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Conical intersections in the photoisomerization and photodissociation of a chiral fluoroethylene derivative ((4-methylcyclohexylidene) fluoromethane)

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Abstract

The photochemical R/S isomerization of the title molecule is of interest as it transforms chiral isomers. The reaction is believed to involve a S_1/S_0 conical intersection (CI) similar to the well-known H-atom migration one found for ethylene. Here, we report a new, different CI; subsequent to crossing this CI, the molecule is expected to form primarily the enantiomeric isomer in solution, whereas in the absence of collisions it is likely to dissociate into a vinylidene biradical and a vibrationally and rotationally excited HF. The low energy of this CI suggests it as a major deactivation pathway after electronic excitation.
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1. Introduction

The chiral (4-methylcyclohexylidene) fluoromethane (4MCF) molecule [1] was the focus of some interest in the last few years as it is one chiral molecule whose R/S photoisomerization converts one enantiomer into the other [2,3]. It has been suggested that this molecule might serve as a substrate in a laser control experiment [4]. This potential application led to several theoretical papers on the mechanism of the photo-reaction which is still under debate. The possibility of competition with photodissociation in these reactions was pointed out [5] for a different chiral molecule, as well as for the smaller fluoroethylene molecule [6]. We propose that in the absence of collision-induced vibrational relaxation dissociation products can be formed in this system from the same conical intersection that leads to the chiral isomer. Moreover, under collision-free conditions the dissociation channel is likely to dominate.

Some of us have recently [7] characterized the electronically excited states involved in the UV absorption spectrum of the 4MCF. A relatively small active space in a MRCI/SA-2-CAS(2,2)/DZ1 calculation provided partial mapping of the lowest two singlet excited states potential surfaces and the conical intersections (CIs) connecting them. The work focused on the motion along the double bond torsion and the pyramidalization of each carbon, coordinates which are believed to be important for the non-radiative crossing to the ground state. These energy profiles gave some indication on the location of degeneracy points, but it was established that these particular internal coordinates alone are not enough to describe the system's photophysics. As for other olefins [8], the minimum energy gap along these potentials alone was still too large to explain the R/S isomerization process [9], and geometry relaxation needs to be taken into account. In addition, the possible dissociation modes, which are expected in analogy with fluoroethylene [6,10] (vinyl fluoride), were not explored. Three degeneracy points involving the torsional and pyramidalization coordinates were located and all of them were correlated with equivalent crossing points

in fluoroethylene. It was suggested that the CIs of this system could be further analyzed using the method of elementary reaction coordinates and the geometrical phase effect (GPE) [11].

In this Letter, we apply this method (referred to as the Longuet-Higgins (LH) loop method [11–15]) to further explore the potential surface of this relatively large molecule. In this work the CASSCF method with a larger active space was used (CAS(12,12)/cc-pVDZ). This active space is large and flexible enough to allow the incorporation and optimization of most relevant nuclear coordinates.

In the present study, Longuet-Higgins loops that contain conical intersections are constructed by using reaction coordinates. Possible reaction products serve as anchors for these loops, and these are chosen so that the loop will be phase inverting [16]. One loop is analogous to that enclosing the well-known ethylene CI for H-migration. Its anchors are the two isomers obtained upon torsion by 180° around the C=C double bond and the carbene formed by H-atom migration [17,18]. A second CI, of considerably lower energy, is found by replacing the carbene by the HF elimination products (see Fig. 1). Due to the formation of the stable HF molecule in its ground state, the latter CI turns out to be much lower in energy than the former, and therefore is potentially more important in the photochemistry of this type of molecules. An advantage of the LH loop method is that it allows easy distinction between different CIs: CIs leading to different products in the electronic ground state are necessarily distinct CIs [19].
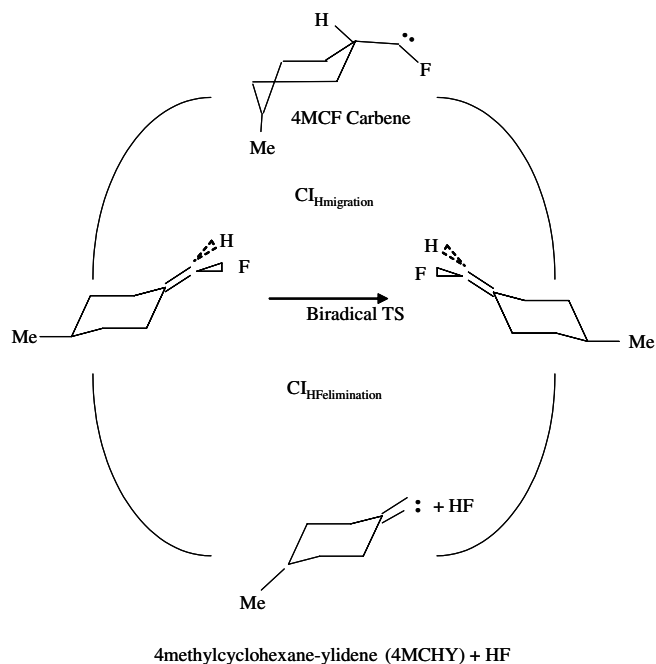

Fig. 1. The two LH loops used in the search for conical intersections. In each loop the two coordinates leading to the conical intersection (the only ones along which the degeneracy is removed) are the torsion and the coordinate connecting the third anchor (4MCF carbene or 4MCHY + HF) with the transition state along the torsion coordinate.

2. Method

The LH method has been described in detail in previous publications [20,21]. The search for CIs is based on the properties of the electronic ground state minima and transition states connected to the CIs. For both CIs considered in this Letter, the two minima (enantiomers) resulting from the torsion around the C=C double bond were used as anchors. Therefore, the torsion coordinate is one of the coordinates used in the search. The second coordinate connects the *R/S* isomerization transition state with the minimum of the third anchor. The third anchor was either the 4MCF carbene formed by a hydrogen atom migration from the terminal carbon atom across the double bond, or the 4-methylcyclohexylidene-methylidene (4MCHY) biradical plus an HF molecule. Fig. 1 shows the structures of the anchors and the LH loops used for the searches. Both loops are phase inverting and therefore each encircles a CI. Since the *R/S* isomerization transition state has a perpendicular structure it belongs to the C_s point group, whereas the ground state molecules (the *R* and *S* isomers) have no symmetry elements. The third anchors in the two loops also have a symmetry plane, making it possible to search for the CIs under a C_s-symmetry restriction.

The CASSCF calculations were performed using the cc-pVDZ basis set as implemented in the GAMESS program suite [22]. Some structures were optimized using the procedure by Bearpark et al. [23], implemented in the GAUSSIAN program suite [24]. The active space included 12 electrons in twelve orbitals: the $\pi\pi*$ orbital pair and 10 σ orbitals, half of them occupied, the other half virtual. State-average calculations were used for the CIs. Transition states were optimized using the standard method of Schlegel [25]. Calculations were made assuming C_s symmetry for all species except the ground state minima (C_1 symmetry).

3. Results and discussion

A biradical transition state for the 4MCF *R/S* isomerization was located at the CAS(12,12)/cc-pVDZ level of theory, 3.15 eV (72.7 kcal/mol) above the minimum. A CI associated with H-atom migration, well-known from studies of ethylene [17,18] was located using a carbene as a third anchor, lying at 6.72 eV (155 kcal/mol) above the minimum. These numerical values compare fairly well to those reported in Ref. [7] at the MRCI level of theory for 4MCF (2.8 and 5.24 eV for the TS and H-migration CI, respectively) and for the H-migration CI of C_2H_3F (6.38 eV). The two coordinates leading to this CI are the torsion and the H-migration from the terminal methylene C atom to its neighboring C atom.

A different CI was found using the other LH loop (Fig. 1), in which the third anchor was the vinylidene biradical – HF pair formed upon geminal elimination. The energy of this anchor (a minimum [26]) was calculated to be 2.23 eV (51.4 kcal/mol) above the 4MCF minimum whereas that of the CI enclosed by the loop was 5.33 eV
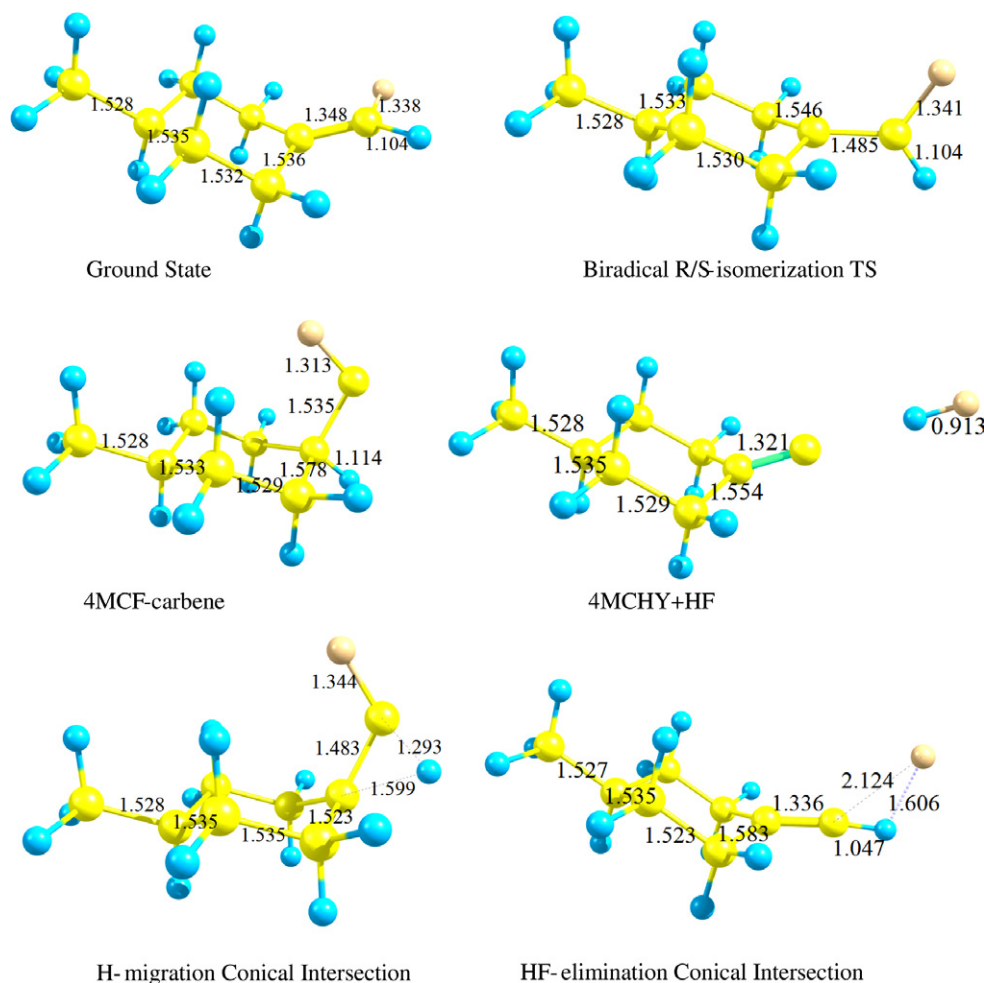
Fig. 2. Geometries of the optimized structures. Three ground state (GS) structures, one transition state (TS), and two conical intersections (CIs). Distances are in Å.

(123 kcal/mol). This CI thus lies at a much lower energy than the H-migration one, and therefore, it is expected to play an important role in the photophysics of this type of systems. In this case torsion is again one of the coordinates leading to the CI, but the second one is mainly the distance between the HF center of mass and the rest of the molecule plus the H–F distance. The geometries of the optimized structures are shown in Fig. 2 and their corresponding energies are listed in Table 1.

As seen in Fig. 2, the structure of the H-migration CI is similar to that reported in Ref. [7]. In contrast, the HF-elimination CI has no obvious analog in the previous work, although the relatively long C–F bond found for one of the CI, termed as twisted MXS (minimum energy crossing point) in Ref. [7], might indicate that the two structures belong to the same $3n - 8$ hypersurface defining the CI (n is the number of atoms). The structure of the HF-elimination CI might also be interpreted as a CI leading to F-atom elimination due to the large C–F distance (2.123 Å) and the short C–H distance −1.047 Å. This possibility was checked using two methods. First, the charge distribution of the A′ state at the CI geometry was calculated (Fig. 3). As can be

Table 1
Calculated energies and dipole moments μ (in Debyes) of some species (CAS(12,12)cc-pVDZ)

Species	Energy[a]	μ, D
4MCF GS	−410.10151 Hartree	2.07
4MCHY + HF	$\Delta\Delta E = 51.4$	na
4MCHM radical + F-atom	$\Delta\Delta E = 105.2$	–
4MCF carbene	$\Delta\Delta E = 60.6$	2.33
Biradical TS	$\Delta\Delta E = 72.7$	2.07
CI$_{H-migration}$ (1A′/1A″)[b]	$\Delta\Delta E = 154.7$	A′ 1.6[c]
		A″ 1.7
CI$_{HF elimination}$ (1A′/1A″)	$\Delta\Delta E = 122.7$	A′ 9.8[c]
		A″ 0.6
4MCHY* + HF[d]	$\Delta\Delta E = 125.2$	–

[a] kcal/mol above the ground state of 4MCF, whose absolute energy is listed in row 2.
[b] Preliminary optimization of the CI$_{H-migration}$ (the H-migration CI) by the GAUSSIAN program suite at the CAS(8,7)cc-pVDZ level, then recalculated at the CAS(12,12)cc-pVDZ level using GAMESS.
[c] Dipole moments calculated near the CI.
[d] A″ excited state of the 4MCHY+HF pair at the Franck–Condon geometry see Fig. 5.

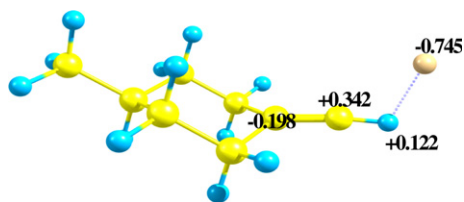seen, the F atom assumes a large negative charge and moves away essentially as an F⁻ anion.

Fig. 3. Charge distribution of the A′ state near the HF-elimination CI.

Second, the minimum energy path (MEP) on the 1A′ surface connects this HF-elimination CI with the GS minimum of the 4-methylcyclohexylidene-methylidene (4MCHY) without a barrier. As the system moves from the excited state to the GS, the C–F distance initially increases and the F atom is moving outwards essentially as a F⁻ anion (with the two electrons formerly forming the CF bond attached to it, as

indicated by the Mulliken charge distribution of the A′ state nearby to the CI shown in Fig. 3). Further along the MEP the F⁻ anion draws nearer to the H atom and detaches it a proton H⁺, leaving two electrons on the carbon atom. Fig. 4 shows a few snapshots taken along the path from the CI to the ground state. More snapshots are shown in the Supplementary material. The data clearly demonstrate that the CI found leads without a barrier to HF elimination.

The charge transfer character of the new CI is indicated by the calculated dipole moments of the two states at geometry slightly off the degeneracy. The A′ state has a dipole moment of 9.8 D, whereas the A″ state of only 0.6 D (cf. Table 1).

A partial energy level diagram along the coordinates leading to the two CIs is shown in Fig. 5; this diagram focuses on the vicinity of the conical intersections.
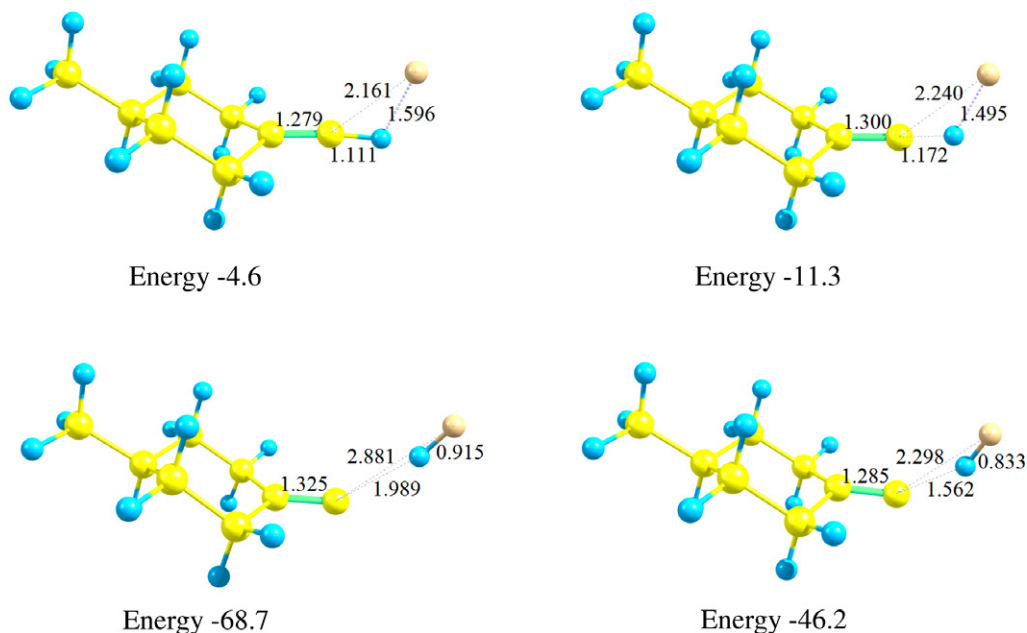

Fig. 4. Some snapshots showing (clockwise from upper left) the evolution of the system from the HF-elimination CI to the ground state. The energies (kcal/mol) relative to the CI are shown for all structures.
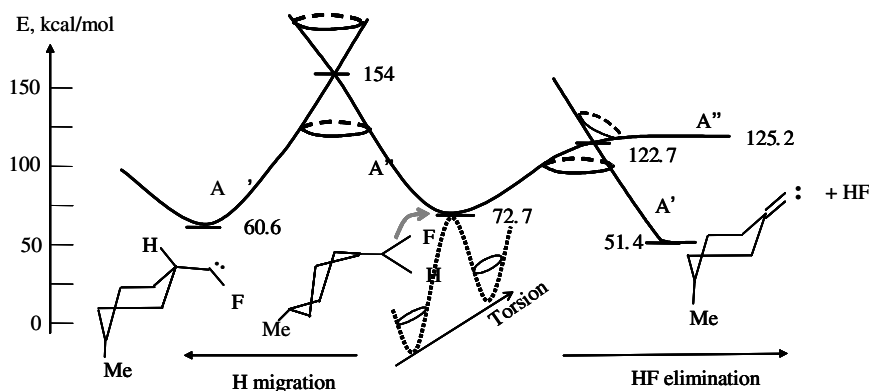

Fig. 5. A schematic energy level diagram showing the two low-lying CIs and ground state transition states of 4MCF based on CAS(12,12)/cc-pVDZ calculations. Torsion (connecting the E and Z isomers) is one of the coordinates leading to both CIs. The second one is either the H-migration or the HF elimination reaction coordinates. All energies refer to singlet electronic excited states.

We have searched for the lowest-lying CI reported in Ref. [7], termed there as the twisted MXS. According to the LH theorem, it would arise if two transition states of perpendicular structure were found on the round state potential surface, as for instance reported for the formaldiminium cation [27,28]. Using the CASSCF(12,12)/cc-pVDZ method, no ionic state was found on the ground state. However, a relatively low lying excited state of A′ symmetry was located at 104.4 kcal/mol. At the same geometry, the energy of the A″ ground state was a mere 7.6 lower in energy. A search for a crossing at the vicinity of this point, as well as at the geometry reported in Ref. [7], did not result in a curve crossing. In view of the small energy separation between the ground state and the excited singlet, this location may still be considered as a funnel for radiationless transition, perhaps with a somewhat reduced efficiency compared to a real crossing. It is noted that this near crossing lies at a lower energy than the new HF-elimination CI.

It is well-known that vinyl fluoride yields HF as a major product upon UV excitation [29]; moreover, the nascent HF molecule is rotationally and vibrationally excited leading to laser action in the infrared range [30,31]. 4MCF is expected to undergo a similar reaction, as it may be viewed as a vinyl fluoride derivative with a similar near UV spectrum and low lying electronically excited states of similar nature. As Fig. 4 shows, the calculation suggests an explanation for the large yield of rotationally excited HF molecules: the torque built up in the parent molecule on the way to the HF-elimination CI, leads to a rotational motion of HF with respect to the main frame of the molecule. The dissociation itself takes place on the ground state potential surface, but conservation of angular momentum means that HF will come out with a large excess of rotatory energy.

The HF-elimination CI can also lead to F atom dissociation, leaving a (4-methylcyclohexylidene)methyl (4MCHM) radical. However, even though initial excitation provides the system with sufficient excess energy, this process has a much higher barrier on the ground state (105 kcal/mol according to our CASSCF(12,12)/cc-pVDZ calculation, Table 1) and it is therefore likely to be less important. In Fig. 5 the A″ species lying on the excited potential surface at the geometry of the A′ (ground state) 4MCHY- HF pair is also shown for completeness sake.

4. Conclusions

In this Letter, a novel mechanism for the photoisomerization of 4MCF is proposed. It differs from the one usually associated with ethylene derivatives by the nature of the CI which is mediating the reaction. A new CI associated with HF elimination was located. Due to the large electron affinity of the fluorine atom, the calculated energy of this CI is considerably lower than that of the usual H-atom migration CI. The energy of this CI is expected to be lowered in polar solvents because of the large dipole

moment of the A′ state at geometries near the conical intersection; in contrast, the energy of the covalent-type conical intersection (associated with H-atom migration) should not be strongly affected by the solvent.

In summary, in liquid solutions, irradiation is expected to yield mainly the chiral isomer upon C=C rotation. In the gas phase, however, passage through the new CI is expected to lead to dissociation. The predicted major product is a strongly vibrationally and rotationally excited HF molecule. Crossing through the covalent CI, on the other hand, is not expected to yield HF as a major product. Thus, the two CIs may be distinguished by the nature of the products observed in the gas phase.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2007.06.072.

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