respectively)]; (b) a *balanced* treatment of both the *dynamic* and *nondynamic* correlation effects within the TD CCSD approach, resulting in the same level of accuracy for the ground singlet and triplet square structures as the one provided by the *best*, CCSDT method; (c) faster convergence of the TD CC correlation expansion manifested by smaller deviations between the corresponding CCSD and CCSD(T) results [compare, e.g. the CCSD(T), "triple excitation" corrections to the ground state isomerization barrier of CB, 5.8 kcal mol^{-1} and 0.1 kcal mol^{-1}, for the single- and two-determinant CC methods, respectively].

In addition to the ground state singlet and triplet potential surfaces, we also examined the rhombic distortion path for the first excited singlet state of CB in comparison with the results from previous, multireference correlated calculations. Contrary to the ground state, *rectangular* isomerization process, the TD CC stabilization energy for the *rhombic* valence tautomerization was found to be much more sensitive to the level of correlation treatment as well as to the choice of the reference orbitals (Table VI). The final, TD CCSD(T) value of the activation barrier with inclusion of the ZPE correction was in a close agreement with the corresponding MCSCF result of Nakamura *et al.* (1.8 and 1.3 kcal mol^{-1}, respectively). Nevertheless, considering the computational aspects of the present TD CC calculations, it will be the focus of our future study to determine the effects of (a) improving the DZP basis set employed; (b) extending the two-determinant active reference space; and (c) including the anharmonic corrections to the vibrational energies, on the final values of the pertinent isomerization energies.

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[55] It is well known [see Refs. 1,16(b)] that the final state wave function, $^1B_{1g}$ for the square GS of CB can be alternatively expressed in terms of delocalized and localized orbital representations. Numerically, the former orbitals can be obtained by solving the HF problem for the square, D_{2h} geometry with *a rectanglelike* orientation of the carbon atoms, while the latter representation can be furnished by the square, D_{2h} calculations for *a rhombuslike* position of the carbon frame (see Table I for corresponding coordinates). As a consequence of its delocalized (localized) description, the resulting GS wave function of CB at the square geometry is of a closed-shell (open-shell) structure.

[56] Based on the MCSCF vibrational energy data published in Ref. 15 we found a discrepancy between the values of ZPE, reported by the authors and the corresponding, recalculated corrections. For the GS rectangular distortion, e.g., the recalculated value differed from the original result (1.6 kcal mol^{-1}) by more than 0.7 kcal mol^{-1} with the final value of the interconversion barrier being lowered to 2.48 kcal mol^{-1}.