

Study of UV-Photoexcitation and Ultrafast Dynamics of HCFC-132b (CF₂ClCH₂Cl)

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INTRODUCTION

The issue of greenhouse gas emissions to the atmosphere and the ozone hole depletion phenomenon are topics of major importance. The main compounds reported as contributors to this fact are the chlorofluorocarbons (CFCs)¹. These were replaced by the hydrochlorofluorocarbons (HCFCs)². The understanding of HCFC's photodissociation is of great importance for the elucidation of their behavior in the upper atmosphere.

The aim of this research is to compute excited-states properties with TD-DFT methodology and compare with CASPT2 results. Nonadiabatic dynamics calculations were also performed to investigate the photochemical deactivation process of HCFC-132b (CF₂ClCH₂Cl).

METHODS

Static calculations and excited-states properties were calculated at TD-DFT (CAM-B3LYP and ω B97XD functional) and CASPT2 levels with Gaussian 09 and MOLCAS programs, respectively. In all calculations aug-cc-pVDZ (C, F and H)/d-aug-cc-pVDZ (Cl) basis set was used.

UV photoabsorption spectrum calculation was carried out and simulations of ultrafast gas phase nonadiabatic dynamics were performed, taking into account 25 electronic states at TD- ω B97XD level starting in two different spectral windows (8.5 \pm 0.25 and 10.0 \pm 0.25 eV), using Newton-X program interfaced with Gaussian 09.

RESULTS AND DISCUSSION

Excited states calculations at the TDDFT level are in good agreement with CASPT2 results, correctly predicting the main excited-states properties.

Experimental data measured at 147 nm (~8.43 eV)³ is in very good agreement with our simulations. The excited state lifetime is 106 and

191 fs for the 8.5 and 10.0 eV spectral excitation windows, respectively.

Internal conversion to the ground state occurred through several different reaction pathways with different products, where 2Cl, C-Cl bond breakage, and HCl are the main photochemical paths in the low-excitation region, representing 95% of all processes. On the other hand, HCl, HF, and C-Cl bond breakage are the main reaction pathways in the higher excitation region, with 77% of the total yield. Figure 1 shows the main decay process for HCFC-132b.

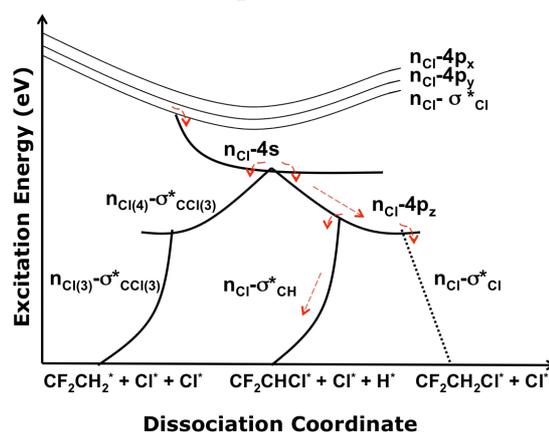


Figure 1. Main photochemical pathways for HCFC-132b.

CONCLUSIONS

For HCFC-132b, TD-DFT performed quite well in the description of excited states properties. Gas phase non-adiabatic dynamic simulations correctly predict the photochemical reaction paths. We have also observed a direct influence of spectral excitation window on products distribution and photodecay lifetime.

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