IDENTIFICATION OF GAS PHASE DNA BASES SPECIFIC ISOMERS VIA HIGH ACCURACY SINGLE PHOTON IONIZATION AND *AB INITIO* COMPUTATIONS

Majdi HOCHLAF

Université Gustave Eiffel

OBJECTIVES

- **Accurate determination of ionization energies** of isolated gas phase medium-sized molecules and investigation of **the vibrational structure of involved ionic states**, including their mutual vibronic couplings.
- **Treatment of tautomers, rotamers, conformers** in the ground state, after photoionization, and in competition with other intramolecular processes.
- Study of **fragmentation of the molecular cations** at low and high internal energies.
- Study of the evolution of the covalent character of **hydrogen bonding** upon substitution, i.e., examination of electronic effects (acceptor, donor, etc.)

Major questions:

→How to get medium-sized molecules in gas phase?

→What to measure?

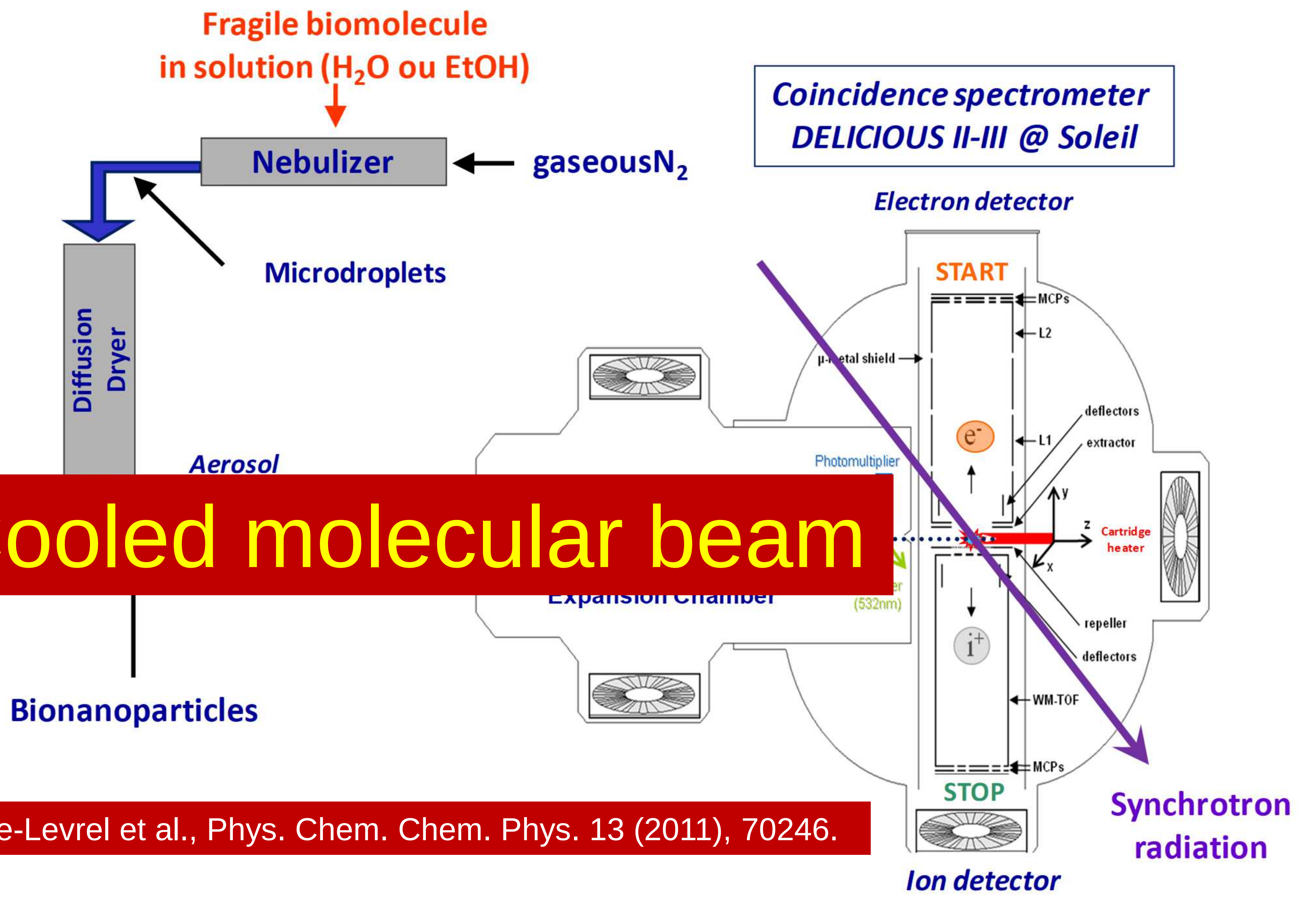
→Pb of autoionization vs. direct photoionization

→What to compute?

→How to compute accurate properties for these relatively large species

VUV SINGLE PHOTOIONIZATION OF NABS @ DESIRS BEAMLINE (SYNCHROTRON SOLEIL)

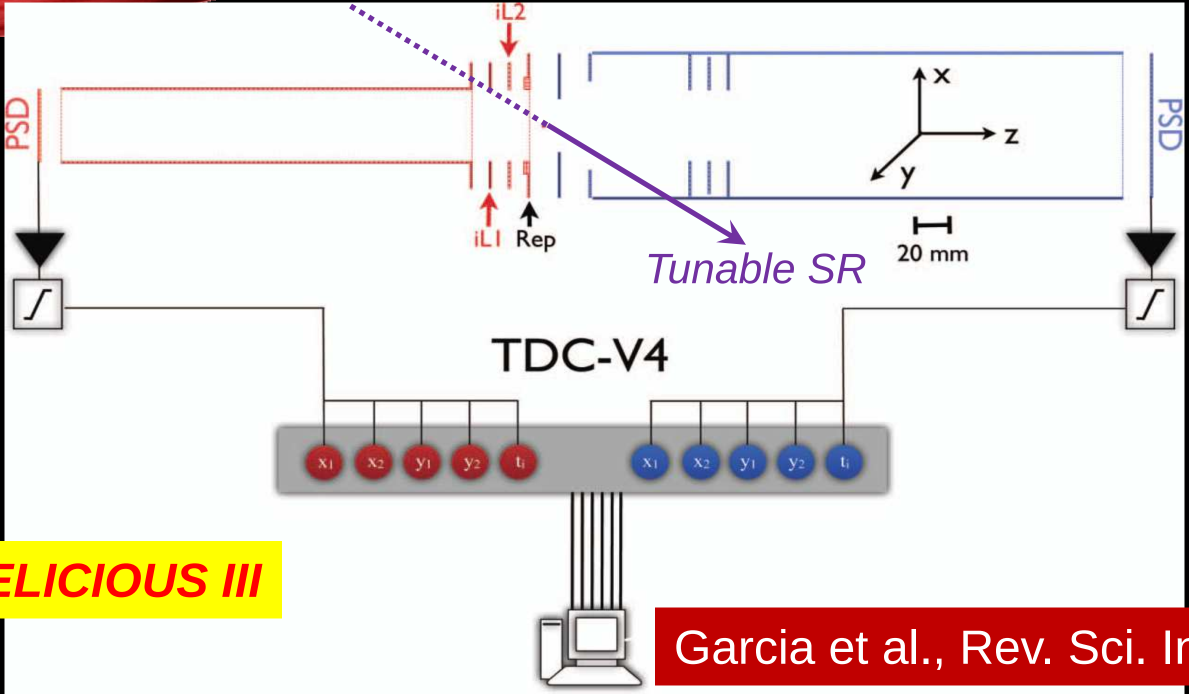
Desorption of “bionanoparticles” on a hot tip



Cooled molecular beam

Gaie-Levrel et al., Phys. Chem. Chem. Phys. 13 (2011), 70246.

Methods used: DELICIOUS III, coincidence spectroscopy, imaging



SOLEIL SYNCHROTRON

DESIRS beamline

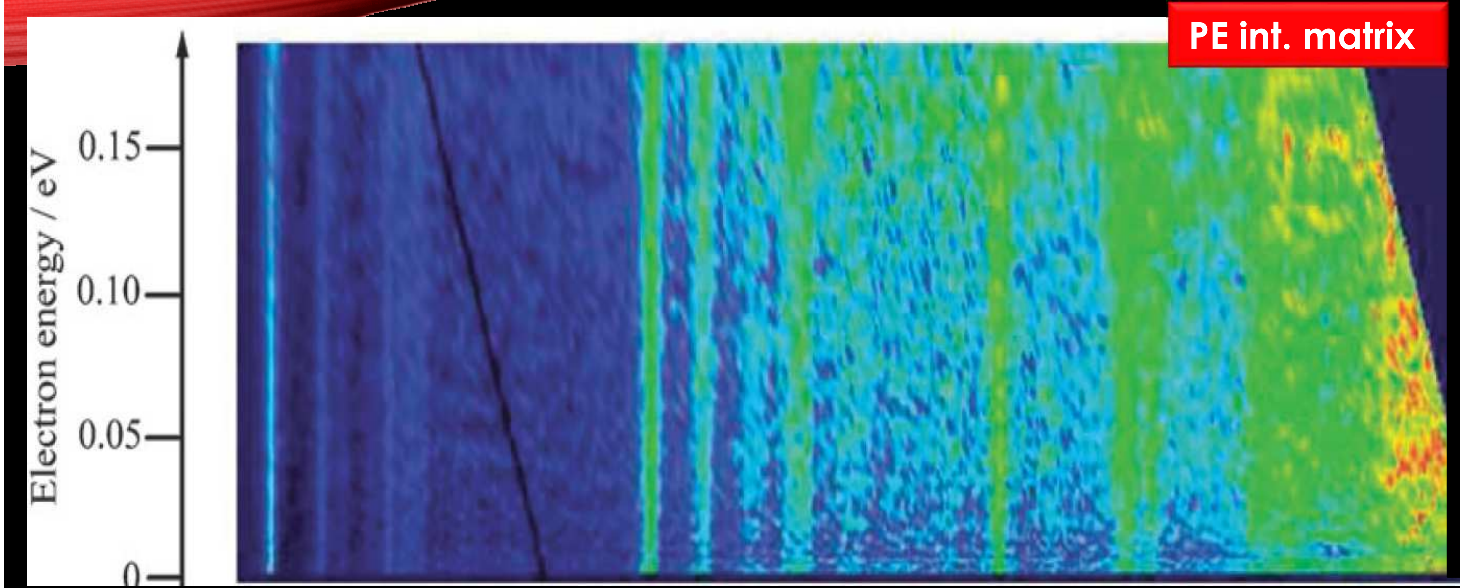
DELICIOUS III

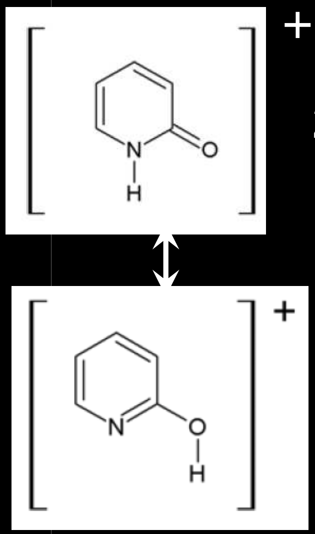
Garcia et al., Rev. Sci. Instrum. 84 (2013), 053112.

DELICIOUS III: multipurpose instrument available @ DESIRS beamline (permanent end station)

- **Jet-cooled molecules**
- **Detection of electrons and ions in coincidence , as a function of photon energy and kinetic energy released (using imaging techniques)**
- **PI mass spectrometry, PEPICO, TPEPICO**
- **High resolution (threshold) photoelectron spetroscopy (about 1 meV), TPES, Slow-PES (SPES)**

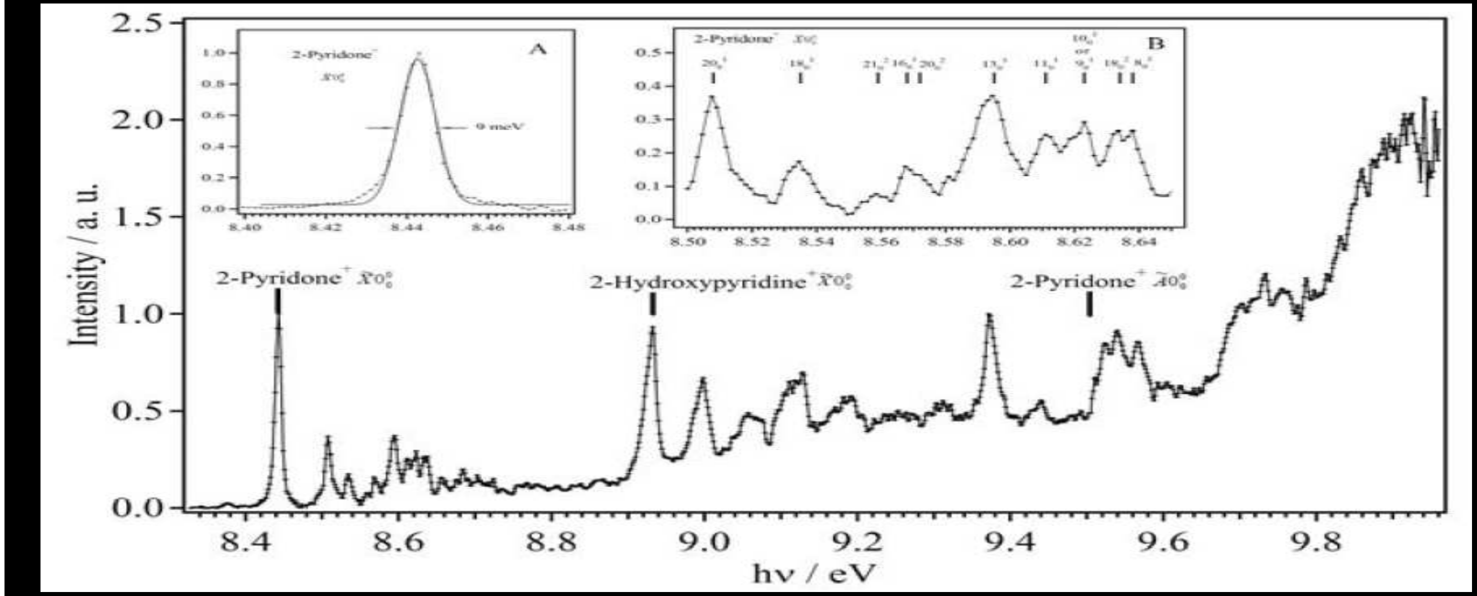
Slow PhotoElectron Spectroscopy: 2-Pyridone





2-PY$^+$

2-HP$^+$



2-Pyridone and 2-Hydroxypyridine

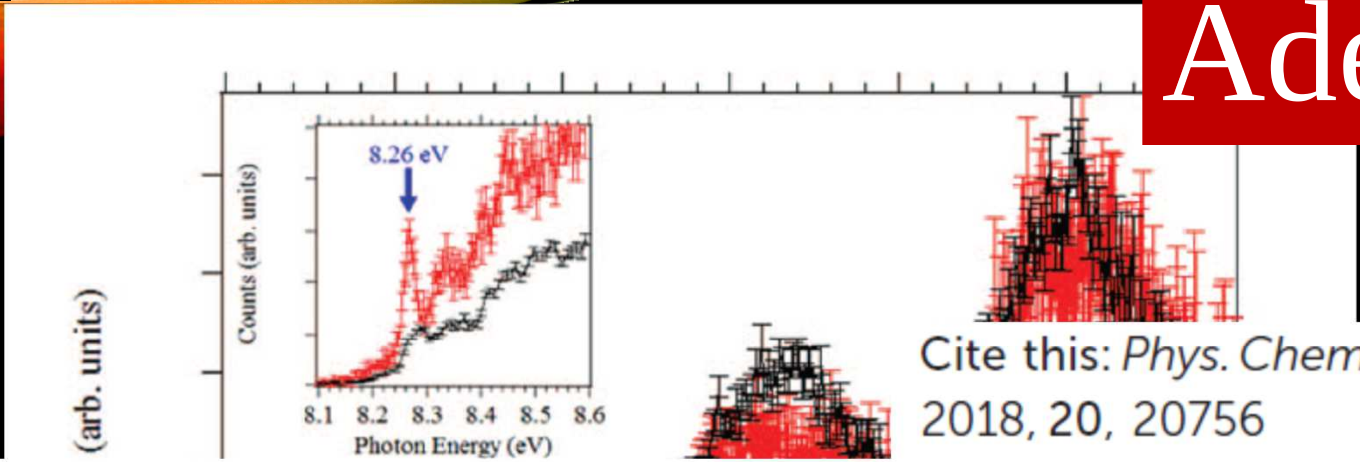
SPES

KE_{max} = 75 meV

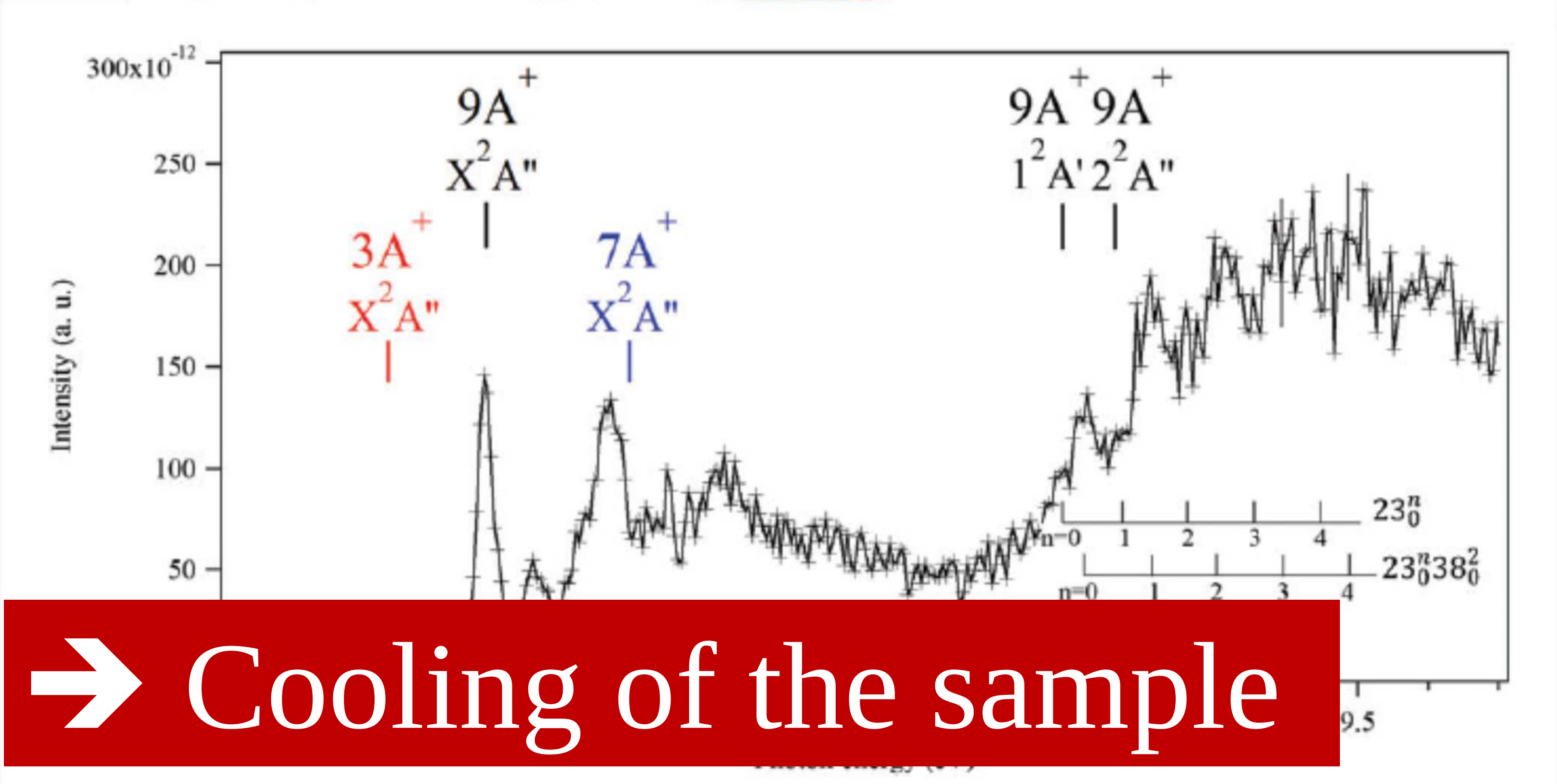
Briant et al., PRL **109**, 193401 (2012).

Poully et al., PCCP **12**, 3566 (2010).

Adenine



Cite this: *Phys. Chem. Chem. Phys.*, 2018, 20, 20756



→ Cooling of the sample

THEORETICAL COMPUTATIONS

Characterization of medium sized molecular systems

- Ground state computations: A*b initio* (MP2, CCSD(T), CCSD(T)-F12) and DFT computations using the recently developed/implemented functionals and methods: Prediction of the equilibrium structures and their energetics and vibrational spectra

Benchmarking DFT methods vs. newly implemented explicitly correlated methods

→ F12 methods: Consideration of large amount of electron correlation

→ F12➔ DFT: Extension to large molecular systems

➔MOLPRO: http://www.molpro.net

➔ GAUSSIAN: www.gaussian.com

→ Consideration of Core-Valence (CV), Relativistic effects (RS), …

- Electronic excited states: Multi configurational approaches: CASSCF, MRCI, MRCI+Q (But size inconsistency …) or EOM-CCSD for monoconfigurational electronic states

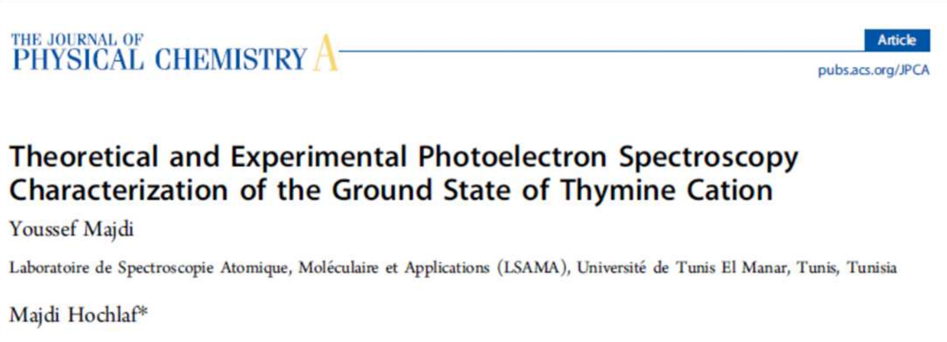
Basis sets:

→Standard methods: aug cc-pVXZ (X > 4 or X = CBS), Dunning and co-workers) + (R)CCSD(T) or CASSCF/MRCI

→Explicitly correlated methods: aug-cc-pVXZ (X=3), cc-pVTZ-F12 (To be used with care, Peterson et al.) + (R)CCSD(T)-F12

→ Efficient composite scheme for computation of IEs of medium sized molecular systems

THYMINE



THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

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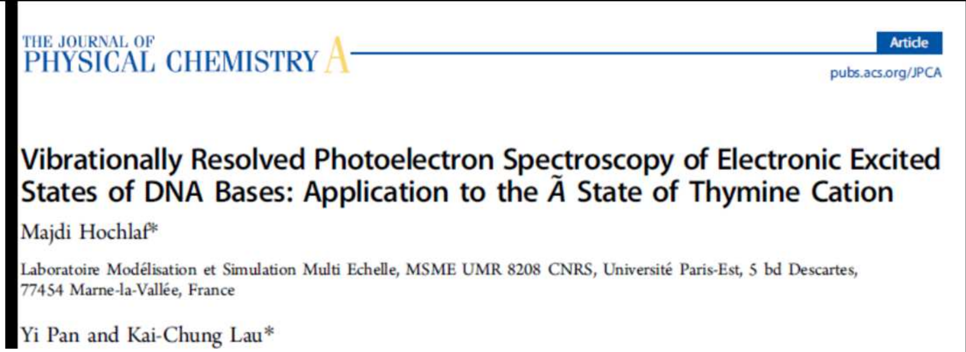
Theoretical and Experimental Photoelectron Spectroscopy Characterization of the Ground State of Thymine Cation

Youssef Majdi

Laboratoire de Spectroscopie Atomique, Moléculaire et Applications (LSAMA), Université de Tunis El Manar, Tunis, Tunisia

Majdi Hochlaf*



THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

Vibrationally Resolved Photoelectron Spectroscopy of Electronic Excited States of DNA Bases: Application to the $\tilde{A}$ State of Thymine Cation

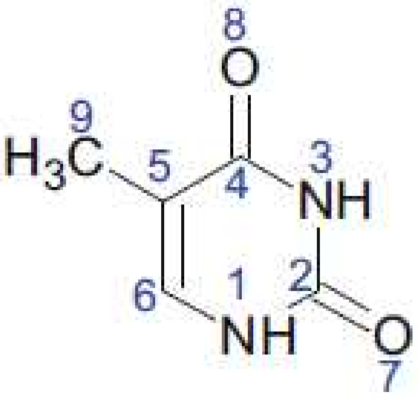
Majdi Hochlaf*

Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, Université Paris-Est, 5 bd Descartes, 77454 Marne-la-Vallée, France

Yi Pan and Kai-Chung Lau*

frontiers in Astronomy and Space Sciences

ORIGINAL RESEARCH
published: 14 October 2021
doi: 10.3389/fspas.2021.757007



Thymine (T)

Identification of DNA Bases and Their Cations in Astrochemical Environments: Computational Spectroscopy of Thymine as a Test Case

Yage Zhao[1], *Majdi Hochlaf*[2] *and Malgorzata Biczysko*[1]*

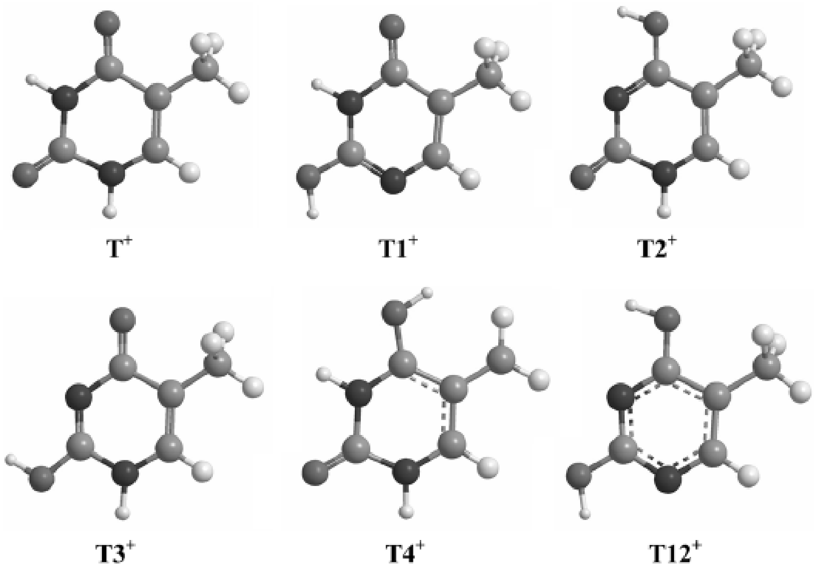
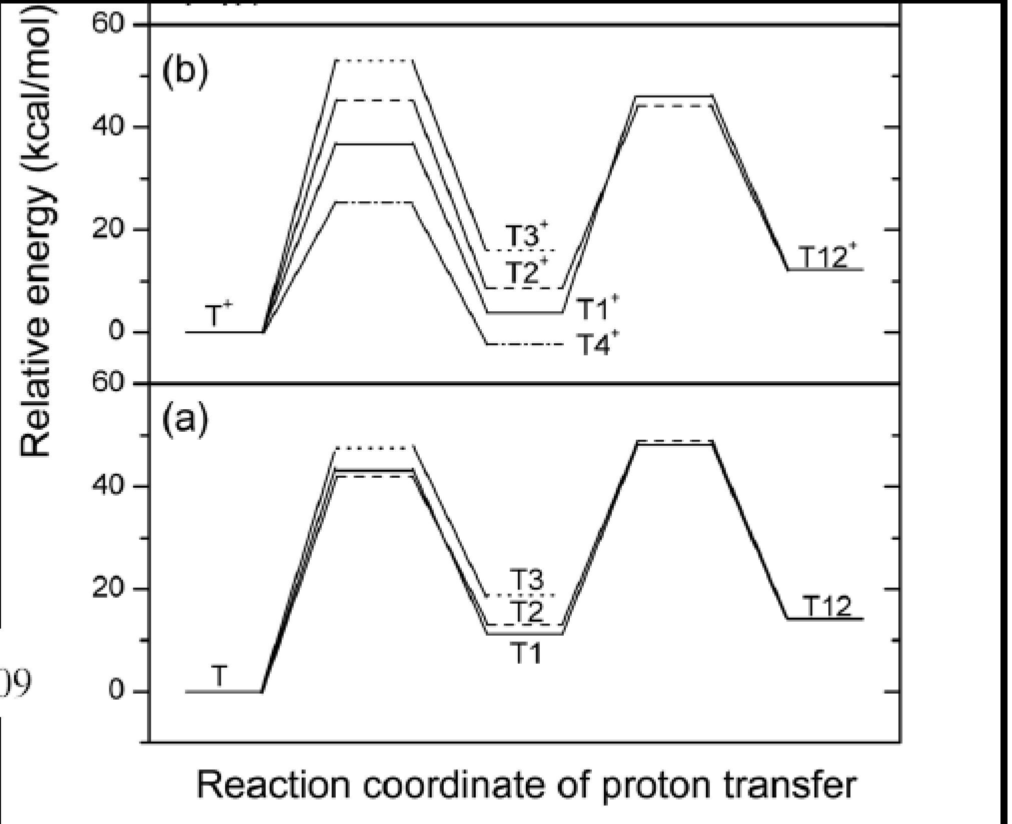


Figure 2. The structures of the tautomers of thymine radical cation optimized at the B3LYP/6-311++G(d,p) level.

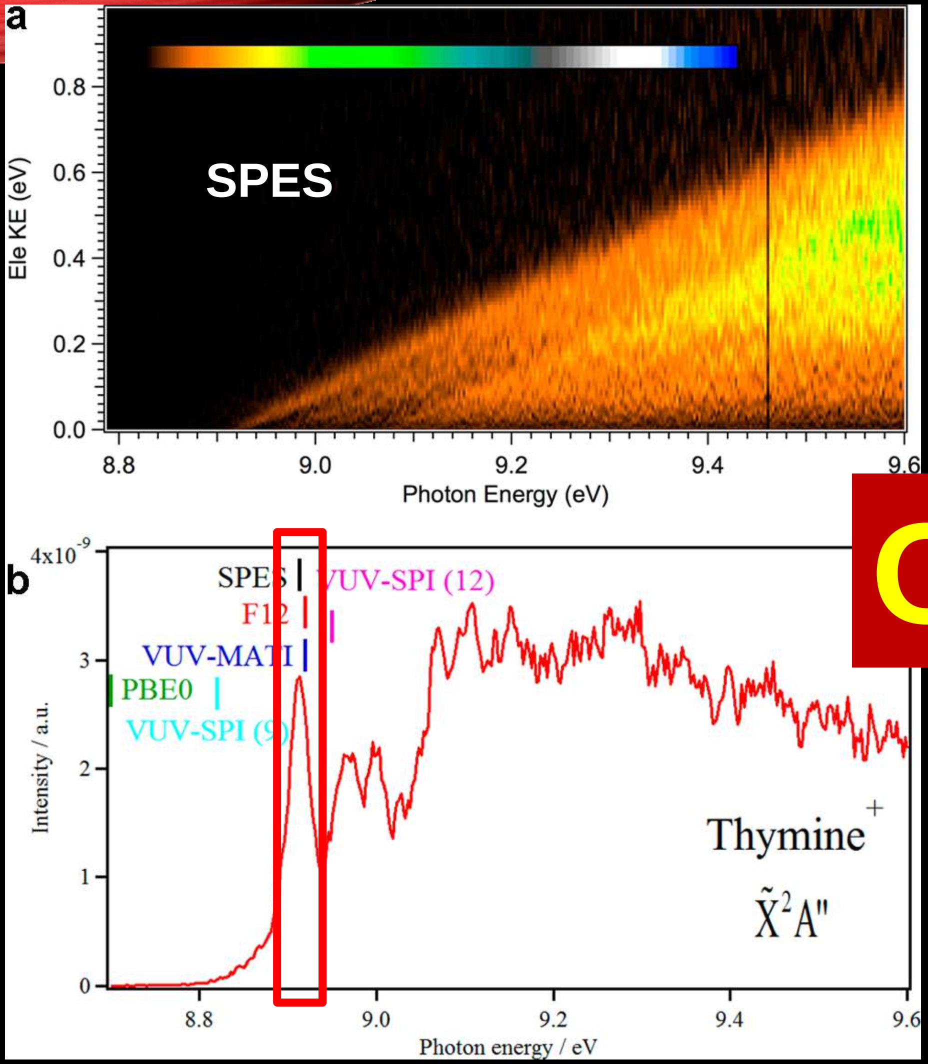
Nam Joon Kim

Bull. Korean Chem. Soc. **2006**, Vol. 27, No. 7 1009

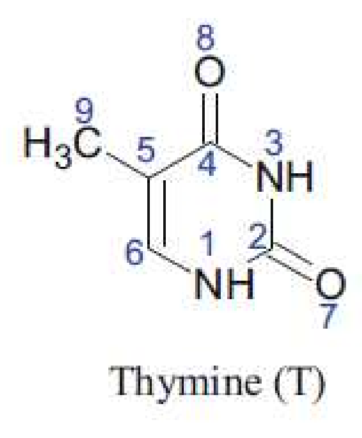
Neutral	$\Delta E_0{}^b$	kc
T	0.00	
T1	11.19	
T2	13.08	
T3	18.76	
T12	14.17	



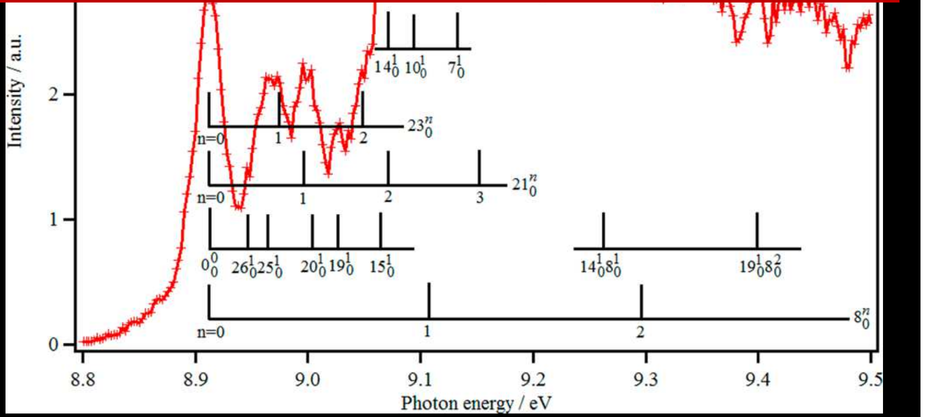
Thymine $^+$ - cation ground state



SOLEIL



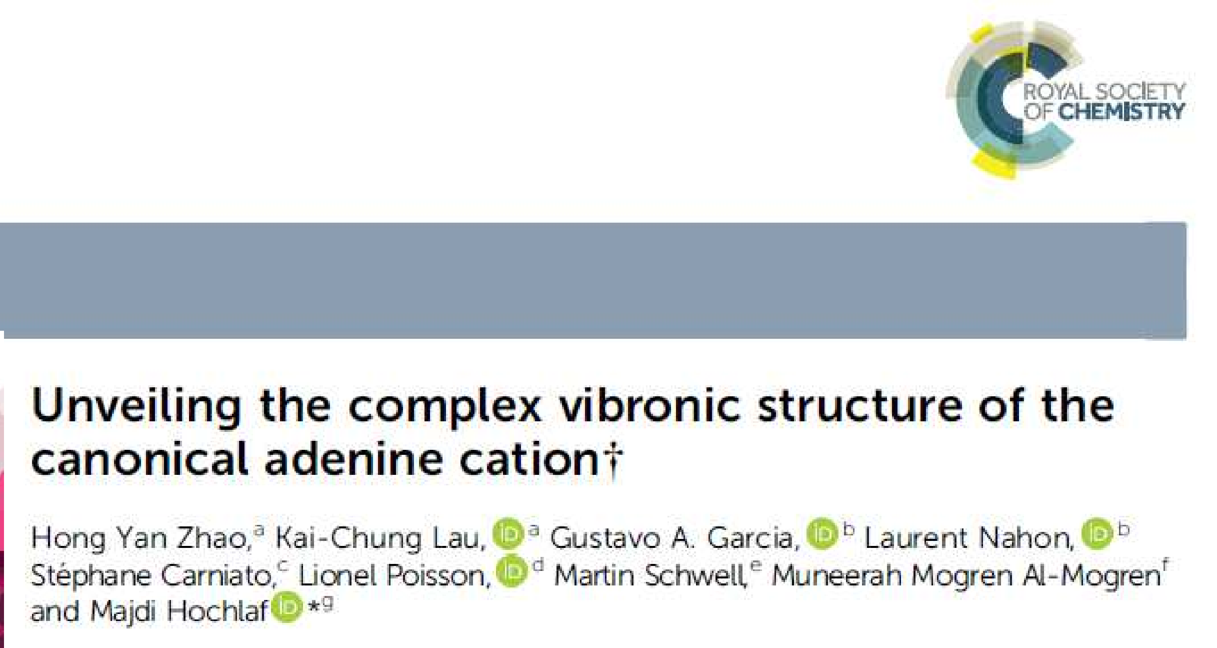
One tautomer



Theo.: **F12** = (R)CCSD(T)-F12/cc-pVTZ-F12+ZPVE
PBE0 (DFT) = PBE0/aug-cc-pVDZ+ZPVE
Expt.: VUV-SPI, VUV-SPI, VUV MATI, SPES

Majdi et al., JPC. A (2015)

ADENINE

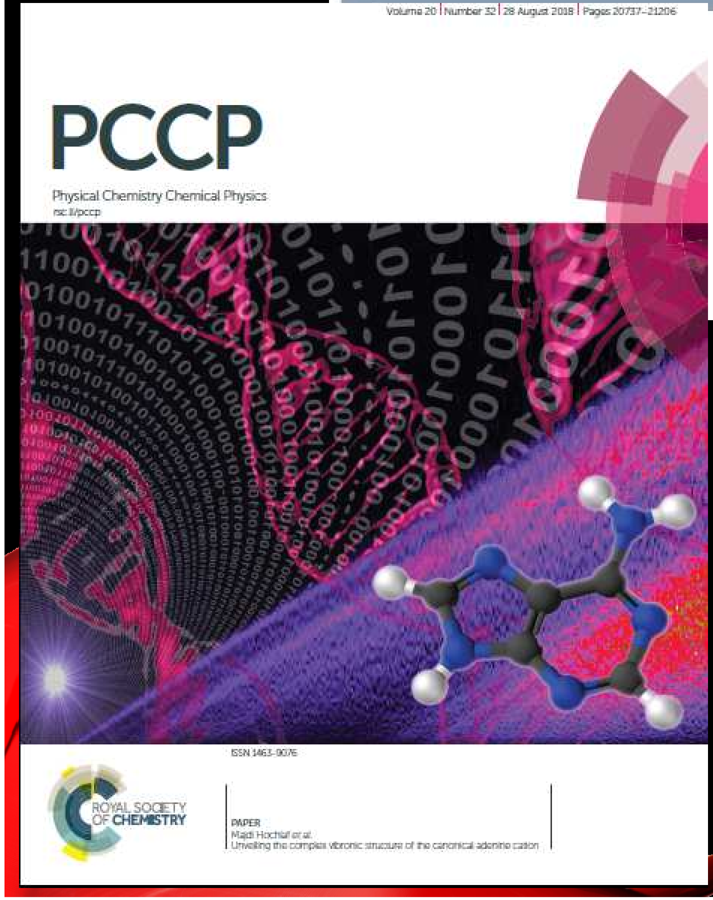


PCCP

PAPER

Unveiling the complex vibronic structure of the canonical adenine cation†

Hong Yan Zhao,[a] Kai-Chung Lau,[a] Gustavo A. Garcia,[b] Laurent Nahon,[b] Stéphane Carniato,[c] Lionel Poisson,[d] Martin Schwell,[e] Muneerah Mogren Al-Mogren[f] and Majdi Hochlaf*[g]



Volume 20 | Number 32 | 28 August 2018 | Pages 20737–21206

PCCP

Physical Chemistry Chemical Physics
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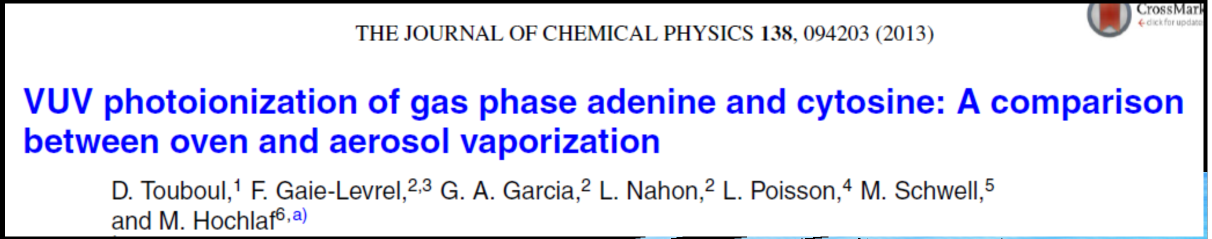
ISSN 1463-9076

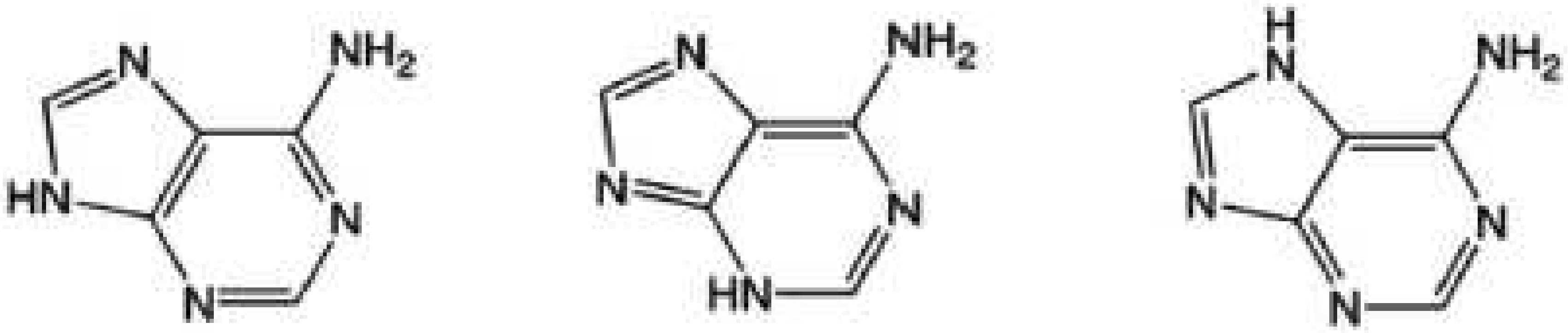
PAPER
Majdi Hochlaf et al.
Unveiling the complex vibronic structure of the canonical adenine cation



THE JOURNAL OF CHEMICAL PHYSICS 138, 094203 (2013)

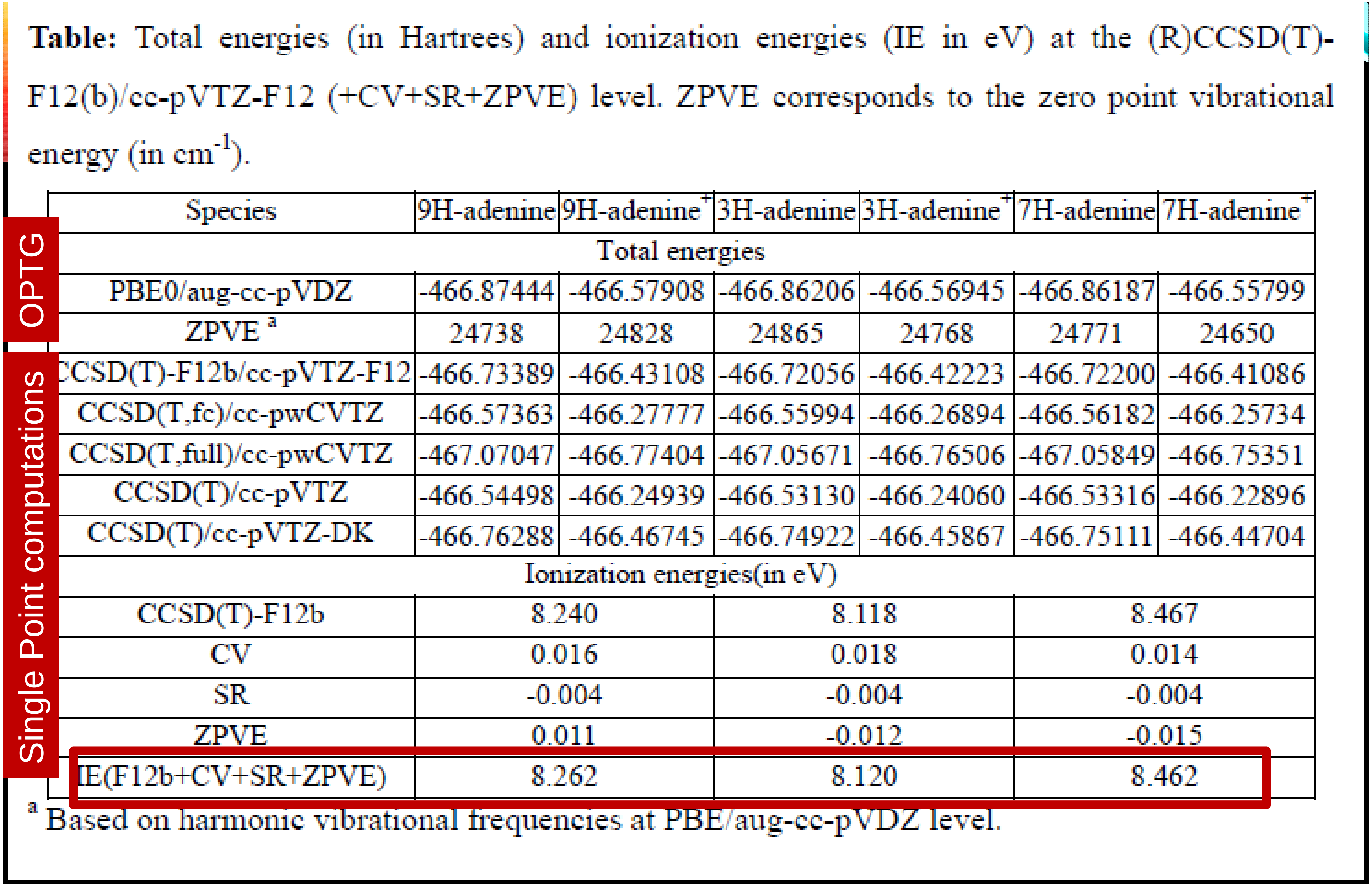
VUV photoionization of gas phase adenine and cytosine: A comparison between oven and aerosol vaporization

D. Touboul,[1] F. Gaie-Levrel,[2,3] G. A. Garcia,[2] L. Nahon,[2] L. Poisson,[4] M. Schwell,[5] and M. Hochlaf[6,a)]



9H-adenine (9A) **3H-adenine (3A)** **7H-adenine (7A)**

Scheme 1 Structures of 9*H*-adenine, 3*H*-adenine and 7*H*-adenine. Between parentheses, we give the symbols used for their designation in the present study. For common atom numbering, please refer to the ESI.†



OPTG

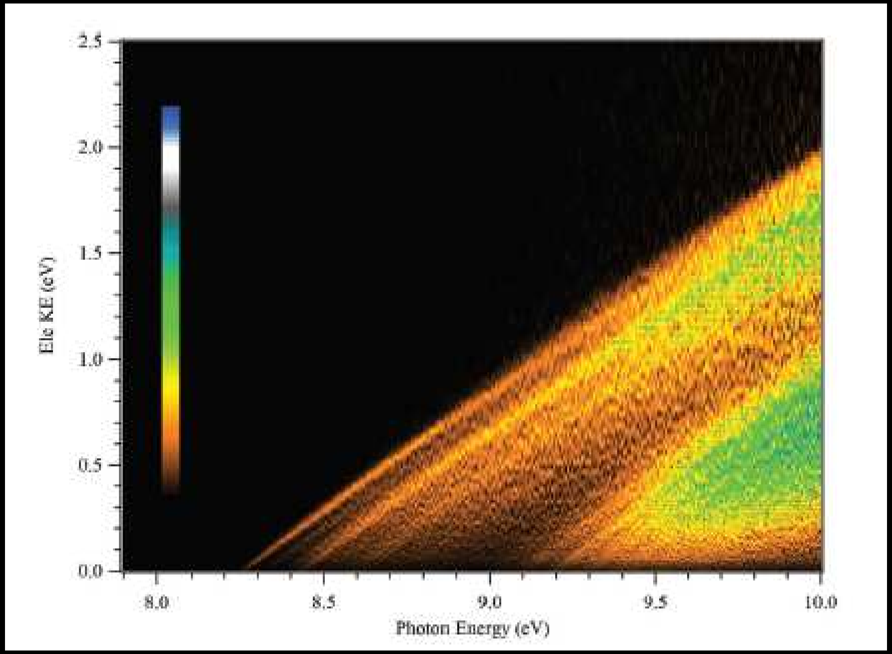
Single Point computations

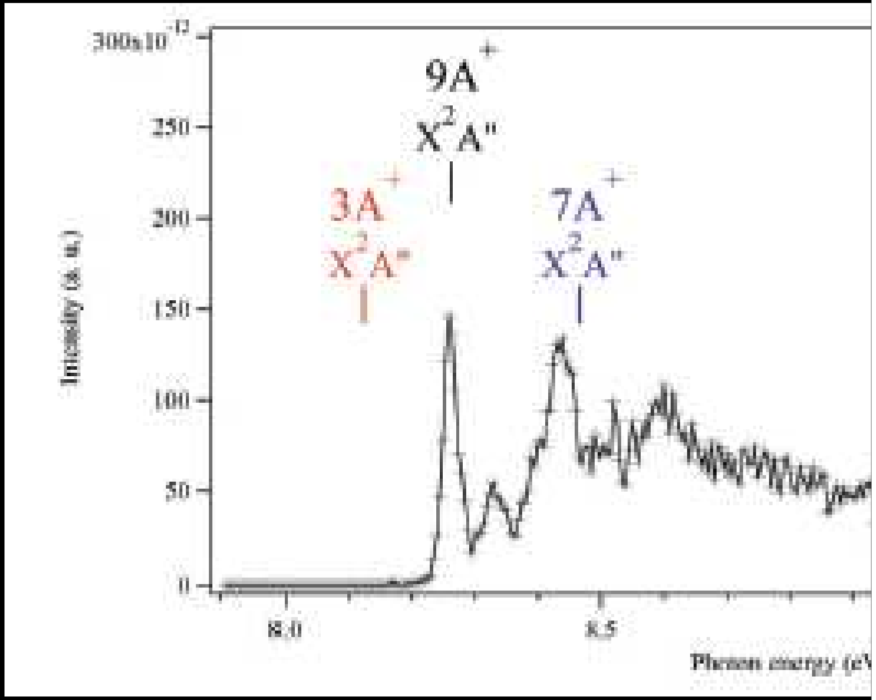
Table: Total energies (in Hartrees) and ionization energies (IE in eV) at the (R)CCSD(T)-F12(b)/cc-pVTZ-F12 (+CV+SR+ZPVE) level. ZPVE corresponds to the zero point vibrational energy (in cm^{-1}).

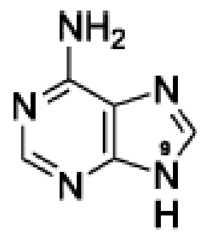
Species	9H-adenine	9H-adenine$^+$	3H-adenine	3H-adenine$^+$	7H-adenine	7H-adenine$^+$
Total energies						
PBE0/aug-cc-pVDZ	-466.87444	-466.57908	-466.86206	-466.56945	-466.86187	-466.55799
ZPVE [a]	24738	24828	24865	24768	24771	24650
CCSD(T)-F12b/cc-pVTZ-F12	-466.73389	-466.43108	-466.72056	-466.42223	-466.72200	-466.41086
CCSD(T,fc)/cc-pwCVTZ	-466.57363	-466.27777	-466.55994	-466.26894	-466.56182	-466.25734
CCSD(T,full)/cc-pwCVTZ	-467.07047	-466.77404	-467.05671	-466.76506	-467.05849	-466.75351
CCSD(T)/cc-pVTZ	-466.54498	-466.24939	-466.53130	-466.24060	-466.53316	-466.22896
CCSD(T)/cc-pVTZ-DK	-466.76288	-466.46745	-466.74922	-466.45867	-466.75111	-466.44704
Ionization energies(in eV)						
CCSD(T)-F12b	8.240		8.118		8.467	
CV	0.016		0.018		0.014	
SR	-0.004		-0.004		-0.004	
ZPVE	0.011		-0.012		-0.015	
IE(F12b+CV+SR+ZPVE)	8.262		8.120		8.462	

[a] Based on harmonic vibrational frequencies at PBE/aug-cc-pVDZ level.

Spectroscopy of a unique tautomer of Adenine$^+$

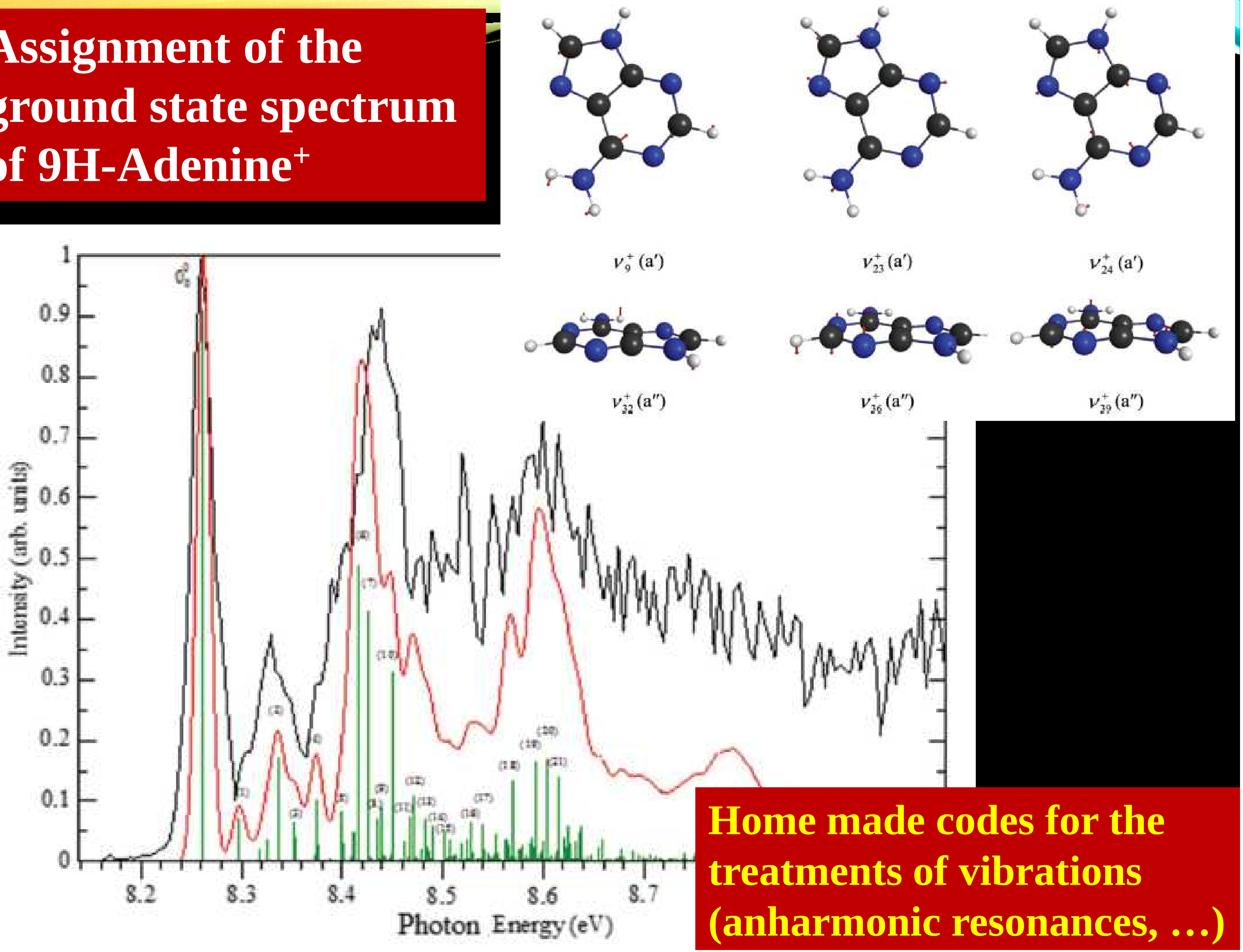






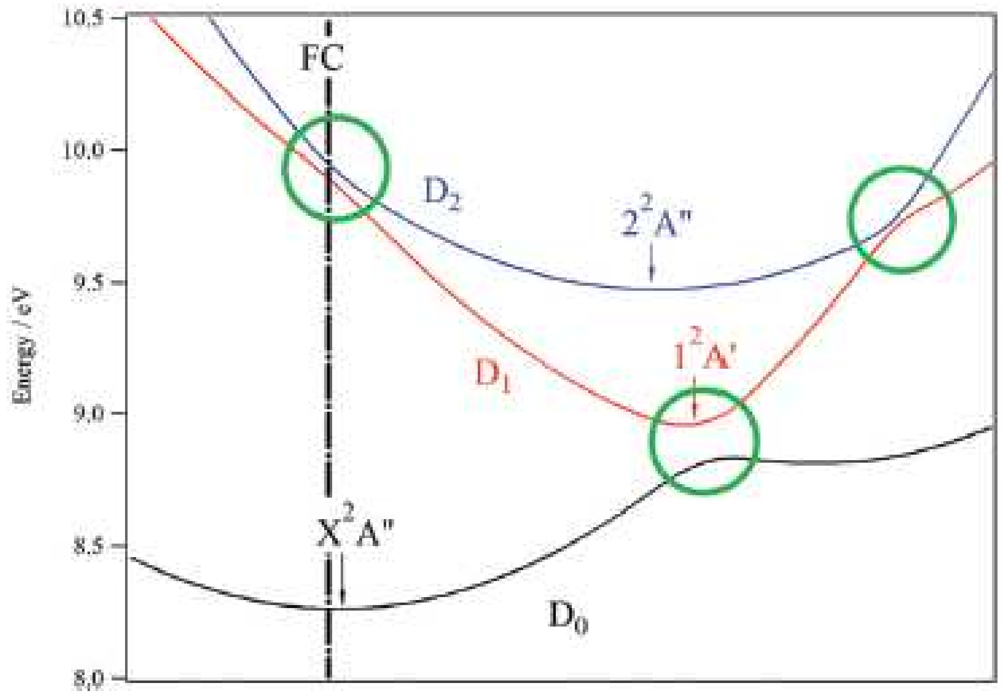
9H – amino

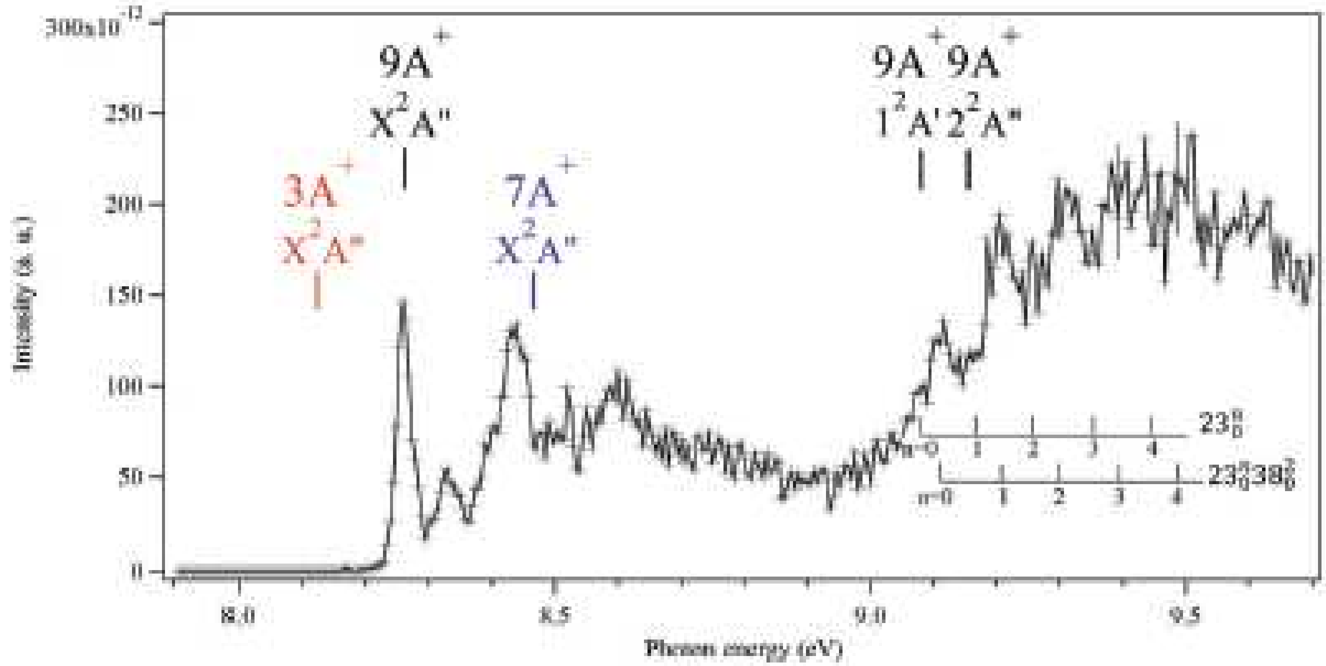
Assignment of the ground state spectrum of 9H-Adenine$^+$



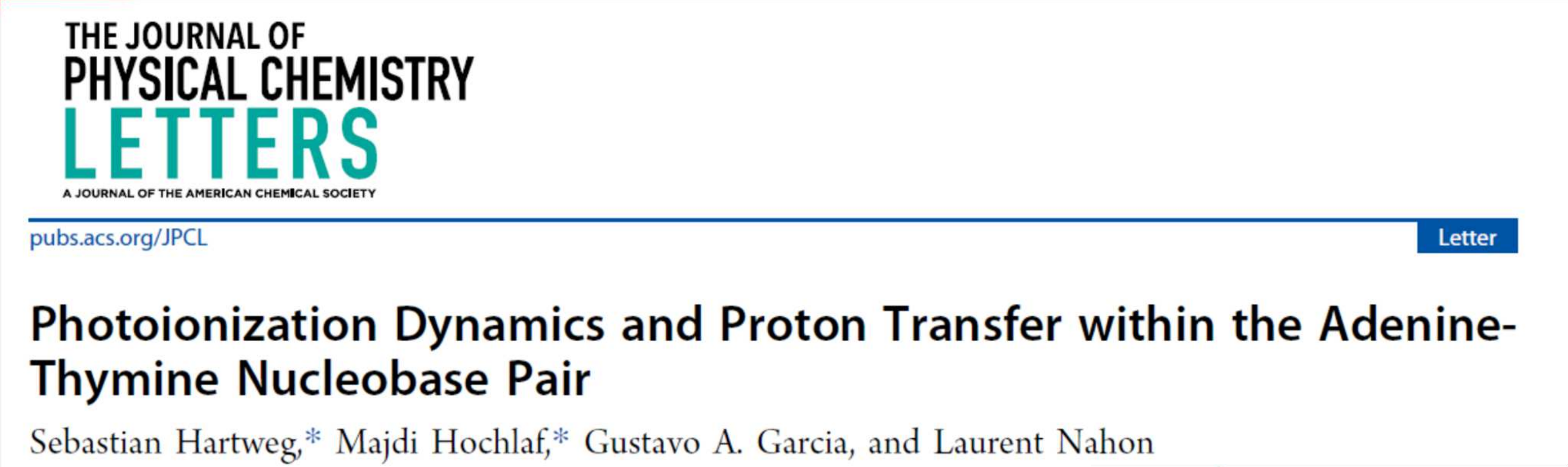
Home made codes for the treatments of vibrations (anharmonic resonances, …)

Electronic excited states of 9H-Adenine$^+$





ADENINE - THYMINE



THE JOURNAL OF
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Letter

Photoionization Dynamics and Proton Transfer within the Adenine-Thymine Nucleobase Pair

Sebastian Hartweg,* Majdi Hochlaf,* Gustavo A. Garcia, and Laurent Nahon

✓ Cite This: *J. Phys. Chem. Lett.* 2023, 14, 3698–3705

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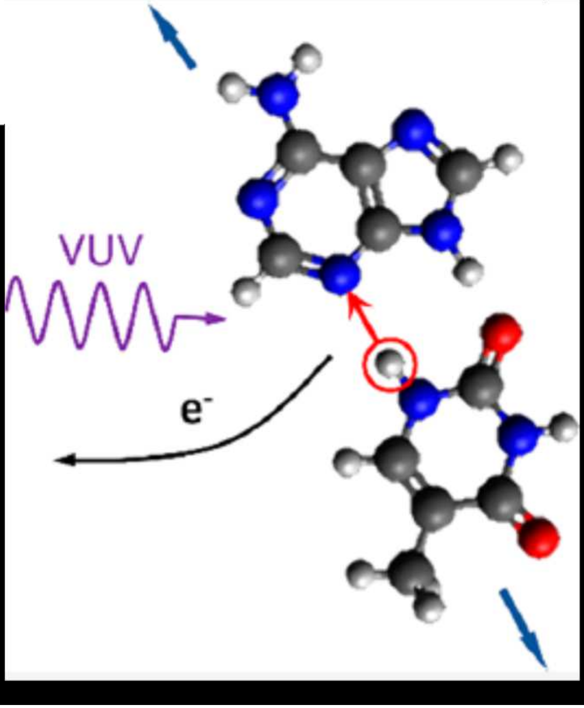
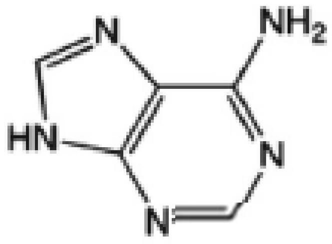
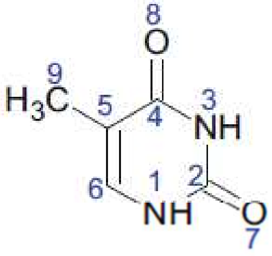
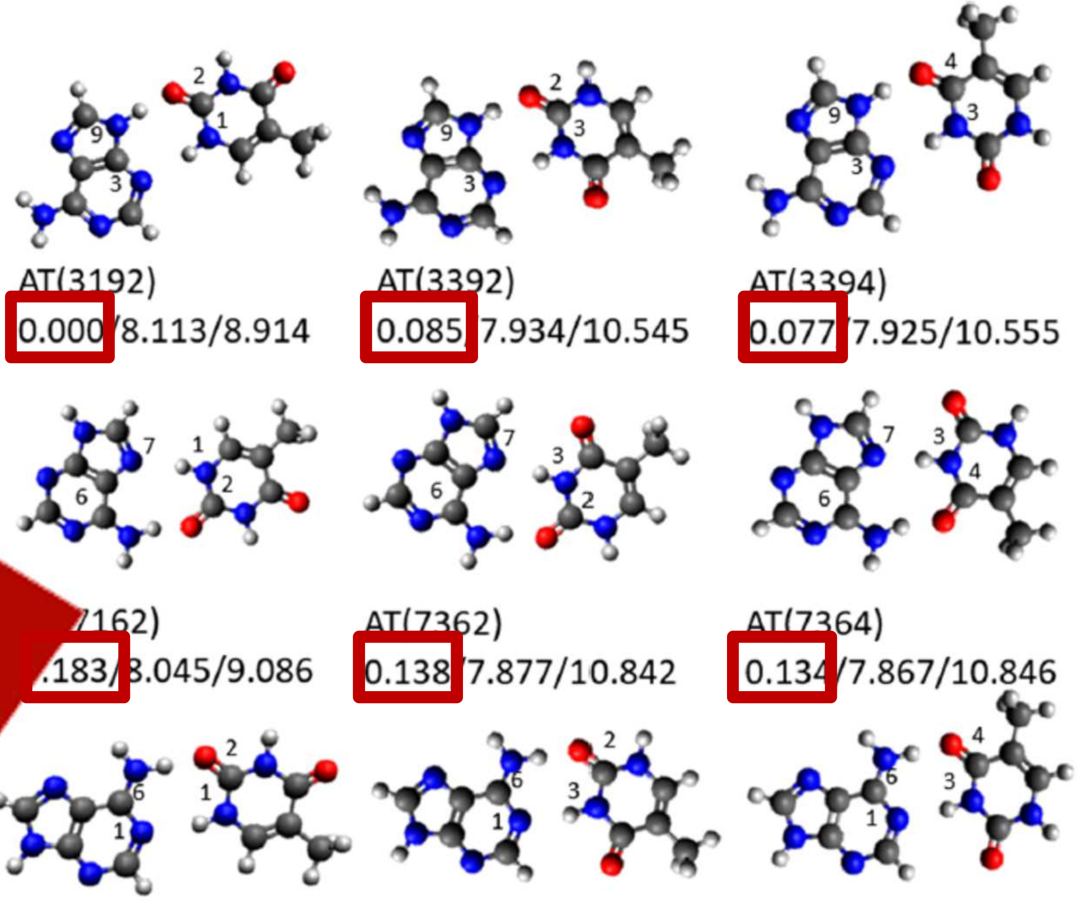




9H-adenine (9A)



Thymine (T)



AT(3192)
0.000/8.113/8.914

AT(3392)
0.085/7.934/10.545

AT(3394)
0.077/7.925/10.555

7162)
.183/3.045/9.086

AT(7362)
0.138/7.877/10.842

AT(7364)
0.134/7.867/10.846

AT(1162)
0.130/8.065/8.778

AT(1362)
0.164/7.897/10.455

AT(1364)
0.160/7.885/10.459

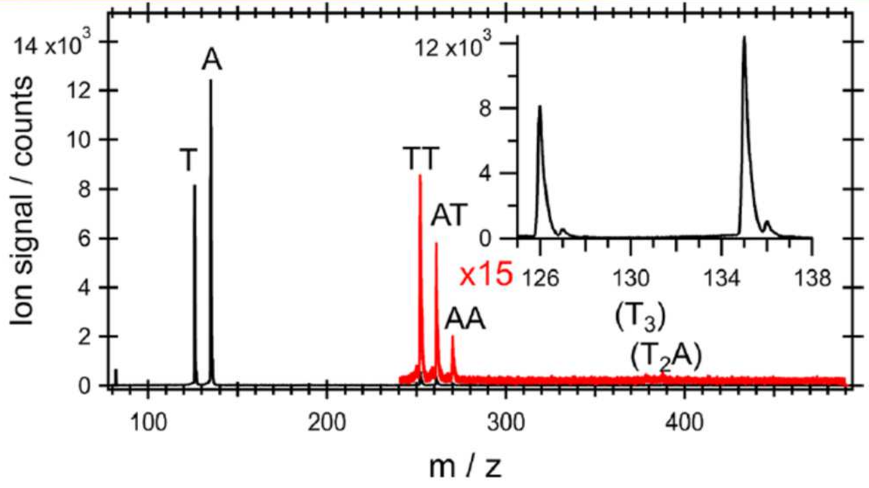


Figure 1. Representative mass spectrum of species in the molecular beam obtained while scanning the photon energy from 8 to 10 eV. Only trace amounts of trimers T_3 and T_2A can be observed.

$$A \rightarrow A^{+} \quad m/z\ 135/136 \tag{1}$$

$$AT \rightarrow T + A^{+} \quad m/z\ 135 \tag{2}$$

$$AA \rightarrow A + A^{+} \quad m/z\ 135 \tag{3}$$

$$AT \rightarrow T(-H) + AH^{+} \quad m/z\ 136 \tag{4}$$

$$AA \rightarrow A(-H) + AH^{+} \quad m/z\ 136 \tag{5}$$

$$T \rightarrow T^{+} \quad m/z\ 126/127 \tag{6}$$

$$AT \rightarrow A + T^{+} \quad m/z\ 126 \tag{7}$$

$$TT \rightarrow T + T^{+} \quad m/z\ 126 \tag{8}$$

$$AT \rightarrow A(-H) + TH^{+} \quad m/z\ 127 \tag{9}$$

$$TT \rightarrow T(-H) + TH^{+} \quad m/z\ 127 \tag{10}$$

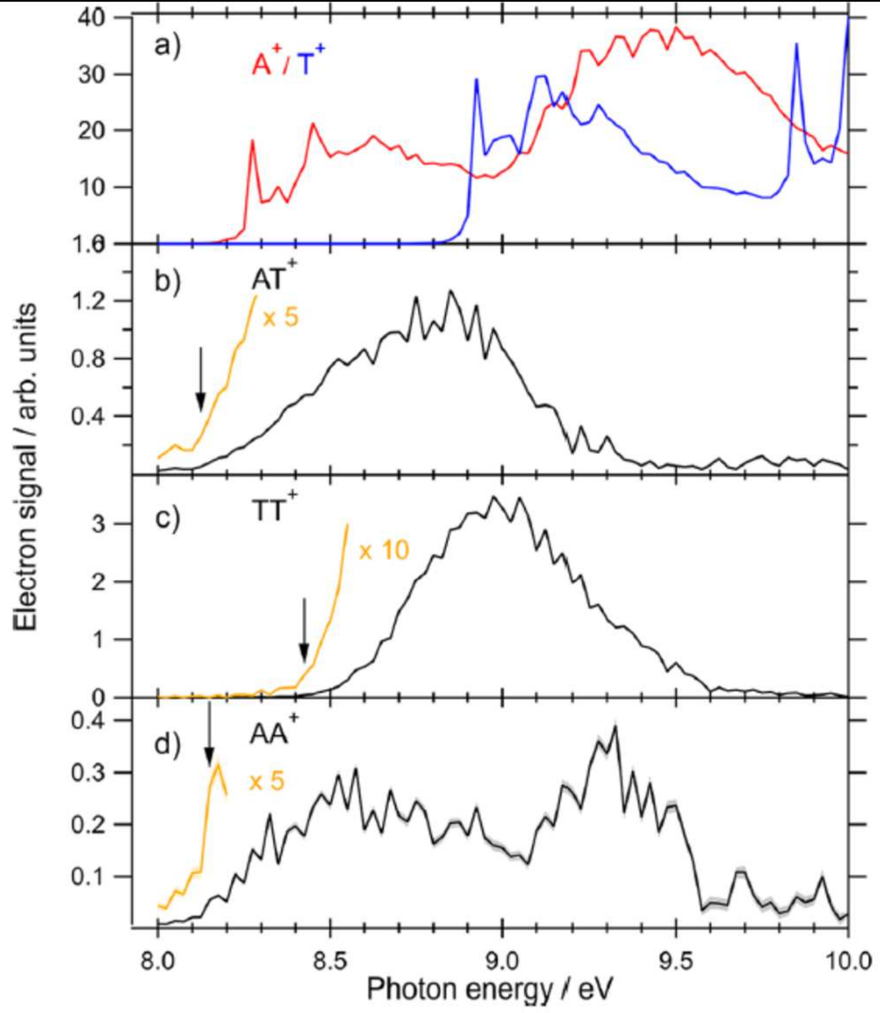


Figure 2. TPES of (a) adenine and thymine (red and blue lines, respectively), (b) the adenine-thymine heterodimer, and the (c) thymine and (d) adenine dimers.

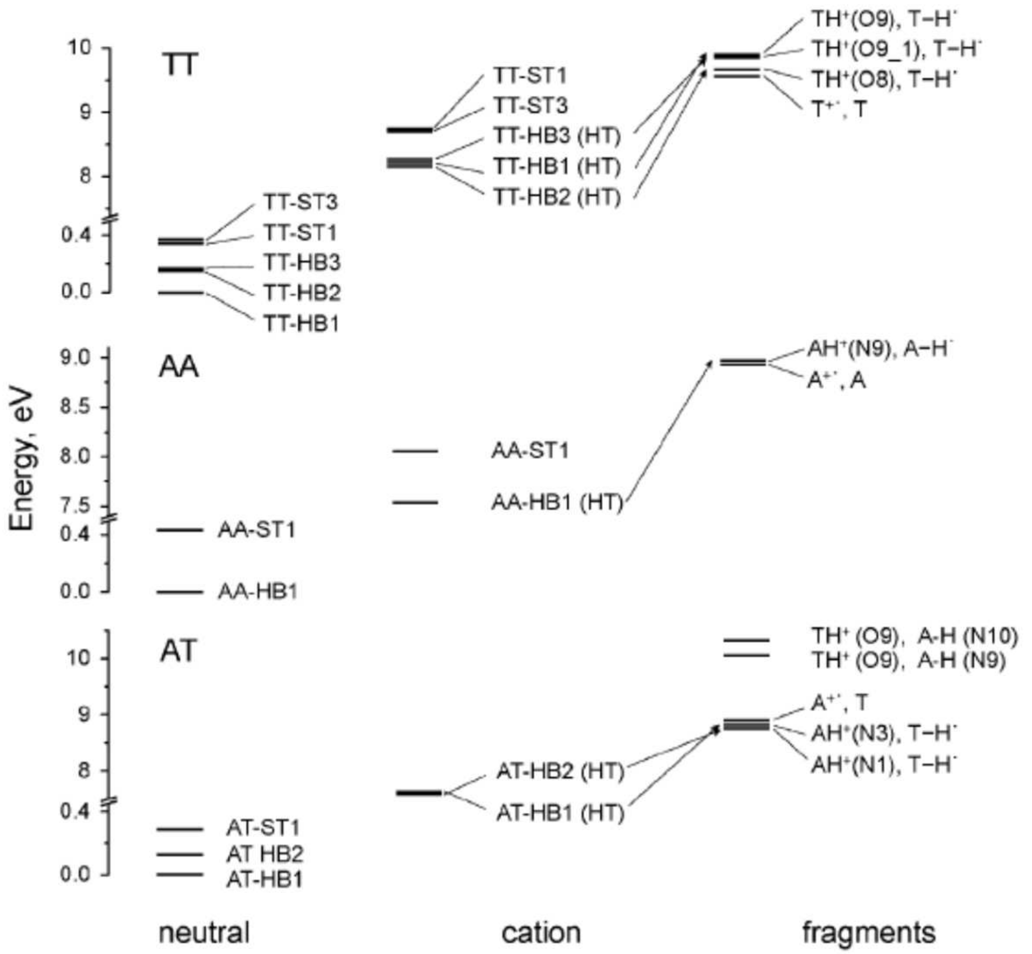


Fig. 13 Relative energies of the ionized dimers and the dissociation products with respect to the lowest energy neutral dimer for each system (TT, AA and AT). The energies are computed with ωB97X-D/6-311 + + G(2df,2dp)//ωB97X-D/6-31 + G(d,p) and include ZPEs. The arrows indicate the channels for direct dissociation of the cationic H-transferred h-boned dimers.

Krylov *et al.*
The effect of π-stacking, H-bonding and electrostatic interactions on the ionization energies of nucleic acid bases

Phys. Chem. Chem. Phys., 2010, **12**, 2292–2307

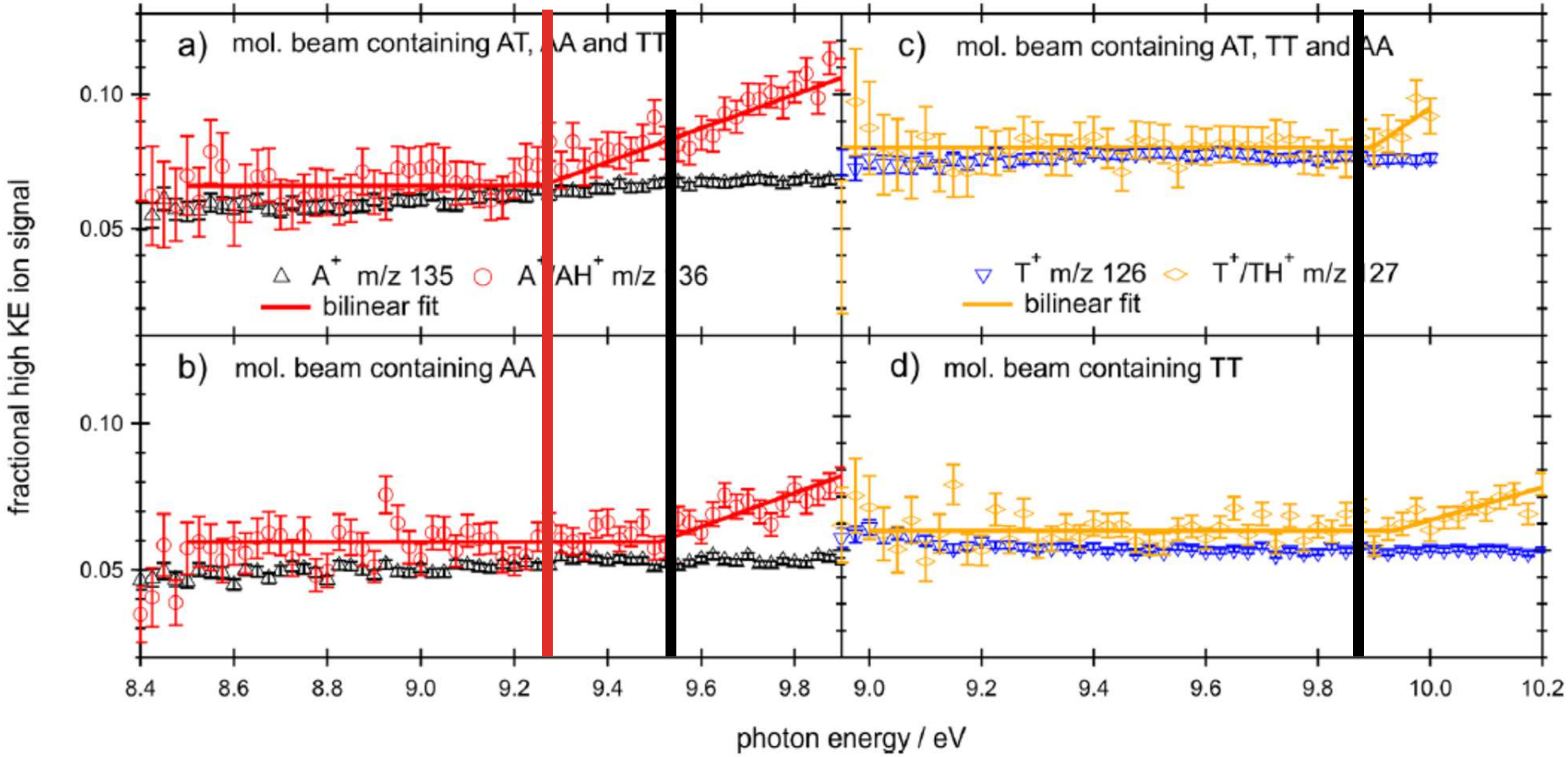


Figure 3. Fractional contributions of high-kinetic energy ions to the total ion signal of a given m/z as a function of the photon energy for a KER threshold fixed at 30 meV. (a and c) Data obtained for mixed molecular beams containing AT, AA, and TT clusters and (b and d) data obtained for pure molecular beams containing either pure A and its clusters or pure T and its clusters but no AT pairs, respectively.

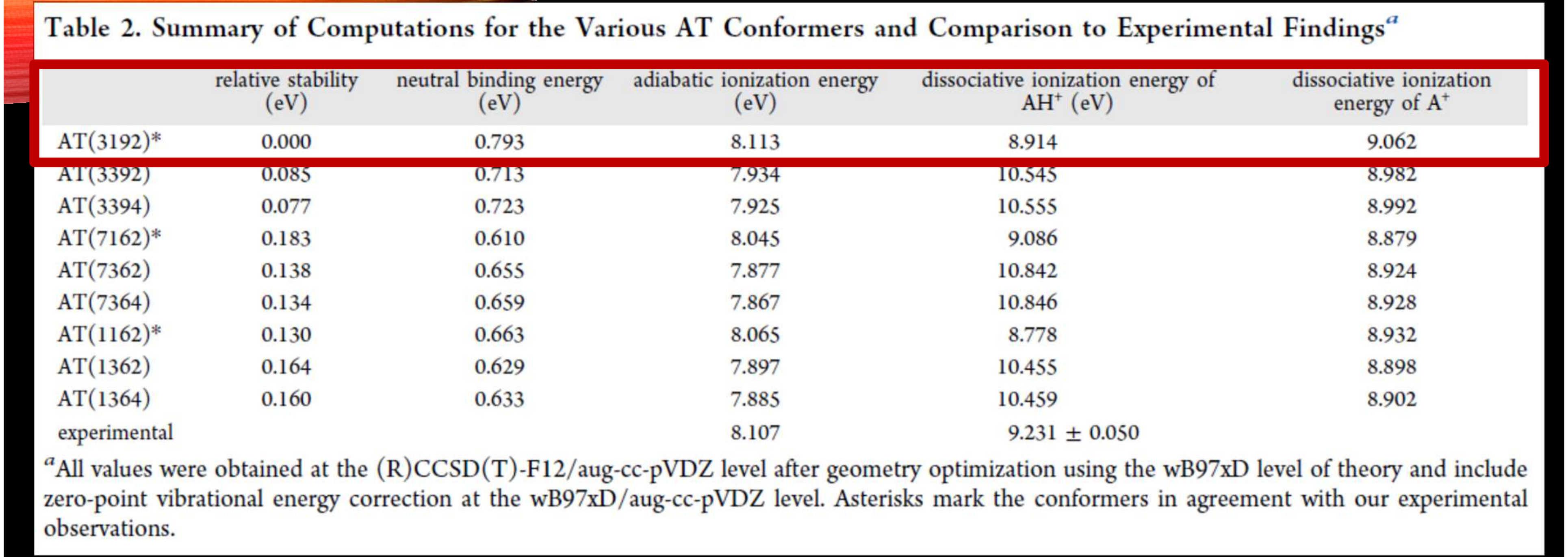
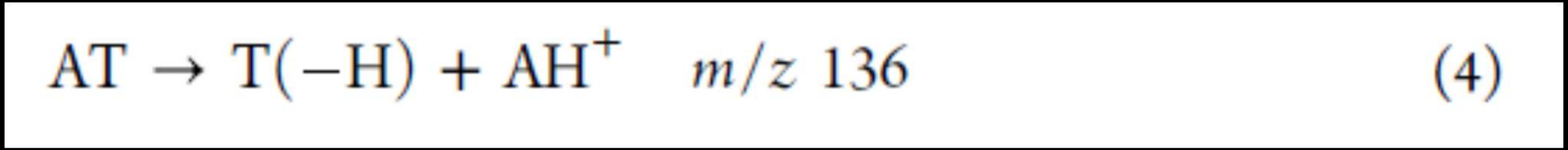


Table 2. Summary of Computations for the Various AT Conformers and Comparison to Experimental Findings[a]

	relative stability (eV)	neutral binding energy (eV)	adiabatic ionization energy (eV)	dissociative ionization energy of AH^+ (eV)	dissociative ionization energy of A^+
AT(3192)*	0.000	0.793	8.113	8.914	9.062
AT(3392)	0.085	0.713	7.934	10.545	8.982
AT(3394)	0.077	0.723	7.925	10.555	8.992
AT(7162)*	0.183	0.610	8.045	9.086	8.879
AT(7362)	0.138	0.655	7.877	10.842	8.924
AT(7364)	0.134	0.659	7.867	10.846	8.928
AT(1162)*	0.130	0.663	8.065	8.778	8.932
AT(1362)	0.164	0.629	7.897	10.455	8.898
AT(1364)	0.160	0.633	7.885	10.459	8.902
experimental			8.107	9.231 ± 0.050	

[a] All values were obtained at the (R)CCSD(T)-F12/aug-cc-pVDZ level after geometry optimization using the wB97xD level of theory and include zero-point vibrational energy correction at the wB97xD/aug-cc-pVDZ level. Asterisks mark the conformers in agreement with our experimental observations.



$$AT \rightarrow T(-H) + AH^+ \quad m/z\ 136 \qquad (4)$$

➔Unique AT conformer

➔Solely proton/hydrogen transfer upon dissociative photoionization

General comments and conclusions

→ Theory:

- Treatment of large or medium sizes (complex) using composite DFT-CCSD(T)-F12 based schemes.
- We have to develop new approaches for FC simulations to consider low frequency modes, anharmonic resonances, …

→ Experiments are still needed to disentangle the complex processes…

➔ NICE COMPLEMENTARY BETWEEN THEORY AND EXPERIMENT.

Atoms, Molecules and Clusters in Motion

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David Lauvergnat (U Paris Saclay)

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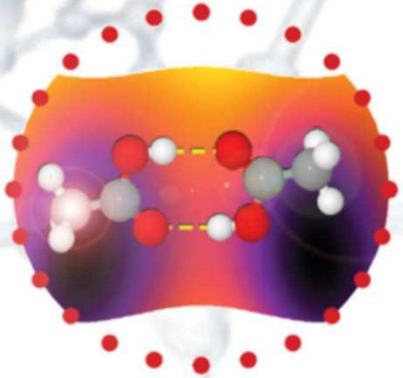

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CYTOSINE

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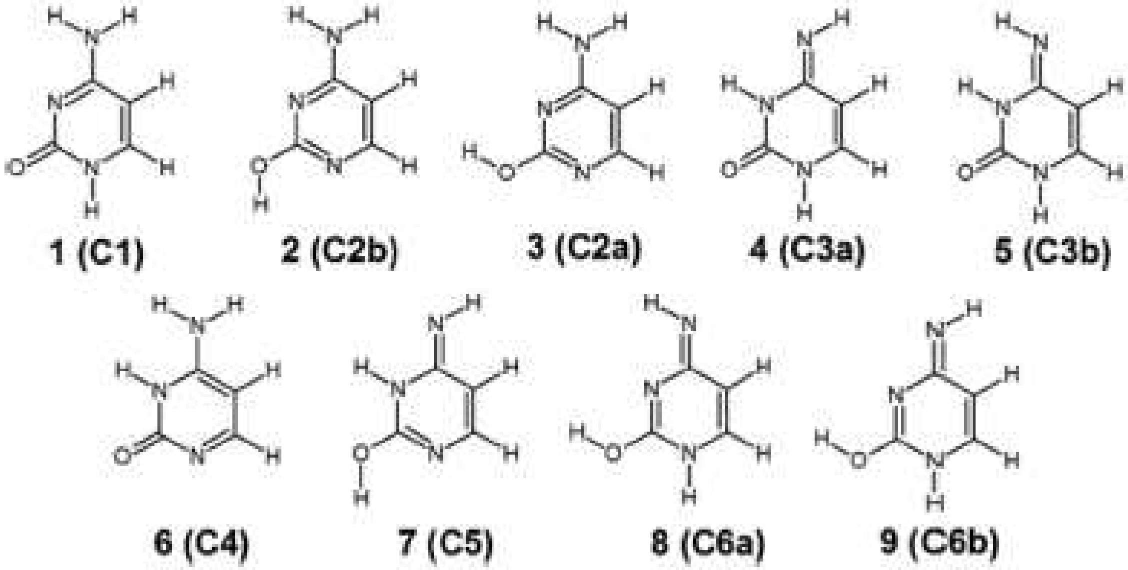
Identifying Cytosine-Specific Isomers via High-Accuracy Single Photon Ionization

Ziyong Chen,[†] Kai-Chung Lau,[*,†] Gustavo A. Garcia,[‡] Laurent Nahon,[‡] Dušan K. Božanić,[‡] Lionel Poisson,[§] Muneerah Mogren Al-Mogren,[||] Martin Schwell,[⊥] Joseph S. Francisco,[#] Ayad Bellili,[∇] and Majdi Hochlaf[*,∇]

Scheme 1. Nine Low-Lying Tautomer and Rotamer Isomers of Cytosine



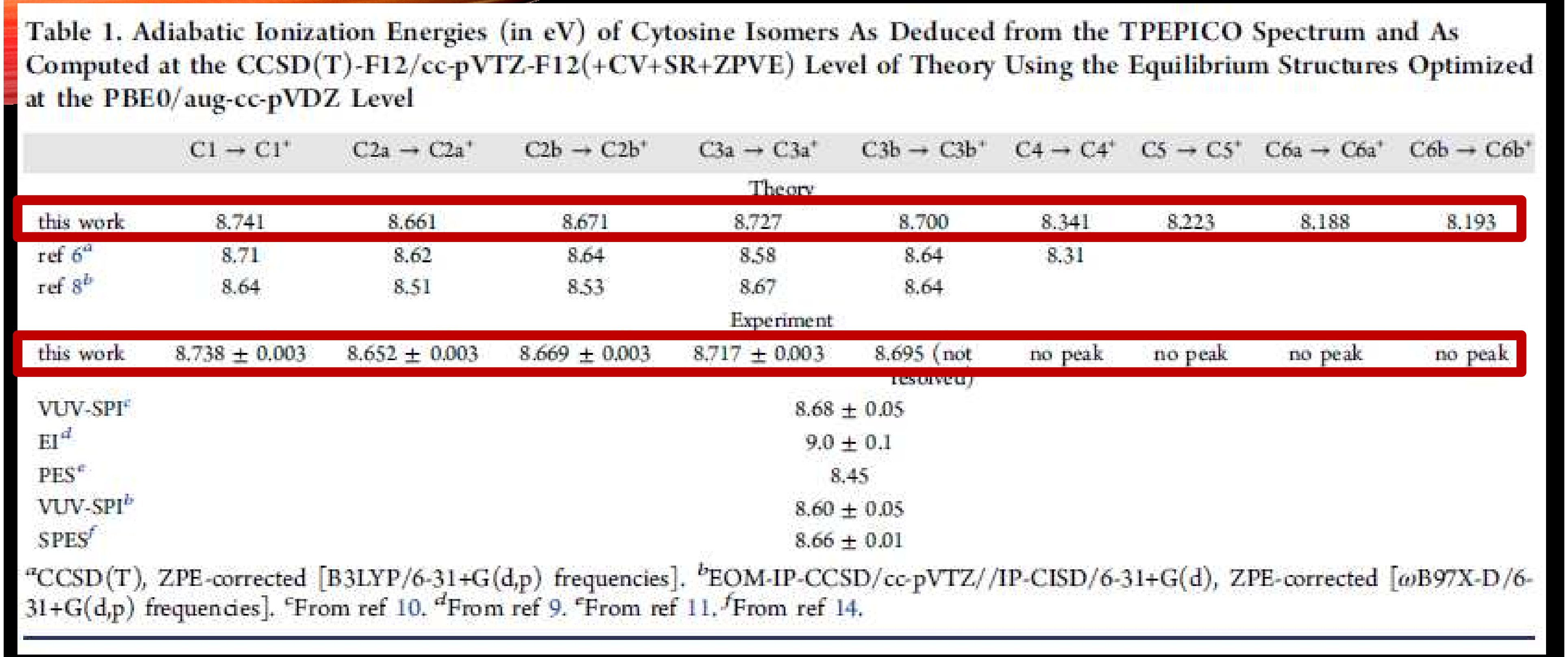


Table 1. Adiabatic Ionization Energies (in eV) of Cytosine Isomers As Deduced from the TPEPICO Spectrum and As Computed at the CCSD(T)-F12/cc-pVTZ-F12(+CV+SR+ZPVE) Level of Theory Using the Equilibrium Structures Optimized at the PBE0/aug-cc-pVDZ Level

	C1 → C1$^+$	C2a → C2a$^+$	C2b → C2b$^+$	C3a → C3a$^+$	C3b → C3b$^+$	C4 → C4$^+$	C5 → C5$^+$	C6a → C6a$^+$	C6b → C6b$^+$
Theory									
this work	8.741	8.661	8.671	8.727	8.700	8.341	8.223	8.188	8.193
ref 6[a]	8.71	8.62	8.64	8.58	8.64	8.31			
ref 8[b]	8.64	8.51	8.53	8.67	8.64				
Experiment									
this work	8.738 ± 0.003	8.652 ± 0.003	8.669 ± 0.003	8.717 ± 0.003	8.695 (not resolved)	no peak	no peak	no peak	no peak
VUV-SPI[c]	8.68 ± 0.05								
EI[d]	9.0 ± 0.1								
PES[e]	8.45								
VUV-SPI[b]	8.60 ± 0.05								
SPES[f]	8.66 ± 0.01								

[a] CCSD(T), ZPE-corrected [B3LYP/6-31+G(d,p) frequencies]. [b] EOM-IP-CCSD/cc-pVTZ//IP-CISD/6-31+G(d), ZPE-corrected [ωB97X-D/6-31+G(d,p) frequencies]. [c] From ref 10. [d] From ref 9. [e] From ref 11. [f] From ref 14.

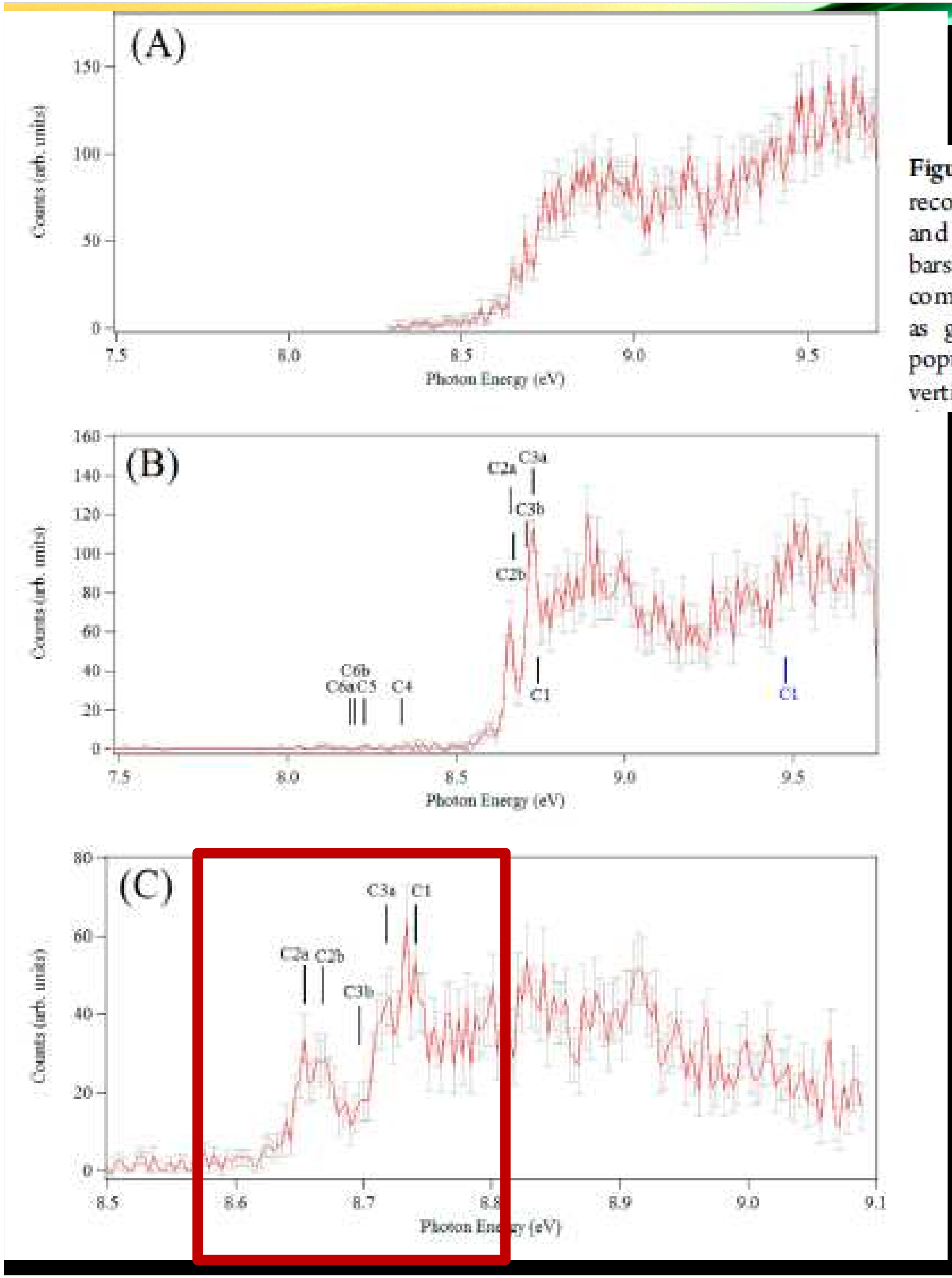
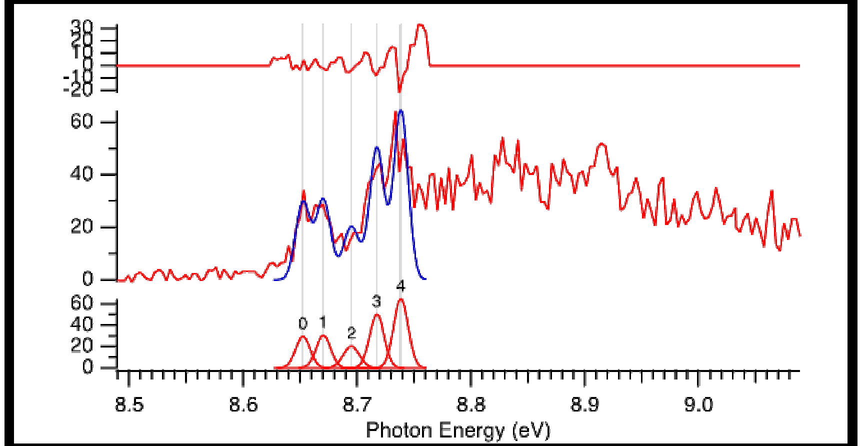
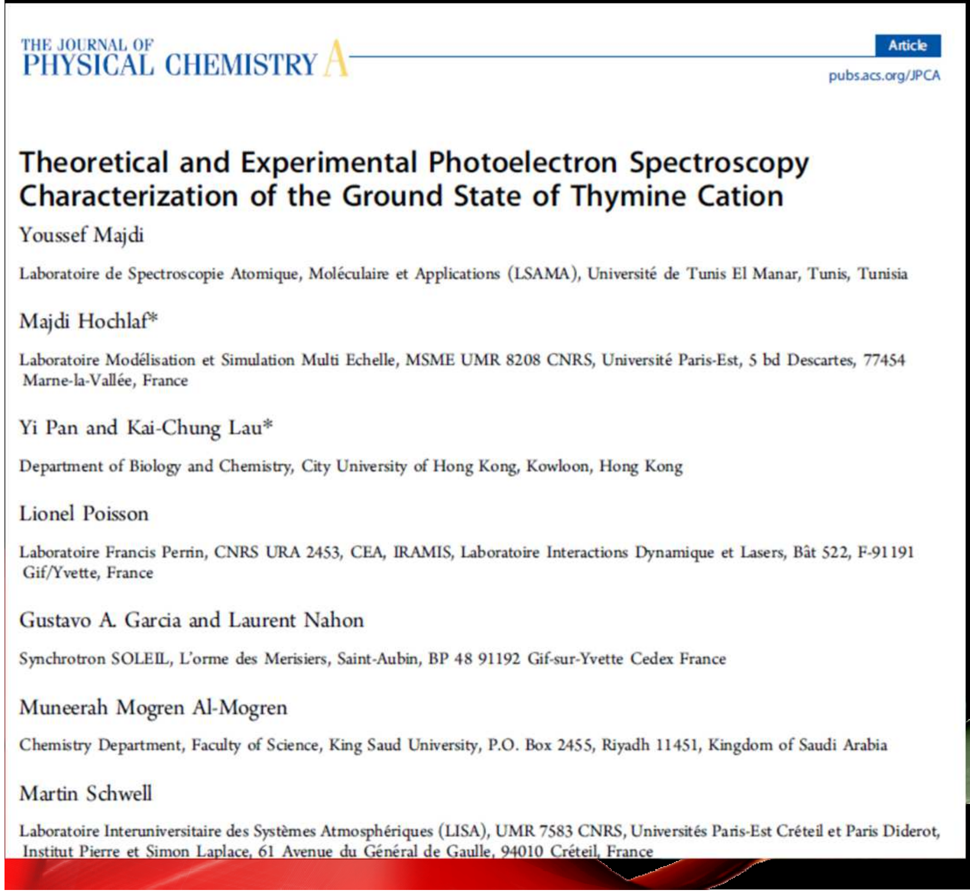


Figure 2. TPEPICO spectra of the cytosine parent (m/z = 111 amu) recorded using (A) an Ar backing pressure of 0.5 bar, (B) Ar at 3 bar and low resolution, and (C) Ar at 3 bar and high resolution. The error bars are shown in gray. In (B), the vertical combs correspond to the computed adiabatic ionization energies (AIEs) of cytosine tautomers as given in Tables 1 and 2. The black (blue) ones are for the population of the cationic ground (first excited) states. In (C), the vertical combs are for the AIEs derived from the fitting of the spectrum



Multi peak fitting of the high resolution spectrum. The upper trace is the residue.

THYMINE



THE JOURNAL OF PHYSICAL CHEMISTRY A
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Theoretical and Experimental Photoelectron Spectroscopy Characterization of the Ground State of Thymine Cation

Youssef Majdi

Laboratoire de Spectroscopie Atomique, Moléculaire et Applications (LSAMA), Université de Tunis El Manar, Tunis, Tunisia

Majdi Hochlaf*

Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, Université Paris-Est, 5 bd Descartes, 77454 Marne-la-Vallée, France

Yi Pan and Kai-Chung Lau*

Department of Biology and Chemistry, City University of Hong Kong, Kowloon, Hong Kong

Lionel Poisson

Laboratoire Francis Perrin, CNRS URA 2453, CEA, IRAMIS, Laboratoire Interactions Dynamique et Lasers, Bât 522, F-91191 Gif/Yvette, France

Gustavo A. Garcia and Laurent Nahon

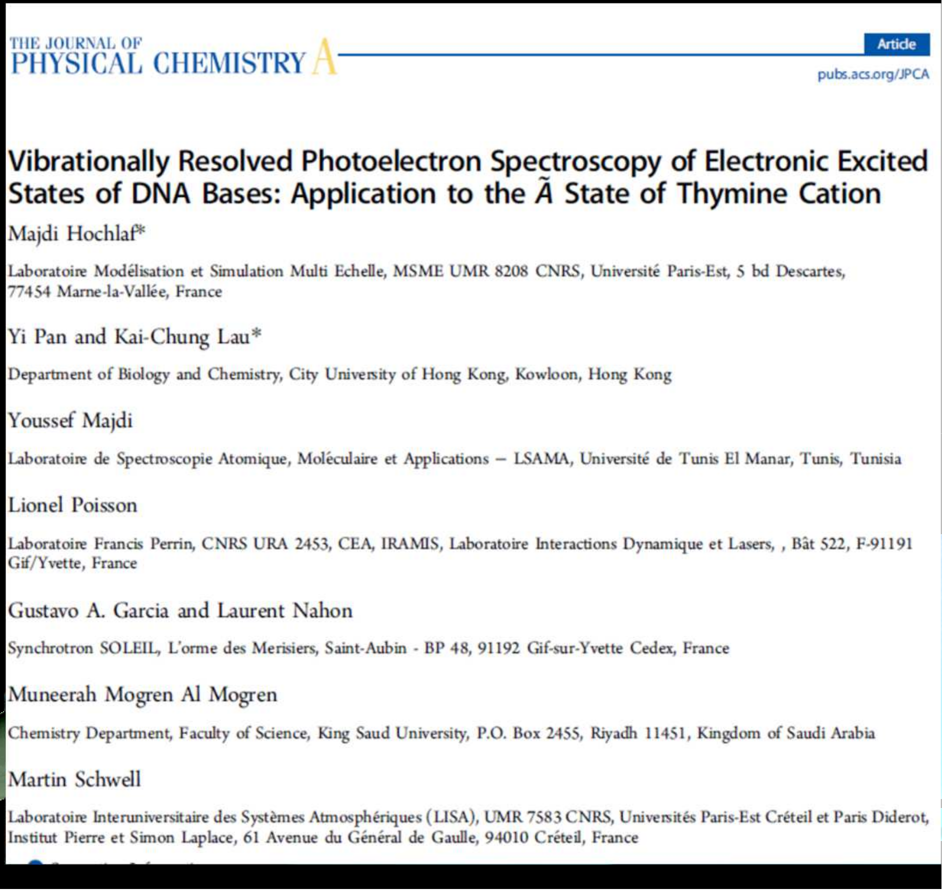
Synchrotron SOLEIL, L'orme des Merisiers, Saint-Aubin, BP 48 91192 Gif-sur-Yvette Cedex France

Muneerah Mogren Al-Mogren

Chemistry Department, Faculty of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Kingdom of Saudi Arabia

Martin Schwell

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583 CNRS, Universités Paris-Est Créteil et Paris Diderot, Institut Pierre et Simon Laplace, 61 Avenue du Général de Gaulle, 94010 Créteil, France



THE JOURNAL OF PHYSICAL CHEMISTRY A
Article
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Vibrationally Resolved Photoelectron Spectroscopy of Electronic Excited States of DNA Bases: Application to the $\tilde{A}$ State of Thymine Cation

Majdi Hochlaf*

Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, Université Paris-Est, 5 bd Descartes, 77454 Marne-la-Vallée, France

Yi Pan and Kai-Chung Lau*

Department of Biology and Chemistry, City University of Hong Kong, Kowloon, Hong Kong

Youssef Majdi

Laboratoire de Spectroscopie Atomique, Moléculaire et Applications – LSAMA, Université de Tunis El Manar, Tunis, Tunisia

Lionel Poisson

Laboratoire Francis Perrin, CNRS URA 2453, CEA, IRAMIS, Laboratoire Interactions Dynamique et Lasers, , Bât 522, F-91191 Gif/Yvette, France

Gustavo A. Garcia and Laurent Nahon

Synchrotron SOLEIL, L'orme des Merisiers, Saint-Aubin - BP 48, 91192 Gif-sur-Yvette Cedex, France

Muneerah Mogren Al Mogren

Chemistry Department, Faculty of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Kingdom of Saudi Arabia

Martin Schwell

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583 CNRS, Universités Paris-Est Créteil et Paris Diderot, Institut Pierre et Simon Laplace, 61 Avenue du Général de Gaulle, 94010 Créteil, France

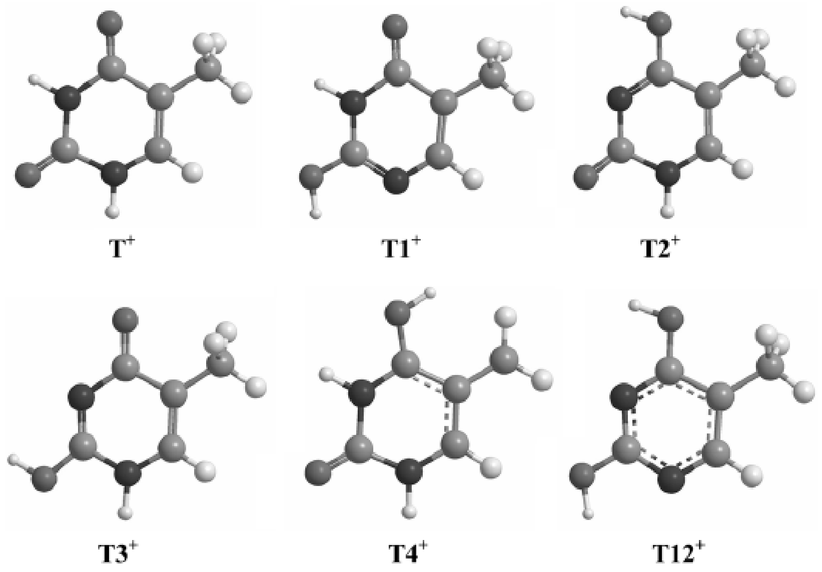
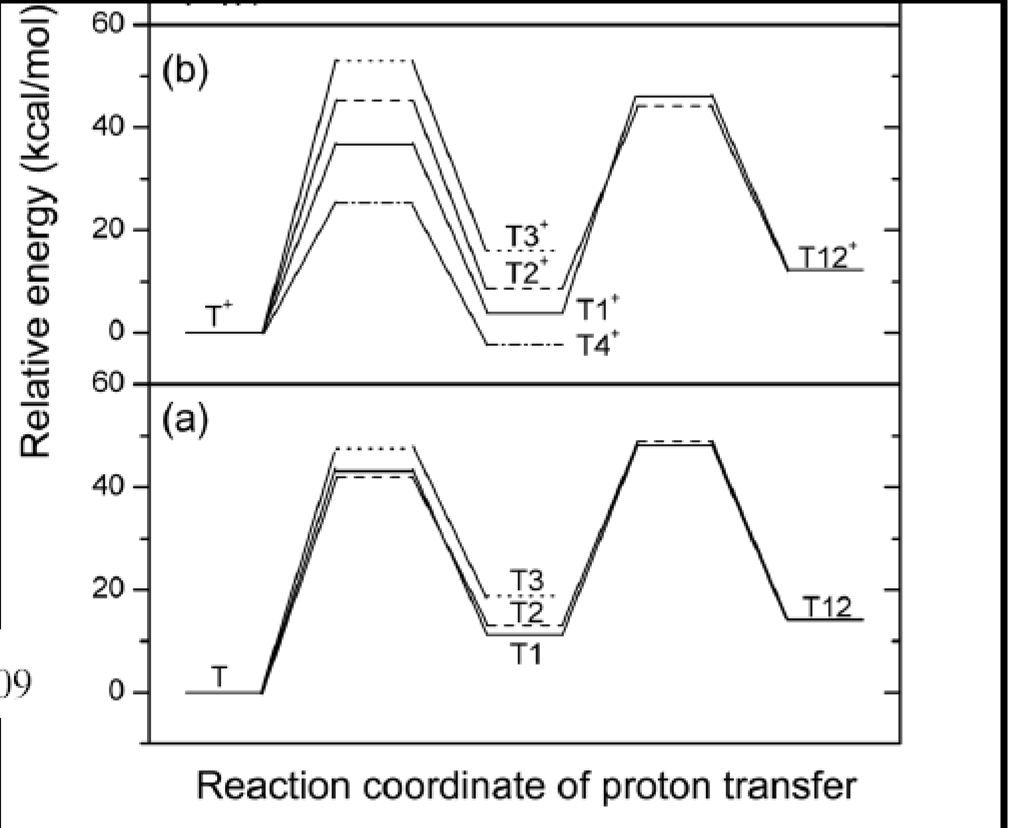


Figure 2. The structures of the tautomers of thymine radical cation optimized at the B3LYP/6-311++G(d,p) level.

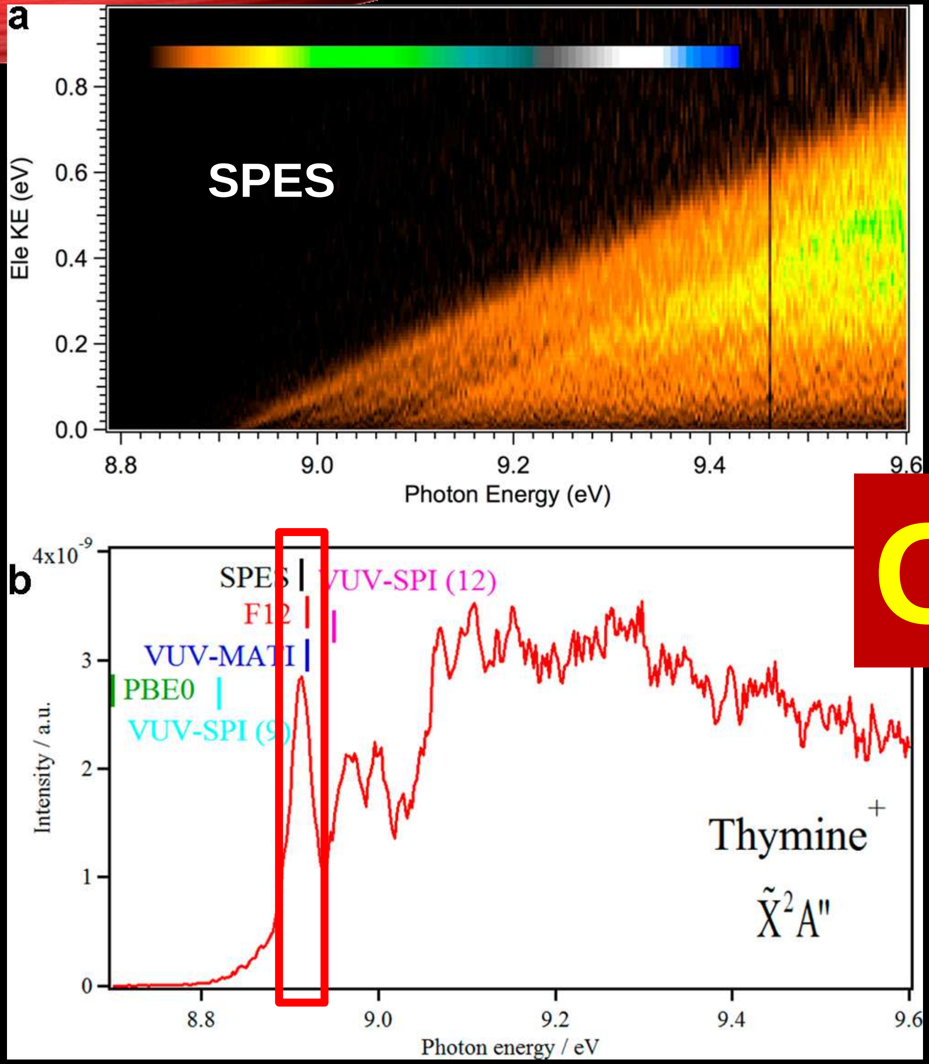
Nam Joon Kim

Bull. Korean Chem. Soc. **2006**, Vol. 27, No. 7 1009

Neutral	$\Delta E_0{}^b$ kc
T	0.00
T1	11.19
T2	13.08
T3	18.76
T12	14.17



Thymine $^+$ - cation ground state



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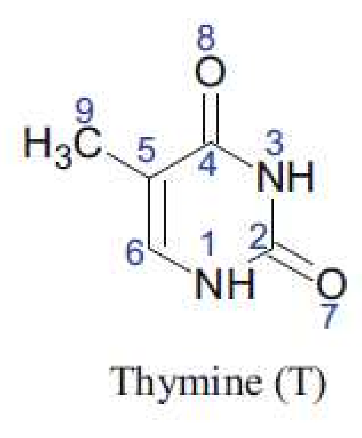
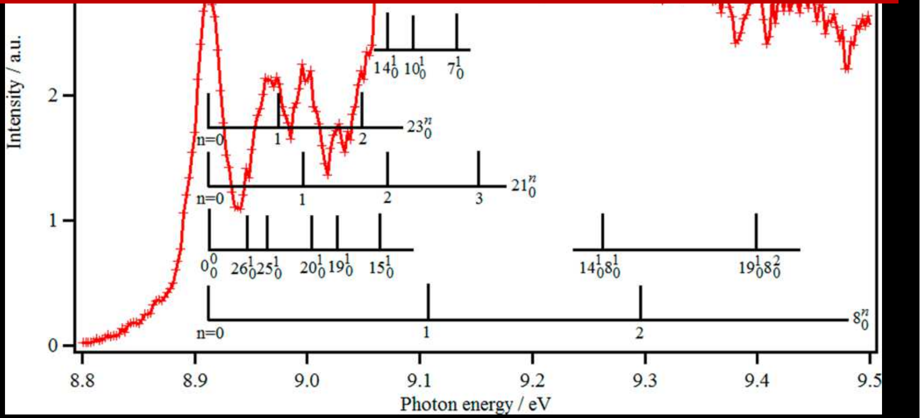
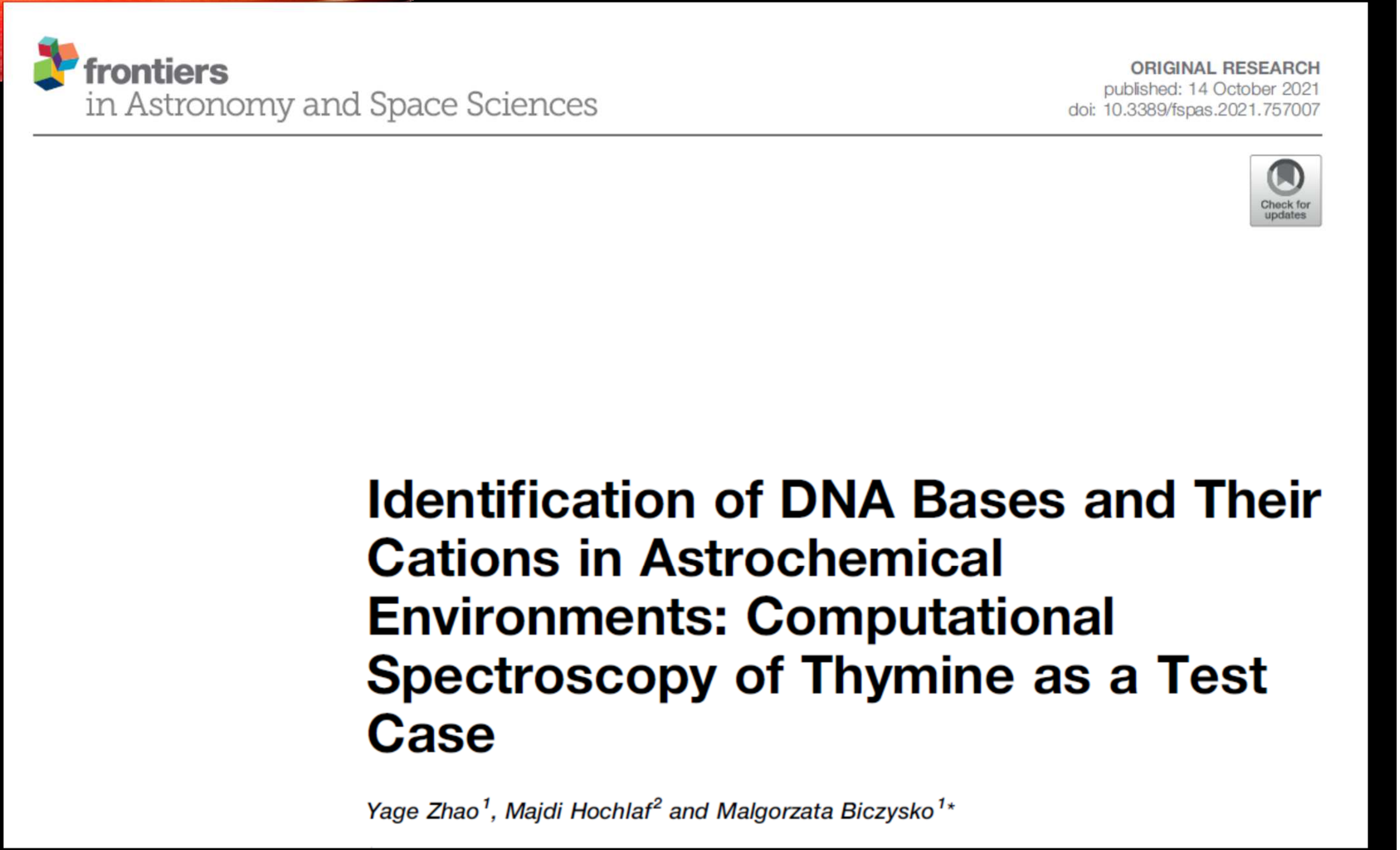


One tautomer



Theo: **F12** = (R)CCSD(T)-F12cc-pVTZ-F12
PBE0 (DFT) = PBE0/aug-cc-pVDZ+ZPVE
Exptl: VUV-SPI, VUV-SPI, VUV MATI, SPES

Majdi et al., JPC. A (2015)



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Identification of DNA Bases and Their Cations in Astrochemical Environments: Computational Spectroscopy of Thymine as a Test Case

Yage Zhao[1], *Majdi Hochlaf*[2] *and Malgorzata Biczysko*[1*]

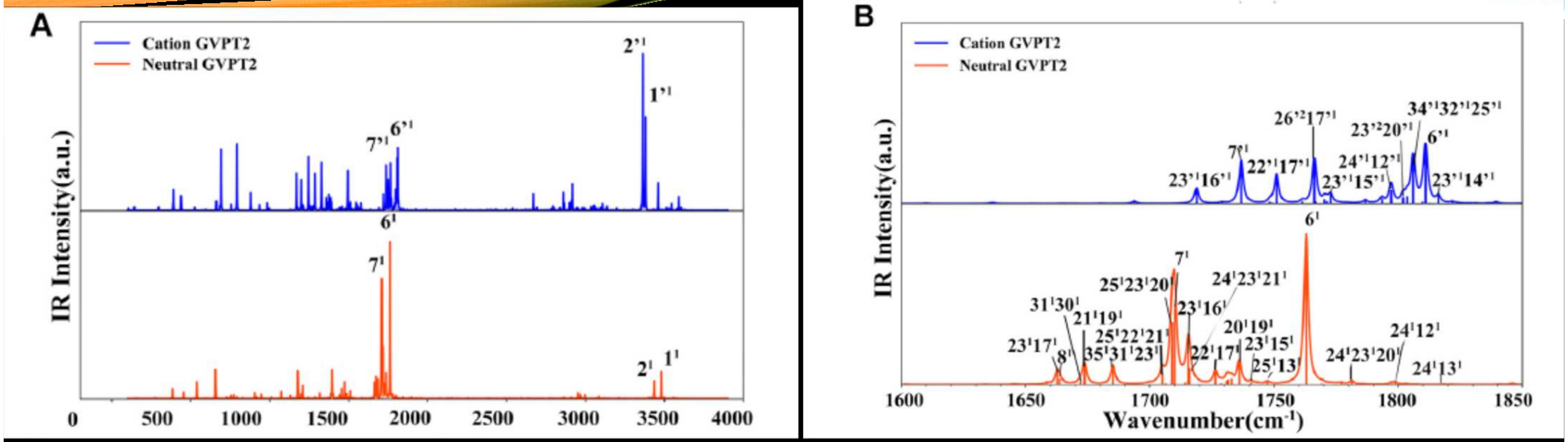


FIGURE 6 | MIR spectra simulated at GVPT2//B2PLYP//B3LYP/AVTZ level. Spectra line-shapes were broadened by Lorentzian functions with HWHM of 1 cm^{-1} **(A)** 100 cm^{-1} - 4000 cm^{-1} range **(B)** The 1600 cm^{-1} -1850 cm^{-1} range related to the modes 6, 7 and the non-fundamentals involved in the Fermi resonances. Most intense bands are assigned as m^n where m is normal mode and n number of quanta (1 fundamentals, 2 overtones).

Theo. vs. Exp. 1: IR region

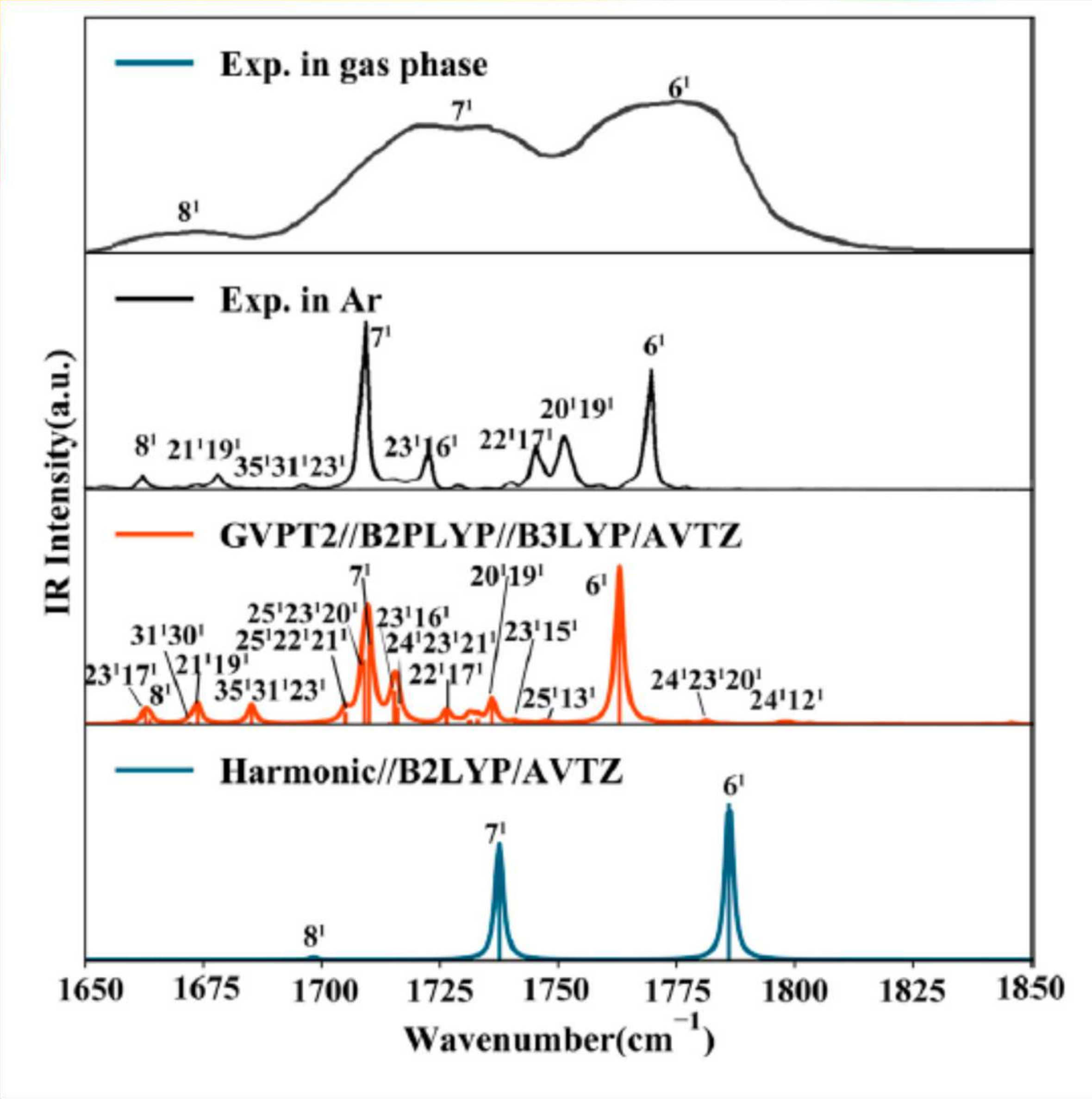


FIGURE 5 | IR spectrum of thymine in the CO stretching range (1650 cm^{-1} - 1850 cm^{-1}). Computed stick spectra were broadened by Lorentzian functions with half width at half-maximum (HWHM) of 1 cm^{-1}. Most significant contributions to intense bands are assigned as m^n where m is the normal mode and n is the number of quanta on this mode (1 fundamentals, 2 overtones). Experimental spectra of gas phase thymine (Colarusso et al., 1997) and of Ar low temperature matrix trapped thymine (Szczepaniak et al., 2000) are shown for comparison.

Theo. vs. Exp. 2: VUV region

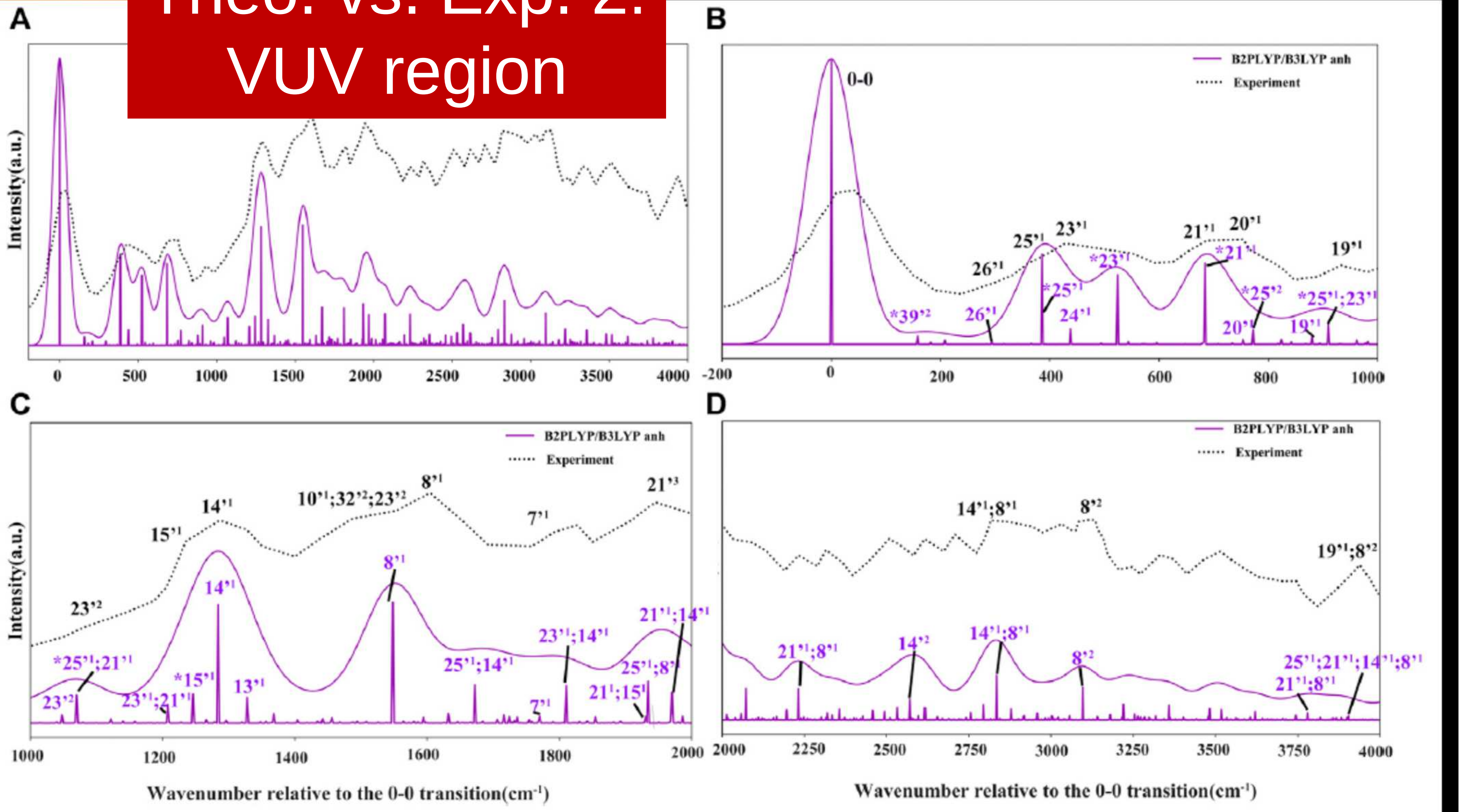
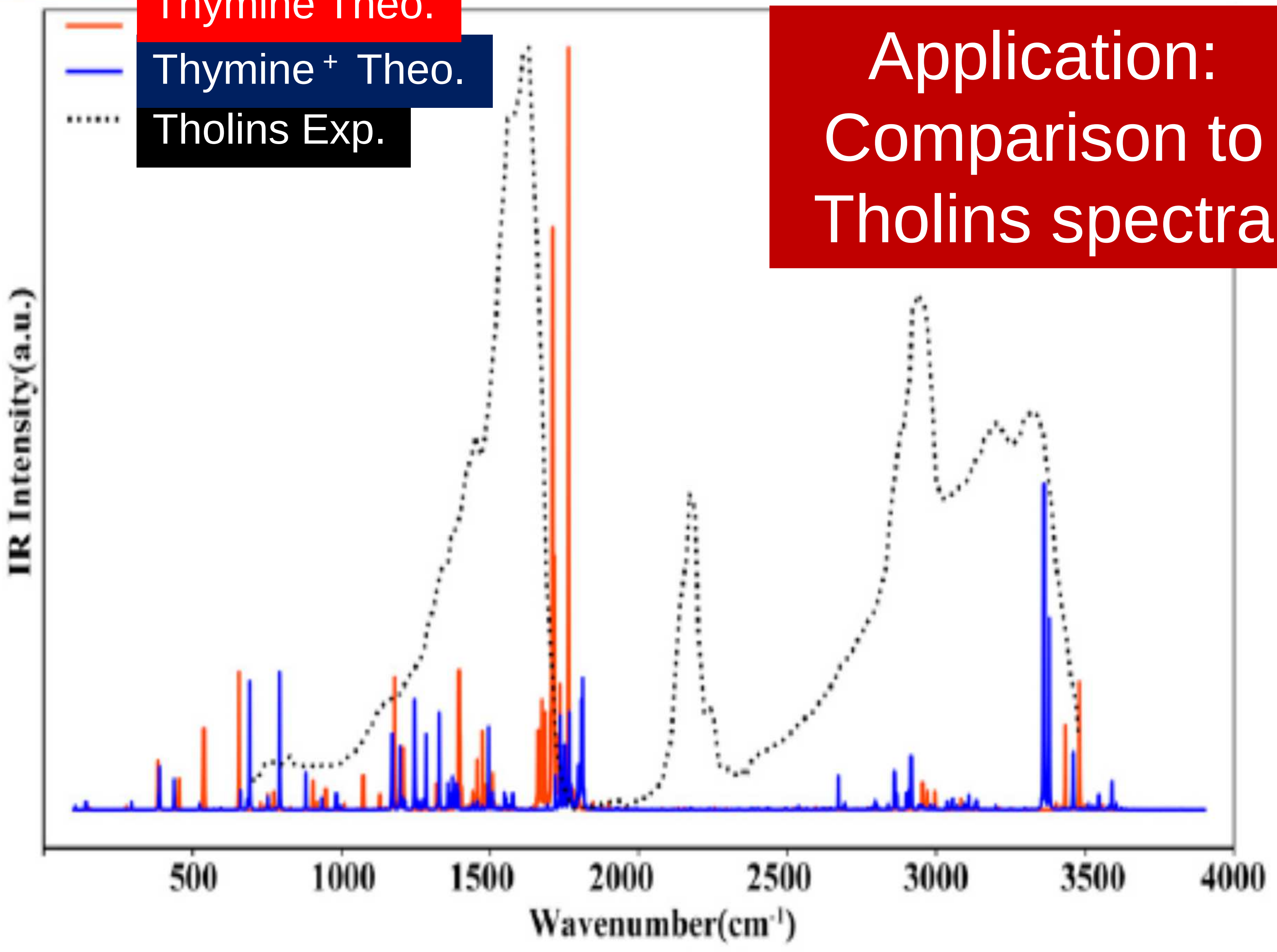


FIGURE 7 | Photoelectron TI AH|FC spectrum (60 K) and SPES experimental spectrum (Majdi et al., 2015). The computed spectrum is represented as single transitions, with most intense ones assigned as m^n, which represents the final vibrational state with n quanta associated to mode m. The convoluted spectra line-shapes have been obtained by broadening with Gaussian function with HWHM of 50 cm^{-1}. Bands observed also in the VUV-MATI experimental spectrum (Choi et al., 2005; Bravaya et al., 2010) are marked by asterisk (*).

Application: Comparison to Tholins spectra



Thymine Theo.

Thymine$^+$ Theo.

Tholins Exp.

FIGURE 8 | Comparison of the simulated IR spectrum of thymine with the experimental spectrum of Tholins (Gautier et al., 2012). GVPT2//B2PLYP//B3LYP/AVTZ stick spectra were broadened by Lorentzian functions with HWHM of 1 cm^{-1}.