Scientific report:

Our attention was focused on the theoretical treatment of photodissociation processes for which a detailed understanding of non-adiabatic effects or interactions at conical intersections has been shown to be essential [1,2]. As a test case, we have undertaken a complete study of the electronic relaxation of the vinoxy radical CH_2CHO in relation with crossed laser-molecular beam experiments [3]. Such a system presents very interesting features, with several conical intersections [4,5], leading to different possible mechanisms according to the radical formation [3,6]. It may be an efficient test case for the study of photon excitation of the C=O group in some biological systems, as for example haemoglobin or the cytosine DNA basis.

The vinoxy radical CH_2CHO plays an important role also in atmospheric and combustion chemistry. Some reactions, in which it takes place, are relevant to the oxidation of the vinyl radical and acetylene [7,8]. In turn, there are also some reactions taking place on the potential energy surface of the vinoxy radical. This attracts great interest of experimentalists. Quite recently, Osborn *et al*. [6] suggested that the photodissociation of the B(^{2}A") state by direct coupling to a repulsive state that correlates to products is probably not the mechanism of predissociation, since the translation energy of photo-fragments is independent of excitation energy. Very recently, Morton *et al*. [3] and Miller *et al*. [3] studied the competition between two unimolecular reactions available to the vinoxy radical. Several measurements on the rate constants of the vinoxy radical have been reported. There are also notable theoretical studies. Yamaguchi *et al*. [9] have performed the vibrational analysis and calculations of Franck-Condon factors of the vinoxy radical. They used the multiconfigurational self-consistent field method to calculate the optimized geometry and energy gradients of molecular states. In turn, Matsika and Yarkony [4] have proposed a predissociation mechanism. They determined the critical points on potential energy surafces using the multi-reference configuration interaction method.

In order to have a more precise insight into these different mechanisms and assess the role of the avoided crossing and conical intersection interactions, we performed an *ab-initio* calculation of the three potential energy surfaces, X(^{2}A") ground state, A(^{2}A') and B(^{2}A") excited states, involved in the photodissociation process. The non-adiabatic interactions have been precised by calculation of the radial coupling matrix elements in the vicinity of the avoided crossings.

To calculate the adiabatic potential energy surfaces we use the complete-active-space multi-configuration self-consistent field (CASSCF) method and multi-reference configuration interaction (MRCI) method. In this approach we do not include spin-orbit interaction. We take the valence triple-zeta (VTZ) basis. All results are obtained by means of the MOLPRO [10] program package. An optimization of the planar geometries in the X(^{2}A") ground state and A(^{2}A'), B(^{2}A") excited states shows three main active degrees of freedom for this process (Fig. 1), the torsion mode $\angle$ H1-C1-C2-O of the two groups H1/C1/H2 and O/C2/H3 around the C-C bond, and the in-the-plane $\angle$ C1-C2-O and dihedral angle $\angle$ H1-C1-C2-H3 corresponding to the breaking of the planar O-C2-H3 equilibrium structure. Adiabatic surfaces have been determined for these three active modes, taken two by two and using the curvilinear coordinates. Of course, planar C_s symmetry of the optimized X(^{2}A"), A(^{2}A') and B(^{2}A") states is broken as out-of-plane motions are considered.
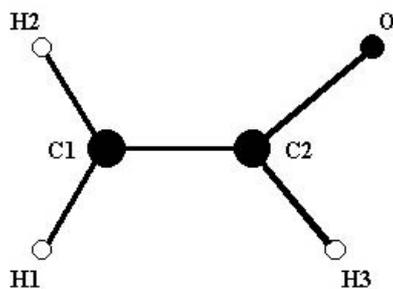
Fig. 1 Geometry of the vinoxy radical

The potential energy surfaces for the ground and first excited states are presented in Fig. 2 and show clearly a very strong interaction on the $\angle$ C1-C2-O / $\angle$H1-C1-C2-O surfaces which is detailed in Fig. 3a. Such an interaction may be assigned to a conical intersection as already noticed by Matsika and Yarkony [4]. The radial coupling has been calculated using a three point numerical differentiation method with a step 0.012°. The non-adiabatic coupling matrix elements are presented in Fig. 3b and appear as a Dirac function as expected for such an interaction. The optimized geometry for this conical intersection corresponds to the angles $\angle$C1-C2-O = 88.8°, torsion angle $\angle$ H1-C1-C2-O = 85.4° and dihedral angle $\angle$ H1-C1-C2-H3 = 45.1°.
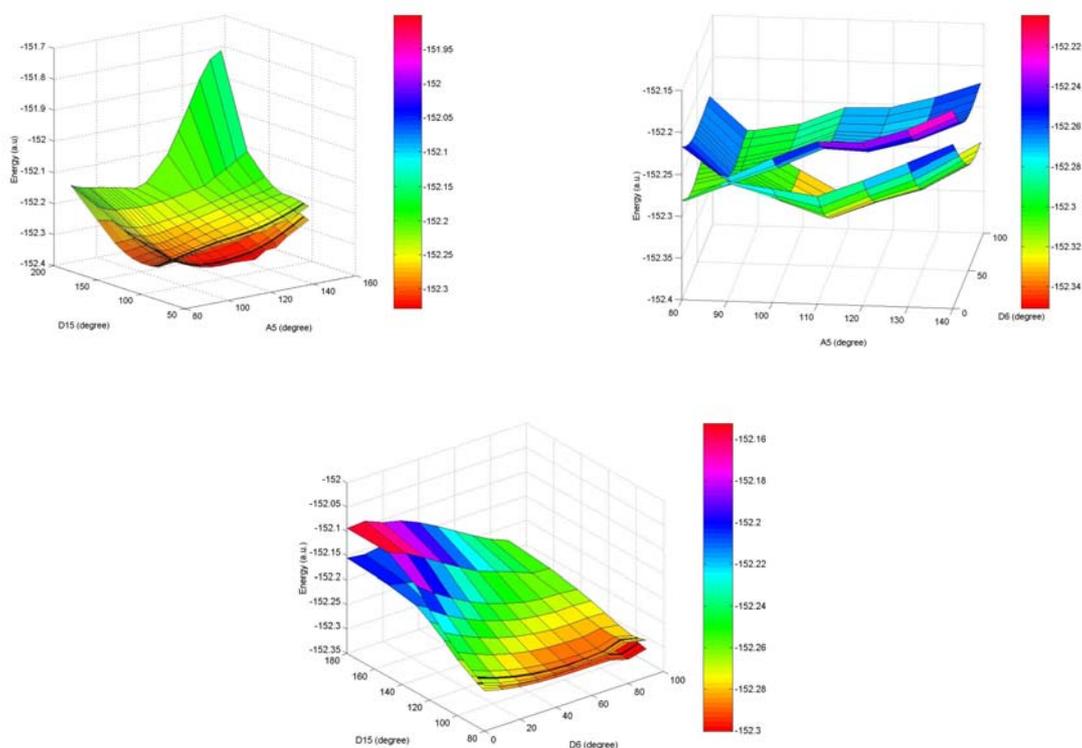
Fig. 2 Adiabatic potential energy surfaces for the X and A states of the vinoxy radical.
A5=$\angle$ C1-C2-O; D15=$\angle$H1-C1-C2-O; D6=$\angle$ H1-C1-C2-H3.
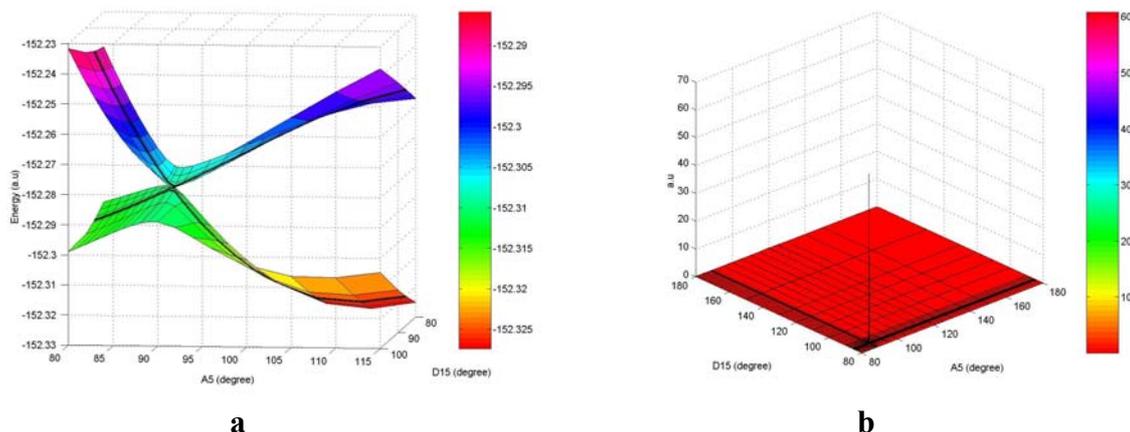
Fig. 3 a: Detail of the potential of the X and A states of the vinoxy radical on the ∠ C1-C2-O/ ∠H1-C1-C2-O surface; **b:** Non-adiabatic coupling matrix element for the same active modes.

The main features of the adiabatic potential energy surfaces for the A and B excited states are presented in Fig. 4 and show a relatively smooth avoided crossing on the ∠ C1-C2-O and ∠ H1-C1-C2-O surfaces between these two excited states. The non-adiabatic radial coupling matrix elements have been calculated numerically and appear to be relatively sharp, around 16.8 a.u. high, and may thus induce an efficient B→A transition. The optimized geometry at the avoided crossing corresponds to the angles ∠C1-C2-O = 115.0° and torsion angle ∠ H1-C1-C2-O = 135.0°.
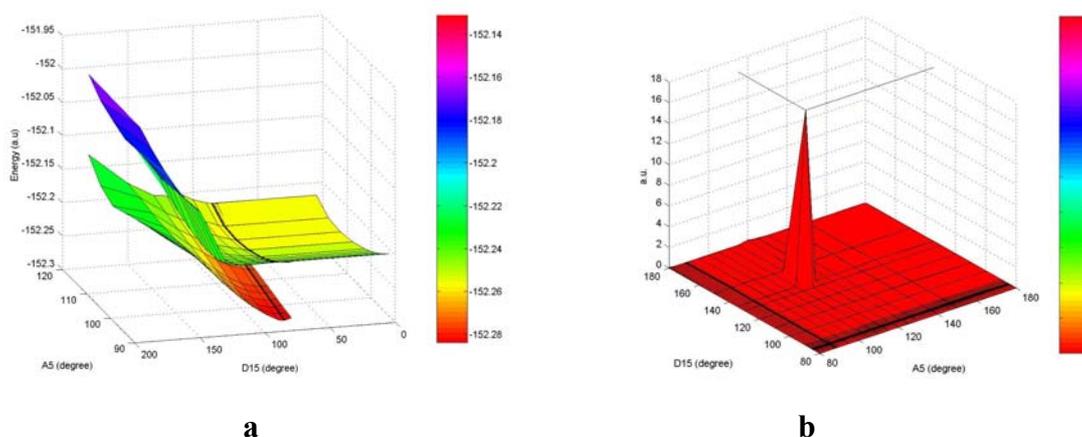
Fig. 7 a: Adiabatic potential energy surfaces for the A and B states of the vinoxy radical on the A5=∠ C1-C2-O/ D15=∠H1-C1-C2-O surface; **b:** Non-adiabatic coupling matrix element for the same active modes.

These molecular *ab-initio* calculations are the first step in the study of photodissociation process. Currently, we focus on conical intersections which are essential to explain formation of ketene during the relaxation of the vinoxy radical [3].. We analyse quantum dynamics in a two-dimensional subspace involving the two main angles: the torsion angle ∠C1-C2-O and the dihedral angle ∠ H1-C1-C2-O. In the framework of a reduced dimensionality method, Dynamics is carried out directly with the internal coordinates used to describe the geometry in the Z-matrix. The spectator coordinates are taken into account by the constrained Hamiltonian technique. In a first approach, the inactive coordinates are simply at the geometry of the

conical intersection between the A and X states of the vinoxy radical. The code Tnum [11] generates numerically but exactly the coefficients of the differential operators occurring in the kinetic energy for any generalized coordinates. Wave-packet simulations are in progress. We illustrate below the evolution of a wave packet prepared in the first diabatic electronic state (A state). Non adiabatic transition occurs every times the wave packet visits the seam between the two diabatic states where the coupling is strong.

a **b**
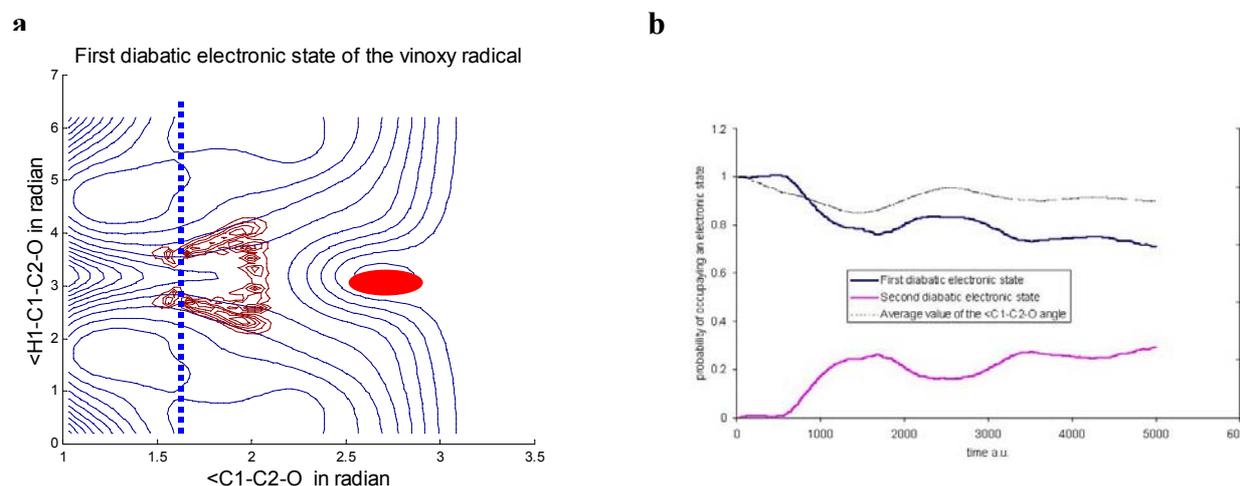
Fig.8 a: Evolution of a Gaussian wave packet prepared in the first diabatic electronic state of the vinoxy radical; *red*: initial wave packet, *brown*: after 10 fs. **b**:Corresponding probability of occupying the two diabatic electronic state and average value of the <C1-C2-O angle.

References

 [1]   "Computational Photochemistry", Ed. M. Olivucci, Elsevier (2004) ; M.A. Robb and M. Olivucci, F. Bernardi, "Photochemistry", in "Encyclopedia of Computational Chemistry", Ed. P. R. Schleyer *et al*., Wiley&Sons (1998).

[2]   M.C. Bacchus-Montabonel, N. Vaeck, B. Lasorne and M. Desouter-Lecomte, Chem. Phys. Lett. **374**, 307 (2003) ; B. Lasorne, M.C. Bacchus-Montabonel, N. Vaeck and M. Desouter-Lecomte, J. Chem Phys. **120**, 1271 (2004).

[3]   M.L. Morton, D.E. Szpunar and L.J. Butler, J. Chem. Phys. **115**, 204 (2001) ; J.L. Miller, L.R. McCunn, M.J. Krisch and L.J. Butler, J. Chem. Phys. **121**, 1830 (2004).

[4]   S. Matsika and D. Yarkony, J. Chem. Phys. **117**, 7198 (2002).

[5]   M.C. Bacchus-Montabonel, K. Piechowska, Y.S. Tergiman and J.E. Sienkiewicz, Int. J. Quant. Chem. (2004, in press)

[6]   D.L. Osborn, H. Choi, D.H. Mordaunt, R.T. Bise and D.M. Neumark, J. Chem. Phys. **106**, 3049 (1997).

[7]   S.G. Davis, H. Wang and W. Tsang, Comunication K4, 5th International Conference on Chemical Kinetics, (16-20 July 2001).

[8]   E. Delbos, P. Devolder, L. El Maimouni, C. Fittschen and M. Hassouna, 8th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, (Torino 17-20 Sept. 2001).

[9]   M. Yamaguchi, T. Momose and T. Shida, J. Chem. Phys. **93**, 4211 (1990).

[10]   MOLPRO is a package of *ab initio* programs written by H.J. Werner and P.J. Knowles with contributions from R.D. Amos, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Leininger, R. Lindh, A.W. Lloyd, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, K. Peterson, R. Pitzer, P. Pulay, G. Rauhut, M. Schütz, H. Stoll, A.J. Stone and T. Thorsteinsson;

H.J. Werner and P.J. Knowles, J. Chem. Phys. **82**, 5053 (1985);

P.J. Knowles and H.J. Werner, Chem. Phys. Letters **115**, 259 (1985);

A. Berning, H.J. Werner, P. Palmieri and P.J. Knowles, Mol. Phys. **98**, 1823 (2000).

[11]   D. Lauvergnat and A. Nauts, J. Chem. Phys. **116**, 8560 (2002).

I accept this report and confirm that Katarzyna Piechowska has spent a month in the Laboratoire de Chimie Physique of the University of Paris-Sud.

Pr Michele Desouter-Lecomte   Katarzyna Piechowska
Laboratoire de Chimie Physique   Department of Theoretical and Mathematical Physics
Universite Paris-Sud (France)   Gdańsk University of Technology (Poland)