アカデミックプログラム［B講演］｜03. 物理化学—構造：口頭B講演

2025年3月29日(土) 9:00 ~ 10:00 [C]C204(第2学舎 2号館 [2階] C204)

[[C]C204-4am] 03. 物理化学—構造

座長：春田 直毅、石川 春人

英語

9:00 ~ 9:20

[[C]C204-4am-01]

炭素およびケイ素芳香族三員環化合物イオンの極低温気相分光：ππ*縮重遷移の分裂と励起状態構造との関係

○小山 雅大[1]、太田 圭[2]、松尾 司[2]、村松 悟[1]、井口 佳哉[1] (1. 広島大、2. 近畿大)

日本語

9:20 ~ 9:40

[[C]C204-4am-02]

高速な輻射冷却を示す炭素クラスター負イオンC_6^-の吸収スペクトルにおける振電構造の再帰属

○高見 哲理[1,2]、春田 直毅[1,2]、加藤 立久[1]、佐藤 徹[1,2] (1. 京大福井セ、2. 京大院工)

日本語

9:40 ~ 10:00

[[C]C204-4am-03]

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

○平田 圭祐[1]、高橋 太星[1]、石内 俊一[1] (1. 東京科学大学)

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

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

Keywords: Aromatic three-membered-ring compound; Gas-phase spectroscopy; Cold ion trap; Electrospray ionization; ππ* 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 $(C_3Ph_3)^+$ 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 ππ* transitions are reflected on electronic spectra. In this study, we performed ultraviolet photodissociation (UVPD) spectroscopy of $(C_3Ph_3)^+$ isolated in a cold (~10 K) ion trap.[2] This study reveals the splitting of the degenerate ππ* transitions in the spectrum and its correlation with the excited-state structures.

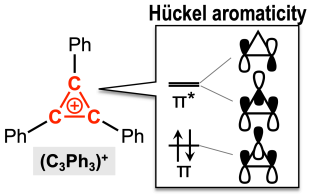

Fig. 1. Structure of target compound and π and π* orbitals at the three-membered-ring.

UVPD spectrum of $(C_3Ph_3)^+$, 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 $(C_3Ph_3)^+$. Actually, the observed band profile cannot be explained by the degenerate ππ* transitions (Fig. 2c), which is predicted in the vertical transition scheme. DFT calculations suggested that the adiabatic transition energies of the two ππ* states (S_1, S_2) are significantly deviated (ΔE > 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, $(C_3Ph_2OH)^+$ and $[Si_3(Eind)_3]^+$.[3]

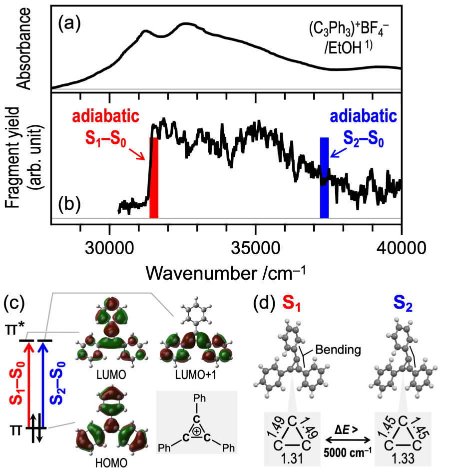

Fig. 2. (a) UV spectrum of $(C_3Ph_3)^+BF_4^-/EtOH$.[1] (b) UVPD spectrum of $(C_3Ph_3)^+$. Bar spectrum represents calculated adiabatic transition energies. (c) Kohn-Sham orbitals of ππ* transitions. (d) Potential minimum structures of $(C_3Ph_3)^+$ at S_1 and S_2.

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

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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 spectrum[4] are reassigned to the vibronic progressions associated with the $\mathrm{C}^2\Pi_g \leftarrow \mathrm{X}^2\Pi_u$ and $\mathrm{D}^2\Pi_g \leftarrow \mathrm{X}^2\Pi_u$ electronic transitions (**Fig. 1**).

Vibronic coupling density (VCD) analysis[5] 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 $\mathrm{A}^2\Sigma_g^+$ and $\mathrm{B}^2\Sigma_u^+$ states, originating from lone-pair-like molecular orbitals. Further, potential softening in the excited states and its effects are also discussed.

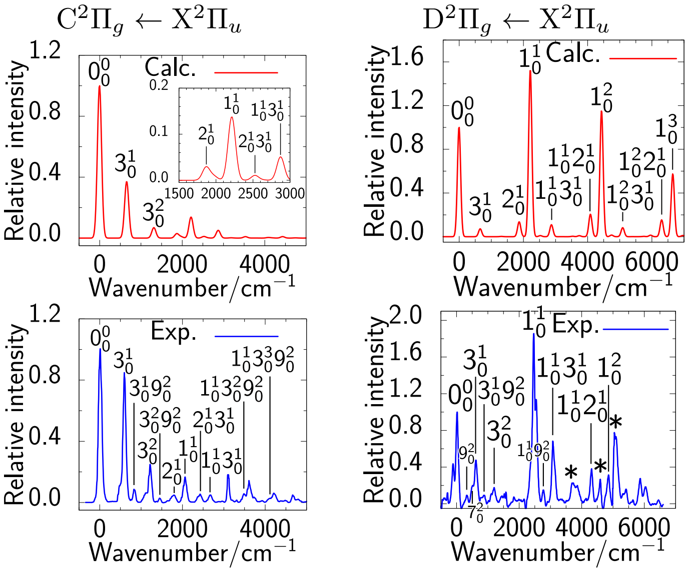


Fig. 1 The simulated absorption spectra of C_6^- (upper row) and the corresponding experimental ones[4] (lower row).

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

（東京科学大[1]）○平田 圭祐[1]・高橋 太星[1]・石内 俊一[1]

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

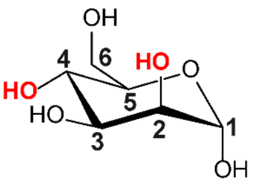
([1]*Institute of Science Tokyo*) ○Keisuke Hirata,[1] Taisei Takahashi,[1] Shun-ichi Ishiuchi,[1]

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.

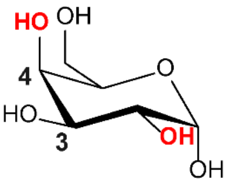
Keywords : Infrared Spectroscopy; Molecular Recognition; Gas-phase Spectroscopy

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。

Mannose



Galactose



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