

アカデミックプログラム [B 講演] | 05. 物理化学—反応：口頭B講演

📅 2025年3月27日(木) 15:55 ~ 17:15 🏢 [C]C401(第2学舎 2号館 [4階] C401)

[[C]C401-2vn] 05. 物理化学—反応

座長：美齊津 文典、堀尾 琢哉

📌 日本語

15:55 ~ 16:15

[[C]C401-2vn-01]

極低温イオントラップ気相分光装置の開発・改良と配位子保護金属クラスターへの適用の試み

○村松 悟¹、四方 嶺宏¹、入口 時代¹、小山 雅大¹、井口 佳哉¹ (1. 広島大)

📌 日本語

16:15 ~ 16:35

[[C]C401-2vn-02]

イオン画像観測法による振電励起された N_3^+ の光解離過程の研究○福富 実¹、渡部 悠¹、小柴 拓実¹、小湊 瑞央¹、菅野 学¹、大下 慶次郎¹、美齊津 文典¹ (1. 東北大)

📌 英語

16:35 ~ 16:55

[[C]C401-2vn-03]

インジウムクラスターの酸化耐性

○小安 喜一郎¹、佃 達哉¹ (1. 東大院理)

📌 英語

16:55 ~ 17:15

[[C]C401-2vn-04]

Dopant effects on the electronic and geometric structures of silver clusters: UV-VIS photodissociation studies

○Olga Lushchikova¹, Miho Hirakawa¹, Yuna Aonuma¹, Ukyo Kawamura¹, Takuya Horio¹, Akira Terasaki¹ (1. Kyushu University)

極低温イオントラップ気相分光装置の開発・改良と配位子保護金属クラスターへの適用の試み

(広島大院先進) ○村松 悟, 四方 嶺宏, 入口 時代, 小山 雅大, 井口 佳哉

Developing and improving a cryogenic ion-trap-based gas-phase spectrometer for applications to ligand-protected metal clusters (*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Satoru Muramatsu, Minehiro Shikata, Jidai Iriguchi, Masahiro Koyama, Yoshiya Inokuchi

We present the current progress in developing and improving a new cryogenic ion-trap-based gas-phase spectrometer designed for cluster compounds. The incorporation of new ion optics including (1) a three-stage ion lens in front of the ion trap and (2) a potential-switch electrode for ion-acceleration into the time-of-flight mass spectrometer significantly enhanced the observed ion intensity. These improvements enabled an attempt for application to a phosphine-protected gold cluster, $[\text{Au}_6(\text{dppp})_4]^{2+}$.

Keywords: gas-phase spectroscopy; photodissociation spectroscopy; cryogenic ion trap; metal clusters; ion-optics simulations

近年の極低温イオントラップによる気相孤立イオン冷却法の進展により、超分子錯体や生体高分子など種々の不揮発性種の気相分光が実現されてきた。この分光法の最たる利点は、スペクトルの高分解能化によって異性体間のわずかな構造を分光学的に明瞭に区別でき、さらには多重共鳴法によって異性体を選別した分光計測が可能になることにある。一方で、最近、配位子保護金属クラスターにおいて、金属コア構造や配位子の配座の違いに由来するエネルギー的に近い異性体が共存するという描像が一般的に確立されつつある。そこで、この気相分光手法を配位子保護金属クラスターに適用することで、各異性体の安定化要因や構造の違いに起因して発現する機能を解明することを目指し、そのための新たな分光装置[1]の開発に着手した。

装置はエレクトロスプレーイオン化 (ESI) 源、八極子イオンガイド (OPIG)、極低温 3 次元四重極イオントラップ (QIT)、飛行時間型質量分析計 (TOF-MS) で構成した (図 1)。特に OPIG と QIT の間を 3 段のイオンレンズで接続し、TOF-MS のイオン加速に円筒形のポテンシャルスイッチ電極を採用することで、イオン検出効率が大幅に (開発当初の数十倍程度に) 改善した。発表では、本装置により実現したホスフィン保護金クラスター $[\text{Au}_6(\text{dppp})_4]^{2+}$ の光解離分光の試みを報告する。

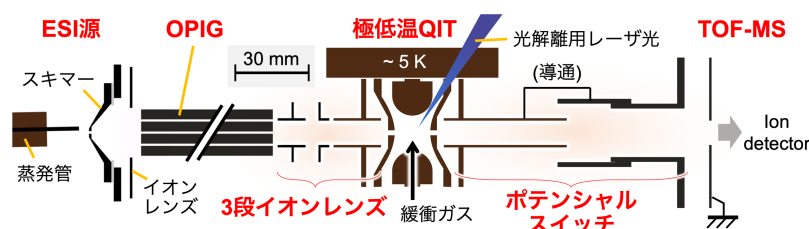


図 1. 製作中の極低温イオントラップ気相分光装置.

[1] Koyama, M.; Muramatsu, S.; *et al. J. Phys. Chem. Lett.* **2024**, *15*, 1493.

【謝辞】本研究を進めるにあたり、東京大学の佃達哉教授および高野慎二郎助教にクラスター試料のご提供を賜りました。ここに深く感謝いたします。

イオン画像観測法による振電励起された N_3^+ の光解離過程の研究

(東北大理¹・東北大院理²) ○福富実¹, 渡部悠², 小柴拓実², 小湊瑞央²,
菅野学², 大下慶次郎², 美齊津文典²

Ion imaging study of the photodissociation dynamics of vibronically excited N_3^+

(¹Faculty and ²Graduate School of Science, Tohoku University)

○Minoru Fukutomi,¹ Yu Watabe,² Takumi Koshiba,² Mizuhiro Kominato,²
Manabu Kanno,² Keijiro Ohshimo,² Fuminori Misaizu²

Linear N_3^+ ion is dissociated to form N_2 and N^+ after UV photoexcitation ($A^3\Pi_u \leftarrow X^3\Sigma_g^-$), in which sharp absorption peaks lie corresponding to vibronically excited states.¹⁾ In this study, energy distributions of the fragments after photodissociation were investigated via different vibronic states by an ion imaging technique. A linearly-polarized photolysis laser was irradiated to mass-selected N_3^+ , and the N^+ fragment ion was detected as a 2D image. As a result, a small amount of the available energy was distributed to the translational energies (Fig. 1), and the balance was partitioned to the rovibrational energies of N_2 . This result is consistent with the potential energy calculation (Fig. 2), which predicts a rotational excitation of the N_2 fragment due to the N_3^+ structural change in the excited state. Also, the dissociation processes were hardly affected by the vibrational excited states.

Keywords: Photodissociation; Ion imaging; Reaction dynamics; Vibronic excitation

直線構造の N_3^+ イオンでは、紫外領域に基底状態 $X^3\Sigma_g^-$ から電子励起状態 $A^3\Pi_u$ の各振動準位への遷移に対応する複数の鋭い吸収ピークが観測される。さらにこの光吸収の後 N_2 と N^+ への解離反応が起こる¹⁾。本研究では、 N_3^+ の光解離過程における初期振電励起状態依存性を、イオン画像観測法を用いて調べた。実験では、励起状態に共鳴した直線偏光のレーザーを質量選別された N_3^+ に照射して、解離生成物 N^+ の散乱速度分布を得た。その結果観測された解離生成物の並進エネルギー E_t の全余剰エネルギー E_{avl} に占める割合 (Fig. 1) は、統計的モデルの 2/3 程度と小さく、中性解離生成物 N_2 の振動回転励起に多く分配されることが分かった。理論計算では、 $N_3^+(A^3\Pi_u)$ は NNN 結合角が折れた準安定構造(▲)をもつ (Fig. 2)。直線構造(●)からこの準安定構造を経由して解離することで N_2 の回転が強く励起されたと考えられる。また、反対称伸縮振動が励起された場合 (3_0^2) でも振動基底状態 (0_0^0) とほぼ同じ並進エネルギー分布となった (Fig. 1)。ゆえに直線性を保つ振動励起では解離過程がほぼ変化しないと考えられる。

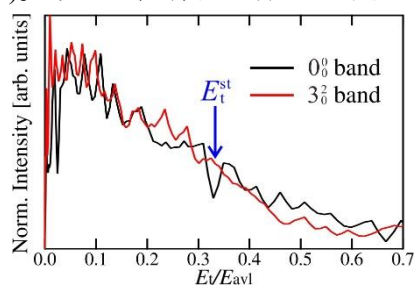


Fig. 1 Translational energy distribution.
 E_t^{st} indicates E_t in the statistical theory.

1) A. Friedmann *et al.*, *J. Phys. Chem.* **98**, 8896 (1994).

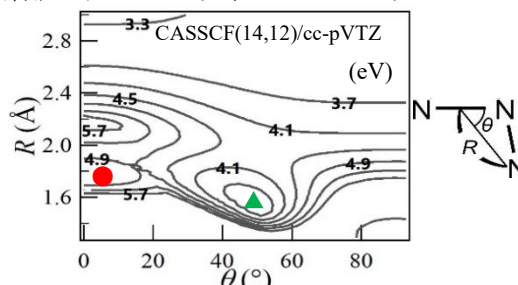


Fig. 2 Potential energy surface of the $A^3\Pi_u$ state.
●: The stable structure of the ground state.
▲: The metastable structure of the $A^3\Pi_u$ state.

Resistance of indium clusters towards oxidation reaction in gas phase

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Keywords: Metal Clusters, TOF Mass Spectrometry, Photoelectron Spectroscopy, DFT Calculations, Pulsed Discharge

Metal clusters, consisting of several to a few hundred metal atoms, attract much attention for their discrete electronic structures with unique geometric structures different from the bulk states. We have attempted to synthesize ligand-protected indium clusters by chemical reduction of In ion in solution and obtained $\text{In}_{15}(\text{PhCO}_2)_{13}$ as the main product.¹ These In clusters were stable against oxidation under aerobic condition similar with the clusters of aluminum in the same 13 group: the magic Al_{13}^- cluster showing poor activity to O_2 in the gas phase demonstrates high stability under atmosphere.² In this study, we investigate the oxidation reactions of naked In_n^- to gain insight into the origin of the resistance to oxidation.

Indium cluster anions were formed by a laser vaporization method and introduced into the reaction cell directly after the source, in which O_2 gas (0.5 MPa) was introduced through a pulse valve (200 μs) and the pulsed discharge (~ 1 kV, 100 μs , 10 Hz) was synchronized with the cluster formation. The formed clusters of In_nO_m^- ($n = 4-8$; $m = 0-3$) were analyzed by a time-of-flight mass spectrometer with a magnetic bottle-type photoelectron energy analyzer.

Figure 1a shows a typical mass spectrum of In_nO_m^- . Less amount of In_nO_m^- was observed for $n \geq 6$ in contrast to $n \leq 5$. According to the previous photoelectron spectra of In_n^- , even-odd alternation was observed for $n \geq 4$:³ even clusters have lower electron affinities than those of odd clusters, suggesting that In_6^- is more active than In_5^- from the point of view of electron pairing. However, no even-odd alternation was observed, but a threshold size was observed in the oxidation reactivity, implying that the origin of the reactivity may be due to the geometric factor. As previously reported theoretically, the structures of In_n^- are planar for $n \leq 5$, while those for $n \geq 6$ are three-dimensional (Fig. 1b-c),⁴ indicating that higher coordination number in three-dimensional structures prevents adsorption of O on In_n^- .

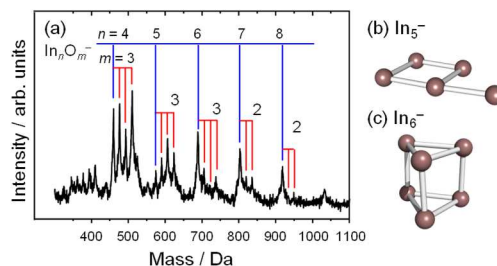


Figure 1. (a) typical mass spectrum of In_nO_m^- , and optimized structures of In_5^- (b) and In_6^- (c).

1) K. Koyasu *et al.* the 17th annual meeting of Japa Society of Molecular Science, **2023**, 3B10. 2) T. Kambe *et al.* *Nature Commun.* **2017**, 2046. 3) M. Gausa *et al.* *Int. J. Mass Spectrom.* **1990**, 102, 227. 4) S. Shi *et al.* *Compt. Theor. Chem.* **2016**, 1079, 47.

Dopant effects on the electronic and geometric structures of silver clusters: UV-VIS photodissociation studies

(¹*Department of Chemistry, Faculty of Science, Kyushu University*) ○ Olga Lushchikova¹, Miho Hirakawa¹, Yuna Aonuma¹, Ukyo Kawamura¹, Takuya Horio¹, Akira Terasaki¹

Keywords: Doped silver clusters, UV-VIS photodissociation spectroscopy, Geometric structure, Electronic structure

Cationic silver clusters doped with a single foreign atom provide an effective platform for testing the two-step Jellium model, wherein the dopant atom modulates the potential within the silver cluster that is otherwise homogeneous. This model was investigated using UV-VIS photodissociation spectroscopy of trapped ions, complemented by TD-DFT calculations. Additionally, reactivity measurements with oxygen were conducted to gain further insight into the position of the dopant within the cluster.

The results for Ag_nSc^+ and Ag_nAl^+ reveal striking differences: fewer silver atoms are required to encapsulate Sc compared to Al, despite both dopants contributing the same number of valence electrons. Figure 1 shows the photodissociation spectra and structural differences between pure and doped silver clusters with the same valence electron count, highlighting the dopants' impact on the cluster's geometry and electronic structure.

To further explore these effects, we extend the study to include other transition metal dopants (V, Mn, Co, Ni). By systematically varying the valence electron count, we examine how different dopants affect the cluster's geometric arrangement and electronic properties. Additionally, we explore how the number of silver atoms alters the electronic structure while maintaining a constant electron count. This approach enables us to disentangle the influences of cluster size and electron count on the electronic behavior.

Our findings provide valuable insights into the interplay between electronic and geometric structures in doped metal clusters, offering a deeper understanding of how dopants modulate cluster properties. These insights are crucial for advancing the design of metal clusters for applications in catalysis and nanotechnology.

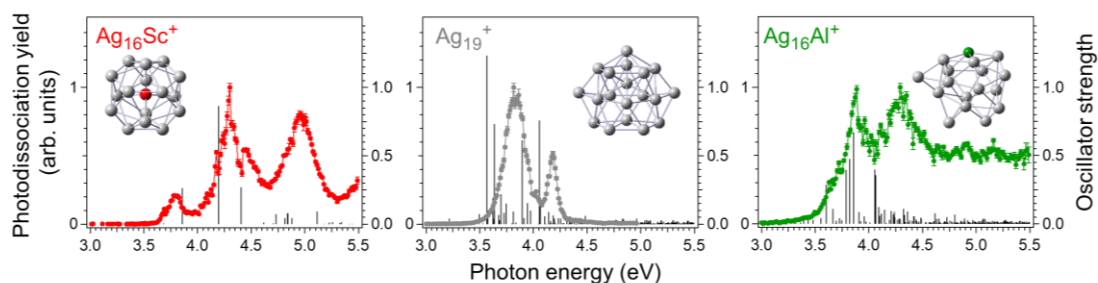


Figure 1: Photodissociation spectra (represented by dots) of $\text{Ag}_{16}\text{Sc}^+$, Ag_{19}^+ , and $\text{Ag}_{16}\text{Al}^+$, all with the same valence electron count, complemented by the best-matching TD-DFT calculations (shown as bars) and corresponding structures.