A THEORETICAL INVESTIGATION OF ELECTRON RELAXATION ACCOMPANYING CORE IONIZATION IN THE SYMMETRY FORMS OF ETHYLENE

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Relaxation energies accompanying core ionization in the planar and twisted form of the C_2H_4 molecule have been computed in terms of single orbital contributions by means of the *ab initio* SCF techniques. It is shown that the 2 eV shift between the core electron binding energies of both symmetry conformers may be attributed to changes in the π-valence electron relaxation when going from the planar to the twisted form of C_2H_4.

The core electron binding and relaxation energies of the two symmetry conformers of the C_2H_6 and C_2H_4 molecules have been recently investigated[1] by the *ab initio* ΔSCF formalism. This study has pointed out that the core electron binding energies (BEs) of the two ethylene symmetry forms (*i.e.* the planar and twisted forms) mutually differ by about 2 eV in contrast to the two forms of ethane (staggered and eclipsed) where the corresponding energy differences are negligible small. The changes of the electron BEs in both these cases has been ascribed to the relacation phenomenon accompanying ionization from the core orbitals. The fact that the relaxation phenomenon becomes so pronounced for the ethylene forms in comparison with the ethane case has been qualitatively explained[1] by the strengthened valence relaxation occuring as a consequence of splitting the highest occupied π molecular orbital in the twisted form of the C_2H_4 molecule. Since the twisted conformer is an unstable molecular species, the above mentioned relaxation cannot be studied experimentally, *e.g.*, by photoelectron spectroscopy. For this reason, the computation is the only tool for studying this problem.

The goal of the present contribution is to investigate in more detail the changes in relaxation energies between the two ethylene symmetry forms and, especially, to verify numerically that the strengthened electron relaxation in the twisted form of C_2H_4 is mainly caused by the effective relaxation of the highest valence electrons. Such a numerical verification can be based on a direct comparison of the individual orbital relaxation energies (REs) of both forms within the model of single orbital relaxation contributions[2,3].

CALCULATIONS

The *ab initio* LCAO MO ΔSCF calculations were performed on the ground and core-hole states of the planar (D_{2h}) and perpendicular (D_{2d}) form of ethylene using the Molecule–Alchemy program package[4]. The contracted Gaussian basis set[5] of triple zeta quality without polarization functions has been employed. The experimental geometry has been used[6] for both forms of ethylene as well as for their ions in agreement with the vertical approximation. In order to describe the K hole as localized, it has been necessary to lower the full molecular symmetries D_{2h} and D_{2d}. Ground and core-hole state MOs obtained from the symmetry unrestricted Hartree–Fock (HF) calculations have been employed in additional HF calculations in which the individual orbital RE contributions were determined using the single orbital relaxation model[2,3]. The presented study of the two ethylene conformers is based on the relative comparison of the two corresponding single orbital RE distributions with the same MO localization. This enables to draw conclusions regardless of the restrictions[7] in the single orbital relaxation model.

RESULTS AND DISCUSSION

Before starting the discussion of the differences of single orbital REs between the two forms of C_2H_4 (Table I), we would like to mention that the difference 2·25 eV between the total REs of both forms does not represent directly the core BE shift in question: it must be corrected by −0·27 eV, the change of the core orbital energy[1,8] occurring between both ethylene forms.

TABLE I

Differences of single orbital relaxation energies between the two forms of C_2H_4 (in eV)

ΔMO (Twisted vs. planar form)	Ionization from $1a_1$, $1a_g$ MOs	Ionization from $1b_2$, $1b_{1u}$ MOs
$1a_1 - 1a_g$	−0·031	0·883
$1b_2 - 1b_{1u}$	0·880	0·021
$2a_1 - 2a_g$	0·005	0·006
$2b_2 - 2b_{1u}$	−0·017	−0·018
$3a_1 - 1b_{2u}$	−0·167	−0·165
$1e \begin{cases} -3a_g \\ -1b_{3g} \end{cases}$	−0·051 / −0·087	−0·050 / −0·097
$2e \quad -1b_{3u}$	1·532	1·530
Sum	2·064	2·120
Directly calculated[a]	2·250	2·253

[a] The differences between the directly calculated total ΔSCF relaxation energies.

It is evident from the data in Table I that the main contribution (1·5 eV) to the 2 eV shift yields the relaxation of the highest valence electrons, although the relaxation contribution of about 0·88 eV from the core region is also significant. The relevant highest occupied valence orbital is in fact the πMO, the orbital under study. Its energy contribution represents about 75% of the core BE shift in question and, therefore, this orbital can be regarded as responsible for the strengthened relaxation of the C_2H_4 twisted form. The mechanism of such relaxation is undoubtedly connected with the change of the π delocalized electron charge into the localized p charges, as a consequence of the transition from the planar to the twisted form of ethylene. This explanation is corroborated by the relation of the corresponding relaxation energy values — the latter is approximately twice as large for the twisted form (3·22 eV) than for the planar form (1·67 eV). The above mentioned energy relation shows that the localized p-orbital system can relax much more effectively than the delocalized π one. Therefore, it is possible to conclude that the reported calculations support the assumption of the strenghtened p valence electron relaxation in the twisted form of the C_2H_4 molecule.

The foregoing discussion includes the case of the unstable molecular form, which is rather uncommon from the experimental (photoelectron spectra) point of view. Nevertheless, we can correlate our conclusions with experimentally more relevant cases, too. The necessary pre-requisite for such an extension is the existence of at least two stable isoelectronic molecules with differently localized valence molecular orbitals. Localization or delocalization is assumed to be a consequence of a suitable molecular symmetry. Two molecules that satisfy the above mentioned requirements are, e.g.. N_2 and CO. The nitrogen molecule has all its MOs symmetrically delocalized while carbon monoxide has them almost localized. From the six occupied MOs of the ground state of CO, four are dominantly localized on the oxygen center (i.e. more electron charge is placed on the oxygen). Thus the core ionization from the oxygen center yields much more RE than that one from the carbon center[7]. The highest occupied MO in both molecules is the πMO which is delocalized in N_2 ($1\pi_u$ orbital) and almost totally localized on oxygen in CO (1π orbital). This situation is in full analogy with that one of the π orbital in the two forms of C_2H_4 — the $1\pi_u$ MO of N_2 corresponds to the $1b_{3u}$ MO of the planar ethylene form, while the oxygen 1π MO of CO corresponds to the $2e$ MO of the twisted conformer. The relative comparison of the single orbital RE values[7] between CO and N_2 shows that the relaxation energy (12·70 eV) of the localized 1π orbital is nearly four times larger than that one of the delocalized $1\pi_u$ one (3·30 eV). In such a way, a strengthened valence electron relaxation takes place in the CO molecule in comparison with N_2, and this relaxation mechanism corresponds to that one of the twisted form of C_2H_4.

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