Development of quantum chemical ab initio methods for accurate simulation of exotic molecules

第三回クラスター階層領域研究会
@東京工業大学(Zoom),
on 18st May, 2020.

横浜市立大学 (Yokohama City Univ.)
大学院生命ナノシステム科学研究科・データサイエンス学部
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    - 3.2. Origin of PAs Variation
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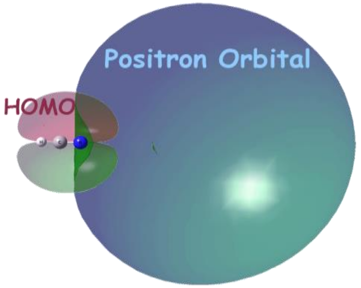
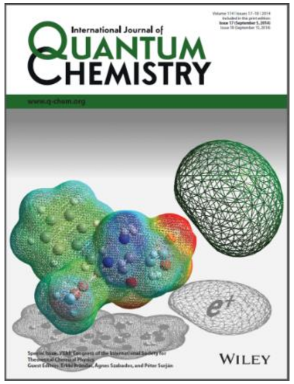
[HCN;e^+]

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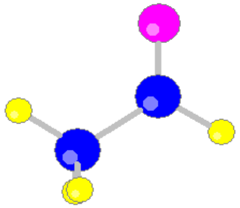
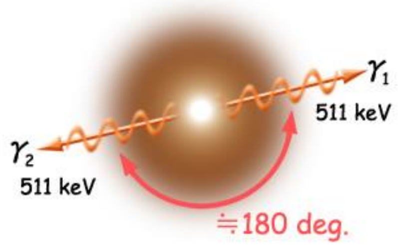

CH_3CHO

1.1. Introduction: Positron technology

➢ Positron (e^+)

- ✓ Anti-particle of an electron (e^-)
  mass= 1, spin=1/2, charge= +1 (atomic unit)
- ✓ Pair annihilation with an e^- and then two photons emission

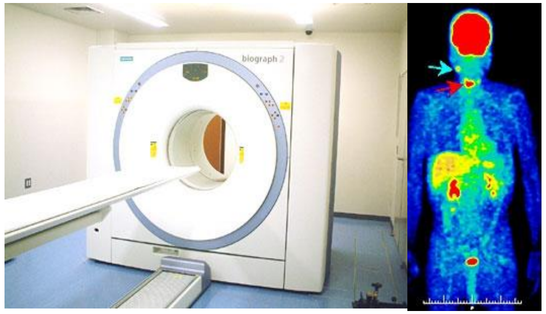


➢ Positron technologies

- PALS (Positron Annihilation Lifetime Spectroscopy)
- ACAR (Angular Correlation of Annihilation Radiation)
- PET (Positron Emission Tomography), etc

Cancer cell imaging

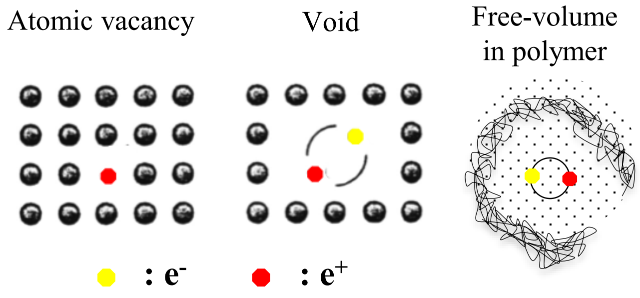
High-sensitive detection of cancer cell in human body



http://www.shinyokohama.jp/

Vacancy detection

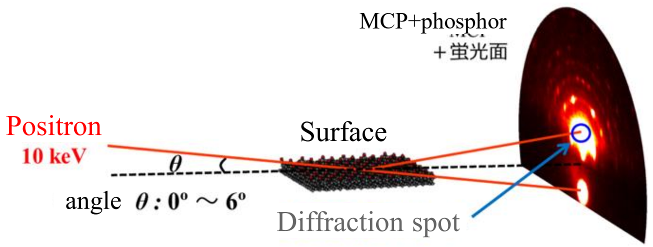
High-sensitive detection of vacancy or void in bulk crystals, polymers, etc.



陽電子計測の科学（日本アイソトープ協会）written in Japanese

Surface analysis

Accurate measurements of geometric and electronic structures on surface



KEK: http://www.kek.jp/ja/NewsRoom/Release/20131121140000/

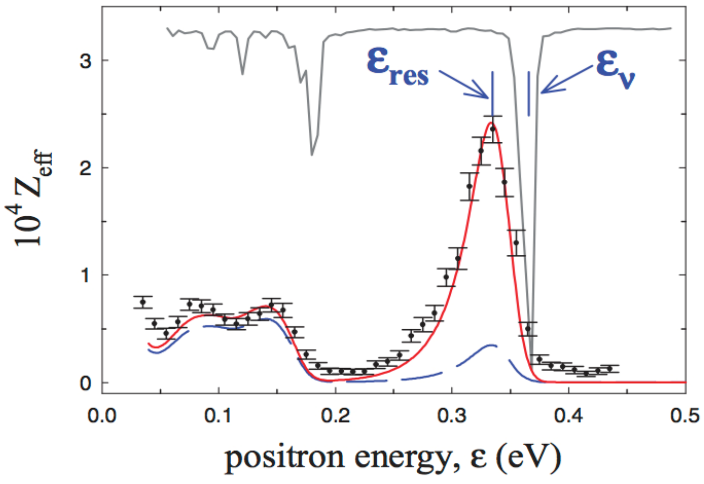
Recently, positron *technologies* are widely used in various fields.

However, the scientific knowledge about fundamental processes of positrons is still unclear at atomic/molecular levels !!

1.2. Experimental PA values !

Experimental side: [1]Danielson, Surko, et al. PRL. 104, 233201 (2010).

Surko and co-workers [1] measured the positron binding to many molecules through vibrational Feshbach resonance (VFR), and estimated the binding energy of a positron (positron affinity, PA) from the difference between VFR and IR spectra



VFR and IR spectra for butane (C_4H_{10}) [1]

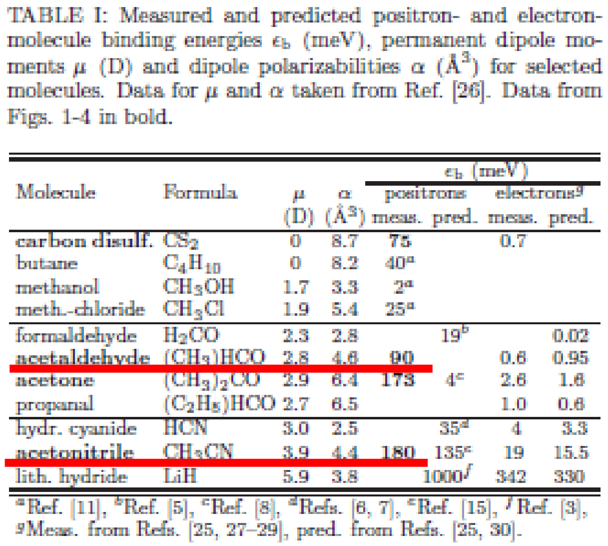
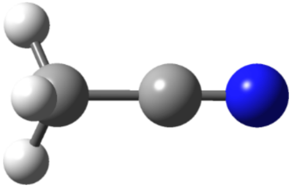
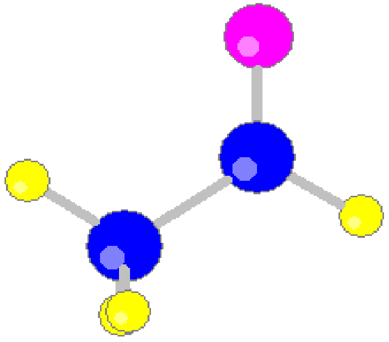


TABLE I: Measured and predicted positron- and electron-molecule binding energies ϵ_b (meV), permanent dipole moments μ (D) and dipole polarizabilities α (Å^3) for selected molecules. Data for μ and α taken from Ref. [26]. Data from Figs. 1-4 in bold.

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**	135^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].





- ***Theoretical interpretation for PA values!***
- ***Development of theoretical procedure!***

PA

$$= E(X) - E([X;e^+])$$

1.3. Purpose

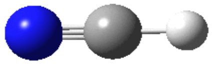
Theoretical elucidation of molecular vibrational effect on positron affinity (PA) values for polyatomic molecules.

- ✓ Theoretical analysis of molecular PA values including the effect of molecular vibrations (***vibrational averaged positron affinity***: **PA_v**)

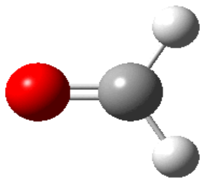
$$\mathrm{PA}_n^{\mathrm{A}} = \int dQ \left\{ E^{\mathrm{A}}(Q) - E^{[\mathrm{A};\mathrm{e}^+]}(Q) \right\} \left| \psi_n^{\mathrm{A}}(Q) \right|^2,$$ **Q** : normal mode coordinate

➡ The PA_v corresponds to the PA value at quantum vibrational states

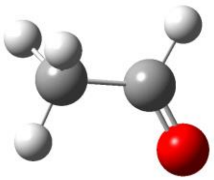
- ✓ Application to hydrogen cyanide (HCN), formaldehyde (H_2CO), and acetaldehyde (CH_3CHO), toward future works for larger molecules.



HCN



H_2CO



CH_3CHO

2.1. Multi-Component MO (MC_MO) method

✓ Total Hamiltonian for a positron-attached molecule:

The non-relativistic Hamiltonian (with atomic unit) of a positron-attached system consisting of *M* nuclei, *N* electrons, and a positron is given by

$$\mathscr{H} = -\frac{1}{2}\left(\sum_{i=1}^{N}\nabla_i^2 + \nabla_p^2\right) \underset{\text{e}^{-}\text{-Nuc.}}{- \sum_{I}^{M}\sum_{i}^{N}\frac{Z_I}{r_{iI}}} \underset{\text{e}^{-}\text{-e}^{-}}{+ \sum_{i}^{N}\sum_{j(>i)}^{N}\frac{1}{r_{iJ}}} \underset{\text{e}^{+}\text{-Nuc.}}{+ \sum_{I}^{M}\frac{Z_I}{r_{pI}}} \underset{\text{e}^{-}\text{-e}^{+}}{- \sum_{i}^{N}\frac{1}{r_{ip}}}$$

✓ Configuration interaction (CI) method

for a positron-attached molecule[1]

$$\left|\Psi_{\mathrm{CI}}(\mathbf{R}_{\mathrm{e}},\mathbf{r}_{\mathrm{p}})\right\rangle = C_{(0,0)}\left|\Phi_0^{\mathrm{e}}(\mathbf{R}_{\mathrm{e}})\right\rangle\left|\varphi_0^{\mathrm{p}}(\mathbf{r}_{\mathrm{p}})\right\rangle + \sum_{L_{\mathrm{e}}}\sum_{L_{\mathrm{p}}} C_{(L_{\mathrm{e}},L_{\mathrm{p}})}\left|\Phi_{L_{\mathrm{e}}}^{\mathrm{e}}(\mathbf{R}_{\mathrm{e}})\right\rangle\left|\varphi_{L_{\mathrm{p}}}^{\mathrm{p}}(\mathbf{r}_{\mathrm{p}})\right\rangle,$$

⇨ $F^{\mathrm{e}}_{L_{\mathrm{e}}}(\mathbf{R}_{\mathrm{e}})$: electronic Slater determinant, $C_{(L_{\mathrm{e}},L_{\mathrm{p}})}$: CI coefficients

$f^{\mathrm{p}}_{L_{\mathrm{p}}}(\mathbf{r}_{\mathrm{p}})$: a positronic molecular orbital,

---

[1] M.Tachikawa, H.Sainowo, K.Iguchi, and K.Suzuki *J. Chem. Phys.* **101** 5925 (1994).

2.1. Multi-Component MO method

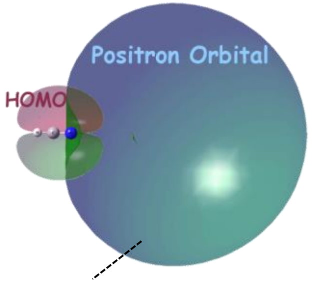
✓ Configuration interaction (CI) method for positronic compounds[1]

- Excited configurations: CISD

Our CISD method contains the single electronic, single positronic, both single electronic - single positronic excitation configurations

→ Pure electron-positron correlation is taken into account.

→ A frozen-core approximation was used for 1s orbital of heavy atoms.

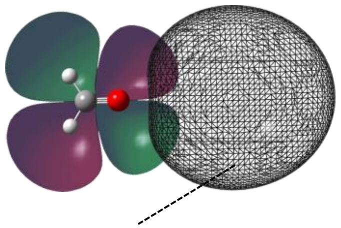


Positron orbital in [HCN;e^+]

- Basis sets:

[HCN;e^+]
- ✓ 6-31++G(2*df*,2*pd*) for e^-
- ✓ 15*s*15*p*3*d*2*f*1*g* Gaussian-type functions for e^+

[H_2CO;e^+]
- ✓ 6-31+G(3*d*2*f*) for e^-
- ✓ 12*s*8*p*6*d*2*f* Gaussian-type functions for e^+



Positron orbital in [H_2CO;e^+]

PA_{HCN} at the equilibrium geometry

HF[2] : 2.0 meV
DMC[2] : 38(5) meV
CISD : 39.6 meV

PA_{H_2CO} at the equilibrium geometry

HF[3] : 1.1 meV
DMC[3] : 25(3) meV
CISD : 25.3 meV

We confirmed that our PA values with **CISD calculation by MC_MO** are in reasonable agreement with those by very accurate **diffusion Monte Carlo (DMC)** ones[2,3].

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[1] M.Tachikawa, H.Sainowo, K.Iguchi, and K.Suzuki; J. Chem. Phys. **101**, 5925 (1994). [2] Y. Kita and M Tachikawa, Euro. Phys. J. D **68**, 116 (2014). [3] Y. Yamada, Y. Kita, and M. Tachikawa, Phys. Rev. A **89**, 062711 (2014).

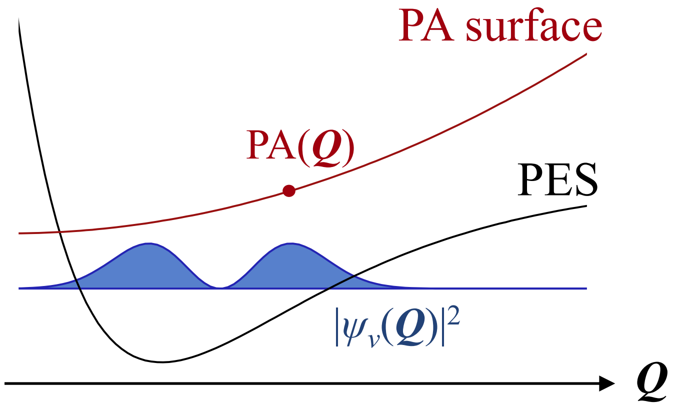
2.2. Vibrational effect on PA

✓ Vibrational averaged PA values[1]

We estimated "***vibrational averaged* PA values**", which correspond to the PA value on molecular vibrational state.

$$\mathrm{PA}_{\nu}^{\mathrm{A}} = \int d\boldsymbol{Q} \left\{ E^{\mathrm{A}}(\boldsymbol{Q}) - E^{[\mathrm{A;e^{+}}]}(\boldsymbol{Q}) \right\} \left| \psi_{\nu}^{\mathrm{A}}(\boldsymbol{Q}) \right|^{2},$$

$\boldsymbol{Q}$: normal mode coordinate



$E^{\mathrm{A}}(\boldsymbol{Q})$ - $E^{[\mathrm{A;e^{+}}]}(\boldsymbol{Q})$: ***vertical* PA at *Q*** ➡ by MC_MO (CISD) method [1]

ψ_{ν}^{A} ***: v-th vibrational wave function*** ➡ by vibrational QMC method [2,3]

$\int d\boldsymbol{Q}$ ***: integration over configuration space*** ➡ by Monte Carlo integration (Metropolis method)

---

[1] M.Tachikawa, H.Sainowo, K.Iguchi, and K.Suzuki; J. Chem. Phys. **101**, 5925 (1994). [2] Y. Kita and M Tachikawa, Euro. Phys. J. D **68**, 116 (2014). [3] Y. Yamada, Y. Kita, and M. Tachikawa, Phys. Rev. A **89**, 062711 (2014).

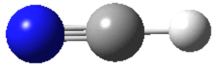
3.1. Vibrational PA values of HCN

PA at equilibrium geom.

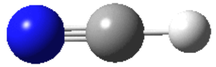
HF : 2.0 meV
DMC : 38(5) meV
CISD : 39.6 meV

Normal modes of HCN

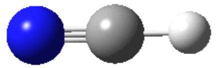
Bending mode

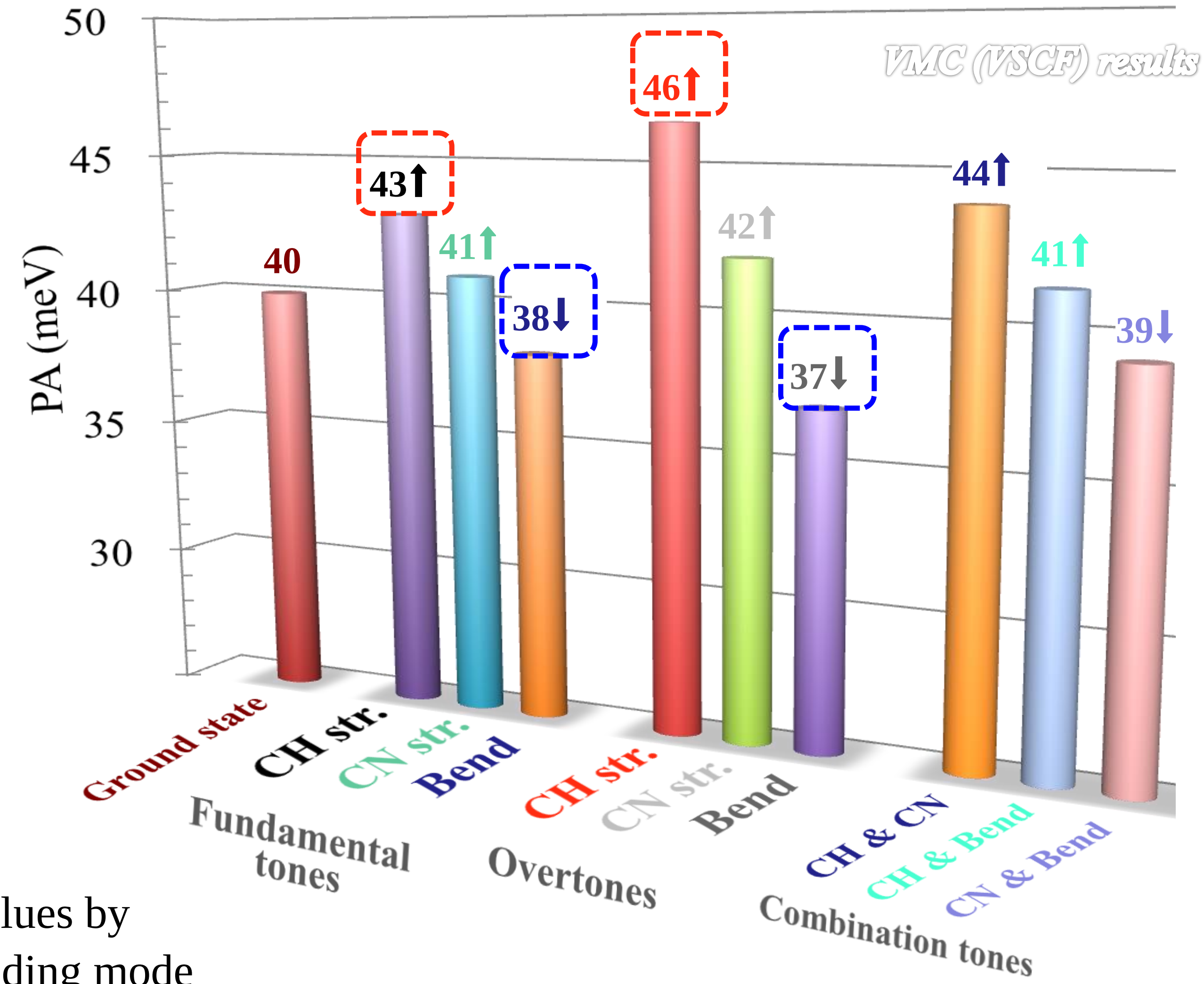


CN stretching



CH stretching





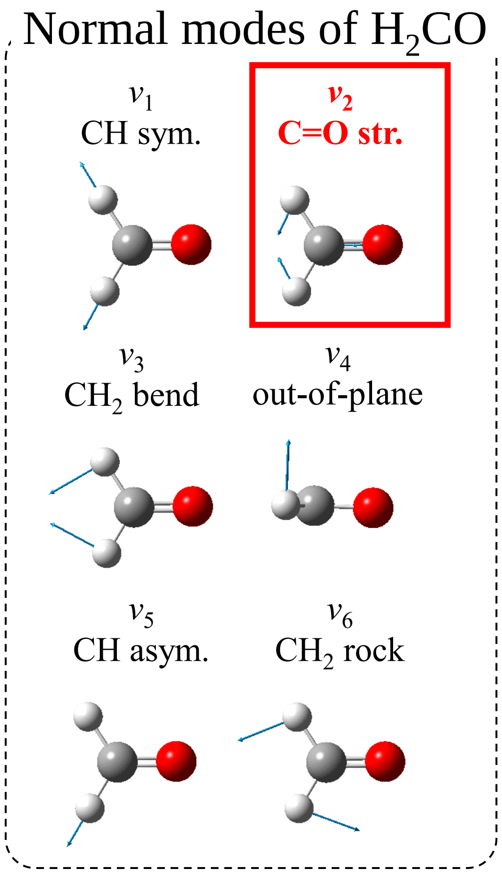
✓ ***Deenhancements*** of PA values by the vibrational excitations of bending mode

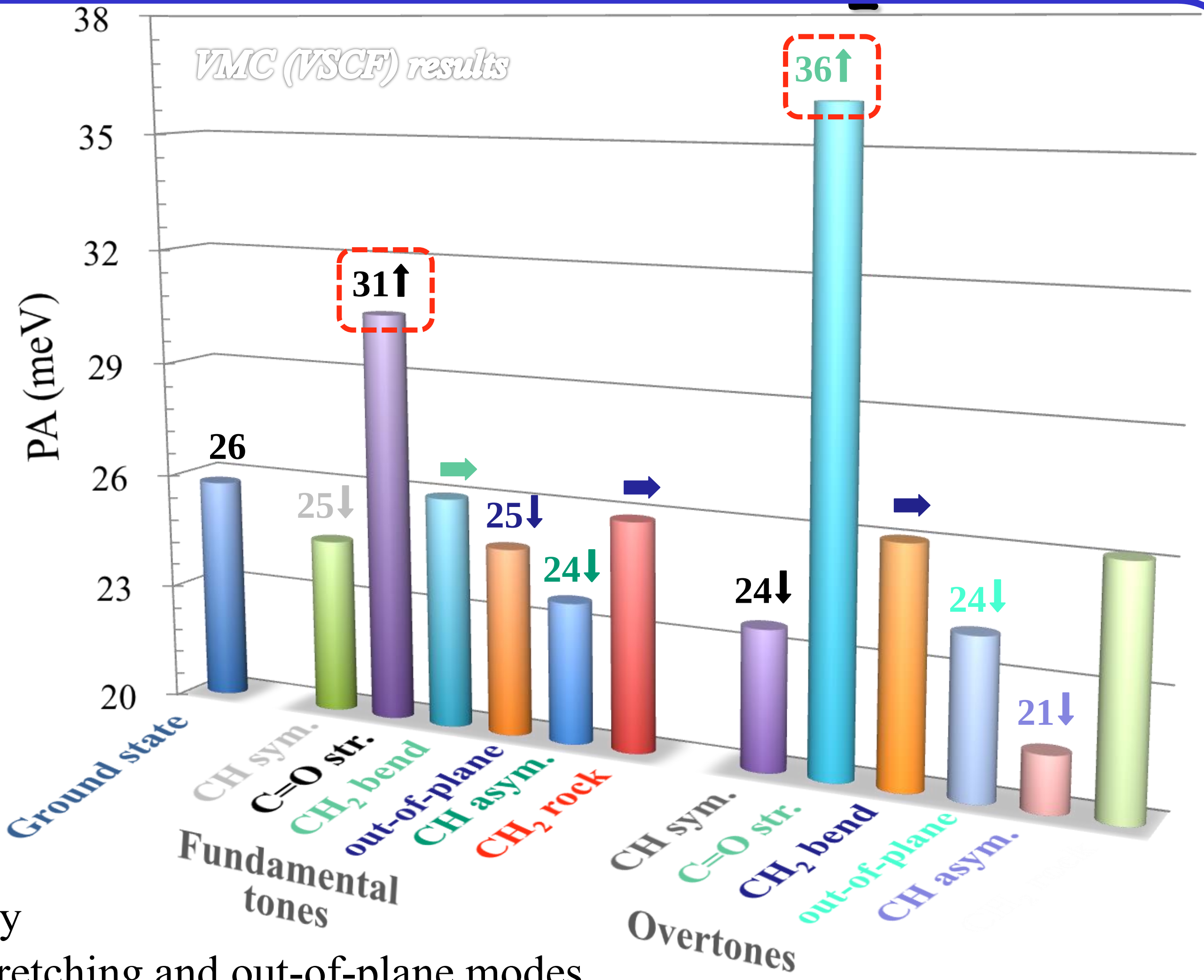
✓ ***Enhancements*** of PA values by the excitations of CH and CN stretching modes

➡ The excitation of CH str. mode gives the largest PA enhancement:

$PA_{v=1}$(CH str.)= 43.02(1) meV (8%↑), $PA_{v=2}$(CH str.)= 46.34(2) meV (16% ↑)

3.1. Vibrational PA values of H_2CO





✓ ***Deenhancements*** of PA values by the excitation of CH sym./asym. stretching and out-of-plane modes

✓ ***Enhancements*** of PA values by the excitation of C=O stretching mode

⇨ The excitation of C=O str. mode gives the largest PA enhancement:

$PA_{v=1}$(CO str.)= 30.7(1) meV (19%↑), $PA_{v=2}$(CO str.)= 36.1(1) meV (40%↑)

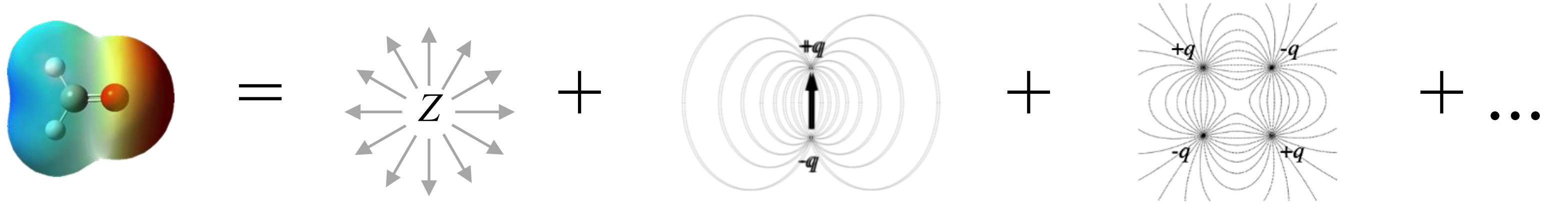
PA at equilibrium geom.

HF : 1.1 meV
DMC : 25(3) meV
CISD : 25.3 meV

3.2. The origin of PA variations

Dominant properties of a parent molecule in the interaction with an attached positron

✓ **Permanent electrostatic interaction with a parent molecule**



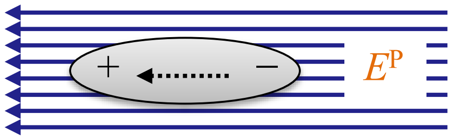
total charge distribution

total charge (Z)
→ zero for neutral mole.

dipole moment ($\boldsymbol{d}$)

quadrupole moment ($\boldsymbol{Q}$)

✓ **Interaction with the induced dipole moment due to a positron attachment**



induced dipole: $\boldsymbol{d}^{\mathrm{I}} = \alpha \times E^{\mathrm{P}}$

α : dipole-polarizability, E^{P} : electric field from a positron

In this modeling, we assumed that the interaction energy between a positron (+1 charge) and the parent molecule linearly depends on d, Q, and α.

e.g. dipole : $\frac{1}{4\pi\varepsilon_0 r^2}\boldsymbol{r}\cdot\boldsymbol{d}$ (or $\boldsymbol{d}^{\mathrm{I}} = \alpha E^{\mathrm{P}}$), quadrupole : $\frac{3}{8\pi\varepsilon_0 r^3}\sum_{i,j}^{x,y,z} Q_{ij} r_i r_j$

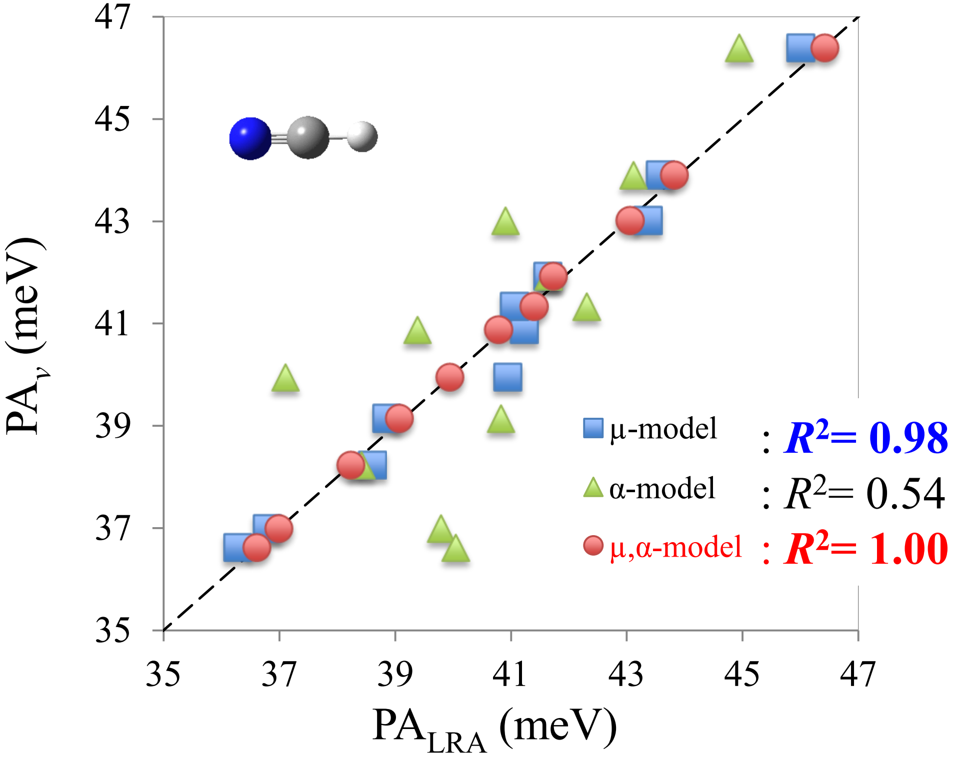
➡ It is strongly expected that the **linear regression analysis (LRA)** using $\boldsymbol{d}$, $\boldsymbol{Q}$, and $\boldsymbol{\alpha}$ of the parent molecule can be useful for explaining the origin of PA variations.

$$\mathrm{PA}_{\mathrm{LRA}} = c_\mu \mu_v + c_Q Q_v + c_\alpha \alpha_v + c_0,$$

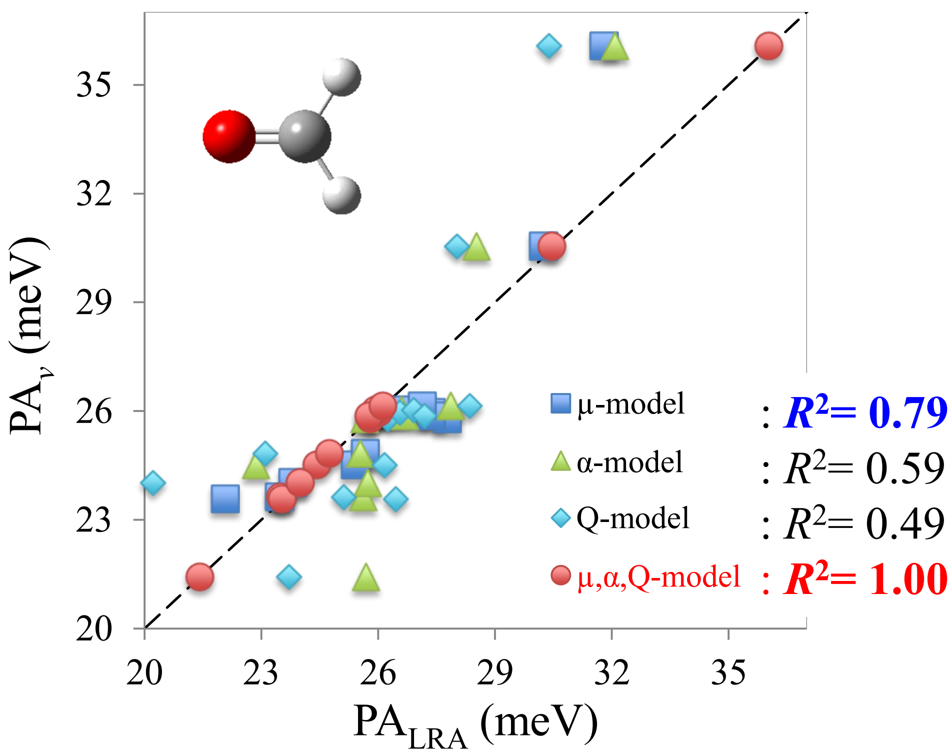
μ_v, Q_v, α_v : vibrational averaged μ, Q, and α at each state

3.2. The origin of PA variations

✓ **PA values of HCN in each state**



✓ **PA values of H_2CO in each state**



- ✓ For both molecules, the PA variations are well described by the change in both the multipole moment and dipole-polarizability.
- ✓ In the linear regression analyses, the dipole (*μ*) model gives the largest R^2 values for both molecules.

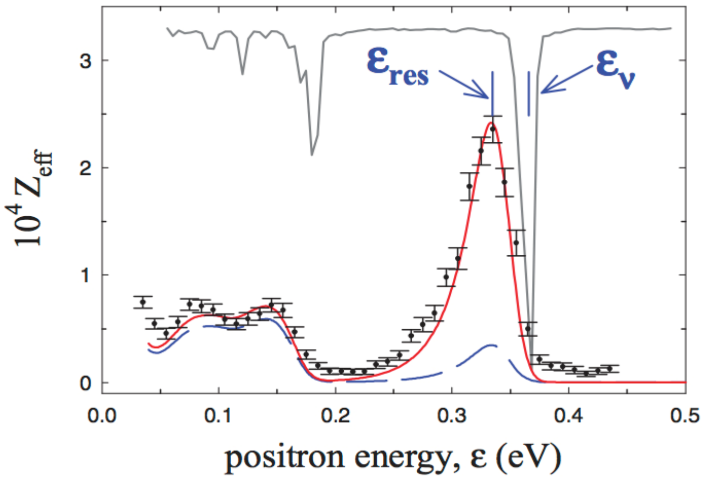
➡ **The origin of PA variations is mainly the change in the multipole moment by vibrational excitations**

1.2. Experimental PA values !

Experimental side:

[1]Danielson, Surko, et al. PRL. 104, 233201 (2010).

Surko and co-workers [1] measured the positron binding to many molecules through vibrational Feshbach resonance (VFR), and estimated the binding energy of a positron (positron affinity, PA) from the difference between VFR and IR spectra



VFR and IR spectra for butane (C_4H_{10}) [1]

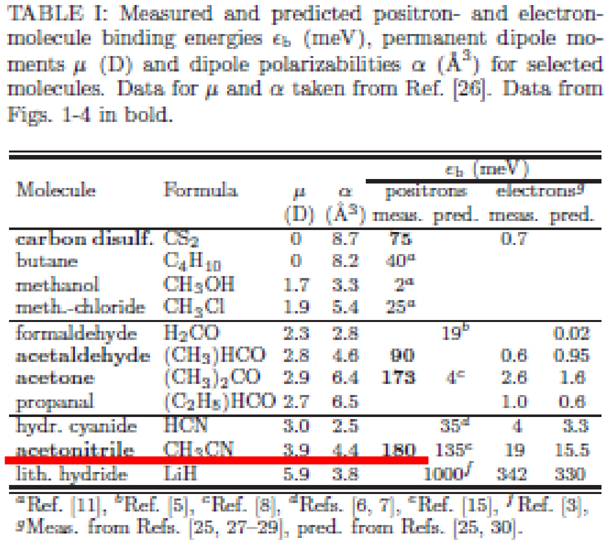
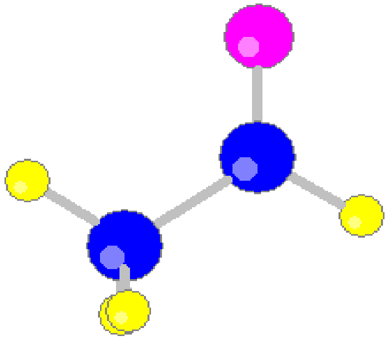


TABLE I: Measured and predicted positron- and electron-molecule binding energies ϵ_b (meV), permanent dipole moments μ (D) and dipole polarizabilities α (Å^3) for selected molecules. Data for μ and α taken from Ref. [26]. Data from Figs. 1-4 in bold.

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**	135[e]	19	15.5
lith. hydride	LiH	5.9	3.8		1000[f]	342	330

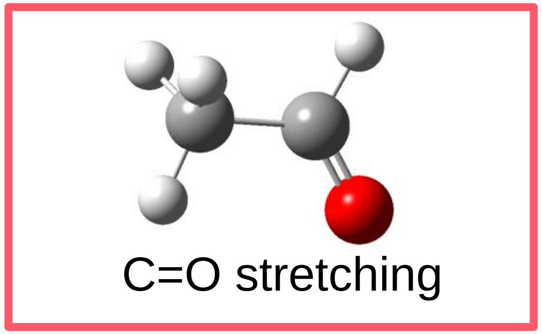
[a] Ref. [11], [b] Ref. [5], [c] Ref. [8], [d] Refs. [6, 7], [e] Ref. [15], [f] Ref. [3], [g] Meas. from Refs. [25, 27–29], pred. from Refs. [25, 30].

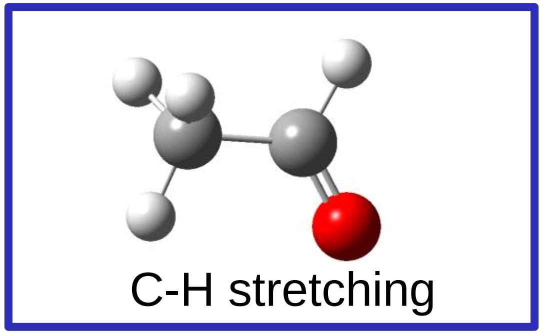


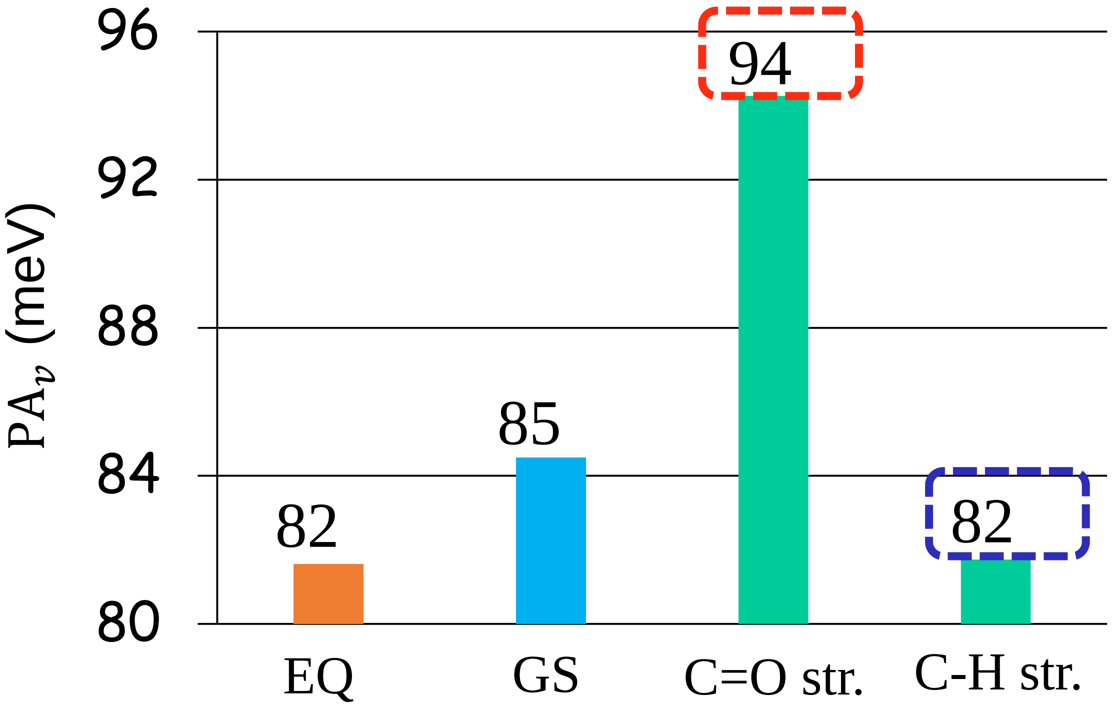
PA(CH_3HCO)
=90 meV

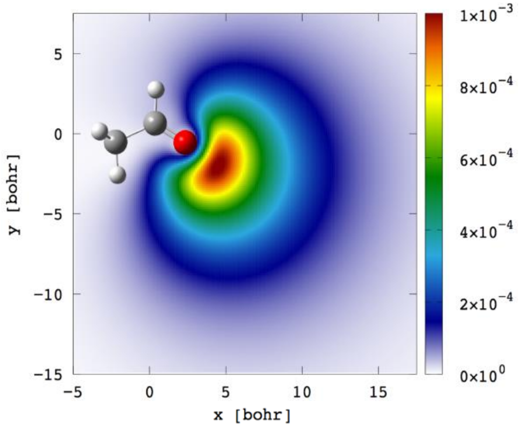
3.3. Vibrational PA values of CH_3CHO

NMs of CH_3HCO









✓ ***Deenhancements*** of PA values by the excitation of C-H stretching mode

✓ ***Enhancements*** of PA values by the excitation of C=O stretching mode

Two stretching modes of aldehyde (-CHO) group affect on PA$_v$ values of CH_3CHO molecule.

4. Summary

To elucidate the molecular vibrational effect on positron affinities (PAs), we analyzed the vibrational averaged positron affinity of HCN, H_2CO, and CH_3CHO molecules at various vibrational excited states.

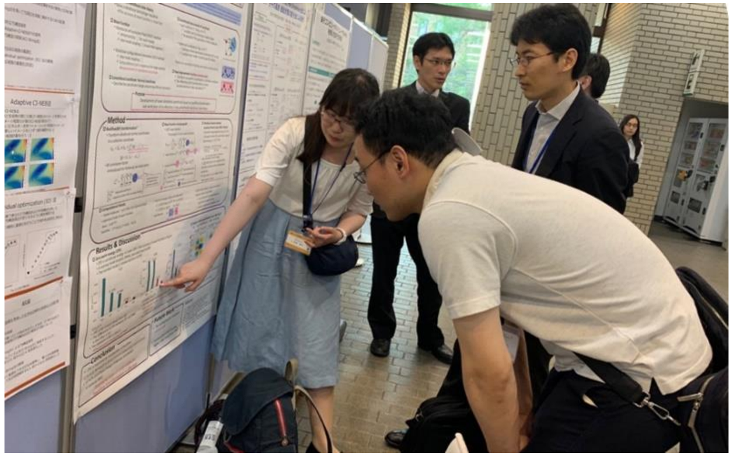
- ✓ The largest PA enhancement are found for the vibrational excitation of CH stretching mode for HCN, and that of C=O stretching mode for H_2CO

  ➡ The PA variations mainly arises from the change in the multipole moment and dipole-polarizability by vibrational excitations

  ➡ The change in permanent dipole moments is dominant in the PA variations.

- ✓ In CH_3CHO molecule, the vibrational averaged PA values for the C-H and C=O stretching modes are 82 and 94 meV, respectively, which can be compared with the corresponding experimental PA value of 90meV.

石井桐子（Ｄ１）
第22回理論化学討論会優秀ポスター賞
（QMC法による分子振動）



大場優生（Ｄ３）
ANSCSE23 Student Oral Award
（経路積分によるミューオン化合物）

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