Isotope effect in the dissociation of methanol dications produced by collision with Ar\textsuperscript{8+}

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Abstract. The H/D isotope effect in the ion-pair dissociation processes of doubly charged methanol formed by the impact of low-energy Ar\textsuperscript{8+} was investigated. By multi-hit position-sensitive time-of-flight measurements, the branching ratios of dissociation channels yielding H, H\textsubscript{2} or H\textsubscript{3} fragment ions, or H/D substituted ions, and the kinetic energy release distributions of these dissociation channels were determined for methanol isotopomers.

1. Introduction
Experiments examining the collision of highly charged ions with molecules have addressed a variety of targets, from diatomics to polyatomics, including organic molecules and clusters. Isotope substitution is useful for investigating the complex dissociation dynamics of multiply ionized polyatomic molecules. Strong isotope effects have been reported for ion-pair dissociation of the water dication; the reaction HDO\textsuperscript{2+} \rightarrow H\textsuperscript{+} + OD\textsuperscript{+} takes preference over the reaction HDO\textsuperscript{2+} \rightarrow D\textsuperscript{+} + OH\textsuperscript{+}. These channels also differ considerably in their kinetic energy release (KER) distributions [1, 2]. In the case of the HDO molecule, the D-substitution breaks the C\textsubscript{2v} symmetry of water, which may be a key factor of the strong isotope effects. On the other hand, isotopomers of methanol may present isotope effects while keeping the C\textsubscript{s} symmetry.

Eland and coworkers investigated the ion-pair dissociation of methanol dications by the photoelectron-photoion-photoion coincidence (PEPIPICO) method, also using isotopomers to distinguish between OH and CH bond breakups [3]. They reported that the peaks in the KER distributions were the same for all isotopomers within experimental uncertainty (0.4~0.6 eV). A coincidence study on the dissociation of collisionally prepared methanol dications was reported by De et al. [4], while the details of the isotopic effects remain an open question. In the present study, the branching ratios and KER distributions of various ion-pair dissociation channels of methanol dications were measured, focusing on the effects of H/D substitution.

2. Experimental setup
A projectile beam, 120 keV Ar\textsuperscript{8+}, extracted from a 14-GHz electron cyclotron resonance-ion source at Tokyo Metropolitan University (TMU-ECRIS), hit the target molecule with a 90° crossed-beam configuration. Methanol (CH\textsubscript{3}OH) or methanol-d (CD\textsubscript{3}OH: 99.8% isotope enrichment, or CD\textsubscript{2}OD: 99.8% isotope enrichment) targets prepared using a conventional degassing procedure were introduced into the beam-source chamber through a pin-pole 0.6 mm in diameter, without seed gas. The molecular beam, collimated by a skimmer, crossed the projectile beam and was caught in a liquid
nitrogen trap placed in the collision chamber. The typical operating pressure was $1 \times 10^{-3}$ Pa in the beam-source chamber and $1 \times 10^{-6}$ Pa in the collision chamber.

The position-sensitive time-of-flight (PSTOF) measurement procedure reported previously [5] was employed, except that a fast ADC card (Acqiris DC270) was used for recording PSTOF output signals. Briefly, the fragment ions were accelerated by an electric field (4.90 V/mm) in the drift tube (449 mm) and hit the aluminum plate. Secondary electrons guided by an inhomogeneous magnetic field were accelerated in the opposite direction by this electric field, while maintaining positional information, and were detected by a time- and position-sensitive detector [6]. The TOF measurements were triggered by detection of the projectile passing through the collision area.

3. Results and discussion

3.1. TOF coincidence map

Hereafter, the ion-pair dissociation channel yielding fragment $A^+$ and $B^+$ is denoted by $(A^+, B^+)$, and the number of evaporated atoms associated with the ion-pair dissociation is denoted by $\Delta$. Typical coincidence maps for CH$_3$OH and CD$_3$OH targets are shown in figures 1(a)-(g), where islands indicate events in which $H^+$ (or $D^+$) and heavier counterpart ions were detected in coincidence. Figures 1(a)-(c) show examples of the two-body ion-pair dissociation channels of the dications ($\Delta=0$), figures (d) and (e) are those accompanied with evaporation of neutral species ($\Delta=1$), and figures (f) and (g) are those for the dissociation of multiply ionized methanol, (CD$_3$OH)$^n+$; $n \geq 3$.

The islands in figures (a)-(c) are narrow lines, as the fragment TOFs are well correlated. The intensity ratio of the islands in figures (b)-(c) is 1:20. It is clear that the C-D bond breakup takes preference over the O-H bond breakup, beyond the statistical weight (1:3), while the ratio is less disproportionate than in the case of 30.4-nm photoionization (1:52) [3]. The islands in figures (d) and (e) are broadened due to the momentum shared by the neutral fragment. The propensities of evaporation were derived from figures 1(b)-(e); $H^+$ ejection tends to induce evaporation of $D$, whereas this is not the case for $D^+$ ejection. As will be discussed later, the ratio of $\Delta=1$ to $\Delta=0$ is considered a measure of the average excess energy of the ion-pair dissociation. The propensity given by $I(D^+,CD_2O^+)+I(D^+,CD_2O^-)/I(H^+,CD_2O^-)$ is 0.08, which is also less disproportionate than in the case of photoionization (0.033).

The shapes of the $(H^+, CO^+)$ and $(D^+, CO^+)$ islands are quite different from those of the other islands. The minimum in the middle indicates that $H^+$ or $D^+$ emitted perpendicular to the TOF axis is missing due to relatively high initial kinetic energy given by more violent Coulomb repulsion in
highly ionized methanol. The round shape of the islands is consistent with the assignment, as the coulombic force of the undetected fragment ions would considerably affect the TOFs. For the (H+, CO+) channel, the undetected ion is D+; whereas for the (D+, CO+) channel, the rest is H+ or D+. The Coulomb repulsion of D+ and H+ acting on CO+ would be partly canceled making the island horizontal. No cancellation is expected for the reaction CO+ + D+ + D+. The relative intensities of the islands identified for the ion-pair dissociation channels with Δ = 0, 1 of the three isotopomers are shown in figure 2, together with the results of the photoionization study [3]. The channels for Δ = 2 are certainly identified in the coincidence map (A3 and A2a-c in the list), however, the branching ratios are not determined due to serious overlap with the neighbouring islands.

Figure 2. Branching ratios for the ion-pair dissociation with Δ = 0, indicated by the subscript “0”, and Δ = 1, indicated by the subscript “1”. Target molecules are I: CH3OH, II: CD3OD, III: CD3OH. The results of the photoionization study for CD3OH are shown in IV. Assignment of the channels is listed in the right. The channels for Δ = 2 are certainly identified in the coincidence map (A3 and A2a-c in the list), however, the branching ratios are not determined due to serious overlap with the neighbouring islands.

In comparison with the photoionization study, it is notable that collisional processes induce more evaporation of neutrals (A1 and B1). This trend can be readily understood, as collisional ionization generally allows access to a wide variety of ionic states and enhances vibrational excitations, in contrast to photoionization, which is governed by selection rules and Franck-Condon factors. The aforementioned enhancement of the minor process of O-H bond breakup is consistent with this trend.

3.2. KER of two-body ion-pair dissociation

The KER distributions of the two-body ion-pair dissociation channels for three methanol isotopomers yielding H+ ~ H3+ are shown in figures 3(a)-(c). A general trend observed in these plots is
that the KER distributions for the CH$_3$OH and the CD$_3$OD dissociation channels are similar, especially for H$_2^+$, D$_2^+$ formation and H$_3^+$, D$_3^+$ formation channels, whereas those for the CD$_3$OH dissociation channels are shifted to lower energy. The peak values in figure 3(a) coincide with those reported in the photoionization study within experimental uncertainty, whereas those in figure 3(c) are considerably lower.

As mentioned in section 3.1, the intensity of the (H$^+$, CD$_3$O$^+$) channel was very low, and thus, the two-body charge separation with O-H bond breakup is most likely a minor channel for all the isotopomers. The peaks of the KER distribution differed slightly among the isotopomers, $E_{(H^+,\text{CD}_3\text{O}^+)} < E_{(D^+,\text{CD}_3\text{O}^+)} < E_{(H_3^+,\text{CH}_3\text{O}^+)}$. For the minor channel (H$^+$, CD$_3$O$^+$), which would be energetically unfavorable, showed low-energy shift in KER, similar to the case of photoionization of methanol and the dissociation of HDO$_2^+$ [1].

For the channels yielding H$_2^+$ isotopomers, the KER distributions varied with H/D substitutions, i.e., $E_{(HD^+,\text{CD}_2\text{O}^+)} < E_{(D_2^+,\text{CH}_2\text{O}^+)} < E_{(D_2^+,\text{CD}_2\text{O}^+)} \approx E_{(H_2^+,\text{CH}_2\text{O}^+)}$. This trend was also observed for the channels yielding H$_3^+$ isotopomers. The shift induced by H/D substitution was about 0.2-0.5 eV.

It should be noted that the isotope effect was not prominent when all the H atoms were substituted by D atoms, but was most enhanced by partial substitution. This observation for different target isotopomers is the outcome of a different type of isotope effect from that reported previously for water isotopomers, in which a larger shift ($\sim 1$ eV) was observed between two ion-pair dissociation channels of HDO$_2^+$. Further extension of the target molecules is needed to clarify whether these are specific phenomena for methanol isotopomers or are generally true for organic molecules.

![Figure 3](image-url)

**Figure 3.** KER distribution of two-body ion-pair dissociation channels for three isotopomers. Since the plots are not normalized by Ar$^+$ beam intensity nor accumulation time, the intensity ratio is meaningful only between the two channels for CD$_3$OH. The vertical arrows indicate peaks reported by photoionization study. (a) A$_0$ group, (b) B$_0$ Group, (c) C$_0$ group.

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