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A new technique to study the dissociation of energy-selected neutral intermediates

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Abstract

The dissociation of excited species is one of the most important types of chemical reactions, and it has been investigated by using either molecular collision or photon excitation. Mass spectrometry is suited to generate and probe unstable intermediates in the gas phase and has enabled the investigation of the dissociation of various stable and unstable ions. However, investigation of neutral species using this technique has been difficult because of their lack of electronic charge. In this work we have used mass spectrometry to measure collision-induced dissociation (CID) spectra and charge-inversion spectra of CD_3OH^+ and CH_3OD^+. The major dissociation process in CID was found to involve elimination of a hydrogen atom from the methyl group, whereas dissociation in the charge-inversion mass spectrometer was found to be via elimination of a hydrogen atom from the hydroxyl group. Hydrogen atom elimination from the hydroxyl group has also been reported as the major process in the photo-induced dissociation of neutral methanol. This demonstrates the usefulness of charge-inversion mass spectrometry as a technique for the investigation of the dissociation of neutral intermediates. (Int J Mass Spectrom 202 (2000) A1–A7) © 2000 Elsevier Science B.V.

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1. Introduction

Excited neutral species such as radicals play an important role as intermediates in many chemical reactions, and the study of dissociation of these intermediates is indispensable for building fundamental knowledge about these chemical reactions. Moreover, the understanding of the mechanism of dissociation of neutral species is relevant to a wide range of basic and applied sciences, including molecular physics, quantum electronics, plasma discharge, quantum theory, atmospheric science, space science, environmental science, and material sciences.

The mechanistic features of the dissociation reaction can be determined by studying energy-selected excitation states of the intermediate [1–8]. The dissociation of ions can be studied easily using mass

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spectrometry because the ions can be mass analyzed and detected because of their electronic charge [1,9,10]. Information about unstable neutral species is, however, limited, as analysis of neutral species is difficult because of their lack of electronic charge. Neutralization-reionization mass spectrometry (NRMS) has emerged as a method for the generation and structural characterization of neutral species [11–14]. Recently, chemical reactivity of neutral species in gas phase has been studied by advanced NRMS methods such as the photoexcitation, photoionization, and long-distance NR done by the Turecek group [15–17] and the neutral and ion decomposition difference (NIDD) work carried out by Schwarz and his coworkers. [18,19] Excited unstable neutral species can be produced from the corresponding cations by single-electron transfer in our charge-inversion mass spectrometry [20–22]. In fact, ions corresponding to unstable neutral intermediates, such as the vinylidene cation [21], have been studied using this technique. Dissociation of these neutral intermediates with energies lower than the ionization energy results in the formation of neutral rather than ionic fragments. These neutral fragments are converted into negative ions by electron transfer and detected using the charge-inversion mass spectrometer. Using so-called thermometer molecules, we have shown that charge-inversion mass spectrometry using an alkali metal target is able to yield information about the dissociation of energy-selected neutrals formed via near-resonant neutralization [22]. It is important to demonstrate that this technique can also give insight into the dissociation of neutral species other than thermometer molecules.

2. Experimental

The MS/MS instrument used in this work comprises a double-focusing mass spectrometer (MS-I) to mass separate precursor ions, a 3-cm-long target chamber, and an electric cylindrical electrostatic analyzer (MS-II) to mass analyze secondary ions [20]. In the charge-inversion mass spectrometer, positive ions mass selected by MS-I are made to collide with alkali metal targets, and the resulting negative ions formed on two-electron transfer are mass analyzed by MS-II. Neutralization, dissociation, and negative ion formation take place in the target chamber filled with alkali metal vapor. The alkali metal target is supplied as vapor from a reservoir through a ball valve. The density of the alkali metal in the target chamber is controlled by the temperatures of the target chamber, the ball valve, and the reservoir. Collision-induced dissociation (CID) spectra were measured by changing the polarity of MS-II and the detector and mass analyzing the secondary positive ions exiting the target chamber. Two types of partially deuterated methanol, CD_3OH and CH_3OD (Merck) were studied in this work. The level of deuterium content of both molecules was $>99\%$.

3. Results and Discussion

Fig. 1 shows the CID and charge-inversion mass spectra of the partially deuterated methenols CD_3OH^+ and CH_3OD^+. The target gas used for all these spectra was Cs. Only one strong dissociative peak is observed in the CID spectra. In the CID spectrum of CD_3OH^+ ($m/z = 35$; Fig. 1A), the mass number of the strongest peak is 33, which represents a decrease in mass number of two from the precursor ion. This implies the formation of CD_2OH^+ resulting from elimination of a D atom from the methyl group. In the CID spectrum of CH_3OD^+ ($m/z = 33$; Fig. 1B), the dissociative species associated with the peak at $m/z = 32$ is attributed to the CH_2OD^+ ion resulting from elimination of a H atom from the methyl group. These two CID spectra show definitively that the main CID process of the CH_3OH^+ cation is the elimination of a hydrogen atom from the methyl group. These results also indicate that the scrambling of H atoms and D atoms does not occur in the dissociation of the cations.

No nondissociative negative ions were detected in the charge-inversion mass spectra. The predominant peak in the charge-inversion spectrum of CD_3OH^+ ($m/z = 35$; Fig. 1C) is the peak at $m/z = 34$, which represents a decrease in mass number of one from the

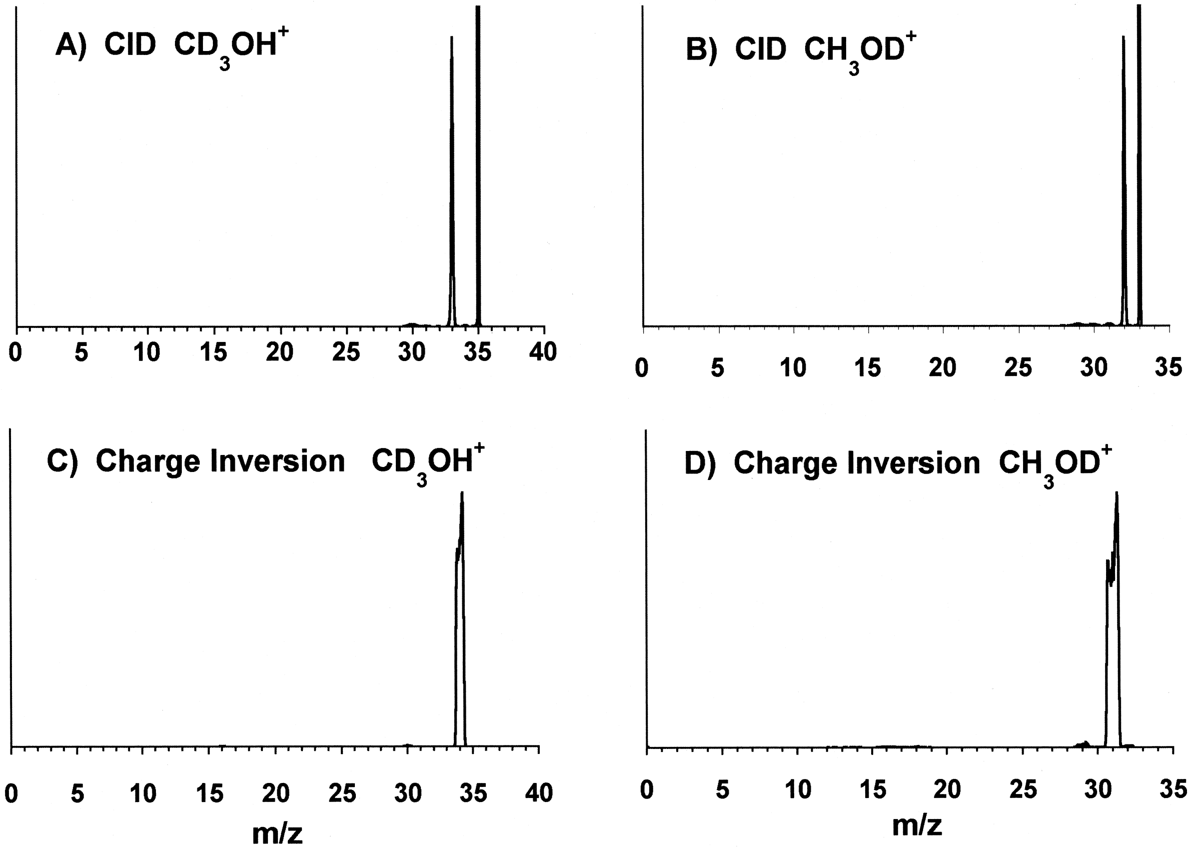

Fig. 1. The CID spectra of CD_3OH^+ (A) and CH_3OD^+ (B) and the charge-inversion mass spectra of CD_3OH^+ (C) and CH_3OD^+ (D). The target gas was Cs.

parent ion. Because the decrease of mass number of one results from the elimination of a H atom, the peak at m/z $= 34$ is attributed to the CD_3O^- ion resulting from elimination of a H atom from the hydroxy group. The predominant peak in the charge-inversion spectrum of CH_3OD^+ (m/z $= 33$; Fig. 1D) is the peak, which has a mass number of two lower than the parent ion. This reduction in mass number by two can be attributed to either the elimination of a D atom from the hydroxyl group or the elimination of two H atoms from the methyl group. As the $CDOH^-$ ion, having a mass number of 31, was not observed in the CD_3OH^+ spectrum (Fig. 1C), the peak corresponding to mass number 33 is attributed to the CH_3O^- ion resulting from elimination of a D atom from the hydroxyl group. Because the activation energy of scrambling of hydrogen atoms is often higher in neutrals than in cations, this assignment, which neglects any scrambling, seems reasonable. These two charge-inversion mass spectra show definitively that the dissociative process of the neutral species involves the elimination of a hydrogen atom from the hydroxyl group. These CID spectra and charge-inversion spectra clearly indicate different dissociation patterns for the cationic species and the neutral species, and this result demonstrates that charge-inversion mass spectrometry is able to yield information about the dissociation of neutral species.

The possibility of the formation of CH_3O^- ions from the dissociation of CH_3OH^{-*} ions formed via double-electron transfer in one collision was excluded on the basis of the density dependence and thermochemical consideration. Although the target density dependence of CH_3O^- ion was not measured directly,

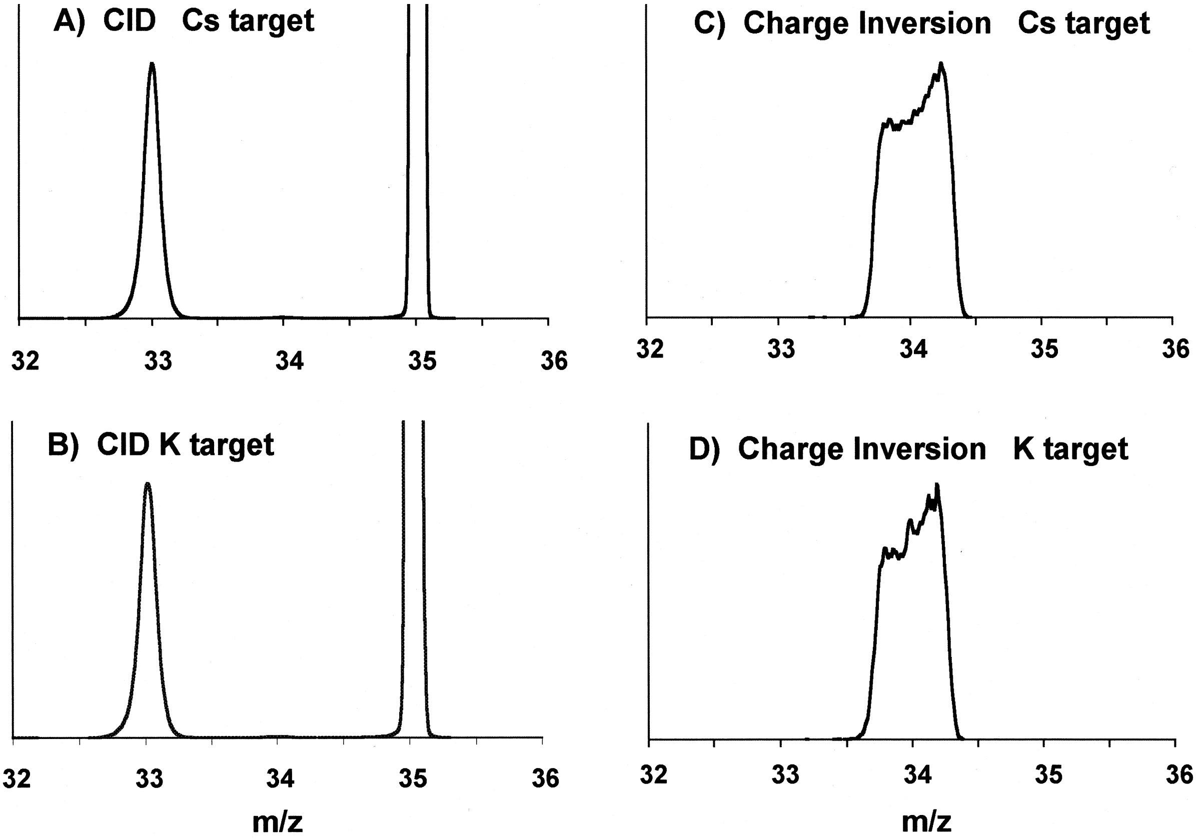

Fig. 2. The CID spectra of CD_3OH^+ using a Cs target (A) and a K target (B) and the charge-inversion mass spectra of CD_3OH^+ using a Cs target (C) and a K target (D).

ion intensities were measured at different densities by controlling the temperature of the reservoir, the ball valve, and the target chamber. It was already confirmed that the formation process of $C_2H_n^-$ ($n = 0,1$) ions from $C_2H_2^+$ ions was successive single-electron transfer in two collisions [21,24]. By comparing the target density dependence of the CH_3O^- ions with that of $C_2H_n^-$ ($n = 0,1$) from $C_2H_2^+$ ions, the formation process of the fragment negative ions detected in this work is attributed to successive single-electron transfer with the dissociation of excited neutrals. The methanol anion radical has not been reported as a stable species to date. Even if a tentative electron affinity of CH_3OH is 0 eV, double-electron transfer in one collision with alkali metal targets Cs and K are 18.2 and 25.3 eV endothermic, respectively. Such a large endothermicity gives a small cross section in the electron transfer process, as discussed in [24] and [25]. Therefore, it is improbable that the dissociation from tentative CH_3OH^{-*} ions is a main process for the formation of CH_3O^- ions.

To show the peak shape more clearly, the CID spectra and charge-inversion spectra are shown expanded in Fig. 2. The peak observed in the CID spectrum using the K target is attributed to CD_2OH^+ ions, and the peak observed in the charge-inversion spectrum is attributed to CD_3O^- ions, as was the case for the Cs target. This result indicates that the dissociation patterns of cationic and neutral species are independent of the type of target.

The shape of the dissociative peaks in the CID spectra in Fig. 2 resembles that of a triangle. This shape is typical of dissociative peaks observed in CID spectra generally and shows dissociation from various

Table 1
Kinetic energy release (KER) values (eV), available energies (eV), and fractions of the KER values to the available energy

Precursor	Cs target	K target	193.3 nm[a]
KER value			
CD_3OH	1.96	1.70	1.59 ± 0.13
CH_3OH	1.84	1.56	1.47 ± 0.12
Available Energy			
	2.45	2.00	1.90
KER Value/Available Energy			
CD_3OH	0.80	0.85	0.82 ± 0.07
CH_3OH	0.75	0.78	0.76 ± 0.06

[a] Data for 193.3 is from ref. [30].

internal energies [9]. Furthermore, the broadening in the internal energy distribution does not contradict the results obtained using so-called thermometer molecules [22]. The peak width of CID spectra obtained using the K target is the same as for the Cs target. These widths are independent of both the target species and precursor ions. This independence of target type agrees with the report that different targets function with similar effectiveness in CID [9].

However, the peak shape of the charge-inversion mass spectra resembles that of a trapezoid. This shape suggests that dissociation is from a state with a specific internal energy [26]. The widths of the dissociative peak for the neutral species (CH_3OH^*) observed in the charge-inversion spectra are much broader than those of the cations in the CID spectra. This difference suggests that the internal energy of the dissociative level in neutral dissociation is much higher than in ion dissociation. As seen in Fig. 2, the peak width of the charge-inversion spectra with the K target is slightly narrower than that for the Cs target. Values for the kinetic energy release (KER), which is the total kinetic energy released in the center-of-mass flame, were calculated from the full width at half maximum (FWHM) of the CH_3O^- peaks, and are listed in Table 1.

Fig. 3 shows the heats of formation of the neutral species and the cations of CH_3OH and those of the fragments. In the CID spectra, the main peak is attributed to CH_2OH^+ ions with lower energy. In the dissociation of cations, a lot of excitation levels are distributed over the lower states, which explains the

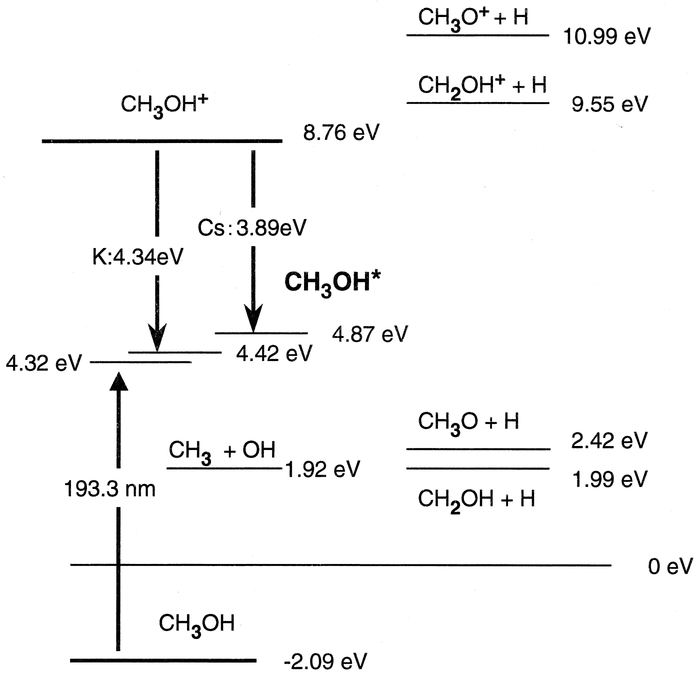

Fig. 3. The heats of formation of the neutral and cationic forms of CH_3OH. Thermochemical values are taken from [27].

experimental results that show that the elimination of a hydrogen atom from the methyl group is the dominant dissociative process. From our previous work on thermometer molecules [22], the neutralization step in the charge-inversion process is via near-resonant electron transfer. Supposing that neutralization is resonant, the energy level of the formed neutral species should be lower than the level of the precursor cation by an amount equal to the ionization energy of the target. The energy levels associated with these resonance processes are also shown in Fig. 3.

Three dissociation processes to $CH_3O + H$, $CH_2OH + H$, and $CH_3 + OH$ are possible energetically, as shown in Fig. 3. Electron affinities of methoxy radical, methyl radical, and hydroxy radical are 1.6, 1.1, and 1.8 eV, respectively; that of hydroxymethyl radical is not reported [27]. The dissociation of excited neutral methanol to $CH_3O + H$ is predominant in the charge-inversion mass spectrometry. Although the dissociation of the excited methanol to $CH_3 + OH$ is energetically possible and the electron affinities of these fragments are positive, negative ions associated with this dissociation process were not observed in the charge-inversion spectra. The negative ion that may be formed from the dissociation process to $CH_2OH + H$ was also not observed. As discussed below in relation to the dissociation of photo-excited methanol [28–33], the channels leading to $CH_3 + OH$ and to $CH_2OH + H$ are not considered to be a main dissociation process of CH_3OH excited in the energy region in this experiment.

The major channel of dissociation induced by photo-excitation of CH_3OH at 193.3 and 157 nm has been reported to be the direct hydroxyl H elimination; $CH_3O + H$ [30–32]. The quantum yield of this process at 193.3 nm was determined to be 0.86 ± 0.10 [30]. The excited CH_3OH produced by this photon was elucidated as being in the 3s Rydberg state [28,29], which is purely repulsive in the O-H coordinate [30–33]. The dissociation time from the Rydberg state is estimated to be shorter than 1 ps, as the dissociation is a direct process via the repulsive 3s surface [31–33]. The broad trapezoidal profile of the CH_3O^- peak in the charge-inversion spectra is attributed to this direct dissociation [26]. The mean free time between neutralization and negative ion formation for the CH_3OH^+ ion is calculated to be ~100 ns from the ion velocity and the length of the target chamber. As the dissociation time is much shorter than the mean free time, dissociation of H atoms from excited CH_3OH molecules takes place before negative ion formation. The KER values and the fractions of the KER values to the available energies are compared with those in the photo-excitation experiment of Satyapal et al. [30] in Table 1. The available energy in the charge-inversion spectra was estimated from the near-resonant state and the energy of dissociative level, as seen in Fig. 3. The available energy of K target was nearly equal to that for 193.3-nm photo-excitation. The close agreement of the KER values and the fractions with different excitation methods in Table 1 provides evidence that in charge-inversion mass spectrometry, the neutralization is resonant, the excited neutrals dissociate to neutral fragments spontaneously, and the negative ions are formed from the neutral fragment by a second electron transfer. The smaller value of the fraction for the Cs target is attributed to the excitation of CH_3O in a higher vibrational level.

The difference between the ions observed in the CID spectra and the charge-inversion spectra indicates that the dissociation patterns of the neutral species and cationic species are definitely different. The width of the dissociative peak and its target dependence show that the electronic state of excited neutrals could be selected using this technique. These results demonstrate that it is possible to study the dissociation of energy-selected neutrals by using charge-inversion mass spectrometry. Because ions of intermediates can be made easily, charge-inversion mass spectrometry makes possible the study of the dissociation of unstable radicals obtained from the parent ions via near-resonant neutralization.

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