

Determination of Energy Minima and Saddle Points Using Multireference Configuration Interaction Methods in Combination with Reduced Gradient Following: The S_0 Surface of H_2CO and the T_1 and T_2 Surfaces of Acetylene

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Abstract: The implementation of the reduced gradient following (RGF) method into the COLUMBUS quantum-chemical program system is reported using the newly developed analytic MR-CISD/AQCC gradient feature. By this combination a very useful tool has been developed for general searches of stationary points on ground- and excited-state energy surfaces. This procedure is applied to the S_0 surface of H_2CO and the T_1 and T_2 surfaces of acetylene. For H_2CO we investigated three minima (formaldehyde, *s*-trans, and *s*-cis hydroxycarbene) and five saddle points. For the T_1 and T_2 states of acetylene the *cis*- and *trans*-minima and the planar and nonplanar saddle points were computed.

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Introduction

Stationary points play a fundamental role for the characterization of potential energy surfaces (PES). In most cases the determination of local minima can be regarded as routine work, because several reliable algorithms are available for that purpose (for reviews see, e.g., refs. 1 and 2). However, the search for saddle points on the PES is significantly more complex and is a nontrivial task even for smaller molecules.^{1,2} The situation is more complicated by the fact that saddle point structures frequently contain significantly stretched chemical bonds and it is, therefore, not always clear whether single reference (SR) methods are sufficient for an accurate description of such structures. The investigation of excited-state surfaces poses still more severe requirements on the quantum chemical method to be used and systematic searches even for minima are much less frequent than corresponding investigations for electronic ground states. In such critical cases multireference (MR) methods are required from which the multireference configuration interaction with singles and doubles (MR-CISD),³ complete active space (CAS),⁴ perturbation theory to second order (CASPT2),⁵ and multireference averaged coupled pair functional (MR-ACPF)⁶ or multireference averaged quadratic coupled cluster (MR-AQCC)^{7,8} are mentioned here. The latter two methods are of interest because they allow the computation of size-extensivity corrections for MR cases based on a variational approach in close analogy to the CI method.

The availability of analytic gradients is, of course, an important practical criterion for the choice of an appropriate computational method for geometry searches. In contrast to the situation found for the SR case, analytic gradients are not so commonly available for MR methods. Many geometry optimizations are being performed only at the multiconfiguration self-consistent field (MCSCF) level. The omission of major parts of dynamic correlation in this approach may lead to significant artifacts. In the last years an efficient MR-CISD gradient method has been developed^{9–11} and implemented into the COLUMBUS program system.^{12–15} Because of the variational character of the above-mentioned MR-ACPF/AQCC methods, analytic gradients can also be computed for these methods in close analogy to the MR-CISD formalism. So far, this gradient formalism has been restricted to MR-CISD calculations based on single-state MCSCF, making the balanced treatment of excited states difficult. Recently, an extension of the MR-CISD gradient method based on state-averaged MCSCF calculations has been developed,¹⁶ concentrating in par-

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ticular on the treatment of excited states. In this implementation local minima and saddle points were determined by the direct inversion in the iterative subspace method for geometry optimization (GDIIS),¹⁷ requiring starting geometries close to the stationary point. Global saddle point searches could not be performed so far within COLUMBUS.

It is the aim of this work to report the implementation of the reduced gradient following (RGF) method, recently developed by Quapp et al.,^{18–20} into COLUMBUS as a tool for global searches of ground- as well as of excited-state PES. The RGF method has been shown to be very flexible and efficient in locating a large variety of saddle points. The computational aspects of saddle point searches using MR quantum chemical methods are similar to those for the SR case. However, there are a number of important practical questions of special interest for MR implementations due to the usually much longer computer times required for a given molecule as compared to SR calculations. Most importantly, second derivatives have to be computed as finite differences of analytical gradients in the present implementation because analytic second derivatives in the MR-CISD approach are not available due to the complexity of the formalism. Because in global PES searches knowledge of the exact Hessian is not necessary, we investigated various possibilities for its approximate evaluation (e.g., simple estimates, update schemes, and quantum chemical calculation with lower-level methods) with the aim of finding a good balance between computational efficiency for the calculation of the Hessian and its reliability, which is still needed for satisfactory convergence of the RGF iterations.

In this work two applications are reported. The first one refers to the determination of minima and saddle points on the S_0 surface of the H_2CO system. Early studies have been performed at MCSCF,²¹ SCF and CISD,^{22,23} and Moller-Plesset perturbation theory^{24,25} levels. These investigations already covered the most important stationary points. More recently, saddle points on S_0 have been studied at the coupled cluster,²⁶ density functional theory (DFT),^{27,28} and quadratic configuration interaction with single, double, and triple [QCISD(T)] levels.²⁹ The most complete investigation on the barrier to unimolecular dissociation to $H_2 + CO$ has been undertaken by Feller et al.³⁰ Extended systematic studies of the S_0 surface using relatively small basis sets have been performed by Quapp et al.,¹⁸ Jensen,³¹ and Bondensgård and Jensen,³² where additional interesting minima and first- and higher-order saddle points have been found and characterized. To our knowledge, no systematic investigations on saddle point structures using MR methods have been undertaken so far. The formaldehyde example is used to investigate the stability of the RGF implementation and to perform new high-level geometry optimizations using the MR-CISD and MR-AQCC methods.

In the second example, stationary points (*cis*- and *trans*-minima, in-plane and out-of-plane saddle points) on the PES of the first two excited triplet states (T_1 and T_2) of acetylene are investigated. These states have been studied previously by various authors.^{33–39} In these investigations only planar structures have been optimized. In the work by Cui et al.,^{40,41} systematic studies on the energy surfaces of several excited states of acetylene, including nonplanar structures, have been performed using the CASSCF and equation-of-motion coupled cluster with single and double (EOM-CCSD)⁴² methods. In the case of the CASSCF

optimizations, substantial fractions of dynamic electron correlation are missing, and in the case of EOM-CCSD the calculations are restricted to SR character. The present investigations comprise the first complete geometry optimizations for the T_1 and T_2 states of acetylene using multireference methods and are part of a general, systematic survey of planar and nonplanar sections of the T_1 – T_4 and S_1 – S_2 PES of acetylene.⁴³

Review of the RGF Procedure

In the RGF method,¹⁸ which is a generalization of the distinguished coordinate method,⁴⁴ the gradient criterion for stationary points

$$\nabla E(\mathbf{x}) = \mathbf{0} \quad (1)$$

is reduced by one equation leading to

$$\frac{\partial E(\mathbf{x})}{\partial x^i} = 0, \quad i = 1, \dots, k, \dots, N \quad (2)$$

where the vector \mathbf{x} represents the nuclear coordinates. In the original formalism¹⁸ the search direction was defined by one individual coordinate, x^k . This formalism was generalized to an arbitrary, fixed search direction, \mathbf{r} , by using the projector equation:¹⁹

$$\mathbf{P}_r \nabla E(\mathbf{x}) = \mathbf{0} \quad (3)$$

where $\mathbf{P}_r \mathbf{r} = \mathbf{0}$ for the fixed search direction \mathbf{r} . Note that eq. (2) is a special case of eq. (3) with the corresponding $(N - 1) \times N$ projector matrix:

$$\mathbf{P}_r = \begin{pmatrix} 1 & \cdots & 0 & 0 & 0 & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdots & 1 & 0 & 0 & \cdots & 0 \\ 0 & \cdots & 0 & 0 & 1 & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdots & 0 & 0 & 0 & \cdots & 1 \\ 1 & k-1 & k & k+1 & N & & \end{pmatrix} \begin{matrix} \text{row} \\ 1 \\ \cdot \\ k-1 \\ k \\ \cdot \\ N-1 \end{matrix} \quad (4)$$

Thus, \mathbf{P}_r is built from the unit vectors orthogonal to the search direction where again the k th unit vector is missing. These reduced gradients of eqs. (2) and (3) define curves connecting stationary points. Starting from a given point (e.g., a minimum) one follows a selected curve to reach the saddle point of interest. A predictor-corrector method is used for tracing these curves. Assuming a curve of points $\mathbf{x}(t)$ fulfilling the $N - 1$ conditions of eq. (3), the tangent \mathbf{x}' to the curve defined by eq. (3) is given as

$$\frac{d}{dt} \mathbf{P}_r \nabla E(\mathbf{x}(t)) = \mathbf{0} = \mathbf{P}_r \frac{d}{dt} \nabla E(\mathbf{x}(t)) = \mathbf{P}_r \mathbf{H}(\mathbf{x}(t)) \frac{d\mathbf{x}(t)}{dt} \quad (5)$$

or

$$\mathbf{P}_r \mathbf{H}(\mathbf{x}(t)) \mathbf{x}' = \mathbf{0} \quad (6)$$

This is a homogeneous system of $N - 1$ linear equations where the coefficients are the elements of the Hessian matrix \mathbf{H} projected by \mathbf{P}_r . Eq. (5) is solved using a QR decomposition. In the predictor step the sequence of points \mathbf{x}_m and \mathbf{x}_{m+1} is computed as

$$\mathbf{x}_{m+1} = \mathbf{x}_m + \frac{StL}{\|\mathbf{x}'_m\|} \mathbf{x}'_m \quad (7)$$

where StL is a steplength parameter.

Because the new point does not satisfy exactly the condition defined in eq. (3), a corrector step is added in which eq. (3) is solved using a Newton–Raphson-like method. In general, the linear combination \mathbf{r} of internal coordinates is used as an initial search direction. For further details of the procedure see refs. 18 and 19 and the web page.²⁰ The use of the metric in internal coordinates is explained in the appendix of ref. 45.

With the RGF method only the global search for a stationary point is performed. For final refinement the GDIIS method¹⁷ is used.

Computational Details

All calculations were performed using the COLUMBUS quantum-chemical program system.^{12–15} Analytical gradients^{9–11,16} of the energy with respect to nuclear coordinates were computed for the MR-CISD³ and MR-AQCC^{7,8} methods. Second derivatives were computed from finite differences of analytic gradients. The atomic orbital (AO) integrals and the AO derivative integrals were calculated using program modules taken from DALTON.⁴⁶ The extended Davidson method (MR-CISD+Q)^{47,48} was used in single point calculations. The RGF and GDIIS¹⁷ optimizations were performed in natural internal coordinates as defined by Fogarasi et al.⁴⁹ The harmonic vibrational frequencies were computed by the program SUSCAL developed by Pongor.⁵⁰

Results and Discussion

Hessian Update in the RGF Procedure

It should be noted that the criterion for the RGF curve [eq. (3)] does not use the Hessian. Therefore, it will be sufficient to use approximations to the Hessian via update methods.² Necessary evaluations of the Hessian needed are generally crucial and time consuming steps, especially in the present MR-CISD case where the Hessian is computed by finite differences from analytic gradients. Quite generally, one will try to perform global saddle-point searches at the lowest computational level possible because of the large computational costs involved in such searches. MCSCF calculations will usually constitute a good starting point. However, in some cases MR-CISD calculations will be required from the beginning because of artificial MCSCF results. The complexity of choices of appropriate procedures is certainly much larger for excited-state calculations as compared to the ground state. No general rules can be given in this case. The present COLUMBUS implementation offers for that purpose a variety of possibilities

with respect to methods used for RGF gradient calculations and for Hessian evaluation, which can be adapted to the respective situation. Some of these possibilities are demonstrated in the following examples.

Several options for approximating the Hessian were investigated. The first one (case 1) is to recompute the Hessian matrix at every point of the RGF search. This is the most expensive case and is intended to serve only as reference for further approximations. A second possibility (case 2) is to calculate the Hessian matrix once at the beginning of the RGF search and use a Hessian update method for all remaining iterations. For this update the method developed by Bofill⁵¹ is used. Case 2 is the cheapest procedure, which will, however, depend significantly on the quality of the Hessian update algorithm. In order to have an alternative to this update-only procedure, we compute in case 3 the Hessian for each predictor step (because the largest geometry changes occur in this step) and use the Hessian update only for the corrector steps. As already noted above, it will not be necessary to compute the Hessian with the same high-level method that is used for the gradient. Either reduced basis sets or a low-level quantum chemical method (such as SCF or MCSCF) will suffice.

Two test examples for the RGF search were chosen: the sequence $M_3 \rightarrow F_1 \rightarrow M_4$ for the out-of-plane saddle point F_1 located between the *s*-trans (M_3) and *s*-cis (M_4) hydroxycarbene (see Fig. 1), and the out-of-plane saddle point located between the *cis*- and *trans*- minima on the PES for the T_1 state of acetylene. For the hydroxycarbene calculations the REDVAL MCSCF wave function and the REDVAL reference space, as described in the following subsection, together with the cc-pVDZ basis set⁵² were used. For the saddle point search on the T_1 surface of acetylene, state-averaged CASSCF(6,6) calculations, including the electronic ground state S_0 and the T_1 state, and MR-CISD calculations with a CAS(4,4) reference configuration set (as described in more detail in the respective subsection below) were carried out.

In Table 1 the number of RGF iteration steps for the two test cases and the three options for the treatment of the Hessian mentioned above are given. Table 1 shows that the number of RGF steps does not vary too much for searches using different options for calculating the Hessian. The number of corrector steps per predictor step ranges between two and three on the average. The calculations for case 2 work very well in all cases and are, of course, the preferred ones. It is interesting to note that in the searches $SP \rightarrow cis$ -acetylene updating the Hessian leads to a smaller number of iterations than for case 1 where the Hessian is calculated exactly. Case 3 is more time consuming and should be reserved for difficult situations where the Hessian update does not work.

The H_2CO PES

In the first step of the search for stationary points on the S_0 PES of H_2CO , the RGF method and the closed shell SCF calculations were used. After a successful localization of stationary points, final GDIIS geometry optimizations were performed using the MR-CISD and MR-AQCC methods and the cc-pVTZ basis set.⁵² For the construction of the reference configurations a reduced valence CAS (REDVAL) space was defined. The active space consisted of the valence orbitals ($1b_2, 5a_1, 1b_1, 2b_2, 2b_1, 6a_1, 3b_2,$

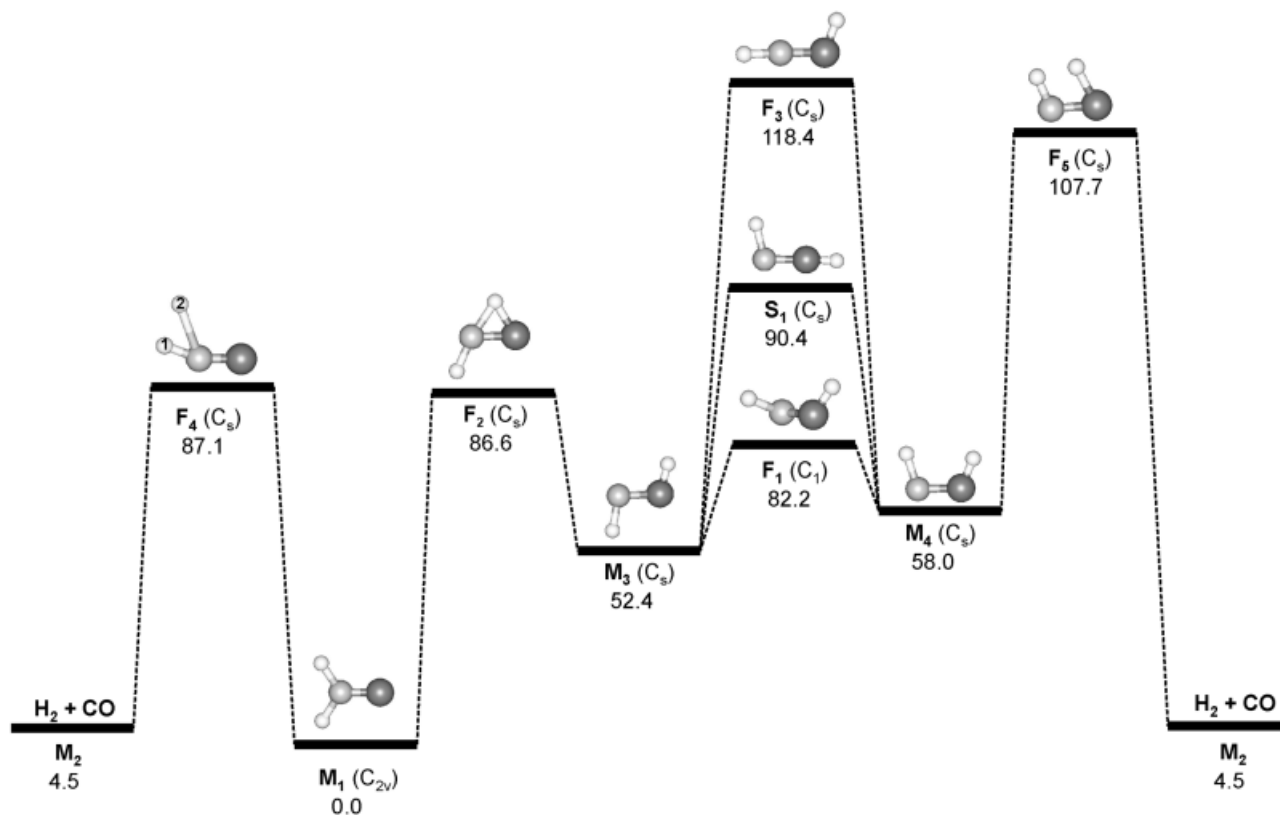


Figure 1. Stationary points on the H₂CO PES. Relative energies (kcal/mol) were computed with the REDVAL-2ex-AQCC method and the cc-pVTZ basis set.

and 7a₁) and eight valence electrons. The 1a₁ – 4a₁ orbitals were kept doubly occupied. The REDVAL space was used in all MCSCF calculations. The reference space for the MR-CISD and MR-AQCC calculations was reduced for computational economy from REDVAL to REDVAL-2ex, which consisted of all one- and two-electron excitations from the four strongly occupied MCSCF orbitals (1b₂, 5a₁, 1b₁, and 2b₂) into the remaining four orbitals (2b₁, 3b₂, 6a₁, and 7a₁) of the REDVAL space. The final expansion space consisted of the reference configurations and all single and double excitations from the reference configurations into all active and virtual orbitals. The 1a₁ and 2a₁ core orbitals were frozen in all post-MCSCF calculations.

Based on the extensive searches for stationary points reported in refs. 18 and 31 the most stable minimum structures and connecting saddle points were chosen. An overview of the selected structures and of the notation used can be found in Figure 1. Four minima, consisting of the C_{2v} global minimum structure M₁ of formaldehyde, the dissociation product H₂+CO (M₂), and the *trans*- (M₃) and *cis*-hydroxycarbene (M₄), were investigated. Starting from these minima, five first-order saddle points (F₁–F₅) and one second-order saddle point, S₁, connecting the different minimum structures as indicated in the figure, were determined.

Geometries for structures M₁ and F₄ and relative stabilities are collected in Table 2. Table 3 shows results for the dissociation products CO and H₂ (structure M₂), and results calculated for M₃,

M₄, F₁, F₂, F₃, and F₅ are given in Table 4. For all structures zero-point energy corrections were determined as well using respective single-reference calculations. In the case of the M₁ structure the REDVAL-2ex reference space was tested against the full REDVAL space. As Table 2 shows, REDVAL-2ex geometries—computed at a significantly reduced computational cost—are in very good agreement with the full REDVAL results. Therefore, the former reference space was used in the following calculations on the remaining formaldehyde structures instead of the full REDVAL approach. For comparison, experimental geometries and CCSD(T) results reported by Feller et al.³⁰ using an aug-cc-pVTZ basis set are given for the M₁ structure as well. All MR methods used in the present work show very good agreement with each other and with the CCSD(T) results. Agreement with experimental geometry data is also good.

The saddle point F₄ leading to the dissociation products CO and H₂ was investigated extensively in previous investigations by several authors.^{18,26–32} The REDVAL-2ex results agree quite well with the CCSD/CCSDT-1 results of Scuseria and Schaefer²⁶ (TZ+2P; see Table 2) and those reported by Feller et al.³⁰ (basis-set extrapolated barrier height 87.4 kcal/mol). Results for the dissociation products CO and H₂ and the reaction energy for the dissociation H₂CO → H₂+CO are collected in Table 3. Reaction energies ΔE_e (REDVAL-2ex-AQCC) are too small by 0.7 kcal/

Table 1. Total Number of RGF Steps for Various Approximations Used for the Hessian Matrix Calculations.

Method ^a	Case 1 ^b	Case 2 ^b	Case 3 ^b
Hydroxycarbene ^c			
SCF (SCF)			
M ₃ → F ₁	14 (6)	16 (6)	15 (6)
F ₁ → M ₄	18 (6)	18 (6)	20 (6)
SR-CISD (SCF)			
M ₃ → F ₁	17 (6)	19 (6)	17 (6)
F ₁ → M ₄	20 (6)	23 (6)	19 (6)
Acetylene (T ₁) ^d			
MCSCF (MCSCF)			
<i>trans</i> → SP ^e	12 (6)	13 (6)	11 (6)
SP ^e → <i>cis</i>	25 (7)	18 (6)	17 (6)
MR-CISD (MCSCF)			
<i>trans</i> → SP ^e	13 (6)	12 (6)	11 (6)
SP ^e → <i>cis</i>	30 (8)	23 (7)	21 (7)

^aMethod for Hessian calculation in parentheses.

^bFor the definition of cases see text. Number of predictor steps in parentheses.

^cSearch direction ∠HCOH; predictor step length = 0.15 rad; corrector step convergence criterion 0.001 aJ/Å and aJ/rad for stretching coordinates and angular coordinates, respectively; cc-pVDZ basis set; for the definition of individual cases see text.

^dSearch direction ∠HCCH; predictor step length = 0.1 rad; corrector step convergence criterion 0.001 aJ/Å and aJ/rad for stretching coordinates and angular coordinates, respectively; cc-pVDZ basis set; for the definition of individual cases see text.

^eOut-of-plane saddle point.

mol as compared to the experimental value. In the extrapolated results by Feller et al.,³⁰ a value of 5.8 kcal/mol was obtained.

For the remaining structures investigated in this work less extensive calculations using either SCF,^{18,31} SR-CISD,²³ or

Table 3. Optimized Bond Lengths (Å) for CO and H₂ and the Reaction Energy for H₂CO → H₂ + CO (kcal/mol).

Method	R _{CO}	R _{HH}	ΔE _e ^a	ΔE ₀ ^{a,b}
REDVAL-2ex-CISD	1.134	0.738	2.9 (4.6)	-4.9 (-3.2) ^c
REDVAL-2ex-AQCC	1.135	0.741	4.5	-3.1 ^d
CCSD/CCSDT-1 ^{e,26}	1.126	0.741	2.7	
Exp.	1.128 ⁵⁵	0.741 ⁵⁵	5.2 ^f	-2.2 ⁵⁶

^aΔE_{MR-CISD+Q} in parentheses.

^bIncluding ZPE correction.

^cZPE correction from SR-CISD.

^dZPE correction from SR-AQCC.

^eCCSD geometry and CCSDT-1 energy at CCSD geometry.

^fSee ref. 26 for the determination of this value.

QCISD³¹ method with basis sets of, at most, polarized DZ quality have been carried out so far. Thus, in these cases our results are expected to give additional information with significantly improved accuracy. Optimized geometries of the *s*-trans hydroxycarbene M₃ and *s*-cis hydroxycarbene M₄ and relative stabilities are collected in Table 4. Starting from the *s*-trans hydroxycarbene M₃, RGF searches were performed with search directions ∠HCOH, ∠HCO, and ∠HOC leading to the saddle points F₁, F₃, and S₁, respectively (see also Fig. 1). In Table 4 comparison is also made with SCF/QCISD results obtained by Jensen³¹ and the DFT-BP calculations of Deng et al.²⁷ as typical representations of previous results available in the literature. Comparing the latter results with the REDVAL-2-ex-AQCC of this work, one finds in many cases acceptable agreement. However, some noteworthy deviations are also observed: in the case of F₁, ≈6° in the HOC angle and ≈0.04 Å in R_{CH} for F₂ using the DFT-BP method. For ΔE_e values we observed in the case of QCISD results deviations of ≈4 kcal/mol for F₂, ≈9 kcal/mol for F₃, and ≈7 kcal/mol for F₅. Different

Table 2. Optimized Bond Lengths (Å), Angles (deg), and Energies Relative to Structure M₁ (kcal/mol) for Structures M₁ and F₄ of H₂CO.

	R _{CO}	R _{CH1}	R _{CH2}	∠H ₁ CO	∠H ₂ CO	ΔE _e ^a	ΔE ₀ ^{a,b}
M ₁							
REDVAL-2ex-CISD	1.208	1.100	1.100	121.9	121.9	—	—
REDVAL-CISD	1.209	1.101	1.101	121.9	121.9	—	—
REDVAL-2ex-AQCC	1.209	1.103	1.103	121.9	121.9	—	—
REDVAL-AQCC	1.210	1.104	1.104	121.9	121.9	—	—
CCSD(T) ³⁰	1.211	1.103	1.103	121.8	121.9	—	—
Exp. ⁵⁴	1.203	1.100	1.100	121.8	121.8	—	—
F ₄							
REDVAL-2ex-CISD	1.170	1.089	1.679	163.7	111.5	86.8 (86.9)	81.4 (81.5) ^c
REDVAL-2ex-AQCC	1.171	1.093	1.675	163.6	111.5	87.1	81.8 ^d
CCSD/CCSDT-1 ^{e,26}	1.163	1.093	1.661	163.1	111.3	86.8	81.4

^aΔE_{MR-CISD+Q} in parentheses.

^bIncluding ZPE corrections.

^cZPE correction from SR-CISD.

^dZPE correction from SR-AQCC.

^eCCSD geometry and CCSDT-1 energy at CCSD geometry.

Table 4. Optimized Bond Lengths (Å), Angles (deg), and Energies Relative to Ground State M_1 (kcal/mol) for the Structures M_3 , M_4 , F_1 , F_2 , F_3 , and F_5 of H_2CO .

	R_{CO}	R_{CH}	R_{OH}	$\angle HCO$	$\angle HOC$	$\angle HOCH$	ΔE_e^a	$\Delta E_0^{a,b}$
M_3								
REDVAL-2ex-CISD	1.317	1.107	0.966	102.2	107.1	180.0	53.0 (52.4)	53.1 (52.5) ^c
REDVAL-2ex-AQCC	1.319	1.113	0.966	102.0	107.2	180.0	52.4	52.5 ^d
SCF/QCISD ^{e,31}	1.299	1.102	0.974				54.0	
DFT-BP ²⁷	1.320	1.125	0.978	102.3	108.1	180.0	52.5	52.5
M_4								
REDVAL-2ex-CISD	1.314	1.121	0.970	106.5	113.6	0.0	57.5 (56.8)	57.1 (56.5) ^c
REDVAL-2ex-AQCC	1.316	1.122	0.971	106.5	113.9	0.0	58.0	57.4 ^d
SCF/QCISD ^{e,31}	1.297	1.110	0.949				59.0	
DFT-BP ²⁷	1.314	1.131	0.987	108.2	116.2	0.0	56.8	56.2
F_1								
REDVAL-2ex-CISD	1.360	1.119	0.961	104.8	114.2	90.4	82.8 (82.6)	80.1 (80.0) ^c
REDVAL-2ex-AQCC	1.360	1.125	0.964	104.8	114.9	91.7	82.2	79.6 ^d
SCF/QCISD ^{e,31}	1.344	1.113	0.946				85.0	
DFT-BP ²⁷	1.353	1.142	0.969	104.9	121.3	90.1	82.5	80.3
F_2								
REDVAL-2ex-CISD	1.309	1.103	1.174	114.5	60.1	180.0	87.2 (86.4)	83.2 (82.4) ^c
REDVAL-2ex-AQCC	1.311	1.087	1.177	114.5	60.0	180.0	86.6	82.2 ^d
SCF/QCISD ^{e,31}	1.270	1.097	1.171		59.3	180.0	91.0	
DFT-BP ²⁷	1.316	1.124	1.176	114.4	61.5	180.0	81.7	78.1
F_3								
REDVAL-2ex-CISD	1.286	1.056	0.981	178.7	111.5	180.0	120.7	119.0
REDVAL-2ex-AQCC	1.289	1.060	0.982	178.4	111.5	180.0	(119.6)	(118.0) ^c
SCF/QCISD ^{e,31}	1.279	1.049	0.954				118.4	116.6 ^d
F_5								
REDVAL-2ex-CISD	1.280	1.355	1.221	101.0	65.7	0.0	109.8	103.8
REDVAL-2ex-AQCC	1.281	1.365	1.223	101.1	65.7	0.0	(107.6)	(101.7) ^c
SCF/QCISD ^{e,31}	1.235	1.430	1.174	97.9	70.0	0.0	107.7	101.8 ^d
DFT-BP ²⁷	1.288	1.373	1.232	102.5	65.7	0.0	115.0	
							103.6	98.1

^a $\Delta E_{MR-CISD+Q}$ in parentheses.^bIncluding ZPE correction.^cZPE correction from SR-CISD.^dZPE correction from SR-AQCC.^eSCF geometry and QCISD energy at SCF geometry [basis set 6-31G(d,p)].

characterizations of structure S_1 (see Fig. 1) have been given in previous studies. It has been reported to be a first-order saddle point in DFT calculations²⁸ and to be a second-order saddle point by Jensen.³¹ The present investigations (SR-CISD/cc-pVDZ) showed that this structure is a second-order saddle point. Therefore, we did not perform further investigations on it as we were interested only in first-order saddle points. The saddle point F_2 (symmetry C_s), located between structure M_1 and the *s*-trans hydroxycarbene M_3 , is of first-order and not of second-order as found in the STO-3G/SCF investigations by Quapp et al.¹⁸

Acetylene

The planar and nonplanar saddle points on the PES of acetylene in the first two triplet states (T_1 and T_2) and the linear ground state geometry were investigated. The RGF saddle point search was performed at the MCSCF level in the cc-pVDZ basis;⁵² for the

subsequent GDIIS geometry refinement MR-CISD and MR-AQCC calculations and the cc-pVTZ basis⁵² set were used. Only the MR-AQCC results, which are considered to be the more accurate ones, are presented here. The active space in the MCSCF calculations consisted of a CAS of six electrons in six orbitals ($3\sigma_g$, $1\pi_u$, $1\pi_g$, and $3\sigma_u$ in $D_{\infty h}$ notation). Because the present calculations are part of a more extensive survey on several excited-state acetylene surfaces, state-averaged MCSCF calculations, including the ground state, the three lowest triplet states, and the two lowest singlet states, were performed in order to get a balanced description of these states. The MR-CISD reference space was constructed from a CAS of four electrons in four orbitals ($1\pi_u$, $1\pi_g$). The expansion space consisted of the reference configurations and all single and double excitations into all active and virtual orbitals. The 1s orbitals of carbon were kept frozen in all post-MCSCF calculations.

Table 5. Optimized Bond Lengths (Å), Angles (deg), and Relative Energies (eV) for Minima and Saddle Points on the S_0 , T_1 , and T_2 Surfaces of Acetylene Calculated at the MR-AQCC Level Using the cc-pVTZ Basis Set.

	R_{CC}	R_{CH1}	R_{CH2}	$\angle H_1CC$	$\angle H_2CC$	$\angle H_1CCH_2$	ΔE_e^a	Ref.
$1^1\Sigma_g^+$ (Ground state, $D_{\infty h}$)								
MR-AQCC	1.210	1.061	1.061	180.0	180.0	—	—	This work
1^3B_2 (<i>cis</i> min., C_{2v})								
MR-AQCC	1.341	1.087	1.087	128.5	128.5	0.0	3.84	This work
CCSD(T)	1.340	1.091	1.091	128.0	128.0	0.0	3.83	Ref. 39
1^3B_u (<i>trans</i> min., C_{2h})								
MR-AQCC	1.349	1.079	1.079	132.2	132.2	180.0	4.14	This work
CCSD(T)	1.345	1.082	1.082	131.5	131.5	180.0	4.18	Ref. 39
$1^3A'$ (Planar saddle pt., C_s)								
MR-AQCC	1.344	1.085	1.060	128.8	175.6	180.0	0.55	This work
SR-CISD/CCSD(T) ^b	1.325	1.088	1.059	127.3	174.0	180.0	0.62	Ref. 36
1^3B (oop saddle point, C_2)								
MR-AQCC	1.366	1.077	1.077	139.6	139.6	106.5	0.58	This work
1^3A_2 (<i>cis</i> min., C_{2v})								
MR-AQCC	1.359	1.091	1.091	130.4	130.4	0.0	4.81	This work
CCSD(T)	1.360	1.095	1.095	130.3	130.3	0.0	4.79	Ref. 39
1^3A_u (<i>trans</i> min., C_{2h})								
MR-AQCC	1.385	1.091	1.091	120.7	120.7	180.0	4.49	This work
CCSD(T)	1.386	1.094	1.094	120.5	120.5	180.0	4.47	Ref. 39
$1^3A''$ (Planar saddle pt., C_s)								
MR-AQCC	1.365	1.104	1.067	119.9	179.8	180.0	0.30	This work
EOM-CCSD	1.360	1.100	1.065	118.2	179.9	180.0	0.26	Ref. 38
1^3A (oop saddle point, C_2)								
MR-AQCC	1.352	1.079	1.079	143.0	143.0	91.7	0.66	This work

^aMinimum-to-minimum excitation energies for minimum structures and energy barriers relative to the *cis* geometry for saddle points.

^bOptimized SR-CISD geometry and TZ CCSD(T) energies.

The linear ground state geometry and the *cis*- and *trans*-minima on the T_1 and T_2 surfaces were optimized first. Both the *cis*- and *trans*-minima are strongly bent, and R_{CC} is stretched by about 0.15 Å as compared to the ground state (see Table V). For comparison, optimized geometries obtained by Sherrill et al.³⁹ from cc-pVTZ CCSD(T) calculations are given in Table V as well. They agree very well with our results. Preliminary basis set extrapolations⁴³ based on MR-AQCC calculations gave for the *cis* T_1 (1^3B_2) structure an excitation energy of 3.93 eV, in very good agreement with the extrapolated value of 3.91 reported by Sherrill et al.³⁹ Zero-point corrections reduce this excitation energy by ≈ 0.05 eV. Thus, we agree with the conclusion of the just-mentioned authors that the experimental estimate of 3.58 eV ($28,900\text{ cm}^{-1}$)⁵³ for ΔE_0 is too low.

Using the RGF method two types of saddle points were determined for the T_1 and T_2 states: a planar one of C_s symmetry and a nonplanar one of C_2 symmetry. The planar saddle point for the T_1 state is of second order. All other saddle points are of first order. The planar saddle point structure can be compared to the SR-CISD results of Vacek et al.,³⁶ which show typical deviations of SR-CISD towards smaller bond distances as compared to the present MR results. SR calculations on the T_2 state meet problems because instabilities for the SCF wave functions have been found by Yamaguchi et al.³⁵ Therefore, the possibility of performing MR

calculations based on MCSCF wave functions is of particular importance here and in general for higher excited states. For the planar saddle point in the T_2 state, comparison can be made with the EOM-CCSD calculations performed by Sherrill et al.³⁸ Agreement with our results is quite good. To our knowledge, out-of-plane saddle points have been investigated only by Cui et al.^{40,41} based on CASSCF and EOM-CCSD calculations. In these cases the reference wave function is dominated by a 1:1 mixture of two configurations and a multireference approach is mandatory. In this work the first post-CASSCF results are presented. In both cases (1^3A and 1^3B) substantial barriers of ≈ 0.6 eV with respect to the planar *cis* structure are observed. In particular, the out-of-plane saddle point of the 1^3A state is of interest. This state crosses for nonplanar geometries with the next higher triplet state, 2^3B . As has been shown by Cui et al.,⁴¹ this crossing is important for the understanding of the photodissociation of acetylene.

Conclusions

The implementation of the RGF procedure into the COLUMBUS program system resulted in a very useful tool for the search and optimization of stationary points at the multireference level for ground states as well as excited states. Because of the generality of

the multireference approach very general and difficult situations can be treated, which leads to new possibilities for accurate determinations of stationary points.

RGF searches were performed for the H₂CO system on the S₀ PES and for acetylene on the T₁ and T₂ PES. In total, eight stationary points for H₂CO and nine stationary points for acetylene have been investigated using the MR-CISD and MR-AQCC methods, respectively. In the case of the transition structures involving hydroxycarbene, the present MR-CISD/AQCC results are a significant improvement compared to previous calculations. In the case of the planar structure F₂ (see Fig. 1), we confirm previous findings²³ that it is a first-order saddle point and not of second order as found in the STO-3G/SCF investigations by Quapp et al.¹⁸ This is another example of the observation³¹ that the number of imaginary frequencies characterizing a saddle point can depend strongly on the computational level. Starting from the *cis*- and *trans*-minima on the T₁ and T₂ surfaces of acetylene, planar and nonplanar saddle points were located.

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References

- Schlegel, H. B. *Adv Chem Phys* 1987, 67, 249.
- Schlegel, H. B. In *Modern Electronic Structure Theory, Part I*; Yarkony, D. R., Ed.; World Scientific: 1995, p 459.
- Shavitt, I. In *Methods of Electronic Structure Theory*; Schaefer III, H. F., Ed.; Plenum Press: New York, 1977, p. 189.
- Roos, B. O. *Adv Chem Phys* 1987, 69, 399.
- Andersson, K.; Malmquist, P.-Å.; Roos, B. O. *J Chem Phys* 1992, 96, 1218.
- Gdanitz, R. J.; Ahlrichs, R. *Chem Phys Lett* 1988, 143, 413.
- Szalay, P. G.; Bartlett, R. J. *J Chem Phys Lett* 1993, 214, 481.
- Szalay, P. G.; Bartlett, R. J. *J Chem Phys* 1995, 103, 3600.
- Shepard, R. *Int J Quant Chem* 1987, XXXI, 33.
- Shepard, R.; Lischka, H.; Szalay, P. G.; Kovar, T.; Ernzerhof, M. *J Chem Phys* 1991, 93, 2085.
- Shepard, R. In *Modern Electronic Structure Theory Part I*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995, p. 345.
- Lischka, H.; Shepard, R.; Shavitt, I.; Pitzer, R. M.; Dallos, M.; Müller, Th.; Szalay, P. G.; Brown, F. B.; Ahlrichs, R.; Böhm, H. J.; Chang, A.; Comeau, D. C.; Gdanitz, R.; Dachsels, H.; Erhard, C.; Ernzerhof, M.; Höchtel, P.; Irle, S.; Kedziora, G.; Kovar, T.; Parasuk, V.; Pepper, M.; Scharf, P.; Schiffer, H.; Schindler, M.; Schüler, M.; Zhao, J.-G. *COLUMBUS, An Ab Initio Electronic Structure Program*, release 5.7; 2001.
- Lischka, H.; Shepard, R.; Brown, F. B.; Shavitt, I. *Int J Quant Chem* 1981, S15, 91.
- Shepard, R.; Shavitt, I.; Pitzer, R. M.; Comeau, D. C.; Pepper, M.; Lischka, H.; Szalay, P. G.; Ahlrichs, R.; Brown, F. B.; Zhao, J. *Int J Quant Chem* 1988, S22, 149.
- Lischka, H.; Shepard, R.; Pitzer, R. M.; Shavitt, I.; Dallos, M.; Müller, Th.; Szalay, P. G.; Seth, M.; Kedziora, G. S.; Yabushita, S.; Zhang, Z. *Phys Chem Chem Phys* 2001, 3, 664.
- Lischka, H.; Dallos, M.; Shepard, R. *Mol Phys*, in press.
- Császár, P.; Pulay, P. *J Mol Struct* 1984, 114, 31.
- Quapp, W.; Hirsch, M.; Imig, O.; Heidrich, D. *J Comp Chem* 1998, 19, 1087.
- Quapp, W.; Hirsch, M.; Heidrich, D. *Theor Chem Acc* 1998, 100, 285.
- Quapp, W. in <http://www.mathematik.uni-leipzig.de/MI/quapp/mrgf.html>.
- Jaffe, R. L.; Morokuma, K. *J Chem Phys* 1976, 64, 4881.
- Goddard, J. D.; Schaefer III, H. F. *J Chem Phys* 1979, 70, 5117.
- Goddard, J. D.; Yamaguchi, Y.; Schaefer III, H. F. *J Chem Phys* 1981, 75, 3459.
- Harding, L. B.; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J Phys Chem* 1980, 84, 3394.
- Frisch, M. J.; Krishnan, R.; Pople, J. A. *J Chem Phys* 1981, 85, 1467.
- Scuseria, G. E.; Schaefer III, H. F. *J Chem Phys* 1989, 90, 3629.
- Deng, L.; Ziegler, T.; Fan, L. *J Chem Phys* 1993, 99, 3823.
- Abashkin, Y.; Russo, N.; Toscano, M. *Theor Chim Acta* 1995, 91, 179.
- Yu, J.-S. K.; Yu, C. *Chem Phys Lett* 1997, 271, 259.
- Feller, D.; Dupuis, M.; Garrett, B. C. *J Chem Phys* 2000, 113, 218.
- Jensen, F. *Theor Chem Acc* 1998, 99, 295.
- Bondensgård, K.; Jensen, F. *J Chem Phys* 1996, 104, 8025.
- Wetmore, R. W.; Schaefer III, H. F. *J Chem Phys* 1978, 69, 1648.
- Lischka, H.; Karpfen, A. *Chem Phys* 1986, 102, 77.
- Yamaguchi, Y.; Vacek, G.; Schaefer III, H. F. *Theor Chim Acta* 1993, 86, 97.
- Vacek, G.; Thomas, J. R.; DeLeeuw, B. J.; Yamaguchi, Y.; Schaefer, H. F. *J Chem Phys* 1993, 98, 4766.
- Malsch, K.; Rebenitsch, R.; Swiderek, P.; Hohlneicher, G. *Theor Chem Acc* 1998, 100, 171.
- Sherill, C. D.; Vacek, G.; Yamaguchi, Y.; Schaefer III, H. F.; Stanton, J. F.; Gauss, J. *J Chem Phys* 1996, 104, 8507.
- Sherill, C. D.; Byrd, E. F. C.; Head-Gordon, M. *J Chem Phys* 2000, 113, 1447.
- Cui, Q.; Morokuma, K.; Stanton, J. F. *Chem Phys Lett* 1996, 263, 46.
- Cui, Q.; Morokuma, K. *Chem Phys Lett* 1997, 272, 319.
- Stanton, J. F.; Bartlett, R. J. *J Chem Phys* 1993, 98, 7029.
- Ventura do Monte, E.; Dallos, M.; Lischka, H. Submitted.
- Rothmann, M. J.; Lohr Jr, L. L. *Chem Phys Lett* 1980, 70, 405.
- Hirsch, M.; Quapp, W.; Heidrich, D. *Phys Chem Chem Phys* 1999, 1, 5291.
- Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Andersen, T.; Bak, K. L.; Bakken, V.; Christiansen, O.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Saue, T.; Taylor, P. R.; Vahtras, O. *DALTON, an ab initio electronic structure program*, Release 1.0; 1997.
- Langhoff, S. R.; Davidson, E. R. *Int J Quantum Chem* 1974, 8, 61.
- Bruna, P. J.; Peyerimhoff, S. D.; Buenker, R. J. *J Chem Phys Lett* 1981, 72, 278.
- Fogarasi, G.; Zhou, X.; Taylor, P. W.; Pulay, P. *J Am Chem Soc* 1992, 114, 8191.
- Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J Am Chem Soc* 1983, 105, 7037.
- Bofill, J. M. *J Comp Chem* 1994, 15, 1.
- Dunning Jr, T. H. *J Chem Phys* 1989, 90, 1007.
- Ahmed, M.; Peterka, D. S.; Suits, A. G. *J Chem Phys* 1999, 110, 4248.
- Duncan, J. L. *Mol Phys* 1974, 28, 1177.
- Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
- Baulch, D. L.; Cox, R. A.; Crutzen, P. J.; Hampson, R. F.; Kerr, J. A.; Troe, J.; Watson, R. T. *J Phys Chem Ref Data* 1982, 11, 327.