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REFERENCE: Short Term Scientific Mission, COST CM0601
Beneficiary: Paulo LIMAO-VIEIRA, New University of Lisbon (PT)
Host: Marie-Jeanne Hubin-Franskin, University of Liège, Belgium
Period: from 24/08/2008 to 29/08/2008 Place: Liège (BE)
Reference code: COST-STSM-CM0601-3179

SCIENTIFIC REPORT

PURPOSE OF VISIT

The scientific mission to the University of Liège was devoted to the experimental spectroscopic valence shell studies of Volatile Organic Compounds (VOC), obtained by experimental high resolution VUV photoabsoprtion spectra collected in the University of Aarhus, Denmark, that have been complemented as far as the electronic state spectroscopy of valence and low ionic states are concerned, by recent High Resolution Electron Energy Loss Spectroscopy (HREELS) and Photoelectron Spectroscopy (PES) obtained by the University of Liège group. A joint publication on previous collaborative work was finished an another two from the present visit are due to be submitted soon on the spectroscopy of isoprene and limonene.

DESCRIPTION OF THE WORK CARRIED OUT DURING THE VISIT

During this STSM, it was possible to analyse some of the PES data previously collected by the Belgian group on propionic acid, a low chain fatty acid. VOCs data (isoprene and limonene) obtained by high resolution VUV photoabsorption and photoelectron spectroscopy was analysed and several assignments have been proposed for the structure observed . The resident lifetimes in the different parts of the atmosphere were deduced from the absolute cross sectional values. It was also established between the parties the next priorities for the set of manuscripts to be written on other VOCs such as alpha- and beta-pinenes.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

A joint publication on low chain fatty acids (propionic, butyric and valeric) has been finished (see a few details on appendix I) to be submitted to Phys. Chem. Chem. Phys. shortly and data on isoprene and limonene carefully analysed to be submitted to a international journal shortly as well. Therefore, during this scientific misson was possible to:

1. compile and analyse the recent PES data of propionic acid and limonene;
2. discussion on the recent assignments, both valence and Rydberg, to propionic, butyric

and valeric acids proposed by the Lisbon group;

3. deconvolution of propionic acid lowest ionic band of the recent PE spectrum. New adiabatic and vertical ionisation energies have been proposed;
4. By making use of the recent TDDFT calculations performed by the group of Denis Duflot in Lille, France, with whom both Lisbon and Liege groups keep a close scientific link, the vertical excitation energies of the three low chain fatty acids have been identified and assigned to the experimental data.

FUTURE COLLABORATION WITH HOST INSTITUTION

This research joint programme will continue. Research will be devoted to the electronoic state spectroscopy of (a) other aeronomic molecular targets; (ii) other relevant molecular targets that may also play an important role from the biological point of view such as longer chain fatty acids.

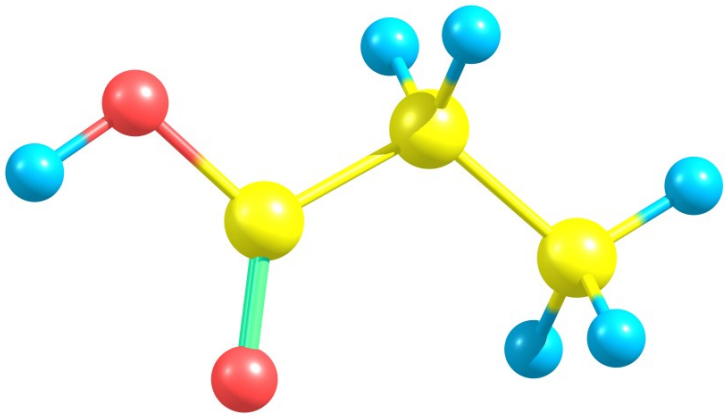
PROJECTED PUBLICATIONS/ARTICLES RESULTING OR TO RESULT FROM THE GRANT

One joint publication is to be submitted to Phys. Chem. Chem. Phys. on low chain fatty acids and two others on the spectroscopy of isoprene and limonene are due shortly. Other publications will emerge during the next months as soon as we compile and analyse the relavant data recorded for other molecules.

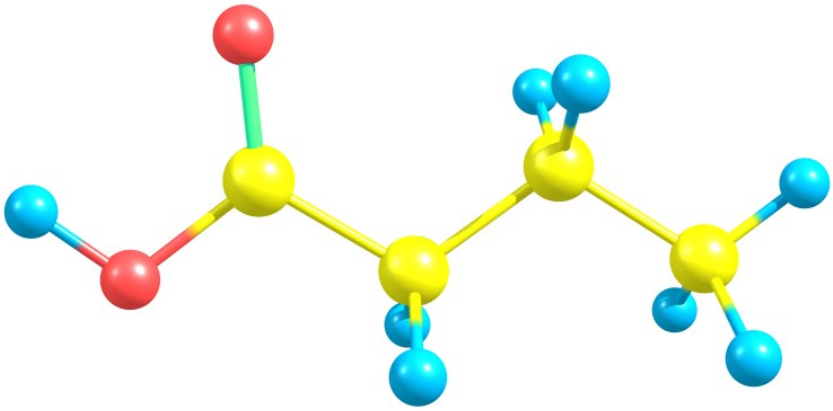
Paulo Limao-Vieira

APPENDIX I - Recent results and data analyses from the STSM to Liège.

Figure 1 – Ground state structure of a) propionic acid C_2H_5COOH, b) butyric acid C_3H_7COOH and c) valeric acid C_4H_9COOH.



a)



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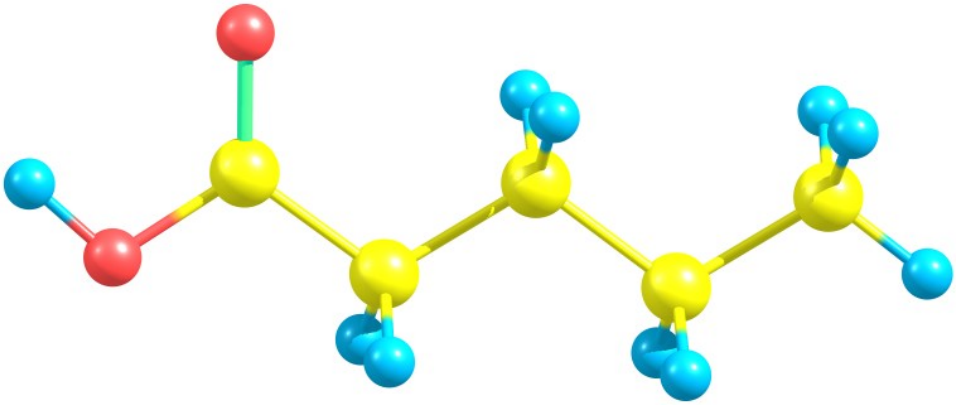

c)

Figure 2a) – High resolution VUV photoabsorption spectrum of propionic acid C_2H_5COOH.

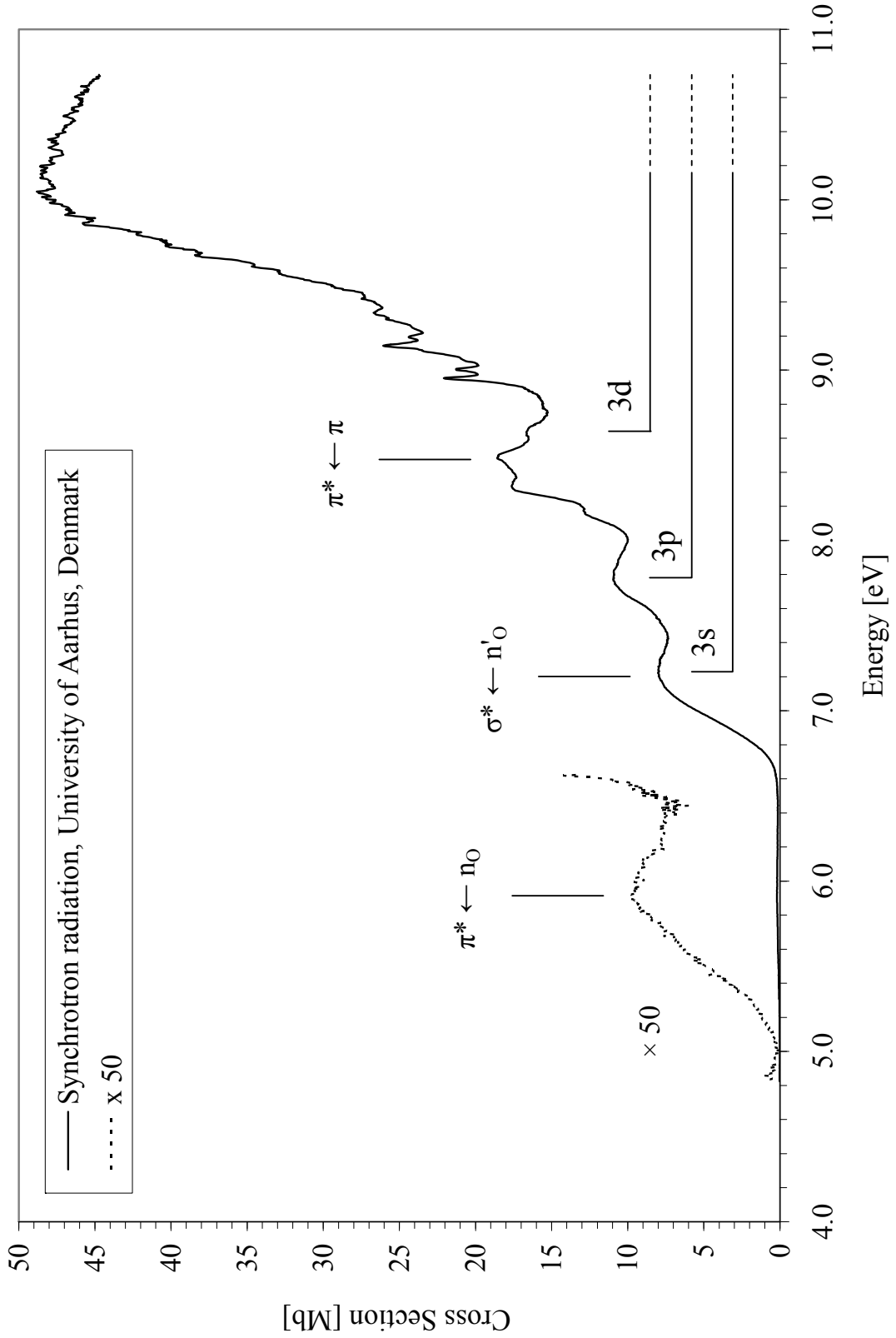

Figure 2b) – High resolution VUV photoabsorption spectrum of butyric acid C_3H_7COOH.

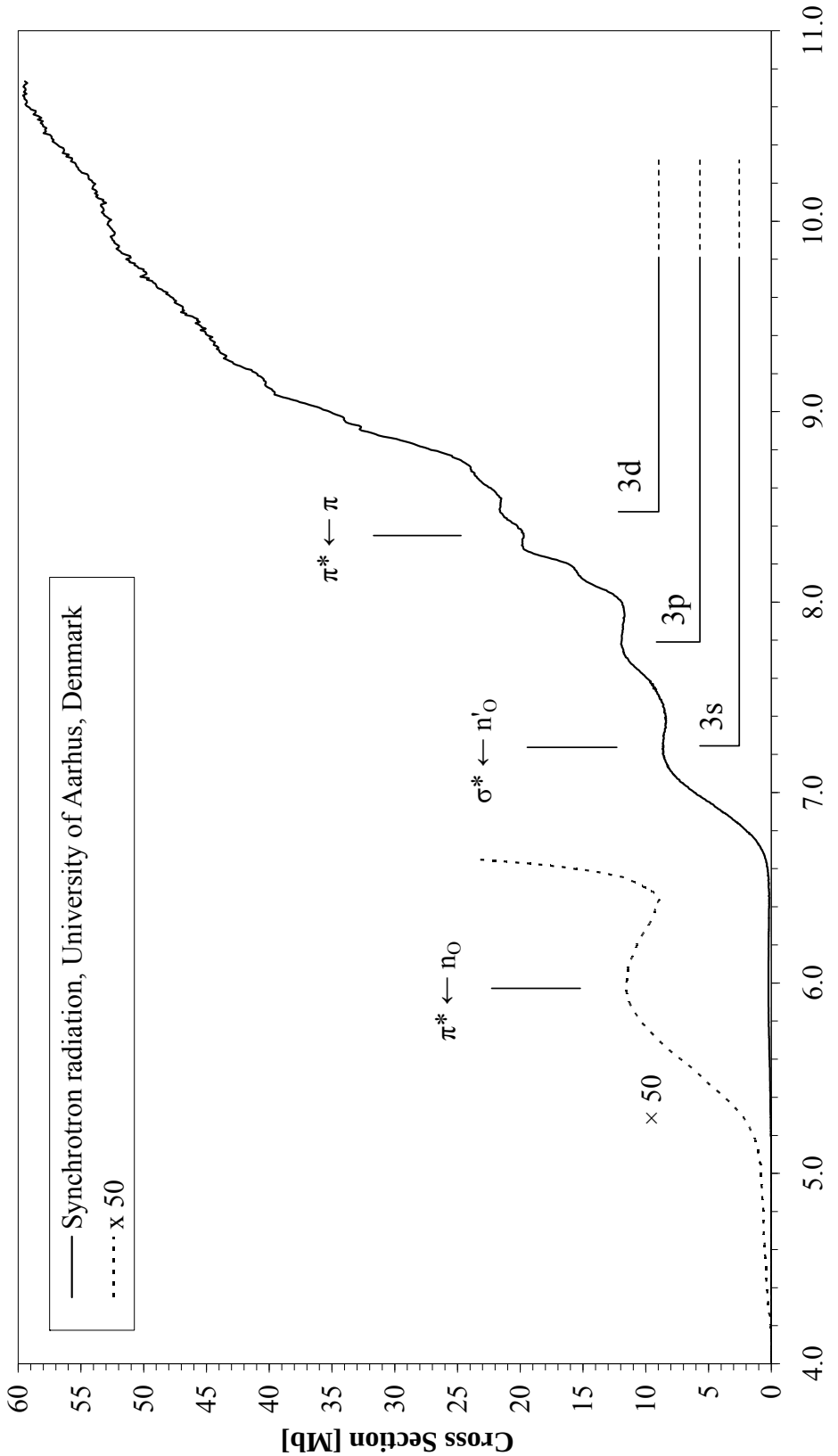

Figure 2c) – High resolution VUV photoabsorption spectrum of valeric acid C_4H_9COOH.

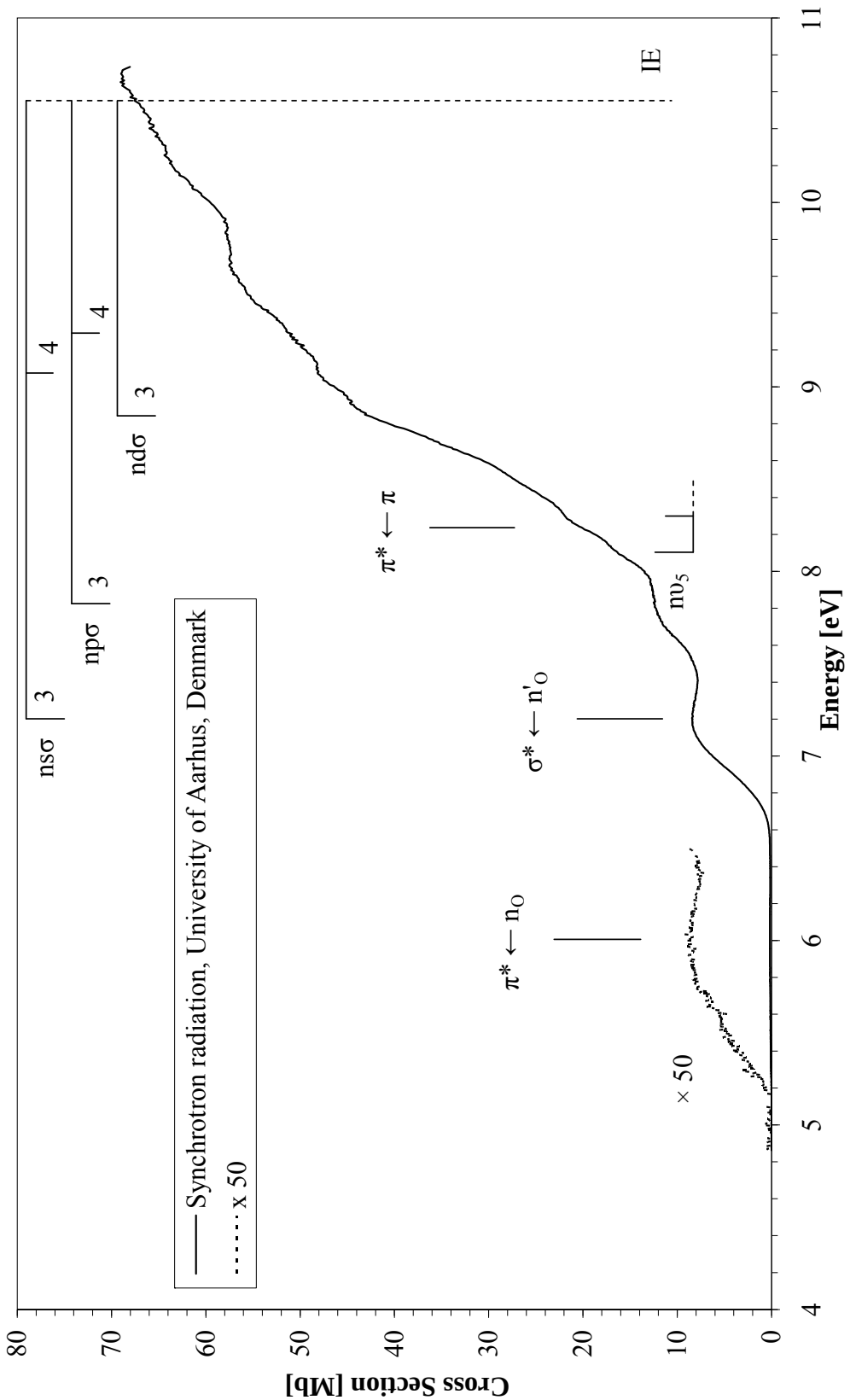

Figure 3 – He(I) photoelectron spectrum of propionic acid C_2H_5COOH.

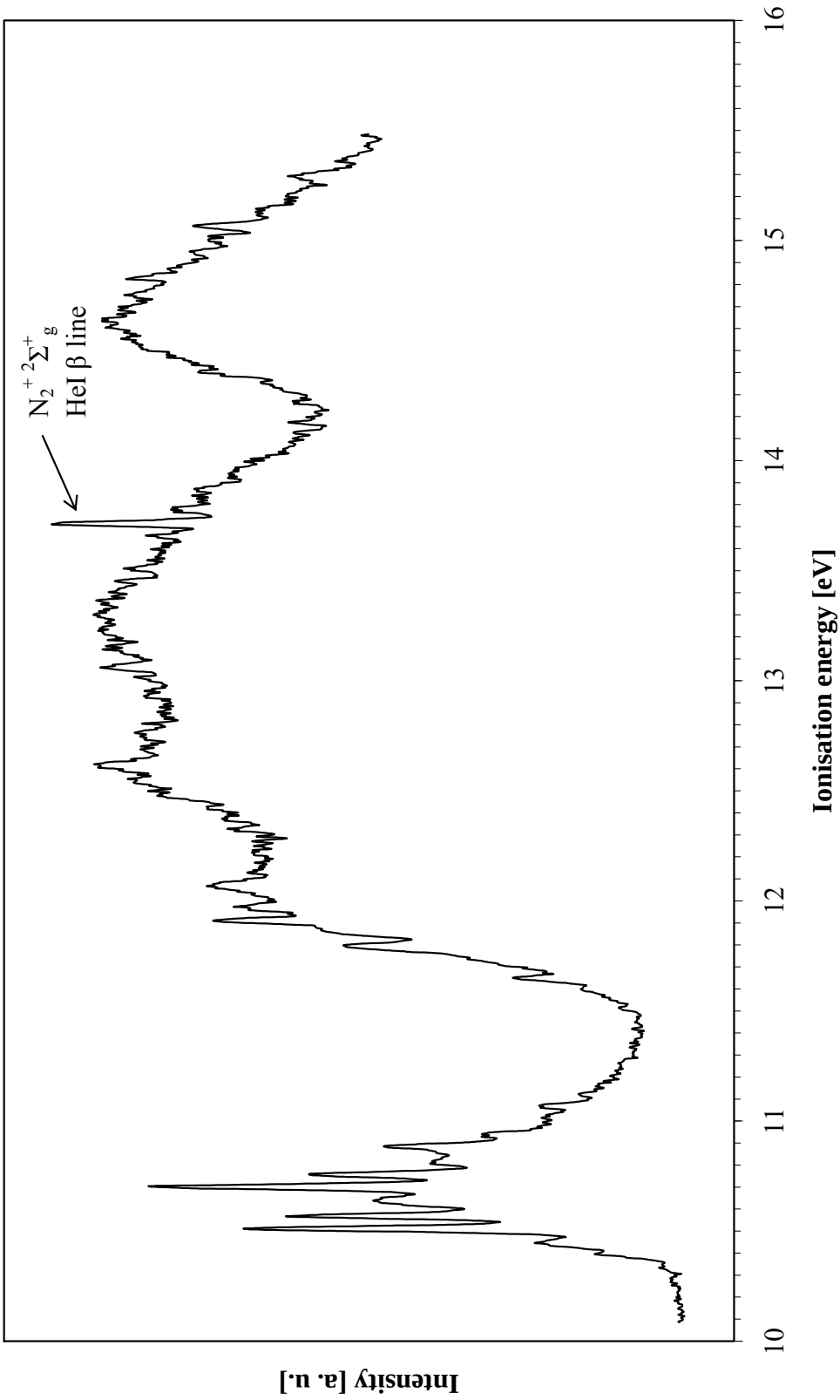

Figure 4 – The first photoelectron band of propionic acid C_2H_5COOH, assigned to ionisation from the $n_O(16a')$ orbital.

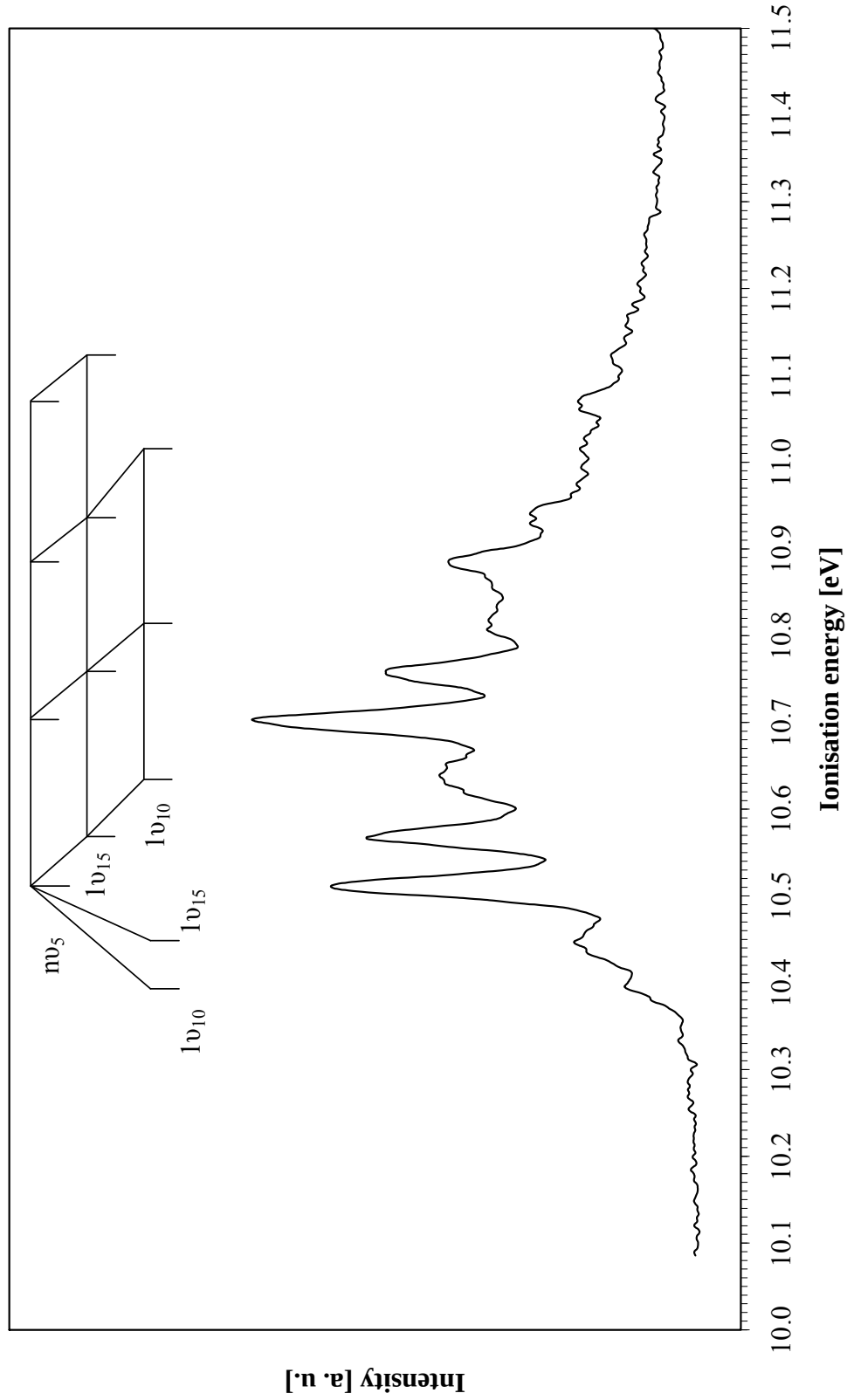

Figure 5 – Vibrational progressions in the 8.0 – 9.0 eV absorption band of C_2H_5COOH.

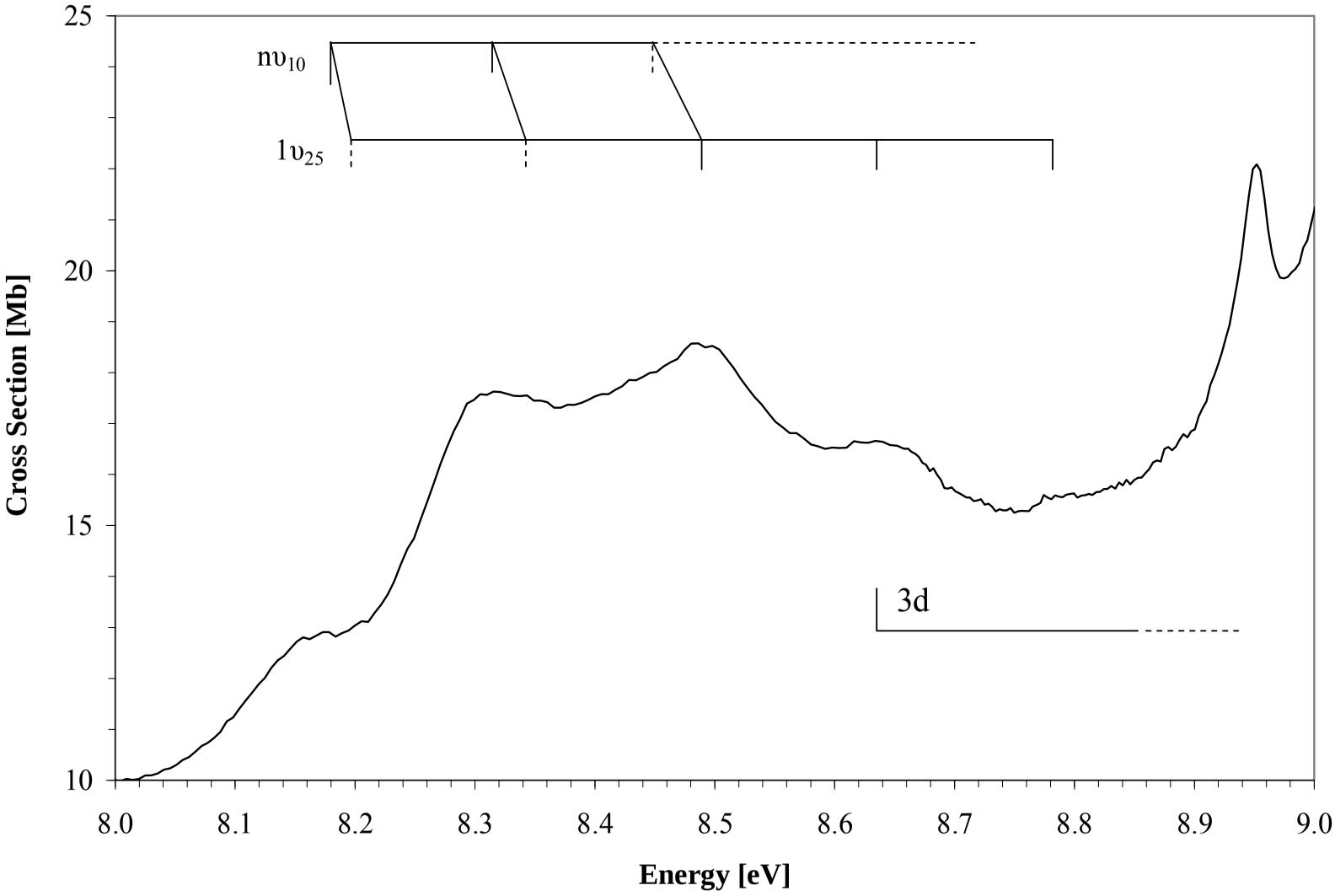
25
20
15
10
8.0
8.1
8.2
8.3
8.4
8.5
8.6
8.7
8.8
8.9
9.0
Cross Section [Mb]
Energy [eV]
nυ10
1υ25
3d

Figure 6 – Vibrational progressions in the 8.5 – 10.8 eV absorption band of C_2H_5COOH.

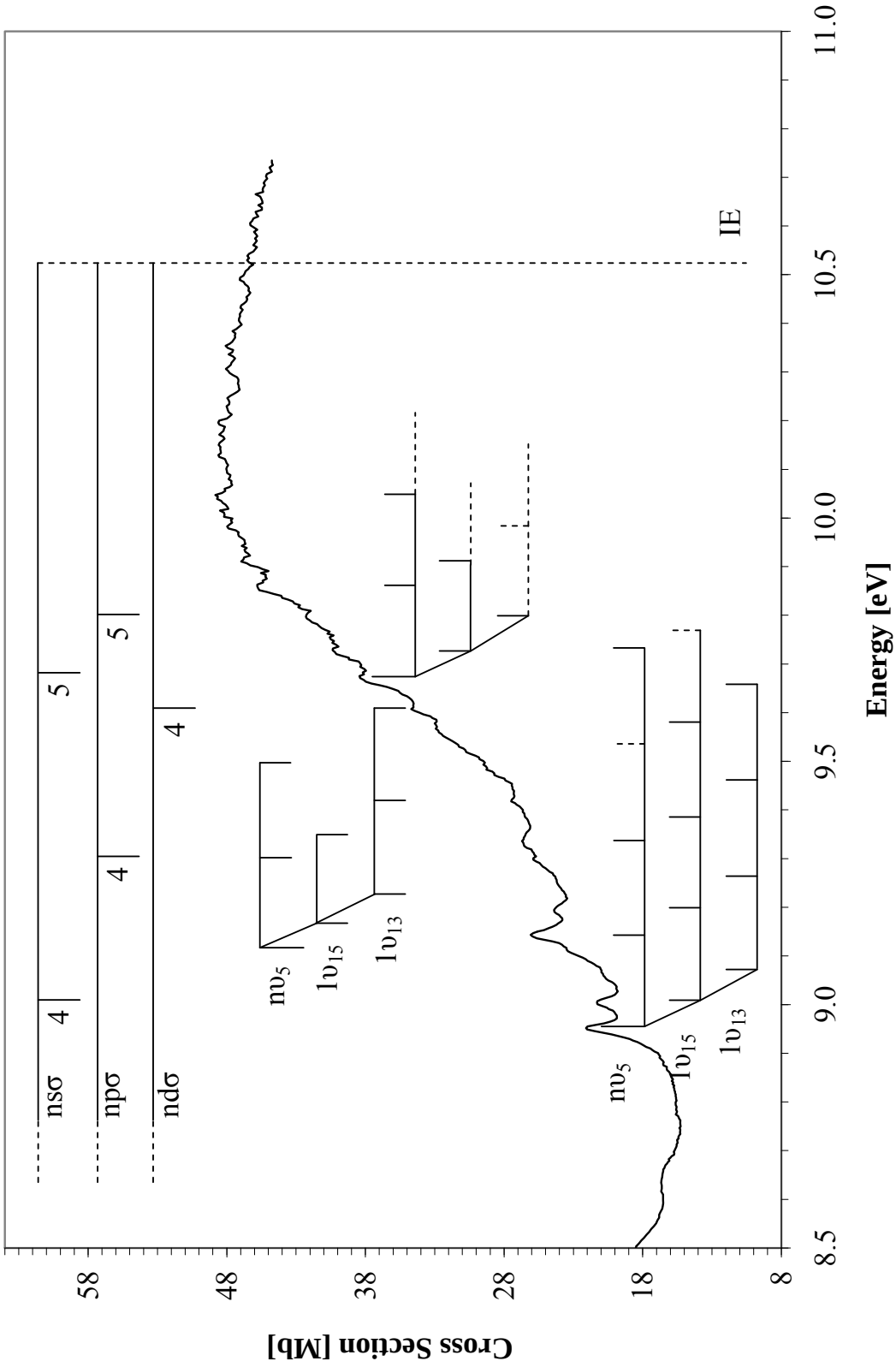

Table 2 – Calculated vertical excitation energies (TDDFT/PBE0/6-311++G**) (eV) and oscillator strengths and experimental transition energies of propionic acid for the present work.

Calculated								Experimental		Transition between
E (eV)	f_L	HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4	Mixed	E (eV)	Cross Section (Mb)	electronic states
5.96	0.0003	π*(C=O)						5.898	0.198	$1\,^1A'' \leftarrow 1\,^1A'$
7.01	0.0473	3sσ/σ*(O-H)						7.221	8.009	$2\,^1A' \leftarrow 1\,^1A'$
7.55	0.0043	3pσ/σ*(O-H)						7.773	10.955	$3\,^1A' \leftarrow 1\,^1A'$
8.10	0.0028	3pσ						7.773	10.955	$4\,^1A' \leftarrow 1\,^1A'$
8.10	0.0014		3sσ/σ*(O-H)							
8.13	0.0015	3pπ								
8.55	0.0029	3dσ						8.634	16.659	$5\,^1A' \leftarrow 1\,^1A'$
8.60	0.1035		π*(C=O)					8.486	18.572	$6\,^1A' \leftarrow 1\,^1A'$
8.75	0.0004		3pσ/σ*(O-H)							
8.81	0.0007			3sσ/σ*(O-H)						
8.89	0.0917			π*(C=O)				9.143	26.068	$7\,^1A' \leftarrow 1\,^1A'$
8.97	0.0006				π*(C=O)					
9.17	0.0003	3dπ								
9.27	0.0439	3dσ								
9.31	0.0028				3sσ/σ*(O-H)					
9.36	0.0001						HOMO-1 → 3pσ + + HOMO-2 → 3pσ/σ*(O-H)			
9.38	0.0072						HOMO-2 → 3pσ/σ*(O-H) + + HOMO-1 → 3pσ			
9.43	0.0068					π*(C=O)				
9.46	0.0094	3dπ								
9.51	0.0102						HOMO-1 → 3pπ + HOMO → 3dσ			

Table 3 – Calculated vertical excitation energies (TDDFT/PBE0/6-311++G**) (eV) and oscillator strengths and experimental transition energies of butyric acid for the present work.

Calculated							Experimental		Transition between electronic states
E (eV)	f_L	HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4	E (eV)	Cross Section (Mb)	
5.95	0.0002	π*(C=O)					5.989	0.234	$1\ ^1A'' \leftarrow 1\ ^1A'$
7.01	0.0532	3sσ/σ*(O-H)					7.229	8.680	$2\ ^1A' \leftarrow 1\ ^1A'$
7.53	0.0030	3pσ/σ*(O-H)					7.778	11.976	$3\ ^1A' \leftarrow 1\ ^1A'$
8.00	0.0005	3pπ							
8.02	0.0066	3pσ					7.778	11.976	$4\ ^1A' \leftarrow 1\ ^1A'$
8.08	0.0009		3sσ/σ*(O-H)						
8.19	0.0048	3dσ					8.486	21.662	$5\ ^1A' \leftarrow 1\ ^1A'$
8.32	0.0067			3sσ/σ*(O-H)					
8.37	0.0242		π*(C=O)						
8.67	0.1250			π*(C=O)			8.486	21.662	$8\ ^1A' \leftarrow 1\ ^1A'$
8.68	0.0047				π*(C=O)				
8.72	0.0005		3pσ/σ*(O-H)						
8.75	0.0293				3sσ/σ*(O-H)				
8.88	0.0012					π*(C=O)			
8.89	0.0002			3pσ/σ*(O-H)					
8.99	0.0028	3dπ							
9.01	0.0078	3dσ							
9.11	0.0055	3dπ							
9.11	0.0210					3sσ/σ*(O-H)			
9.13	0.0399		3pσ						

Table 4 – Calculated vertical excitation energies (TDDFT/PBE0/6-311++G**) (eV) and oscillator strengths and experimental transition energies of valeric acid for the present work.

Calculated								Experimental		Transition between
E (eV)	f_L	HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4	Mixed	E (eV)	Cross Section (Mb)	electronic states
5.95	0.0002	π*(C=O)						6.033	0.185	$1\ ^1A'' \leftarrow 1\ ^1A'$
7.01	0.0523	3sσ/σ*(O-H)						7.204	8.450	$2\ ^1A' \leftarrow 1\ ^1A'$
7.51	0.0077	3pσ/σ*(O-H)						7.862	12.581	$3\ ^1A' \leftarrow 1\ ^1A'$
7.90	0.0011	3pσ						7.862	12.581	$4\ ^1A' \leftarrow 1\ ^1A'$
7.93	0.0003	3pπ								
8.05	0.0003		3sσ/σ*(O-H)							
8.13	0.0055	3dσ								$5\ ^1A' \leftarrow 1\ ^1A'$
8.16	0.0023						HOMO-2 → 3sσ/σ*(O-H) HOMO-1 → 3pσ/σ*(O-H)	7.862	12.581	$4\ ^1A'' \leftarrow 1\ ^1A'$
8.27	0.0087		π*(C=O)							
8.46	0.0021				3sσ/σ*(O-H)					
8.49	0.0016				π*(C=O)					
8.57	0.0074		3pσ/σ*(O-H)							
8.63	0.1174			π*(C=O)				8.338	22.519	$8\ ^1A' \leftarrow 1\ ^1A'$
8.65	0.0090					π*(C=O)				
8.70	0.0065					3sσ/σ*(O-H)				
8.73	0.0142	3dσ						8.850	43.138	$10\ ^1A' \leftarrow 1\ ^1A'$
8.74	0.0087						HOMO-2 → 3pσ/σ*(O-H) HOMO-2 → 3sσ/σ*(O-H)			
8.80	0.0007	3dπ								
8.83	0.0569		3pσ							
8.85	0.0179				3pσ/σ*(O-H)					

Table 5 – Vibrational assignments in the 8.0 – 9.0 eV absorption band of propionic acid C_2H_5COOH.

Energy (eV)	Assignment	ΔE (υ_{10}) (eV)	ΔE (υ_{25}) (eV)
8.178	υ_{00}	-	-
8.195 (s) (d)	$1\upsilon_{25}$	-	0.017
8.316	$1\upsilon_{10}$	0.138	-
8.343 (s) (d)	$1\upsilon_{25}+1\upsilon_{10}$	-	-
8.446 (s) (d)	$2\upsilon_{10}$	0.130	-
8.486	$1\upsilon_{25}+2\upsilon_{10}$	-	-
8.634	$1\upsilon_{25}+3\upsilon_{10}$	-	-
8.784	$1\upsilon_{25}+4\upsilon_{10}$	-	-

(s) means peak shoulder; (d) means diffuse structure.