Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Dissociative photoionization of acetaldehyde in the 10 -19.5 eV VUV range

Pedro Recio,[a] Roger Y. Bello,[b] Gustavo A. García,[c] Alexandre Zanchet,[d] Jesús González-Vázquez,[e, f] Luis Bañares,[a,g] and Sonia Marggi Poullain[a,*]

[a] Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain. E-mail: smarggi@ucm.es

[b] Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain

[c] Synchrotron SOLEIL, L'Orme des Merisiers, St. Aubin, BP 48, 91192 Gif-sur-Yvette, France

[d] Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas, C/ Serrano, 123, 28006 Madrid, Spain

[e] Departamento de Química, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain

[f] Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049 Madrid, Spain

[g] Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanoscience), Cantoblanco, 28049 Madrid, Spain

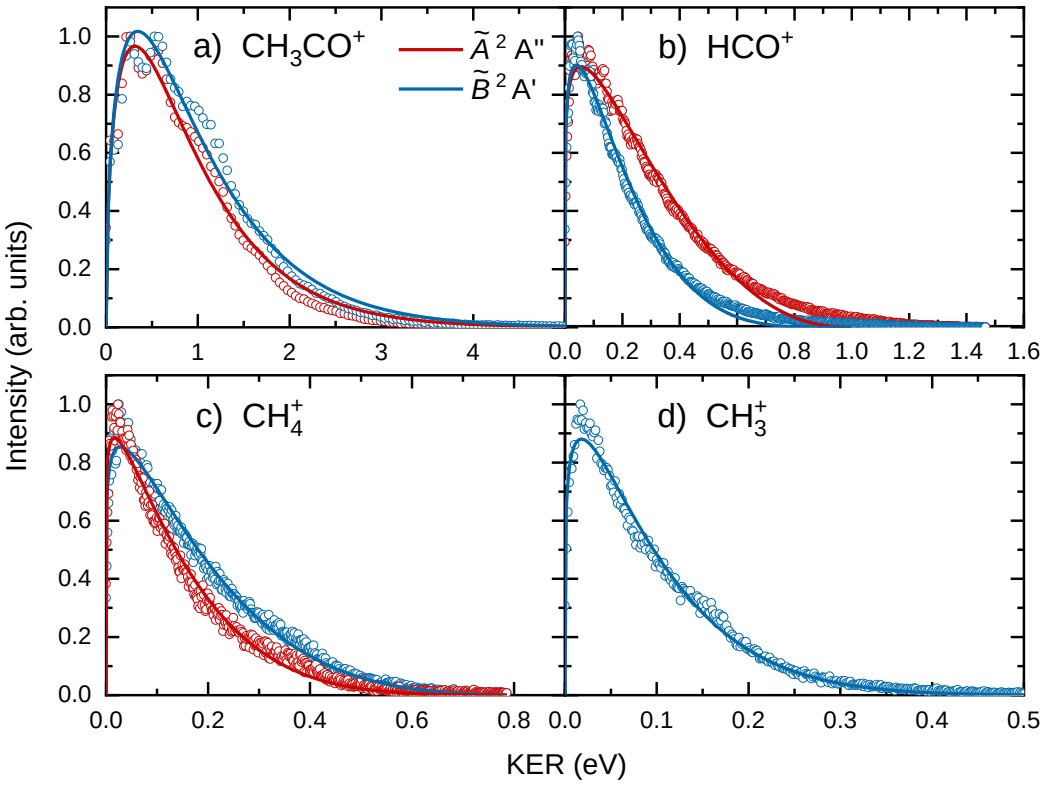

Figure S1: Experimental kinetic energy release (KER) following photoionization at 15 eV for each fragment, obtained by integration of the KECD, depicted in Fig. 3 of the manuscript, over photoelectron energies between 1.3 and 2.2 eV and between 0.5 and 1.3 eV, corresponding to photoionization into the $\tilde{A}$ (^{2}A'') and the $\tilde{B}$ (^{2}A') cationic states, respectively (Panels a-c). All photoelectron energies are taken to obtain the KER for the methyl cation (Panel d) and it is associated to photoionization into highly-vibrationally excited states of the $\tilde{B}$ (^{2}A') state as well as some minor threshold photoionization into $\tilde{C}$ (^{2}A') state.

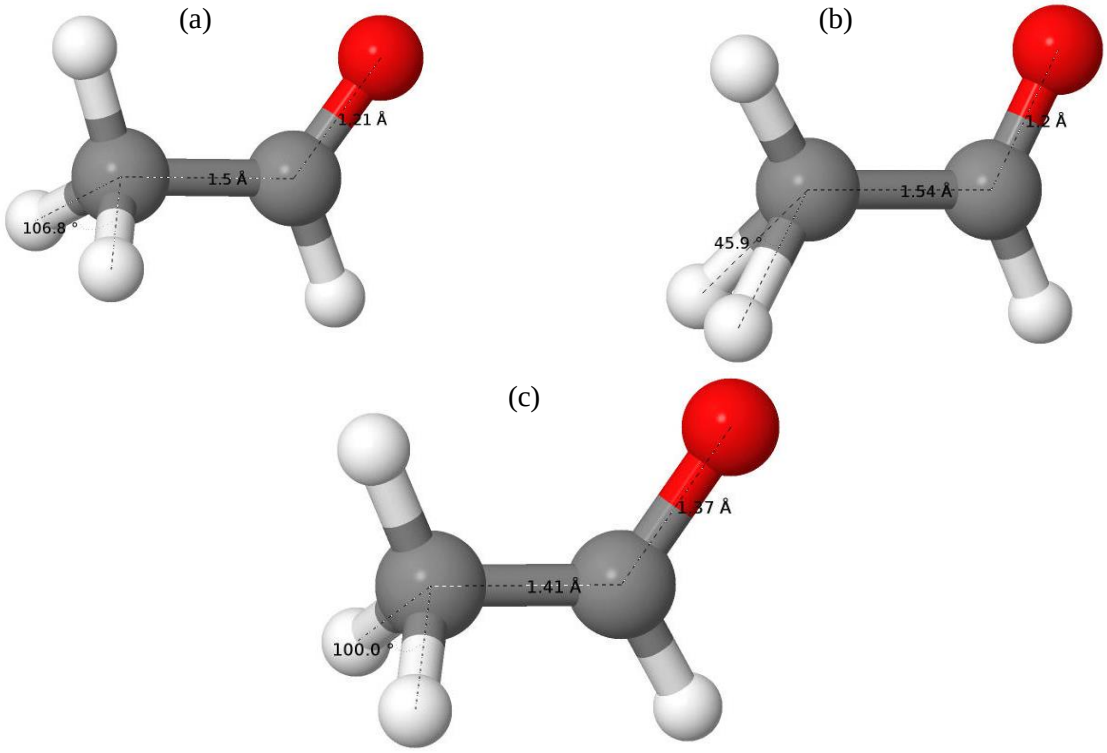

Figure S2: Computed geometry (a) at the equilibrium (*i.e.* vertical photoionization at Franck-Condon) (b) at the conical intersection found between the $\tilde{A}$ (^{2}A'') and the $\tilde{X}$ (^{2}A') ionic states and (c) at the energy minimum of the state. Relevant distances and angles are shown.

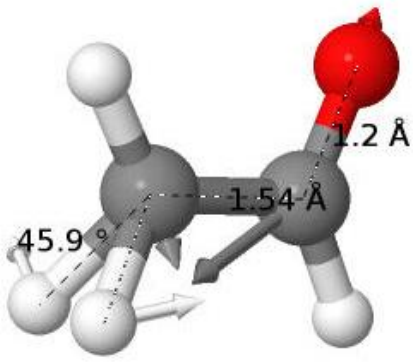

Figure S3: Computed geometry at the at the conical intersection found between the $\tilde{A}$ (^{2}A'') and the $\tilde{X}$ (^{2}A') ionic states (as in Fig. S2). The arrows represent the non-adiabatic vector characterizing the conical intersection.

Geometries for relevant points:

Equilibrium geometry (FC)

O	0.00130272	0.05880247	-1.09163746
C	0.00018129	-0.46168660	0.00601302
C	0.00002435	0.29252579	1.30028092
H	-0.00169774	-1.56264857	0.09542013
H	-0.00085212	1.36309287	1.12077939
H	-0.87466897	0.00702178	1.88533814
H	0.87571045	0.00873529	1.88471542

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Minimum energy for $\tilde{X}$ (^{2}A') state

O	0.00049251	0.04763632	-1.06412626
C	0.00072201	-0.46340391	0.02459259
C	0.00015459	0.32244036	1.32610542
H	-0.00146800	-1.57768914	0.06267646
H	-0.00057487	1.38675627	1.12149812
H	-0.89062556	-0.00565737	1.86493950
H	0.89129932	-0.00423950	1.86522398

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Minimum energy for $\tilde{A}$ (^{2}A'') state

O	0.00066990	0.09011031	-1.15019264
C	-0.00007852	-0.46255724	0.09837356
C	-0.00020799	0.32620755	1.26636007
H	-0.00031794	-1.55550279	0.12904526
H	-0.00043598	1.39752452	1.11072390
H	-0.84825419	-0.04491137	1.87378360
H	0.84862471	-0.04502797	1.87281603

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Conical intersection found between $\tilde{A}$ (^{2}A'') and $\tilde{X}$ (^{2}A')

O	-0.06268321	-0.00184413	-1.17538521
C	-0.00060820	-0.56465536	-0.12095768
C	0.01474324	0.38656067	1.09327174
H	0.03823353	-1.64346454	0.06582331
H	0.04289013	1.46958496	1.01282124
H	-0.49284035	0.00948340	2.13981293
H	0.46026486	0.05017803	2.18552345

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Dissociation limit: $CH_3 + HCO^+$

O	-0.00002009	-10.50752494	-17.22221187
C	-0.00000712	-11.39623957	-16.54750911
C	0.00000323	0.17211526	1.20898424
H	0.00001615	-12.26988963	-15.88605577
H	0.00004153	1.08448687	0.63133820
H	-0.93515992	-0.27564077	1.51077536
H	0.93512622	-0.27566451	1.51086466

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Dissociation limit: $CH_3^+ + HCO$

O	-0.30208331	-10.69166445	-15.76069793
C	0.30025140	-11.52341474	-16.35368151
C	-0.02553478	0.18864938	1.17588273
H	-0.02639314	-11.93889819	-17.34469662
H	-0.04156438	1.12176065	0.61950794
H	-0.95734452	-0.26367584	1.50424019
H	0.92199808	-0.29124654	1.40501877

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Dissociation limit: $CH_4^+ + CO$

O	0.45304599	-10.59526339	-17.86314220
C	-0.47050297	-10.31827246	-17.28416741
C	0.00501510	0.27396913	1.27889968
H	0.16742307	-0.19122969	0.30640819
H	0.93799304	0.69377809	1.64358954
H	-0.73253305	1.06593048	1.18518446
H	-0.35502738	-0.46951169	1.98429072

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Dissociation limit: $CH_3CO^+ + H$

O	0.00005390	0.17358825	-1.22091564
C	0.00002938	0.24774840	-0.10254903
C	-0.00000136	0.39053625	1.33019959
H	-0.00005697	-2.37932375	0.21241902
H	0.00001271	1.45929149	1.55275238
H	-0.89937832	-0.09298273	1.71448098
H	0.89934065	-0.09301489	1.71452250