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PREBIOTIC CHEMISTRY, CHIRALITY

Chiral Recognition in Cold Gas-Phase Cluster Ions of Carbohydrates and Tryptophan Probed by Photodissociation

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Abstract

Chiral recognition between tryptophan (Trp) and carbohydrates such as D-glucose (D-Glc), methyl-α-D-glucoside (D-glucoside), D-maltose, and D-cellobiose in cold gas-phase cluster ions was investigated as a model for chemical evolution in interstellar molecular clouds using a tandem mass spectrometer containing a cold ion trap. The photodissociation mass spectra of cold gas-phase clusters that contained Na^+, Trp enantiomers, and D-maltose showed that Na^+(D-Glc) was formed via the glycosidic bond cleavage of D-maltose from photoexcited homochiral Na^+(D-Trp)(D-maltose), while the dissociation did not occur in heterochiral Na^+(L-Trp)(D-maltose). The enantiomer-selective dissociation was also observed in the case of D-cellobiose. The enantiomer-selective glycosidic bond cleavage of disaccharides suggested that photoexcited D-Trp could prevent chemical evolution of sugar chains from D-enantiomer of carbohydrates in molecular clouds. The spectra of gas-phase clusters that contained Na^+, Trp enantiomers, and D-Glc indicated that enantiomer-selective protonation of L-Trp from D-Glc could induce enantiomeric excess via collision-activated dissociation of the protonated L-Trp. In the case of protonated clusters, photoexcited H^+(L-Trp) dissociated via C_α–C_β bond cleavage in the presence of D-Glc or D-glucoside, where the excited states of H^+(L-Trp) contributed to the enantiomer-selective reaction in the clusters. These enantiomer selectivities in cold gas-phase clusters indicated that chirality of a molecule induced enantiomeric excess of other molecules via enantiomer-selective reactions in molecular clouds.

Keywords Chemical evolution · Molecular cloud · Enantiomer · Chirality · Mass spectrometry

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Introduction

Molecular clouds in the atmosphere play important roles in radiative transfer, precipitation, and optical processes. Ice nucleation on mineral dust, soot, organic molecules, and biological particles has been investigated using a continuous flow diffusion chamber since the 1980s, where freezing and particle sizes were detected by light scattering and polarization (DeMott et al. 2011; Hoose and Möhler 2012). The chemical and physical properties of gas-phase clusters generated in molecular beams have been investigated as a model for atmospheric particles using mass spectrometry (Fárník and Lengyel 2018). Melting points of mass-selected gas-phase water cluster anions were 93 K for $(H_2O)_{48}^-$ and 118 K for $(H_2O)_{118}^-$ (Hock et al. 2009). The melting points of $OH^-(H_2O)_n$ were higher than those of $(H_2O)_n^-$ and lower than those of $H^+(H_2O)_n$ (Schmidt and von Issendorff 2012; Zamith et al. 2013). Gas-phase molecular adsorption on mass-selected hydrogen-bonded cluster ions was investigated to understand heterogeneous nucleation and molecular cloud formation (Fujihara and Shimada 2019).

Molecular clouds also exist in space, where chemical processes of interstellar molecules occur at low temperatures and low densities. Gas-phase ion–molecule reactions related to interstellar chemistry have been investigated using a 22-pole ion trap cooled by a cryogenic refrigerator (Gerlich and Horning 1992; Gerlich and Smith 2006). Chemical formation of biological molecules from interstellar molecules such as H_2O, CH_3OH, CO, CO_2, and NH_3 condensed on a cold surface in vacuum has been investigated as a model for chemical evolution in interstellar ice. Amino acids (Bernstein et al. 2002; Muñoz Caro et al. 2002), small peptides (Gontareva et al. 2009; Abplanalp et al. 2016), and sugar molecules (Meinert et al. 2016) were formed by ultraviolet irradiation of the interstellar ice analogs.

Biomolecules have the ability to recognize molecules and their chirality, which is attributed to homochirality in biomolecules consisting of L-amino acids and D-sugars. The origin of homochirality is one of the most important issues in the study of origins of life (Bonner 1991, Munegumi 2015, Myrgorodska et al. 2017, Nanita and Cooks 2006, Pizzarello and Groy 2011, Ruiz-Mirazo et al. 2014). The enantiomeric excess of amino acids (Cronin and Pizzarello 1997; Engel and Macko 1997) and sugars (Cooper and Rios 2016) observed in meteorites and the chiral molecule observed in a star-forming region (McGuire et al. 2016) suggest an extraterrestrial origin of enantiomeric enrichment.

Mass spectrometric study of amino acid clusters showed that gas-phase serine (Ser) octamers are stable and exhibit a preference for homochirality (Takats et al. 2003; Nanita and Cooks 2006). However, NMR and IR studies indicated that the Ser octamers do not exist in solution (Vandenbussche et al. 2006). Chiral preference of amino acids is different in the gas phase than it is in solution, and it plays an important role in gas-phase clusters. Cryogenic ion traps have been used in laser spectroscopy of cold gas-phase ions (Asvany et al. 2005; Boyarkin et al. 2006; Dhzonson and Maier 2006; Fujihara et al. 2008; Goebbert et al. 2009; Spieler et al. 2018; Wang and Wang 2008). Chiral recognition in isolated systems has been investigated using laser spectroscopy and mass spectrometry (Awad and El-Aneed 2013; Klyne et al. 2018; Lee and Kim 2017; Scuderi et al. 2010; Speranza et al. 2009; Zehnacker 2014). We investigated the structure and reactivity of cold gas-phase clusters as a model for chemical evolution in interstellar molecular clouds. Photoinduced C_α–C_β bond cleavage in cold protonated D-tryptophan, H^+(D-Trp), on a chiral crown ether was suppressed upon increasing the temperature above 170 K, and no difference between the reactivity of D- and L-Trp was observed at 300 K (Fujihara et al. 2014a). These temperatures correspond to those of interstellar and atmospheric molecular clouds, respectively. Photoexcited D-Trp in a cold gas-phase protonated cluster that contained 3 L-Ser molecules was dissociated via the loss of CO_2 (Fujihara et al. 2014c). Enantioselective photoinduced reactions between protonated Trp and disaccharides depended on the structure of disaccharides (Doan and Fujihara 2018). Photoexcitation of cold gas-phase clusters containing protonated Trp enantiomers and disaccharides resulted in photoinduced *C*-glycosylation, which links glucose residues to the indole moiety of Trp via a C–C bond.

The enantiomeric excess of amino acids and sugars in solution was determined from a single photodissociation mass spectrum of cold gas-phase clusters (Fujihara and Maeda 2017; Fujihara and Okawa 2018). This application suggests that study of chemical evolution in interstellar molecular clouds is important for developing analytical methods where the characteristic of each molecule can be utilized based on the history of its chemical evolution.

In this study, chiral recognition between carbohydrates and Trp in cold gas-phase cluster ions was investigated as a model for chemical evolution in interstellar molecular clouds using a tandem mass spectrometer containing a cold ion trap. Structures of carbohydrates used in this study, D-glucose (D-Glc), methyl-α-D-glucoside (D-glucoside), D-maltose, and D-cellobiose, are shown in Fig. 1. D-Maltose and D-cellobiose are disaccharides that consist of two D-Glc units linked by α1,4 and β1,4 bonds, respectively. D-Glucoside was used to maintain the cyclic form of D-Glc, because D-Glc has both cyclic and linear (open-chain) forms, which are represented by the wavy lines in the structures of Fig. 1. The left side of the disaccharides shown in Fig. 1 is a cyclic form similar to D-glucoside, and the right side has both cyclic and open-chain forms similar to D-Glc. D-Glucoside and D-Glc were also used as models for a sugar chain and the terminal end of a sugar chain, respectively, to examine the reactivity of photoexcited Trp with sugar chains. Based on these results, we discussed enantiomer-selective reactions of carbohydrates and amino acids in cold gas-phase clusters and the implications for chemical evolution in interstellar molecular clouds.

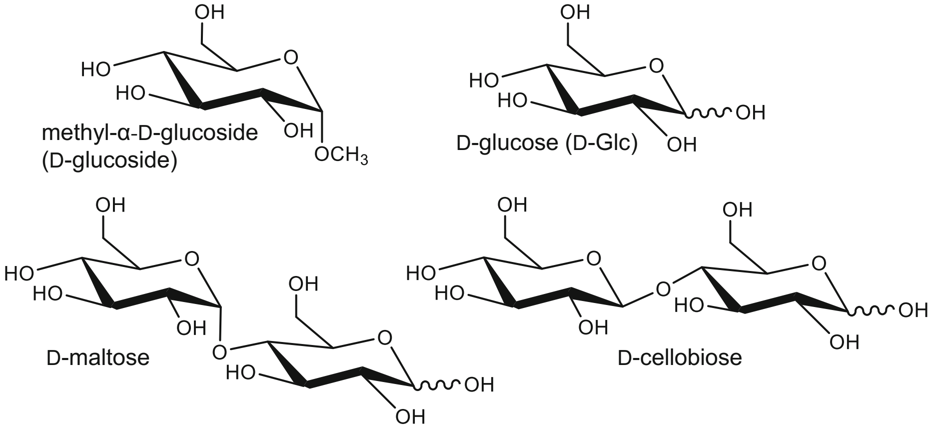

Fig. 1 Structures of carbohydrates used in this study

Materials and Methods

Trp and carbohydrates shown in Fig. 1 were obtained from Nacalai Tesque. The purities were more than 98%. Solutions of Trp (0.5 mM) and a carbohydrate (1.0 mM) in a mixture of water and methanol (50:50, *v*/*v*) containing 1% acetic acid for protonated clusters or NaCl (1.0 mM) for Na^+-containing clusters were used.

A tandem mass spectrometer equipped with a temperature-controlled 22-pole ion trap (8–350 K) was previously described (Fujihara et al. 2014a). Gas-phase cluster ions of Trp and carbohydrates were generated using electrospray ionization of the solutions. The cluster ions were transferred to the gas phase through a capillary, a skimmer, and an octopole ion guide, and were deflected by 90° using an ion bender into a quadrupole mass filter. The mass-selected ions were decelerated into the 22-pole ion trap where the ions were thermalized by multiple collisions with a helium buffer gas, analogous to a thermal bath. The mass-selected and temperature-controlled ions were extracted from the ion trap and irradiated with a photoexcitation laser pulse. The product ions were mass-analyzed using a reflectron time-of-flight spectrometer. The 266-nm photoexcitation laser pulse of 0.8 mJ/pulse was the fourth harmonic of a Nd:YAG laser (Minilite II, Continuum). The excitation laser pulse was not focused to overlap spatially between the ion packets and the laser pulse. Although the dissociation efficiency of precursor ions depended on the laser power and the spatial overlap, the relative ion intensity of fragment ions formed via one-photon absorption of cold gas-phase clusters was independent of them.

Results and Discussion

Enantiomer-Selective Dissociation of Tryptophan

Figures 2a, b show the photodissociation mass spectra of heterochiral H^+(L-Trp)(D-glucoside) and homochiral H^+(D-Trp)(D-glucoside) (*m/z* 399), respectively, at 8 K. The 266-nm photoexcitation laser pulse excited the indole ring of Trp to the $\pi\pi^*$ state. H^+(Trp) (*m/z* 205) formed via detachment of D-glucoside, which was observed in both spectra. H^+(Trp) (*m/z* 205) and NH_3 loss from H^+(Trp) (*m/z* 188) were observed in the spectra, which indicated that the proton associated with Trp in the protonated clusters and that the protonation site was the amino group of Trp (Lioe et al. 2004; Aribi et al. 2004). $NH_2CHCOOH$ loss from the protonated clusters was observed at *m/z* 325 in the spectrum of heterochiral H^+(L-Trp)(D-glucoside), while the loss was not observed in homochiral H^+(D-Trp)(D-glucoside). $NH_2CHCOOH$ loss occurred via C_α–C_β bond cleavage of H^+(L-Trp). In contrast, the energy absorbed by H^+(D-Trp) was released through the detachment of D-glucoside, and the dissociation of H^+(D-Trp) was suppressed. The observations indicated that the C_α–C_β bond cleavage of Trp in protonated clusters was an enantiomer-selective reaction of Trp induced by chiral recognition with glucoside.

Enantiomer-selective C_α–C_β bond cleavage of Trp in protonated heterochiral clusters was reported for aldohexose such as glucose, galactose, talose, altrose, and mannose (Fujihara et al. 2017a; Fujihara and Okawa 2018). The relative ion intensity of $NH_2CHCOOH$-elimination product for glucoside shown in Fig. 2a was larger than that for aldohexose reported previously. The enantiomer-selective reaction of Trp occurred more with glucoside than aldohexose. In this study, glucoside and Glc were used to model the reaction on the sugar chain and at the terminal of the sugar chain, respectively. The results suggest that the enantiomer-selective

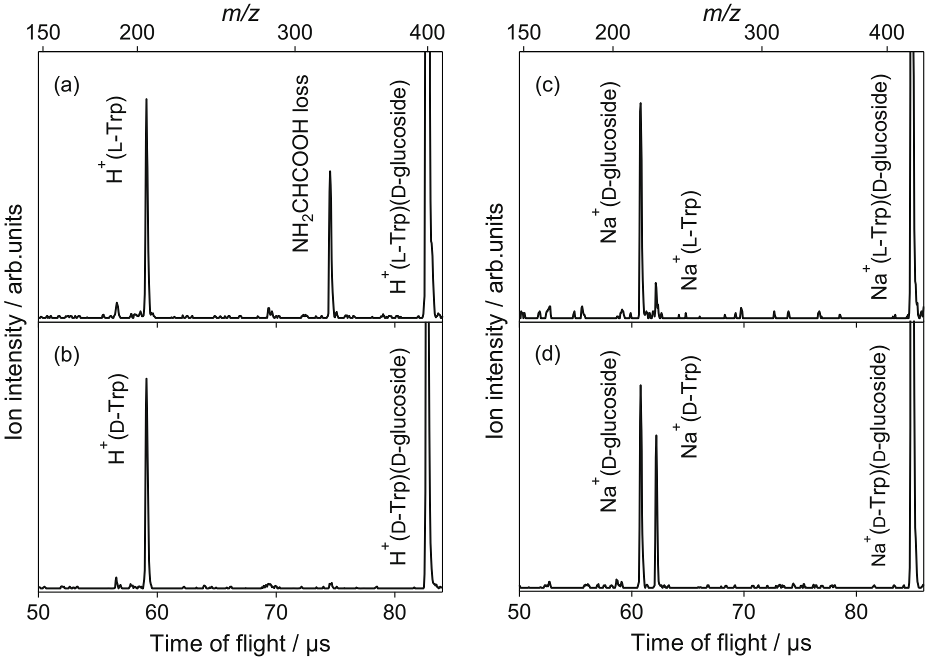

Fig. 2 Photodissociation mass spectra of **a** H^+(L-Trp)(D-glucoside), **b** H^+(D-Trp)(D-glucoside), **c** Na^+(L-Trp)(D-glucoside), and **d** Na^+(D-Trp)(D-glucoside) at 8 K. The irradiation wavelength was 266 nm, which excites the indole ring of Trp to the $\pi\pi^*$ state

reaction of Trp is more favorable on the sugar chain than at the terminal of the sugar chain in the gas phase. The photodissociation mass spectra of cold gas-phase protonated clusters showed that photoexcited L-Trp dissociated via C_α–C_β bond cleavage in the presence of D-glucoside or D-Glc, suggesting the formation of excess D-amino acids from enantiomer-selective dissociation in molecular clouds.

In order to investigate the effects of cations on enantiomer-selective reactions, photoexcitation experiments of Na^+-containing clusters were conducted. Figures 2c, d show the photodissociation mass spectra of heterochiral Na^+(L-Trp)(D-glucoside) and homochiral Na^+(D-Trp)(D-glucoside) (*m/z* 421), respectively, at 8 K. Na^+(Trp) (*m/z* 227) and Na^+(D-glucoside) (*m/z* 217) were observed in both spectra, which were formed by detachment of D-glucoside and Trp, respectively. The relative ion intensity of Na^+(D-Trp) compared to Na^+(D-glucoside) in the spectrum of the homochiral cluster was larger than that of Na^+(L-Trp) in the heterochiral cluster. This indicated that Na^+ affinity of D-Trp compared to D-glucoside was larger than that of L-Trp and that Na^+ recognized the chirality of Trp in the clusters. The spectra of Na^+-containing clusters showed no dissociation of molecules, such as the C_α–C_β bond cleavage observed in Fig. 2a. The difference in reactivity between Na^+-containing and protonated clusters suggests that the proton in clusters plays an important role in the enantiomer-selective reaction of Trp.

C_α–C_β bond cleavage of gas-phase H^+(Trp) photoexcited by a 266-nm laser pulse was reported to be attributed to photoinduced intramolecular electron and proton transfer (Lucas et al. 2008; Grégoire et al. 2009). The broad S_1–S_0 band of the electronic spectrum of cold gas-phase H^+(Trp) narrowed slightly upon hydrogen bonding to a solvent molecule, and vibrationally resolved electronic spectra were obtained for $H^+(Trp)(H_2O)_2$ and

$H^+(Trp)(CH_3OH)_2$ (Mercier et al. 2006; Fujihara et al. 2009). This behavior was ascribed to the decrease in interaction between the ππ* and dissociative πσ* states by hydrogen bonds between the NH_3^+ group of H^+(Trp) and OH groups of the solvent molecules, which increased the excited-state lifetime. In the collision-activated dissociation of H^+(Trp) (*m/z* 205), losses of NH_3, (NH_3 + H_2O), (H_2O + CO), (NH_3 + CH_2CO), and (NH_3 + CO_2) corresponding to *m/z* 188, 170, 159, 146, and 144, respectively, were observed (Aribi et al. 2004; Lioe et al. 2004). These dissociation pathways were not observed in the photodissociation mass spectra shown in Fig. 2a, b. The excited states of H^+(Trp), which induce C_α–C_β bond cleavage, contributed to chiral recognition and the enantiomer-selective reaction in cold gas-phase protonated clusters with carbohydrates.

Enantiomer-Selective Protonation to Tryptophan

Figure 3 shows the photodissociation mass spectra of heterochiral Na^+(L-Trp)(D-Glc) and homochiral Na^+(D-Trp)(D-Glc) (*m/z* 407) at 8 K. Na^+(Trp) (*m/z* 227) and Na^+(D-Glc) (*m/z* 203) were observed in both spectra, which were formed by detachment of D-Glc and Trp, respectively. The relative ion intensity of Na^+(D-Trp) compared to Na^+(D-Glc) was larger than that of Na^+(L-Trp), indicating that Na^+ affinity of D-Trp compared to D-Glc is larger than that of L-Trp, as in the case with D-glucoside. The formation of H^+(L-Trp) (*m/z* 205) was the main reaction pathway of photoexcited heterochiral Na^+(L-Trp)(D-Glc), as shown in Fig. 3a. For homochiral Na^+(D-Trp)(D-Glc), Na^+(D-Glc) formed by the detachment of D-Trp was the main product ion, and the protonation to D-Trp was a minor reaction pathway. The protonation to Trp did not occur in the Na^+-containing clusters with glucoside, as shown in Fig. 2c, d.

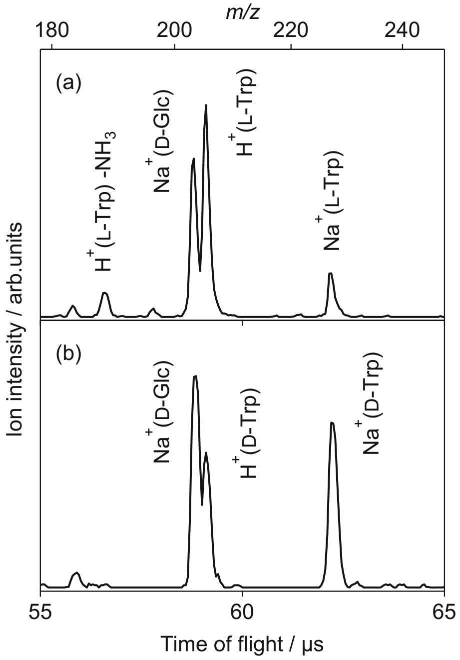

Fig. 3 Photodissociation mass spectra of **a** Na^+(L-Trp)(D-Glc) and **b** Na^+(D-Trp)(D-Glc) at 8 K

Therefore, the protonation in the clusters was attributed to the chain-openable structure of Glc, and this was enantiomer-selective protonation. NH_3 loss from H^+(Trp) (*m/z* 188) was also observed in the spectra, because gas-phase H^+(Trp) dissociated via NH_3 loss with low energy (Lioe et al. 2004; Aribi et al. 2004). It was reported that NH_3-elimination product (*m/z* 188) was formed spontaneously from H^+(Trp) in the field-free region of the reflectron time-of-flight mass spectrometer (Fujihara et al. 2014b). These results suggested that once H^+(L-Trp) formed via protonation to L-Trp from D-Glc in heterochiral Na^+(L-Trp)(D-Glc), H^+(L-Trp) could dissociate via NH_3 loss by low-energy collisional activation. The enantiomer-selective protonation to Trp from Glc could induce enantiomeric excess via collision-activated dissociation of the protonated Trp. In the case of L-Glc, the spectra of heterochiral Na^+(D-Trp)(L-Glc) and homochiral Na^+(L-Trp)(L-Glc) was identical to those of heterochiral Na^+(L-Trp)(D-Glc) and homochiral Na^+(D-Trp)(D-Glc), respectively. For chiral recognition between L-alanine tripeptide and Trp reported previously, H^+(D-Trp) was formed in heterochiral protonated cluster and dissociated via the loss of NH_3 (Fujihara et al. 2017b). The enantiomer-selective reactions reported in this paper was not a real prebiotic start-up scenario for enantiomeric enrichment due to the presence of D-Glc. It was an accidental chiral effect. The enantiomer selectivity observed in the spectra indicates that a chirality of one type of molecule induces enantiomeric excess of other molecules via enantiomer-selective reactions in molecular clouds.

Enantiomer-Selective Glycosidic Bond Cleavage of Disaccharides

Chiral recognition between Trp enantiomers and D-maltose, which is a disaccharide consisting of two D-Glc units linked by α1,4 bond as shown in Fig. 1, was investigated by photoexcitaion of Na^+-containing heterochiral and homochiral clusters. Figure 4 shows the photodissociation mass spectra of heterochiral Na^+(L-Trp)(D-maltose) and homochiral Na^+(D-Trp)(D-maltose) (*m/z* 569) at 8 K. Na^+(D-maltose) (*m/z* 365) formed by the detachment of Trp was observed in both spectra. In the spectrum of homochiral Na^+(D-Trp)(D-maltose) shown in Fig. 4b, Na^+(D-Glc) (*m/z* 203) formed via the glycosidic bond cleavage of D-maltose was observed. The glycosidic bond cleavage did not occur in heterochiral Na^+(L-Trp)(D-maltose), as shown in Fig. 4a. This enantiomer-selective glycosidic bond cleavage was induced by the photoexcitation of D-Trp in homochiral Na^+(D-Trp)(D-maltose). In the presence of D-Trp in Na^+-containing clusters, D-maltose dissociated to D-Glc via glycosidic bond cleavage, suggesting that photoexcited D-Trp could prevent a chemical evolution to sugar chains from D-enantiomer of saccharides in molecular clouds. In contrast, photoexcited L-Trp was detached from D-maltose, and D-maltose did not dissociate. The enantiomer-selective glycosidic bond cleavage was also observed in the case of D-cellobiose, as shown in Fig. 5, which is a disaccharide consisting of two D-Glc units linked by β1,4 bond.

In the collisional activation and infrared photoexcitation of gas-phase Na^+(Trp) and $Na^+(Trp)_2$, the detachment of Trp was the main dissociation pathway and dissociation of Trp was not observed, where Trp was a non-zwitterionic structure having NH_2 and COOH groups (Fujihara et al. 2014b; Polfer et al. 2006; Ruan and Rodgers 2004). In the case of ultraviolet photoexcitation, amino acids in an ice matrix and in cold gas-phase amino acid clusters dissociated via the loss of CO_2 (Ehrenfreund et al. 2001; Fujihara and Maeda 2017; Fujihara et al. 2014c; Oki and Fujihara 2018). It was difficult to conclude that the observed enantiomer-selective reaction of Na^+-containing clusters happened in the ground or in the excited electronic states from the photodissociation mass spectra. Information regarding the geometric

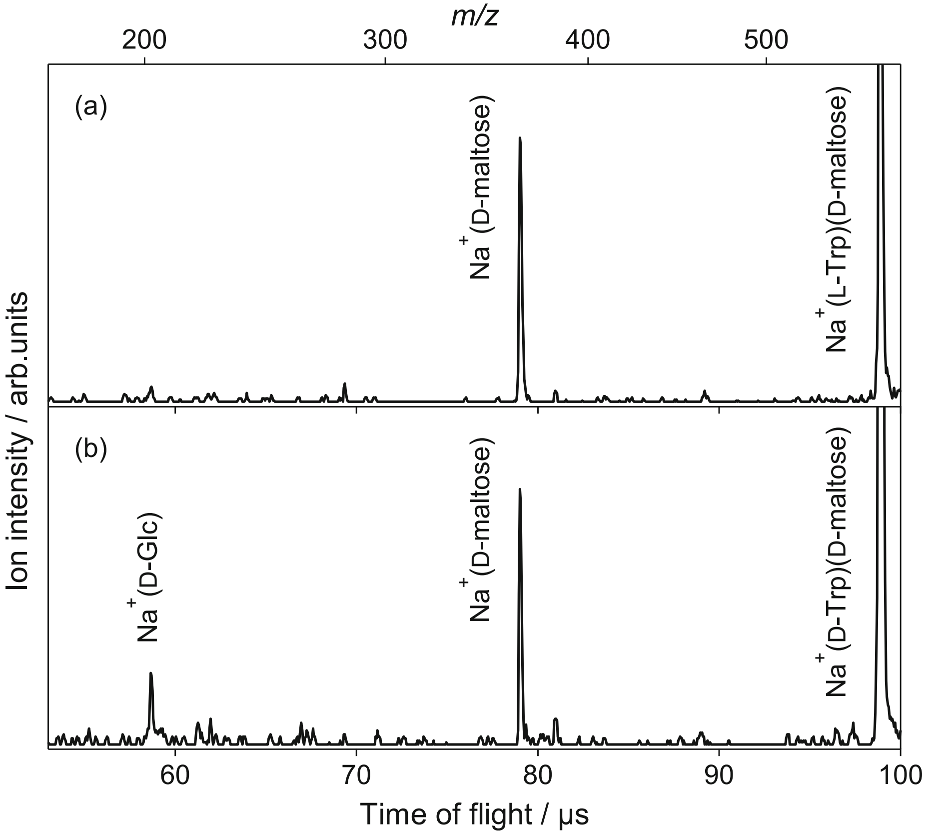

Fig. 4 Photodissociation mass spectra of **a** Na$^+$(L-Trp)(D-maltose) and **b** Na$^+$(D-Trp)(D-maltose) at 8 K

and electronic structures of the gas-phase clusters is indispensable for understanding the relationships between chiral recognition and the enantiomer-selective reactions.

Conclusions

Enantiomer-selective reactions in cold gas-phase cluster ions were investigated by mass spectrometry as a model for chemical evolution in interstellar molecular clouds. The photodissociation mass spectra of cold gas-phase protonated clusters containing Trp and monosaccharides showed that H$^+$(L-Trp) dissociated via C_α–C_β bond cleavage in the presence of D-enantiomer of monosaccharides. In contrast, the energy absorbed by H$^+$(D-Trp) was released through the detachment of D-enantiomer of monosaccharides, and the dissociation of H$^+$(D-Trp) was suppressed. The excited states of H$^+$(L-Trp) contributed to the enantiomer-selective dissociation.

For Na$^+$-containing clusters, the enantiomer-selective protonation to L-Trp from D-Glc could induce enantiomeric excess via low-energy collision-activated dissociation of the protonated L-Trp. In the case of disaccharides, D-maltose and D-cellobiose dissociated to D-Glc via glycosidic bond cleavage in cold gas-phase clusters containing photoexcited D-Trp and Na$^+$. This

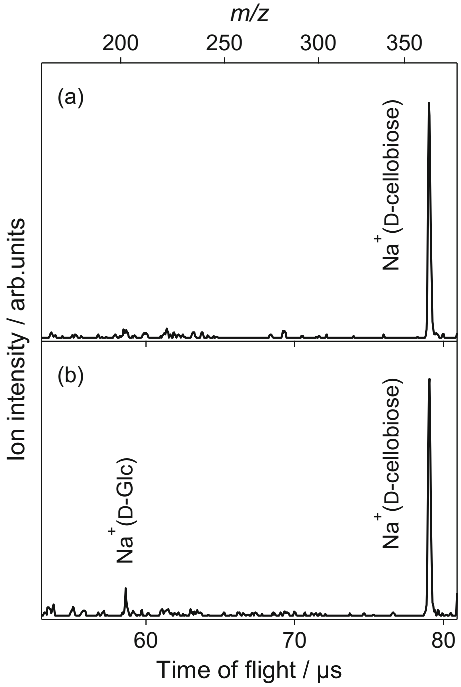

Fig. 5 Photodissociation mass spectra of **a** Na$^+$(L-Trp)(D-cellobiose) and **b** Na$^+$(D-Trp)(D-cellobiose) at 8 K

suggested that D-Trp could prevent chemical evolution to sugar chains from the D-enantiomer of saccharides in molecular clouds. The enantiomer selectivity between Trp and disaccharides in cold gas-phase clusters was consistent with the homochirality of biomolecules consisting of L-amino acids and D-sugars.

The enantiomer selectivities indicated that chirality of a molecule could induce enantiomeric excess of other molecules via enantiomer-selective reactions in molecular clouds. Mass spectrometry-based methods are useful for examining the reactivity of molecules in molecular clouds.

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Compliance with Ethical Standards

Conflict of Interest None.

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