Bound states of positron with nitrile species with several multi-component molecular theories

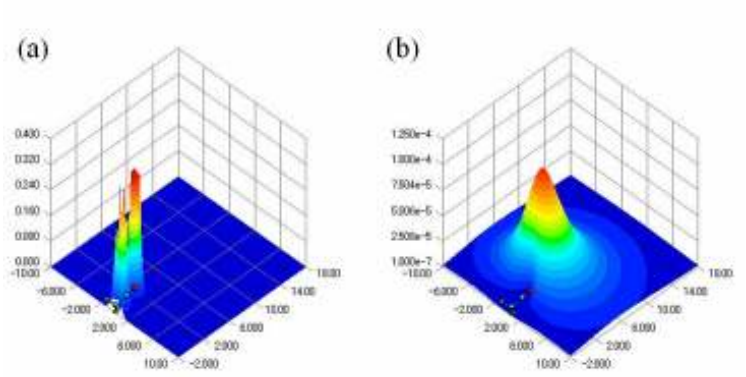
"International Workshop on Positrons in Astrophysics"
@Hotel Alpin Palace, Murren, Switzerland,
on 20-23, March 2012

Masanori Tachikawa
(Yokohama-city University)

YOKOHAMA CITY UNIVERSITY

Today's talk

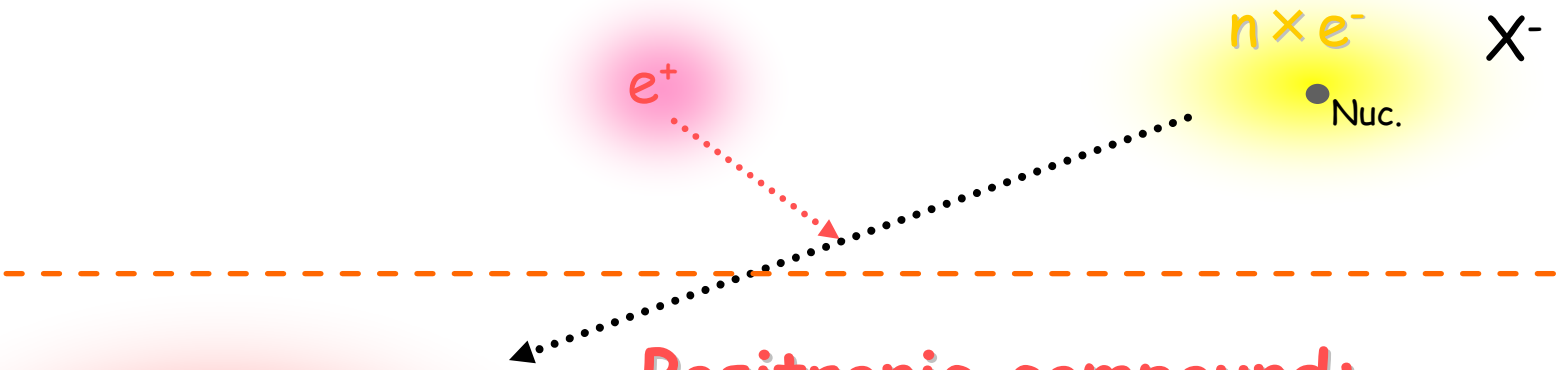
1. Introduction
   1.1. Positronic compounds
2. Theory
   2.1. Multi-Component Molecular Orbital (MC_MO)
   2.2. Multi-Component Quantum Monte Carlo (MC_QMC)
3. Results and discussion
   3.1 Positronic nitrile compounds
4. Summary & Future plans



- Y. Kita, R. Maezono, M. Tachikawa, M. Towler, and R. J. Needs, **J. Chem. Phys.** *131*, 134310 (2009).
- M. Tachikawa, Y. Kita, and R. J. Buenker, **Phys. Chem. Chem. Phys.**, *13*, 2701 (2011).

1.1. Introduction: Positronic compounds

When a positron interacts with atom/molecule, they can form a meta-stable "positronic compound" before pair annihilation.



Positronic compound:

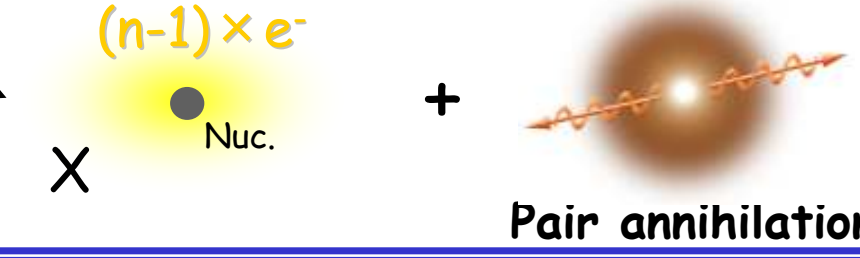
→ Electronic & Positronic Structure ?

→ Stable Geometry ??

$[X^-; e^+]$

Theoretical analysis is indispensable!

life-time
: 10^{-7} ~ 10^{-10} sec.



1.2. Experimental PA values !

Dipole enhancement of positron binding to molecules

J. R. Danielson, J. J. Gosselin, and C. M. Surko
Department of Physics, University of California at San Diego, La Jolla, CA 92093
(Dated: May 12, 2010)

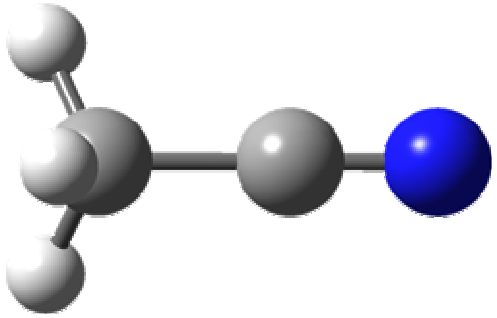
Measurements of positron-molecule binding energies are made for molecules with large permanent dipole moments (> 2.7 debye), by studying vibrational-Feshbach-mediated annihilation resonances as a function of incident positron energy. The binding energies are relatively large (e.g., ≥ 90 meV) as compared to those for similar sized molecules studied previously and analogous weakly bound electron-molecule (negative ion) states. Comparisons with existing theoretical predictions are discussed.

TABLE I: Measured and predicted positron- and electron-molecule binding energies ϵ_b (meV), permanent dipole moments μ (D) and dipole polarizabilities α (Å^3) for selected molecules. Data for μ and α taken from Ref. [26]. Data from Figs. 1-4 in bold.

Molecule	Formula	μ (D)	α (Å^3)	ϵ_b (meV) positrons meas.	positrons pred.	electrons[g] meas.	electrons[g] pred.
carbon disulf.	CS_2	0	8.7	**75**		0.7	
butane	C_4H_{10}	0	8.2	40[a]			
methanol	CH_3OH	1.7	3.3	2[a]			
meth.-chloride	CH_3Cl	1.9	5.4	25[a]			
formaldehyde	H_2CO	2.3	2.8		19[b]		0.02
acetaldehyde	$(CH_3)HCO$	2.8	4.6	**90**		0.6	0.95
acetone	$(CH_3)_2CO$	2.9	6.4	**173**	4[c]	2.6	1.6
propanal	$(C_2H_5)HCO$	2.7	6.5			1.0	0.6
hydr. cyanide	HCN	3.0	2.5		35[d]	4	3.3
acetonitrile	CH_3CN	3.9	4.4	**180**	125[e]	19	15.5
lith. hydride	LiH	5.9	3.8		1000[f]	342	330

[a]Ref. [11], [b]Ref. [5], [c]Ref. [8], [d]Refs. [6, 7], [e]Ref. [15], [f]Ref. [3], [g]Meas. from Refs. [25, 27–29], pred. from Refs. [25, 30].

J. R. Danielson, J. J. Gosselin, and C. M. Surko, Phys. Rev. Lett. **104, 233201 (2010).**



acetonitrile

PA(CH_3CN)=180 meV

PA (Positron Affinity) =E(X)-E([X;e^+])

2.1. Multi-Component MO (MC_MO)

- **Total Hamiltonian (N electron、1 positron、M fixed nuclei):**

$$H_{tot} = \sum_{i=1}^{N} h^e(i) + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} + h^p(p) - \sum_{i=1}^{N} \frac{1}{r_{pi}}$$

$$h^e(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}}, \qquad h^p(p) = -\frac{1}{2}\nabla_p^2 + \sum_{A=1}^{M} \frac{Z_A}{r_{pA}},$$

- **Total wavefunction:**

$$\left|\Psi_{tot}\right\rangle = C_{00}\left|\Phi_0^e\right\rangle\left|\Phi_0^p\right\rangle + \sum_{IJ}{}' C_{IJ}\left|\Phi_I^e\right\rangle\left|\Phi_J^p\right\rangle$$

$\left|\Phi_0^e\right\rangle\left|\Phi_0^p\right\rangle$ ⟶ **Hartree-Fock**

$\sum_{IJ}{}' C_{IJ}\left|\Phi_I^e\right\rangle\left|\Phi_J^p\right\rangle$ ⟶ **Configuration Interaction**

1. Hartree-Fock (HF) equations:

Electrons: $f^e\varphi_i^e = \varepsilon_i^e\varphi_i^e$ $\qquad f^e = h^e + \sum_i^N (J_i - K_i) - J_p$

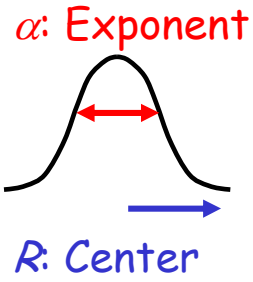
Positron : $f^p\varphi_p^p = \varepsilon_p^p\varphi_p^p$ $\qquad f^p = h^p - \sum_i^N J_i$

2.1.Multi-Component MO (MC_MO)

1. LCAO expansion → HF Roothaan equations:

Electrons: $\varphi_i^e = \sum_\mu \chi_\mu^e C_{\mu i}^e$ $\quad \mathbf{F}^e\mathbf{C}^e = \mathbf{S}^e\mathbf{C}^e\boldsymbol{\varepsilon}^e$

Positron: $\varphi_p^p = \sum_\mu \chi_\mu^p C_{\mu p}^p$ $\quad \mathbf{F}^p\mathbf{C}^p = \mathbf{S}^p\mathbf{C}^p\boldsymbol{\varepsilon}^p$



[*] STF: I. L. Thomas, PR (1969). ECG: L. Adamowicz, PRL (2002). GTF: H. Nagao, IJQC (1996), Y. Shigeta, JCP (1999), H. Nakai, JCP (2003), S. Hammes-Schiffer, JCP (2005), C.D.Sherrill, MP (2004). DFT: E. K. U. Gross, PRL (2001).

2. Correlation: Configuration Interaction (CI)

$$H_{tot} = \sum_{i=1}^{N} h^e(i) + \underbrace{\sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}}}_{E_{ee}} + h^p(p) \underbrace{- \sum_{i=1}^{N} \frac{1}{r_{pi}}}_{E_{ep}}$$

$$\left|\Psi_{tot}\right\rangle = C_{00}\left|\Phi_0^e\right\rangle\left|\Phi_0^p\right\rangle + \sum_{IJ}{}' C_{IJ}\left|\Phi_I^e\right\rangle\left|\Phi_J^p\right\rangle$$

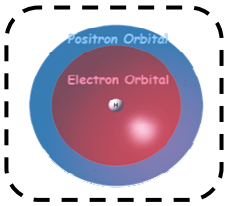
|IJ> : I-electron excitation [IO]
J-positron excitation [OJ]
I-elec & J-pos excitation [IJ]

[*] MP2: M. Tachikawa, K. Iguchi, and K. Suzuki, J. Chem. Phys. 101, 5925 (1995). Gradient: M. Tachikawa, K. Mori, H. Nakai, and K. Iguchi, Chem. Phys. Lett. 290, 437 (1998). CI: M. Tachikawa, Chem. Phys. Lett. 350, 269 (2001), Chem. Phys. Lett. 360, 494 (2002). R. J. Buenker, M. Tachikawa, M. Kimura, et al., Phys. Rev. A73, 022705 (2006).

2.1.Multi-Component MO (MC_MO)

Correlation between e^- and e^+ is indispensable

$[H^-;e^+]$



MC_MO(HF) -0.666950 (hartree)

$[e^-/e^+$= 10s/10s]

-0.769167 (85%)

MC_MO(Full CI) [1]

$[e^-/e^+$= 6s3p2d1f/6s3p2d1f]

−0.789196705

ECG [2]

[1] M. Tachikawa; Chem. Phys. Lett. 350 269 (2001)
[2] J. Mitroy; Phys. Rev. A 73 054502 (2006).
[3] J. Mitroy, M. W. J. Bromley and G. G. Ryzhikh, J. Phys. B35 81 (2002), -0.7750785(L=3, STF), -0.7867761(L=9, STF)

2.2.Multi Component QMC (MC_QMC)

Trial Wave function Ψ_T : $\Phi = \Psi_{\text{trial}} = e^{J(\mathbf{R})}\Psi_{\text{HF}}(\mathbf{R})$

(A) MC_MO

$$f^e = h^e + \sum_i^{Ne}(J_i - K_i) - \sum_p^{Np} J_p$$

$$f^p = h^p + \sum_p^{Np}(J_p - K_p) - \sum_i^{Ne} J_i$$

(B) MC_QMC (Jastrow factor)

$$\begin{aligned} J(\mathbf{R}) &= J(\mathbf{R}_e, \mathbf{R}_I, \mathbf{r}_p) \\ &= \sum_i^N \sum_{j(>i)}^N \underbrace{u_{ij}(r_{ij})}_{e^- \text{-} e^-} + \sum_i^N \sum_I^M \underbrace{\chi_I(r_{iI})}_{e^- \text{-Nuc.}} + \sum_i^N \sum_{j(>i)}^N \sum_I^M \underbrace{f_{ijI}(r_{iI}, r_{jI}, r_{ij})}_{e^- \text{-} e^- \text{-Nuc.}} \\ &\quad + \sum_i^N \underbrace{u_p(r_{ip})}_{e^- \text{-} e^+} + \sum_i^M \underbrace{\chi_p(r_{pI})}_{e^+ \text{-Nuc.}} \end{aligned}$$

Variational Monte Carlo [VMC] method:

- Energy is obtained by using Metropolis sampling.
- Parameters in trial WF can be optimized under variational principles

Diffusion Monte Carlo [DMC] method :

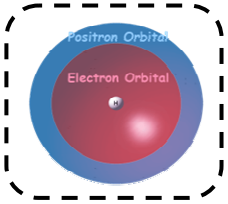
- Projection to ground state by using imaginary-time dependent Schrödinger equation

$$\lim_{\tau \to \infty} \Phi(\mathbf{R}, \tau = it) \to \Psi_{\text{Exact}}(\mathbf{R})$$

2.2.Multi Component QMC (MC_QMC)

Correlation between e^- and e^+ is indispensable

$[H^-;e^+]$



MC_MO(HF) -0.666950 (hartree)

[e^-/e^+= 10s/10s]

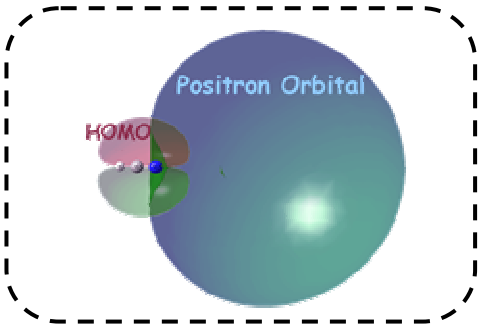
VMC
-0.78675(6)

DMC
-0.78920(11)

-0.769167 (85%)
MC_MO(Full CI) [1]
[e^-/e^+= 6s3p2d1f/6s3p2d1f]

−0.789196705
ECG [2]

$[HCN;e^+]$



MC_MO(HF) -92.90074 (hartree)

[e^-/e^+= 6-311++G(2d,2p)
/15s 15p 6d 2f]

VMC
-93.2591(5)

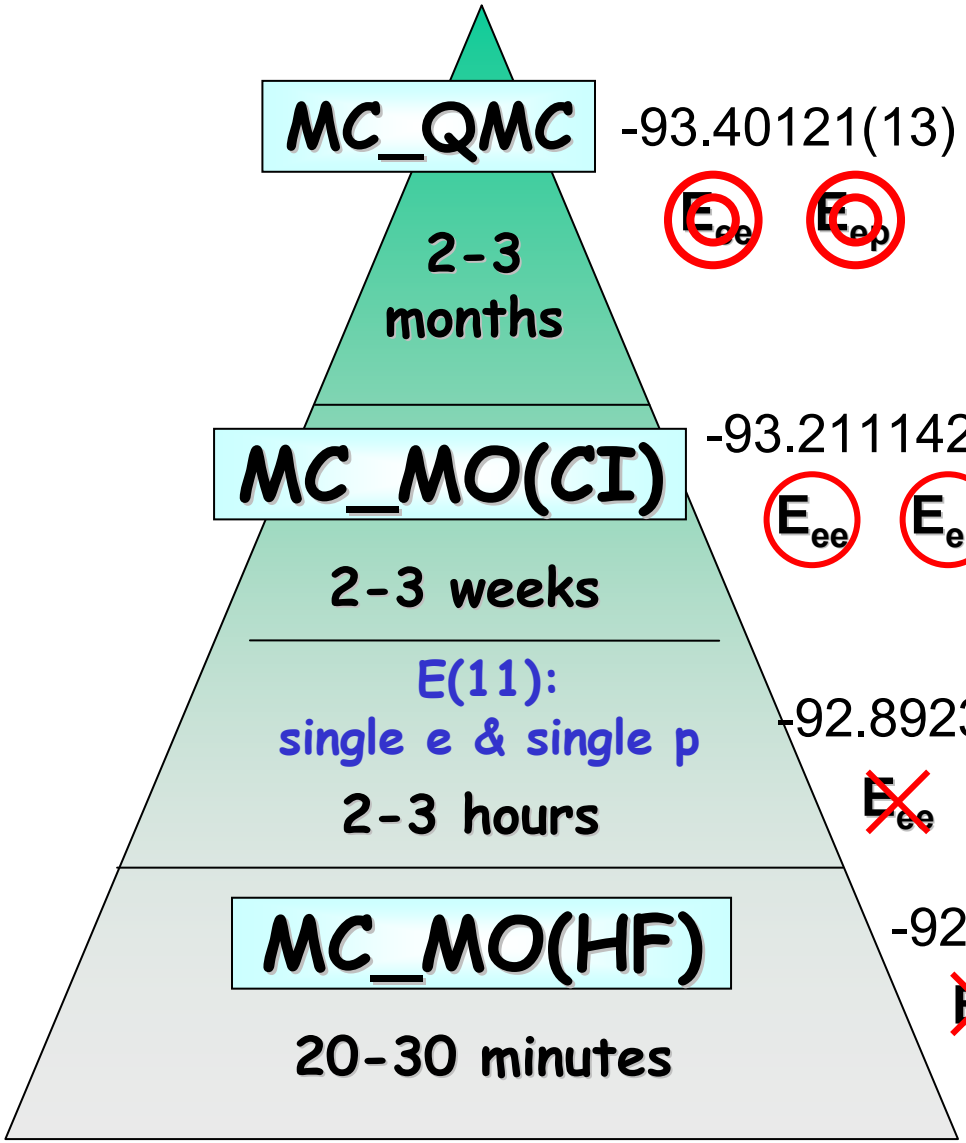
DMC
-93.40121(13) [5]

-92.901915
CISD [4]
[e^-: 6-311++G(2d,2p)
e^+: 6-311++G(2d,2p)
+ 10s GTF (off-atom)]

PA(meV)
HF + 1.8
DMC +38(5)

[1] M. Tachikawa; Chem. Phys. Lett. 350 269 (2001)
[2] J. Mitroy; Phys. Rev. A 73 054502 (2006).
[3] J. Mitroy, M. W. J. Bromley and G. G. Ryzhikh, J. Phys. B35 81 (2002), -0.7750785(L=3, STF), -0.7867761(L=9, STF)
[4] H. Chojnacki and K. Strasburger, Mol. Phys. 104 2273 (2006)
[5] Y. Kita, R. Maezono, M. Tachikawa, M. Towler, and R. J. Needs, J. Chem. Phys. 131 134310 (2009)

2.3. Hierarchie of computational methods



	E(HCN;e⁺)	E(HCN)	PA(HCN)
MC_QMC	-93.40121(13) au	-93.39986(12) au	38(5) meV
MC_MO(CI)	-93.211142 au	-93.209851 au	35 meV
E(11): single e & single p	-92.892320 au	-92.890994 au	36 meV
MC_MO(HF)	-92.891061 au	-92.890994 au	1.8 meV

•Electronic 6-31++G(2df,2pd)

•Positronic [15s15p3d2f1g]

[4] H. Chojnacki and K. Strasburger, Mol. Phys. 104 2273 (2006)

1.2. Experimental PA values !

Dipole enhancement of positron binding to molecules

J. R. Danielson, J. J. Gosselin, and C. M. Surko
Department of Physics, University of California at San Diego, La Jolla, CA 92093
(Dated: May 12, 2010)

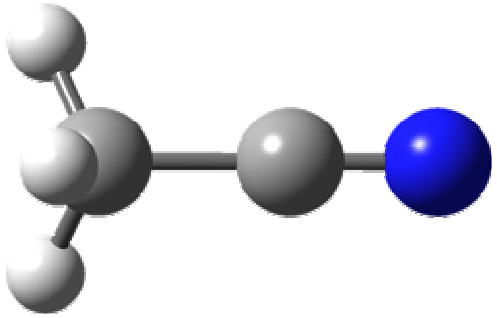
Measurements of positron-molecule binding energies are made for molecules with large permanent dipole moments (> 2.7 debye), by studying vibrational-Feshbach-mediated annihilation resonances as a function of incident positron energy. The binding energies are relatively large (e.g., ≥ 90 meV) as compared to those for similar sized molecules studied previously and analogous weakly bound electron-molecule (negative ion) states. Comparisons with existing theoretical predictions are discussed.

TABLE I: Measured and predicted positron- and electron-molecule binding energies ϵ_b (meV), permanent dipole moments μ (D) and dipole polarizabilities α (Å^3) for selected molecules. Data for μ and α taken from Ref. [26]. Data from Figs. 1-4 in bold.

Molecule	Formula	μ (D)	α (Å^3)	ϵ_b (meV) positrons meas.	positrons pred.	electrons[g] meas.	electrons[g] pred.
carbon disulf.	CS_2	0	8.7	**75**		0.7	
butane	C_4H_{10}	0	8.2	40[a]			
methanol	CH_3OH	1.7	3.3	2[a]			
meth.-chloride	CH_3Cl	1.9	5.4	25[a]			
formaldehyde	H_2CO	2.3	2.8		19[b]		0.02
acetaldehyde	$(CH_3)HCO$	2.8	4.6	**90**		0.6	0.95
acetone	$(CH_3)_2CO$	2.9	6.4	**173**	4[c]	2.6	1.6
propanal	$(C_2H_5)HCO$	2.7	6.5			1.0	0.6
hydr. cyanide	HCN	3.0	2.5		35[d]	4	3.3
acetonitrile	CH_3CN	3.9	4.4	**180**	125[e]	19	15.5
lith. hydride	LiH	5.9	3.8		1000[f]	342	330

[a]Ref. [11], [b]Ref. [5], [c]Ref. [8], [d]Refs. [6, 7], [e]Ref. [15], [f]Ref. [3], [g]Meas. from Refs. [25, 27–29], pred. from Refs. [25, 30].

J. R. Danielson, J. J. Gosselin, and C. M. Surko, Phys. Rev. Lett. **104, 233201 (2010).**



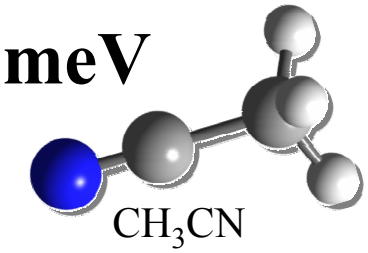
acetonitrile

PA(CH_3CN)=180 meV

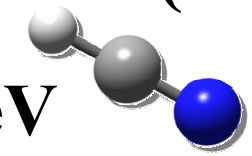
PA (Positron Affinity) =E(X)-E([X;e^+])

3.1. PAs of nitrile species

PA=135 meV
(4.23D)

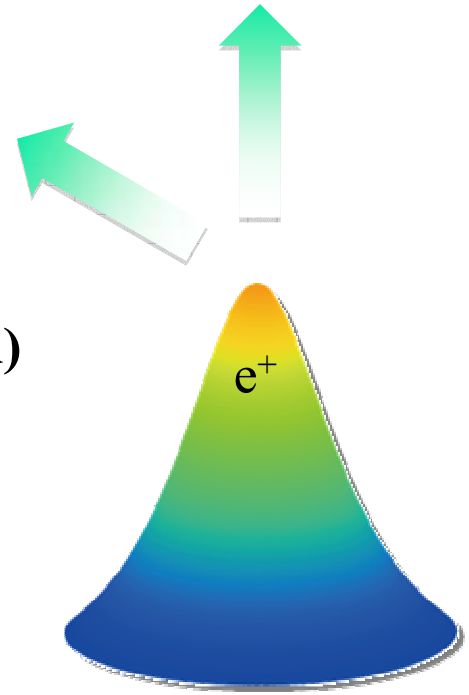


PA_{exptl}= 180 meV



PA=36 meV
(3.29D)

- **Electronic 6-31++G(2df,2pd)**
- **Positronic [15s15p3d2f1g]**
- **CI ([10], [01], and [11])**

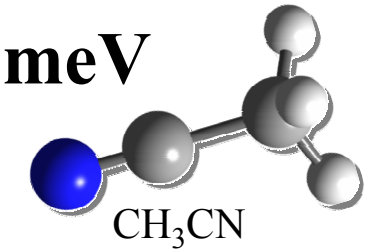


Positron (e^+) adsorption

Within 25% of the recent experimental value of 180 meV by Danielson et al. [Phys. Rev. Lett. 104, 233201 (2010)].

3.1. PAs of nitrile species

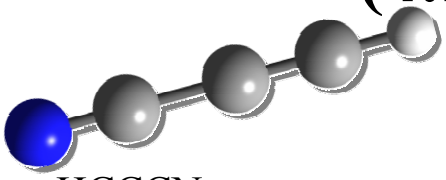
PA=135 meV
(4.23D)



CH_3CN

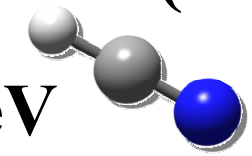
PA_{exptl}=
180 meV

PA=87 meV
(4.12D)

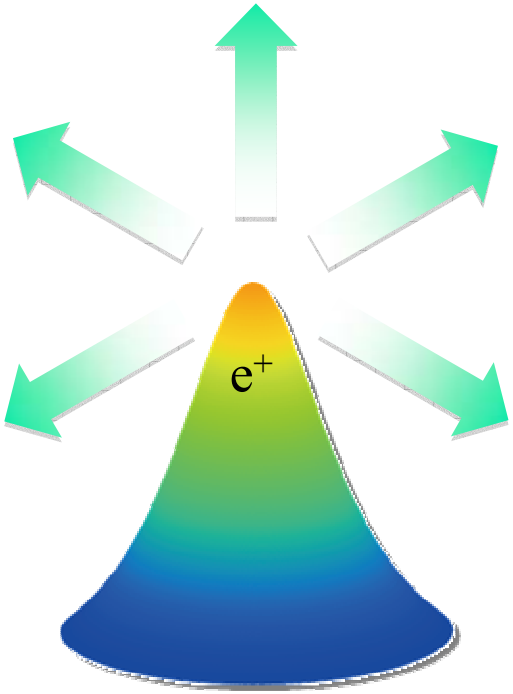


HCCCN

PA=36 meV
(3.29D)

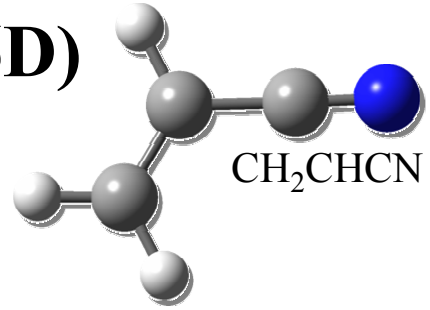


HCN



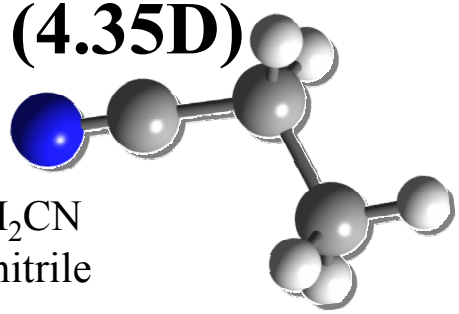
Positron (e^+) adsorption

PA=155 meV
(4.36D)



CH_2CHCN

PA=164 meV
(4.35D)



CH_3CH_2CN
Propionitrile

PA_{exptl}=225 meV
(Private communication)

The PA values are strongly correlated with the dipole moments.

M. Tachikawa, Y. Kita, and R. J. Buenker, Phys. Chem. Chem. Phys., *13*, 2701 (2011).

4. Summary

- **Development of Multi-Component molecular theory:**
  - Multi component molecular orbital (MC_MO) from Hartree-Fock (HF) to Configuration Interaction (CI)
  - Multi component quantum Monte Carlo (MC_QMC)

- **Application of positronic nitrile species:**
  - We have obtained 135 meV as PA(CH_3CN), which is 75% of the recent experimental value of 180 meV.
  - The PA values are strongly correlated with the dipole moments.

- **(Near) future Plans:**
  - Vibrational effect on positronic molecules
  - PAs for non-polar molecules

Acknowledgement

- Prof. R.J Buenker (Wuppatal Univ.)
- Prof. R.J Needs (Cambridge Univ.)
- Dr. Yukiumi Kita (Assistant Prof.)
- Dr. Taro Udagawa (Gifu Univ.)
- Mr. Katsu Koyanagi (M1 student)

- TOKYU Car (東急車輛)
  for electric power
  of our computer systems

TOKYU CAR CORPORATION

- JST
  PREST(03-06), CREST(07-08)
- KAKENHI
  KIBAN(B), Sakaki and Fujii
  Tokutei, Material-Design, etc
- YCU
  Strategic Research Project