Photochemistry of ethylene: A multireference configuration interaction investigation of the excited-state energy surfaces

M. Barbatti, J. Paier, and H. Lischka
Institute for Theoretical Chemistry and Structural Biology, University of Vienna, A-1090 Vienna, Austria

(Received 23 June 2004; accepted 25 August 2004)

Multireference configuration interaction with singles and doubles (MR-CISD) calculations have been performed for the optimization of conical intersections and stationary points on the ethylene excited-state energy surfaces using recently developed methods for the computation of analytic gradients and nonadiabatic coupling terms. Basis set dependence and the effect of various choices of reference spaces for the MR-CISD calculations have been investigated. The crossing seam between the $S_0$ and $S_1$ states has been explored in detail. This seam connects all conical intersections presently known for ethylene. Major emphasis has been laid on the hydrogen-migration path. Starting in the $V$ state of twisted-orthogonal ethylene, a barrierless path to ethylidene was found. The feasibility of ethylidene formation will be important for the explanation of the relative yield of cis and trans H$_2$ elimination. © 2004 American Institute of Physics. [DOI: 10.1063/1.1807378]

I. INTRODUCTION

The ethylene molecule plays a fundamental role for the understanding of photoisomerization processes and in particular the ultrafast energy conversion through nonadiabatic transitions. Quantum chemical calculations on excited-state energy surfaces of ethylene and on nonadiabatic couplings have a very long tradition. One of the first theoretical attempts to perform a global exploration of the ethylene energy surfaces and to explain the fast conversion from the valence to the ground state observed in photoexcitation experiments is due to Ohtome. In that work, an extended investigation on the excited-state potential energy surfaces of the first valence states was performed using multireference configuration interaction (MR-CI). Besides other features of the energy surfaces, the relevance of a hydrogen migration path under $C_2v$ symmetry restriction, where one H atom migrates from one CH$_2$ group to the other one was proposed. Along this path a crossing between the $S_0$ and $S_1$ states was found. Later on, Freund and Klessinger pointed out that a symmetry-unrestricted search revealed that the minimum energy intersection between the two states had one of the CH$_2$ groups pyramidalized from one CH$_2$ group to the other one was proposed. During the pyramidalization process, ethylene reaches a conical intersection between the $S_1 (V)$ and the $S_0 (N)$ states, through which it can return rapidly to the ground state in a nonradiative way.

To complete this qualitative view of the ethylene photodynamics, we should note additionally that at a torsion angle of around 80° the V state crosses the Z state, and that these two states remain approximately degenerate up to 90°. Recently, in wave packet dynamics simulations, Viel et al. have shown that due to this fact 100 fs after the initial photoexcitation to the V state, around 10% of population is in the Z state. Furthermore, Rydberg states, into which the vertically excited valence states are embedded, are destabilized by the torsion. Starting from a torsional angle of about 70°, the V and Z states are located below the Rydberg states. From there on one can expect that only these two states are of interest for the subsequent dynamics to the ground state.

This view of the photodynamics of ethylene has been supported by new experimental evidence indicating also that (i) the conversion from the V to the N state occurs in a very short time interval of around 10 to 45 fs (Refs. 14 and 15) and that (ii) the H$_2$ molecule formation in ethylene photofragmentation occurs to 58% by the 1-1 elimination where the H$_2$ formation proceeds from H atoms belonging to the same CH$_2$ group.

In ab initio multiple spawning (AIMS) studies the twisted-pyramidalized conical intersection is regarded as the main effective funnel to the ground state, although other conical intersections had been theoretically characterized for the ethylidene and hydrogen migration structures. On the other hand, the results of the experiments of Ref. 16 also decreased by a torsional motion around the C–C bond from the planar geometry to a twisted-orthogonal structure in which the two CH$_2$ groups are rotated by an angle of 90° to each other. From this twisted-orthogonal structure, the energy of the $S_1$ state is further reduced by pyramidalization of one of the CH$_2$ groups. During the pyramidalization process, ethylene reaches a conical intersection between the $S_1 (V)$ and the $S_0 (N)$ states, through which it can return rapidly to the ground state in a nonradiative way.

Nowadays, the view of the ethylene photodynamics is based on the following features of the energy surfaces (Refs. 4, 9, and 10 and references therein). After a vertical $\pi\pi^*$ excitation to the first valence state, (V state in the Merer-Mulliken notation), the potential energy of the system is...
show that 42% of the H₂ formation occurs by cis and trans eliminations, which involve H atoms belonging to different CH₂ groups. This is an indication that the H-migration process still plays an important role in the photodynamics of ethylene.

In contrast to the AIMS and wave packet dynamics investigations mentioned above, molecular dynamics simulations performed with semiempirical methods show at the time of the first surface hopping (around 50 fs) the presence of H-migration/ethylidene structures in addition to the twisted-pyramidalized one. In these simulations, the presence of H-migration/ethylidene structures is characterized by the large angular asymmetry of the two H atoms at one of the CH₂ groups, and, at the same time, by the large pyramidalization angle. This facts can be interpreted as evidence of ethylidene formation.

Recently, other authors have also pointed out the necessity to take into account the hydrogen migration in the interpretation of ethylene photochemistry. Lin and co-workers have shown that a RRKM kinetic model including the hydrogen migration and ethylidene structures predicts very well the product yields for the H₂ and H eliminations. Experimental results of O’Reilly et al. suggest that for excitation energies between 11.7 and 21.4 eV the ethylene isomer should be an important intermediate in the CH₃ + CH and CH + CH + H₂ dissociation processes. Mestagh et al. claim the necessity of a more complete discussion of the nonadiabatic processes involved in the ethylene photodynamics, including the hydrogen-migration path.

A comprehensive study of the photoreactions of ethylene requires first of all a reliable and balanced description of several energy surfaces. Even though substantial progress has been achieved since the early investigations of Petrolongo and co-workers, especially by the surveys of Ben-Nun et al. and Krawczyk et al., many questions have still to be solved, e.g., geometry optimizations and conical intersections should be performed at a significantly higher computational level than limited single-point searches or the complete active space self-consistent field (CASSCF) or semiempirical optimizations. Furthermore, reaction paths and intersection seams need to be investigated in more detail than has been done before. It is the purpose of the present work to use in particular the recently developed methods for the computation of analytic gradients and nonadiabatic coupling terms at the MR-CI level for that purpose. The availability of these quantities at the MR-CI level represents a significant progress especially for optimizations of minima on the crossing seam in comparison to previous calculations based on CASSCF calculations only. The results and the experience obtained in this work will be used as basis for dynamics studies to be carried out as next step.

II. COMPUTATIONAL DETAILS

State-averaged multiconfiguration self-consistent field (SA-MCSCF) and multireference configuration interaction with singles and doubles (MR-CISD) calculations were carried out. In the SA-MCSCF calculations equal weights were used for all states. Several active spaces were chosen in the MCSCF calculations. For the description of valence states, the simplest wave function was a CAS(2,2) in the π and π⁺ orbitals. State averaging was performed over the three valence states N, V, and Z. The same CAS(2,2) was used as reference space in the subsequent MR-CISD calculations. The final expansion space in terms of configuration state functions (CSFs) for the MR-CISD calculations consisted of the reference configurations and of all single and double excitations thereof into all internal and external orbitals. No individual selection scheme with respect to single CSFs was applied in contrast to the procedures used in the multireference double-excitation CI (MRD-CI) approach of Buenker and Peyerimhoff (see also Ref. 27). The symmetry of the reference configurations was restricted to the state symmetry and the interacting space restriction was applied. The two core orbitals were always kept frozen in the post-MCSCF calculations. Analogous principles for the construction of the CI wave function were applied for the larger reference spaces described below. The CAS(2,2)-ref calculations were used for the determination of the MXS, for the calculation of stationary points and for the cuts of the potential energy surface in the pyramidalization and hydrogen migration studies. The aug-cc-pVDZ basis was selected in these calculations. Size-extensivity corrections were taken into account by means of the extended Davidson correction and will be denoted by +Q.

Larger reference spaces and basis sets were chosen in order to verify the CAS(2,2)-ref results. A restricted direct product (RDP) space constructed for all σ orbitals was added to the original CAS(2,2). The RDP space is composed of ten orbitals grouped in five subspaces, one for each σ bond, i.e., four [(σσ*)ₐₐ] pairs and one [(σσ*)ₐₚ] pair. Each σ* subspace is restricted to singlet pairing. The MCSCF calculation based on the RDP wave function resulted in localized orbitals very similar to those obtained in generalized valence bond (GVB) calculations. The same RDP wave function was used as reference in the subsequent MR-CI calculations. Two basis sets were used in this case. The aug-cc-pVDZ basis and an aug'-cc-pVTZ basis. The latter one was derived from the original aug-cc-pVTZ set by omitting the augmented functions on the carbon atoms and the augmented d functions on the hydrogen atoms. The RDP reference space contains 96 CSFs, which results in a CI expansion space of about 14 million CSFs for the aug-cc-pVDZ basis set and 38 million CSFs for the aug'-cc-pVTZ basis.

For the joint calculation of valence and Rydberg states, the (ππ*)-CAS(2,2) was augmented by four auxiliary (AUX) orbitals representing the 3s and 3p Rydberg orbitals. Only single excitations were allowed from the CAS to the AUX space. In addition to the three valence states N, V, and Z, four Rydberg states (π-3s, π-3p, π-3p, and π-3p) were considered leading to a state-averaging over seven states at the MCSCF level. The same configuration space was used as reference space in the MR-CISD calculations and is denominated as MR-CISD/SA-7-CAS(2,2)+aux. A d-aug-cc-pVDZ basis was chosen in order to take into account the diffuseness of the Rydberg orbitals.

Analytic MR-CISD gradients were computed using the

Downloaded 30 Nov 2004 to 131.130.39.6. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp
procedures described in Refs. 21–24. Determination of the MXS were performed using the analytic MR-CI nonadiabatic coupling vectors$^{25}$ and the direct inversion in the interactive subspace (GDIIS) procedure developed in Ref. 26. Standard GDIIS optimization$^{28}$ was used for the determination of stationary points. Natural internal coordinates were constructed according to the prescriptions given in Ref. 39.

All calculations were performed using the COLUMBUS program system.$^{40–43}$

III. RESULTS AND DISCUSSION

A. Effect of computational level on geometries and energies

Figure 1 shows selected geometric parameters describing the main structures that will be discussed in the present work. Table I presents the respective energetic results. The main coordinates studied are defined in Fig. 2. Cartesian coordinates of all structures investigated are given in the supplementary material stored electronically.$^{44}$

The planar structure was optimized on the ground state surface and corresponds to the ground state energy minimum. The staggered and eclipsed ethylidene structures were optimized for the ground state as well. The twisted-orthogonal ethylene and the $C_3v$ ethylidene structures were optimized on the $V$ state surface. The other three structures, which correspond to conical intersections between the $S_0$ and $S_1$ states, were optimized as MXS.

As we can see in Fig. 1, the increase of the reference space from CAS(2,2) to RDP and using the aug-cc-pVDZ basis leads to a small increase of the C–H and C–C distances. On the other hand, increase of the basis set at the RDP level from aug-ccVDZ to aug'-cc-pVTZ has the opposite effect of decreasing the internuclear distances. Relatively small changes of 0.1–0.2 eV in energy differences are observed when comparing results obtained with the three computational levels used in Table I. Overall, these calculations show that the CAS(2,2) reference space and the aug-cc-pVDZ basis provide a good compromise for our survey of the energy surfaces for the valence states of ethylene.

B. Vertical excitations, twisting, and Valence-Rydberg splittings

Vertical excitations from the planar ground state $N(\pi^2)$ to the two valence states, $V(\pi\pi^*)$ and $Z(\pi\pi^*)$ and to the $3s$ and $3p$ Rydberg states will be considered here. Rydberg states$^{45–48}$ and the valence character of the $V$ state$^{49–51}$ have been intensively investigated by other authors. In the present work we intend to summarize briefly the main results that will be relevant for our discussion.

At the ground-state-equilibrium geometry, the energy spectrum of ethylene shows an embedding of the valence $V$ state into the Rydberg $3s$ and $3p$ states around 8 eV. The excitation energies for the Rydberg transitions calculated at the MR-CISD/1Q level are in very good agreement with experimental results. For the $N-V$ transition, our best theoretical value is 0.14 eV higher than the experimental band maximum. Several authors have pointed out that the experimental value might not correspond to a purely vertical excitation.$^{10,52}$ The difficulties in the computation of the $N-V$ excitation are well documented (see Refs. 49 and 50 and references therein). The largest computational level employed up to date predicts a value of 7.69 eV.$^{50}$ Our MR-CISD+Q results agree well with those of the earlier MRD-CI calculations of Petrongolo et al.$^2$ The CASSCF re-
TABLE I. Main CSFs contributing to each state and respective excitation energies (in eV) calculated at several levels, Pl—planar; To—twisted-orthogonal; Py—twisted-pyramidalized conical intersection; Hm—H-migration conical intersection; Et—ethylidene conical intersection; C₃ᵥ—C₃ᵥ ethylidene conical intersection; St—staggered ethylidene; Ec—eclipsed ethylidene.

<table>
<thead>
<tr>
<th>State</th>
<th>CFS</th>
<th>L1</th>
<th>L1Q</th>
<th>L2</th>
<th>L2Q</th>
<th>L3</th>
<th>L3Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pl</td>
<td>1¹A₉</td>
<td>π²π*¹</td>
<td>0.00 a</td>
<td>0.00 b</td>
<td>0.00 c</td>
<td>0.00 d</td>
<td>0.00 e</td>
</tr>
<tr>
<td></td>
<td>1¹B₁₉</td>
<td>π¹π*¹</td>
<td>8.08</td>
<td>7.88</td>
<td>7.99</td>
<td>7.79</td>
<td>8.02</td>
</tr>
<tr>
<td></td>
<td>2¹A₈</td>
<td>π⁰π*²</td>
<td>13.12</td>
<td>12.15</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>To</td>
<td>1¹B₁</td>
<td>π⁰π<em>¹ − π⁰π</em>⁺</td>
<td>3.09</td>
<td>2.95</td>
<td>3.04</td>
<td>2.92</td>
<td>3.13</td>
</tr>
<tr>
<td></td>
<td>1¹A₁</td>
<td>π²π*⁻</td>
<td>5.66</td>
<td>5.43</td>
<td>5.63</td>
<td>5.30</td>
<td>5.68</td>
</tr>
<tr>
<td></td>
<td>1¹B₂</td>
<td>π¹π*²</td>
<td>5.69</td>
<td>5.53</td>
<td>5.68</td>
<td>5.42</td>
<td>5.72</td>
</tr>
<tr>
<td>Py</td>
<td>1¹A</td>
<td>π¹π*¹</td>
<td>4.83</td>
<td>4.61</td>
<td>4.74</td>
<td>4.40</td>
<td>4.83</td>
</tr>
<tr>
<td></td>
<td>2¹A</td>
<td>π²π*⁰</td>
<td>4.83</td>
<td>4.58</td>
<td>4.74</td>
<td>4.46</td>
<td>4.83</td>
</tr>
<tr>
<td>Hm</td>
<td>1¹A*</td>
<td>π¹π*¹</td>
<td>5.40</td>
<td>5.18</td>
<td>5.38</td>
<td>5.15</td>
<td>5.38</td>
</tr>
<tr>
<td></td>
<td>1¹A'</td>
<td>π²π*⁰</td>
<td>5.40</td>
<td>5.27</td>
<td>5.38</td>
<td>5.20</td>
<td>5.38</td>
</tr>
<tr>
<td></td>
<td>2¹A'</td>
<td>π⁰π*²</td>
<td>8.85</td>
<td>8.64</td>
<td>8.79</td>
<td>8.48</td>
<td>8.88</td>
</tr>
<tr>
<td>Et</td>
<td>1¹A'</td>
<td>π²π<em>⁰ − π⁰π</em>⁻</td>
<td>4.46</td>
<td>4.55</td>
<td>4.49</td>
<td>4.46</td>
<td>4.49</td>
</tr>
<tr>
<td></td>
<td>1¹A*</td>
<td>π¹π*¹</td>
<td>4.47</td>
<td>4.56</td>
<td>4.49</td>
<td>4.46</td>
<td>4.49</td>
</tr>
<tr>
<td></td>
<td>2¹A'</td>
<td>π⁰π<em>² + π⁰π</em>⁺</td>
<td>5.62</td>
<td>5.62</td>
<td>5.62</td>
<td>5.59</td>
<td>5.64</td>
</tr>
<tr>
<td>C₃ᵥ</td>
<td>1¹E</td>
<td>π¹π*¹</td>
<td>4.58</td>
<td>4.67</td>
<td>4.61</td>
<td>4.69</td>
<td>4.59</td>
</tr>
<tr>
<td></td>
<td>1¹E</td>
<td>π²π*⁻</td>
<td>4.58</td>
<td>4.68</td>
<td>4.61</td>
<td>4.69</td>
<td>4.60</td>
</tr>
<tr>
<td></td>
<td>1¹A₁</td>
<td>π⁰π<em>² + π⁰π</em>⁺</td>
<td>5.60</td>
<td>5.60</td>
<td>5.61</td>
<td>5.59</td>
<td>5.61</td>
</tr>
<tr>
<td>St</td>
<td>1¹A'</td>
<td>π⁰π*⁰</td>
<td>3.22</td>
<td>3.25</td>
<td>3.24</td>
<td>3.24</td>
<td>3.30</td>
</tr>
<tr>
<td></td>
<td>1¹A*</td>
<td>π¹π*¹</td>
<td>5.06</td>
<td>5.10</td>
<td>5.08</td>
<td>5.11</td>
<td>5.11</td>
</tr>
<tr>
<td></td>
<td>2¹A'</td>
<td>π⁰π*²</td>
<td>7.84</td>
<td>7.77</td>
<td>7.86</td>
<td>7.77</td>
<td>7.87</td>
</tr>
<tr>
<td>Ec</td>
<td>1¹A'</td>
<td>π⁰π*⁰</td>
<td>3.28</td>
<td>3.30</td>
<td>3.29</td>
<td>3.30</td>
<td>3.35</td>
</tr>
<tr>
<td></td>
<td>1¹A*</td>
<td>π¹π*¹</td>
<td>5.10</td>
<td>5.14</td>
<td>5.12</td>
<td>5.15</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>2¹A'</td>
<td>π⁰π*²</td>
<td>8.06</td>
<td>7.99</td>
<td>8.07</td>
<td>7.98</td>
<td>8.07</td>
</tr>
</tbody>
</table>

*E = −78.335 953 a.u., L1 = MR-CISD/SA-3-CAS(2,2)/aug-cc-VDZ.
*a = −78.365 265 a.u., L1Q = MR-CISD/Q/SA-3-CAS(2,2)/aug-cc-VDZ.
*b = −78.349 642 a.u., L2 = MR-CISD/SA-3-RDP/aug-cc-VDZ.
*c = −78.370 776 a.u., LQ = MR-CISD/Q/SA-3-RDP/aug-cc-VDZ.
*d = −78.414 017 a.u., L3 = MR-CISD/SA-3-RDP/aug-cc-VTZ.
*e = −78.439 182 a.u., LQ = MR-CISD/Q/SA-3-RDP/aug-cc-VTZ.
*f = ΔE_{exp}=5.5 eV (Ref. 53).

FIG. 2. Definition of the main angular coordinates employed in the present work.
It is well known that after ππ* excitation, ethylene undergoes C–C stretching and C–C torsion (angle \( \tau \) in Fig. 2). The effect of C–C stretching on the relative energies of the \( N, V \), and Rydberg states is displayed in Fig. 3. The barrier to the torsion in the ground state is 3.00 eV at our best computational level (see Fig. 4). This value agrees well with the 3.06 eV obtained by Krawczyk et al.\(^{10} \) at the MS-CASPT2 level. The energy gap between the \( N(S_0) \) and \( Z(S_1) \) states for the twisted orthogonal geometry is 2.55 eV at the MR-CISD/SA-3-RDP/aug\(^5\)-cc-pVTZ level. When Davidson correction is taken into account, this value is reduced to 2.35 eV. This latter value compares well with the 2.32 eV found by Krawczyk et al.\(^{10} \) at the MS-CASPT2 level.

During the C–C stretch, the \( V \) state is stabilized with respect to the Rydberg states (see Fig. 3). However, the relative stabilization is not enough to achieve a sufficient separation of the \( V \) state from the Rydberg states at the C–C distances given in the figure. On the other hand, the torsion around the C–C bond has a strong effect, as we can see in

![Fig. 3](image)
This large asymmetry in the C–H bonds of the twisted-pyramidalized MXS indicates H-migration character of one of H atoms of the pyramidalized CH\textsubscript{2} group to the other group. The pseudomigrating atom is 1.73 Å apart from the other carbon atom, while the second hydrogen atom of the CH\textsubscript{2} group shows a distance of 2.15 Å to the other carbon atom. In Sec. III E, the connection between the twisted-pyramidalized MXS and the H-migration intersection will be discussed in more detail.

The energy of the twisted-pyramidalized MXS is 4.83 eV above the planar ethylene ground-state structure at the MR-CISD/SA-3-RDP/aug'-cc-pVTZ level, or 4.50 eV if the Davidson correction is taken into account. This result agrees well with the SA-2-CASSCF\textsubscript{(4/7)} results of Toniolo \textit{et al.}\textsuperscript{17} At the MS-CASPT2 level, Krawczyk \textit{et al.}\textsuperscript{10} found an energy of 6.53 eV for the twisted-pyramidalized MXS. This value is significantly too high due to the restrictions imposed in their 6D model of nuclear degrees of freedom.

**D. Hydrogen migration and ethylidene**

From the twisted-orthogonal structure of ethylene a hydrogen-migration path to ethylidene (CH\textsubscript{3}CH) exists.\textsuperscript{4,5,6} The H-migration path (Fig. 6) was started at the twisted-orthogonal structure (θ=124°). At each point, the coordinate θ (see Fig. 2) was frozen, while all other coordinates were optimized. The symmetry was restricted to the C\textsubscript{s} point group. The H-migration path was calculated for the N (1\textsuperscript{1}A\textsuperscript{\textsc{a}}) and V (1\textsuperscript{1}A\textsuperscript{\textsc{t}}) states.

Similar to the case of pyramidalization and antisymmetric scissoring,\textsuperscript{54} the hydrogen migration breaks the quasidegeneracy of the V/Z states at the twisted-orthogonal structure. As a consequence, the phenomenon of sudden polarization occurs as in the other two, just-mentioned cases. The dipole moment along the C–C direction increases from zero at the twisted-orthogonal geometry to 1 Debye when θ is varied just by 10°.

In the ground state, the ethylene-ethylidene isomerization is blocked by a 3 eV barrier (see Fig. 6, top). The situation is completely different in the first excited state, for which, as we can see in Fig. 6 (bottom), there is no barrier to H migration.

In Fig. 7 the H migration is characterized by the evolution of the internal coordinates R\textsubscript{CC}, α, and φ and β (see Fig. 2) with the H-migration angle θ. The angle φ, defined as 360°−(α+θ), is the HCH angle. During the migration, the C–C distance decreases to a minimal value of about 1.35 Å at θ=70° (Fig. 7, top). As will be shown below, this is the angle at which the minimum of the conical intersection occurs. From this point on, the CC distance increases rapidly. At the beginning of the migration, α increases almost linearly, while the angle φ is approximately constant around 115° (Fig. 7, second and third graphs). This indicates that the CH\textsubscript{2} containing the migrating H atom shows a rocking mo-
tion almost rigidly around the carbon atom. At approximately \( \theta = 50^\circ \), the angle \( \phi \) starts to increase quickly, while the angle \( \alpha \) stabilizes around 180°. An analogous situation can also be observed in the pyramidalization angle \( \beta \) of the group that is accepting the migrating atom. These behaviors occur because the migrating hydrogen atom finally leaves its original group and binds to the other carbon atom forming a CH3 group.

A characteristic of the hydrogen migration path is that starting from the twisted-orthogonal geometry (right-hand side of Fig. 6), it is possible to reach two different isomers of ethylidene, the staggered \( \alpha = 105.2^\circ \) and the eclipsed \( \alpha = 251.7^\circ \) conformations. The staggered structure is just 0.05 eV more stable than the eclipsed one.

At the top of Fig. 6 in which the geometry was optimized on the ground state surface, only the path finishing in the staggered isomer is displayed. The eclipsed case is quite similar. At the bottom of the same figure (optimization for the V state), the path shown does not finish in one of the two isomers, but in a point connecting them. This point corresponds to a highly symmetric \( C_{3v} \) structure, also identified by Toniolo et al.\(^{17} \) When the molecule reaches the \( C_{3v} \) structure, the ground and the first valence states collapse into a degenerate \( E \) state. The degeneracy is split by bending of the angle \( \alpha \). The variation of the \( S_0 - S_2 \) energies with \( \alpha \) for fixed \( \theta \), but optimizing all other coordinates, is displayed in Fig. 8. From this figure we can observe how in the course of the hydrogen migration path a double well is developed at the ethylidene structure. The cuts in terms of the coordinate \( \alpha \) give also information about the location of crossings and avoided crossings between the \( S_0 \) and \( S_1 \) states. In Fig. 8 we can see that there is a pattern of two crossings, one on the staggered side and the other on the eclipsed side, up to \( \theta \) around 54°. After that, the \( 1^1A' \) and the \( 1^1A'' \) states do not change order during the formation of the double well on the \( 1^1A'' \) surface, until collapsing into one single intersection, corresponding to the \( C_{3v} \) structure \((\theta = 28.7^\circ)\). At the ethylidene ground state, the \( C_{3v} \) structure represents a barrier of 1.37 eV for the staggered/eclipsed isomerization through the rotation of \( \alpha \).

The effect of the rigid torsion on the hydrogen migration path is shown in Fig. 9. For the \( S_1 \) state, the minimum energy path occurs at \( \tau = 90 \). The \( S_1 \) and \( S_0 \) surfaces cross at \( \tau = 90 \) and \( \theta = 72 \), which allows a diabatic hydrogen migration on the \( 1^1A' \) state from \( \theta = 120 \) (ethylene) to \( \theta = 30 \) (ethylidene) without barrier. The optimization of this crossing and its role in the crossing seam will be discussed in the following section.

E. The \( S_0/S_1 \) crossing seam

On the H-migration path exist two known conical intersections between the \( S_0 \) and \( S_1 \) states, the H migration\(^4 \) and the ethylidene one.\(^9 \) Both structures have \( C_s \) symmetry. They were fully optimized at the three computational levels used in this work. Geometrical parameters are shown at Fig. 1 and

![FIG. 7. Variation of geometrical parameters during the hydrogen migration for the first excited state. \( \phi = 360° - (\alpha + \theta) \) is the HCH angle. Calculations performed at the same level as given in Fig. 5. The planar ground-state ethylene energy is the energy zero.](image)

![FIG. 8. Potential energy curves for the angle \( \alpha \) at several fixed \( \theta \) values optimized on the \( 1^1A' \) state. Calculations performed at the same level as given in Fig. 5. The planar ground-state ethylene energy is the energy zero.](image)
it was possible to locate a starting point on the crossing seam also within the $S_1$ optimization procedure under $C_2$ symmetry restriction, which corresponds to the H-migration intersection ($\theta = 72^\circ$) (see Fig. 1 and Refs. 4, 17).

From the hydrogen migration structure on the energy of the seam increases up to a maximum at $\theta = 54^\circ$. From there, the seam splits; one part extends in the direction of increasing $\theta$ and small $\alpha$ angles ($50^\circ < \alpha < 120^\circ$) forming “super-staggered” structures. In the other part, the energy decreases until it reaches the $C_{3v}$ structure. Near the $C_{3v}$ intersection there is the ethylidene MXS. From this conical intersection, the energy increases to large $\theta$ and $\alpha$ values. After $\theta$ around $60^\circ$ and $\alpha$ around $230^\circ$ we could not localize any other point on the seam.

Recently, Laino and Passerone have shown$^{57}$ that the H-migration conical intersection is indeed not a minimum on the crossing seam, but a saddle point connecting two symmetrically equivalent twisted-pyramidalized MXSs. This path on the seam is also shown in Fig. 10 by varying the pyramidalization angle $\beta$.

Therefore, the three most pronounced $S_0/S_1$ intersections for ethylene—twisted-pyramidalized, the H migration and ethylidene—are connected by just one complex seam, which involves structures from scissored up to ethylidene. With the exception of the superstaggered structures, all regions of this seam can be reached within the initial photoexcitation energy to the $V$ state.

F. Ethylene dissociation

After having reached the $S_0/S_1$ seam, ethylene can switch rapidly to the ground state. Due to its high internal energy, several dissociation channels ($C_2H_2 + H_2$, $C_2H_3 + H$, and $C_2H_2 + 2H$) are available. Experimental results show$^{16}$ that the dissociation products have large and broadly distributed amounts of translational energy, and, in particular, $42\%$ of the eliminated $H_2$ are formed by cis/trans isomerization, which necessarily involves H-migration processes.

Two other results from this experiment also deserve attention: (i) cis and trans eliminations have the same probability and (ii) the translational energy distributions of the $H_2$ fragments are approximately the same. These results indicate that the underlying H-migration process should start in a situation in which cis and trans eliminations are equivalent. This would be the case if the H migration started near the twisted-orthogonal structure, i.e., before the pyramidalization (which leads also to strongly nonequivalent H atoms) takes place. Consequently, the conversion to the ground state is expected to occur in regions of the seam near the H migration or ethylidene conical intersections.

An overview of possible H and $H_2$ dissociation paths has been given by Evleth and Sevin$^{56}$ based on calculations using relatively small basis sets and restricted CI expansions. In the present work we want to discuss possible reaction paths for $H_2$ dissociation only starting on certain strategic locations on the seam. Figure 11 shows the potential energy paths for $H_2$ elimination starting at three important points of the seam, the twisted-pyramidalized MXS, the ethylidene by fixing $\theta$ in $124^\circ$ and increasing $\alpha$ up to $187.6^\circ$. From this structure, which we have called “scissored,” the seam extends to smaller $\theta$ angles. The energy on the seam decreases up to a local minimum under $C_2$ symmetry restriction, which corresponds to the H-migration intersection ($\theta = 72^\circ$) (see Fig. 1 and Refs. 4, 17).

Two other results from this experiment also deserve attention: (i) cis and trans eliminations have the same probability and (ii) the translational energy distributions of the $H_2$ fragments are approximately the same. These results indicate that the underlying H-migration process should start in a situation in which cis and trans eliminations are equivalent. This would be the case if the H migration started near the twisted-orthogonal structure, i.e., before the pyramidalization (which leads also to strongly nonequivalent H atoms) takes place. Consequently, the conversion to the ground state is expected to occur in regions of the seam near the H migration or ethylidene conical intersections.

An overview of possible H and $H_2$ dissociation paths has been given by Evleth and Sevin$^{56}$ based on calculations using relatively small basis sets and restricted CI expansions. In the present work we want to discuss possible reaction paths for $H_2$ dissociation only starting on certain strategic locations on the seam. Figure 11 shows the potential energy paths for $H_2$ elimination starting at three important points of the seam, the twisted-pyramidalized MXS, the ethylidene.

FIG. 10. Sketch of the $S_0/S_1$ crossing seam. Calculations performed at the same level as given in Fig. 5. The planar ground-state ethylene energy is the energy zero.
HCCH is 0.12 eV only. 58 were used for H$_2$ dissociation. In case of the H-migration case, the dissociation leads to the products HCCH

For the ethylidene MXS, and the H-migration conical intersection. These curves were obtained by simultaneous extension of the C–H distances for two neighboring H atoms. Optimization of the remaining coordinates were performed for S$_0$ in two steps. For each set of new C–H distances of the hydrogen pair, the distance between the two hydrogen atoms was optimized first keeping all other coordinates frozen at the original values of the MXS structure. Next, the C–H and H–H distances for the hydrogen pairs were fixed and all other coordinates were optimized. For the twisted-pyramidalized MXS (Fig. 11, top), the two H atoms of the pyramidalized CH$_2$ group were used for H$_2$ dissociation. In case of the H-migration MXS (Fig. 11, middle), the migrating H atom and its neighbor in the original CH$_2$ group were chosen for H$_2$ formation. For the ethylidene MXS (Fig. 11, bottom), the pair of hydrogen atoms consisted of two hydrogen atoms of the CH$_3$ group. In the twisted-pyramidalized and H-migration cases, the dissociation products are CCH$_2$+H$_2$. In the ethylidene case, the dissociation leads to the products HCCH+H$_2$. The asymptotic limits are 4.10 eV for the H$_2$+CCH$_2$ products and 2.4 eV for the H$_2$+HCCH products, computed at the MR-CISD/SA-3-CAS(2,2)/aug-cc-pVDZ level using a supermolecule approach. These values are reduced to 4.02 and 2.31, respectively, if the Davidson correction is taken into account. The energetic barrier for conversion from CCH$_2$ to HCCH is 0.12 eV only.$^58$

In all three cases, the potential curves in Fig. 11 show that after return to the ground state the system has enough energy to dissociate into the H$_2$+C$_2$H$_2$ products. For the dissociation from the twisted-pyramidalized MXS, a small barrier of 0.37 eV is present. In the case of ethylidene the barrier is 0.79 eV. For the dissociation from the H-migration structure, the barrier is 2.11 eV, which should be large enough to diminish the probability of the H-migration conical intersection to be an effective exit to a fast dissociation process.

Under the naive hypothesis that the nonadiabatic transition occurs with the same frequency in the twisted-orthogonal region as in the ethylidene region of the seam, and that after this transition a fast H$_2$ elimination takes place, we may expect that (i) half of the H$_2$ elimination is formed by 1-1 elimination in the twisted-pyramidalized case and (ii) the other half is divided between cis and trans eliminations (ethylidene case). As the twisted-pyramidalized region should be more directly accessible than the ethylidene region, one will also expect a shift of this 50%:50% proportion in the direction of an increasing of 1-1 H$_2$ elimination. In addition, due to the symmetry of the ethylidene structure, cis and trans eliminations should occur with the same probability and with the release of similar amounts of translational energy. Although we have to emphasize the simplicity of this model, it is remarkable that all these conclusions are in qualitative agreement with the experimental results cited at the beginning of this section.

G. Dynamics of the photoexcited ethylene

As we have seen in Sec. III E, the crossing seam between the S$_0$ and S$_1$ states extends over a wide variety of structures. Therefore, we should expect that not only the twisted-pyramidalized MXS but also other regions of this seam will contribute to the internal conversion. The importance and the efficiency of each one of these regions for the radiationless decay of ethylene cannot be inferred adequately by static PES studies. Nevertheless, a qualitative overview of the most relevant processes can be obtained. After a vertical excitation to the first valence state, the gradient points mainly along the C–C stretch and torsion coordinates. During the torsion, energetically favorable paths toward the seam, especially in direction to the pyramidalization,$^6$ but also to H migration and ethylidene regions (Fig. 9) become available.

Recently, three dynamics investigations have been performed on the time evolution of photoexcited ethylene. Viel et al.$^{12}$ have studied the wave packet evolution within the first 100 fs. Their work clarifies very nicely the interplay of the C–C stretch and torsional modes and the role of the S$_1$/S$_2$ couplings via antisymmetric CH$_2$ bending in the early stages of the dynamics. However, the geometrical limitations imposed by their six-dimensional model (equivalence of the four C–H bonds and the omission of the CH$_2$ rocking mode) does not allow an adequate exploration of the S$_0$/S$_1$ seam. As a consequence, the S$_0$/S$_1$ intersection at the twisted-pyramidalized structure is too high in energy (see Sec. III C). Therefore, the slope from the twisted-orthogonal to the twisted-pyramidalized geometries is too small in the work by Viel et al., which will lead to a delay in reaching the
twisted-pyramidalized MXS and in the internal conversion to the ground state.

By means of ab initio molecular dynamics, Martínez et al. have claimed\(^a\)\(^{\cdots}\)\(^d\)\(^8\) that the twisted-pyramidalized MXS should be the main channel for the radiationless transfer between the V and the ground state of ethylene. However, these authors do not give any quantitative evaluation of the efficiency of the hydrogen migration or ethylidene conical intersections. Finally, the results of the semiclassical surface hopping dynamics simulations based on the semiempirical AM1 method obtained by Granucci et al.,\(^9\) despite predicting a too short lifetime of the V state, show evidence for radiationless transfer occurring also near the ethylidene MXS. This finding connects to our discussion at the end of Sec. III F indicating that other regions of the seam beyond the twisted-pyramidalized should also be considered as candidates to the nonadiabatic processes in ethylene.

### IV. CONCLUSIONS

In the present work recently developed MR-CI methods for the computation of analytic gradients and nonadiabatic coupling terms have been employed for the full optimization of stationary points and conical intersections on the ethylene PES. For that purpose basis sets up to cc-pVTZ quality and flexible MR-CISD wave functions including all valence orbitals into the reference space have been used. In this way fully consistent results have been achieved at a post CASSCF level between the geometry optimization method and the final energy calculation in comparison to the usual procedure of CASSCF optimizations and subsequent single-point MR-CI/CASPT2 calculations. In summary, our calculations basically confirm the previously reported CASSCF MXS structures computed at the CASSCF level.\(^9\) These structures are located in the valence region and the dynamical electron correlation for the intersecting states seems to be quite similar. However, in cases where the dynamical electron correlation differs significantly between the two intersecting states, the CASSCF results are likely to show artifacts. Actually, such an example can be found in the present work in the form of the crossing between Rydberg and valence states on torsion. The differences between Rydberg and valence excitations computed at the CASSCF and MR-CISD/MR-CISD+Q levels have been described in Sec. III B. The crossings computed at the CASSCF level (not shown in this work) are shifted by about 40° to larger torsional angles as compared to the MR-CISD level (see Fig. 4). In order to obtain better CASSCF results, much larger active spaces would be necessary. Even though such an increase in the active space is certainly possible for ethylene, the extension to larger systems will encounter limits soon and introduce ambiguities due to the specific choice of the active space. Even though the MR-CISD approach has its natural limits as well, the dynamic electron correlation is certainly described more reliably in this way. The availability of analytic MR-CISD gradients and nonadiabatic couplings is certainly another asset.

Beyond the determination of selected structures on the ethylene energy hypersurface, the \(S_0/S_1\) seam has been investigated in more detail. It has a very complex structure connecting all conical intersections presently known for ethylene. We have also demonstrated that by starting from three characteristic points of the seam there are paths to \(H_2\) elimination accessible at the energy of the initial \(\pi\pi^\ast\) excitation. Starting from the twisted-orthogonal geometry, one H atom can migrate from one \(\text{CH}_2\) group to the other without barrier. Thus, ethylidene should be easily accessible during the photodynamical process. This fact is also important for the explanation of the relative yield of cis and trans \(H_2\) elimination.

### ACKNOWLEDGMENTS

The authors acknowledge support by the Austrian Science Fund within the framework of the Special Research Program F16 and Project No. P1442-CHE. M.B. thanks for the financial support from CNPq, Brazil. The calculations were performed in part on the Schrödinger II Linux Clusters of the Vienna University Computer Center.