

Academic Program [Oral B] | 03. Physical Chemistry -Structure- : Oral B

📅 Sat. Mar 29, 2025 9:00 AM - 10:00 AM JST | Sat. Mar 29, 2025 12:00 AM - 1:00 AM UTC 🏛️
[C]C204(C204, Bldg. 2, Area 2 [2F])

[[C]C204-4am] 03. Physical Chemistry -Structure-

Chair: Naoki Haruta, Haruto Ishikawa

🇬🇧 English

9:00 AM - 9:20 AM JST | 12:00 AM - 12:20 AM UTC

[[C]C204-4am-01]

Cold gas-phase spectroscopy of aromatic three-membered-ring carbon and silicon compound ions: correlation between splitting of degenerate $\pi\pi^*$ transitions and excited-state structures

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🇯🇵 Japanese

9:20 AM - 9:40 AM JST | 12:20 AM - 12:40 AM UTC

[[C]C204-4am-02]

Reassignment of the Vibronic Structure in the Absorption Spectrum of Carbon Cluster Anion C_6^- Exhibiting Fast Radiative Cooling

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🇯🇵 Japanese

9:40 AM - 10:00 AM JST | 12:40 AM - 1:00 AM UTC

[[C]C204-4am-03]

Molecular-level approach to glycan recognition in immune systems: Cryogenic ion spectroscopy of a partial peptide in mannose-binding proteins with monosaccharide

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Cold gas-phase spectroscopy of aromatic three-membered-ring carbon and silicon compound ions: correlation between splitting of degenerate $\pi\pi^*$ transitions and excited-state structures

(¹Graduate School of Advanced Science and Engineering, Hiroshima University, ²Faculty of Science and Engineering, Kindai University) ○ Masahiro Koyama,¹ Kei Ota,² Tsukasa Matsuo,² Satoru Muramatsu,¹ Yoshiya Inokuchi¹

Keywords: Aromatic three-membered-ring compound; Gas-phase spectroscopy; Cold ion trap; Electrospray ionization; $\pi\pi^*$ transition

Hückel 2π aromaticity, found in three-membered-ring carbon/silicon cations, is characterized by a π orbital and two degenerate π^* orbitals (Fig. 1). UV-vis absorption spectrum of $(\text{C}_3\text{Ph}_3)^+$ in solution, firstly reported over 60 years ago, exhibits several broad bands (Fig. 2a).¹ However, assignments of these bands still remain unresolved, hiding how the degenerate $\pi\pi^*$ transitions are reflected on electronic spectra. In this study, we performed ultraviolet photodissociation (UVPD) spectroscopy of $(\text{C}_3\text{Ph}_3)^+$ isolated in a cold (~ 10 K) ion trap.² This study reveals the splitting of the degenerate $\pi\pi^*$ transitions in the spectrum and its correlation with the excited-state structures.

UVPD spectrum of $(\text{C}_3\text{Ph}_3)^+$, generated by electrospray ionization of bromide precursor (C_3BrPh_3), exhibited several broad bands even under the cold gas-phase conditions (Fig. 2b). This result indicates that the broad profile is intrinsically determined by excited-state dynamics of $(\text{C}_3\text{Ph}_3)^+$. Actually, the observed band profile cannot be explained by the degenerate $\pi\pi^*$ transitions (Fig. 2c), which is predicted in the vertical transition scheme. DFT calculations suggested that the adiabatic transition energies of the two $\pi\pi^*$ states (S_1 , S_2) are significantly deviated ($\Delta E > 5000$ cm^{-1} ; Fig. 2d), well explaining the spectrum and unveiling the crucial contribution of structural relaxations on the excited-state potential surfaces. In the presentation, we further extend the study to other three-membered-ring carbon/silicon compound ions, $(\text{C}_3\text{Ph}_2\text{OH})^+$ and $[\text{Si}_3(\text{Eind})_3]^+$.³

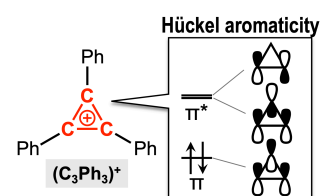


Fig. 1. Structure of target compound and π and π^* orbitals at the three-membered-ring.

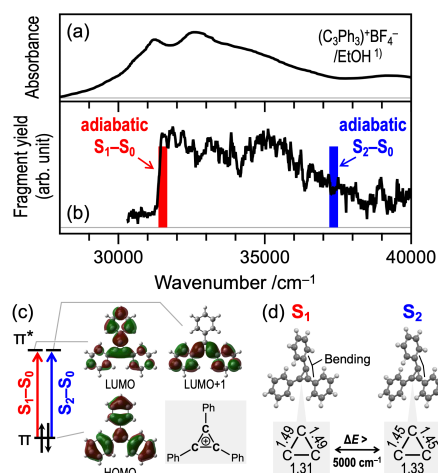


Fig. 2. (a) UV spectrum of $(\text{C}_3\text{Ph}_3)^+\text{BF}_4^-/\text{EtOH}$.¹ (b) UVPD spectrum of $(\text{C}_3\text{Ph}_3)^+$. Bar spectrum represents calculated adiabatic transition energies. (c) Kohn-Sham orbitals of $\pi\pi^*$ transitions. (d) Potential minimum structures of $(\text{C}_3\text{Ph}_3)^+$ at S_1 and S_2 .

1) Breslow, R.; *et al. J. Am. Chem. Soc.* **1958**, *80*, 5991. 2) Koyama, M.; *et al. J. Phys. Chem. Lett.* **2024**, *15*, 1493. 3) Ohno, R.; *et al. J. Am. Chem. Soc.* **2024**, *146*, 24911.

Reassignment of the Vibronic Structure in the Absorption Spectrum of Carbon Cluster Anion C_6^- Exhibiting Fast Radiative Cooling

(¹Fukui Institute for Fundamental Chemistry, Kyoto University, ²Graduate School of Engineering, Kyoto University) ○Tetsuri Takami,^{1,2} Naoki Haruta,^{1,2} Tatsuhisa Kato,¹ Tohru Sato^{1,2}

Keywords: Inverse Internal Conversion; Density Functional Theory; Vibronic Coupling; Recurrent Fluorescence; Interstellar Medium

Linear carbon cluster anions such as C_6^- have been thought to be promising candidates for interstellar molecules. Recent experiments have found that C_6^- exhibits fast radiative cooling from its highly vibrationally excited states via inverse internal conversion (IIC) in a collision-free vacuum system.^{1,2} Since IIC is driven by vibronic coupling,³ the vibronic structures of C_6^- are of theoretical importance. In the present study, we employ time-dependent density functional theory (TD-DFT) to calculate the absorption spectrum of C_6^- ; thereby, peaks in the experimental spectrum⁴ are reassigned to the vibronic progressions associated with the $C^2\Pi_g \leftarrow X^2\Pi_u$ and $D^2\Pi_g \leftarrow X^2\Pi_u$ electronic transitions (**Fig. 1**).

Vibronic coupling density (VCD) analysis⁵ reasonably explains prominent peaks in the experimental spectra. We also show the pseudo-Jahn–Teller distortion along the mode $\nu_4(\sigma_u^+)$ caused by the pseudo-degeneracy of $A^2\Sigma_g^+$ and $B^2\Sigma_u^+$ states, originating from lone-pair-like molecular orbitals. Further, potential softening in the excited states and its effects are also discussed.

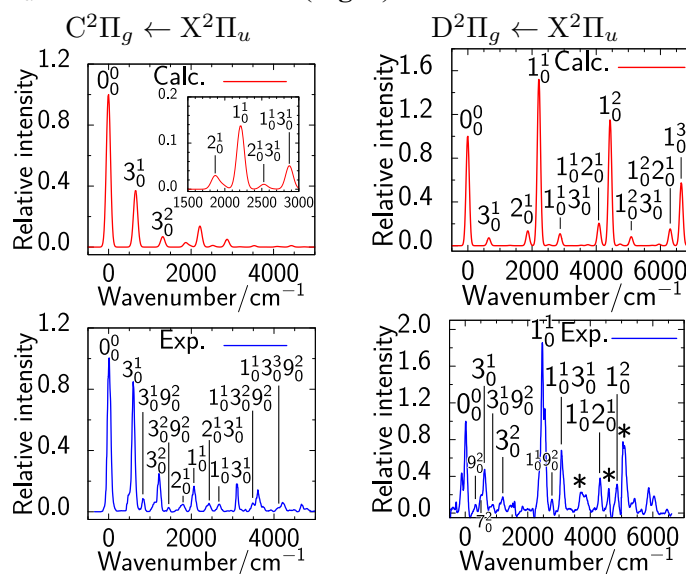


Fig. 1 The simulated absorption spectra of C_6^- (upper row) and the corresponding experimental ones⁴ (lower row).

- 1) G. Ito *et al.*, *Phys. Rev. Lett.* **2014**, *112*, 183001.
- 2) Y. Ebara *et al.*, *Phys. Rev. Lett.* **2016**, *117*, 133004.
- 3) W. Ota, M. Uejima, and T. Sato, *Bull. Chem. Soc. Jpn.* **2023**, *96*, 582.
- 4) P. Freivogel *et al.*, *J. Chem. Phys.* **1997**, *107*, 22.
- 5) T. Kato, N. Haruta, T. Sato, *Vibronic Coupling Density: Understanding Molecular Deformation*, Springer, Singapore, **2021**.

免疫システムにおける糖鎖認識機構への分子論的アプローチ：マンノース結合型タンパク質部分ペプチド-糖複合体の冷却イオン分光

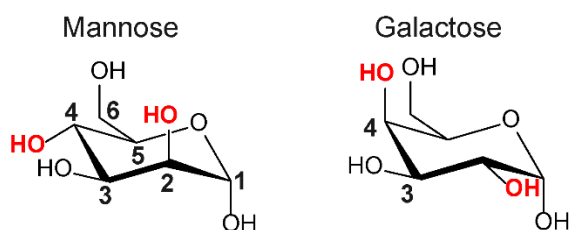
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Molecular-level approach to glycan recognition in immune systems: Cryogenic ion spectroscopy of a partial peptide in mannose-binding proteins with monosaccharide (¹*Institute of Science Tokyo*) ○Keisuke Hirata,¹ Taisei Takahashi,¹ Shun-ichi Ishiuchi,¹

The immune system is based on the identification of self and non-self. Mannose-binding proteins (MBPs) recognize mannose, a monosaccharide unique to the surface of pathogens, which activates the system of pathogen elimination. On the other hand, they do not bind galactose, which is unique to human erythrocytes. In this study, we aimed to elucidate the mechanism of the immune system in MBPs at the molecular level by utilizing the cutting-edge gas-phase infrared spectroscopy.

Keywords : *Infrared Spectroscopy; Molecular Recognition; Gas-phase Spectroscopy*

免疫系の基本は、自己と非自己を識別する能力である。細胞表面の糖鎖は細胞の種類や状態を示す指標であり、病気や免疫に深く関与する。糖鎖を認識する糖結合タンパク質をレクチンといい、マンノース結合レクチン (MBL) は病原体糖鎖特有のマンノース (図) に結合し、免疫反応を誘導して病原体の分解を促進する。一方で MBL はヒト赤血球特有のガラクトース (図) には結合しない。X 線結晶構造解析では、MBL 中の Ca^{2+} がマンノースの特定の部位と結合することが判明している¹が、ガラクトースとの結晶構造が得られていないため、この選択性の理由は不明である。そこで本研究では、糖と MBL の結合部位、さらには Ca^{2+} を組み合わせた複合体を気相中に取り出し、赤外分光法を用いて MBL の糖認識メカニズムを解明することを目指した。その結果、マンノース、ガラクトースともに Ca^{2+} に対して 3 つの OH 基で配位する三配位構造を取り、両者に構造的な違いはほとんど見られないことが分かった。実際のタンパク質では多数の水分子があることが分かっており、MBL の糖認識に水和が重要であることが示唆された。



1) K. K.-S. Ng *et al.*, *J. Biol. Chem.* **1996**, 271, 663.