ARTICLES

Excitation Mechanism in the Collision-Induced Dissociation of Methane Molecular Ion at Kiloelectronvolt Translational Energy

Hee Seung Lee and Myung Soo Kim*

Department of Chemistry and the Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Korea

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Collision-induced hydrogen loss from methane molecular ion has been studied at kiloelectronvolt laboratory translational energy by using mass-analyzed ion kinetic energy spectrometry (MIKES). The kinetic energy release (KER) distribution evaluated from the MIKE profile is bimodal: a small KER component arising from vibrational excitation and a large KER component from electronic excitation. CH$_4^+$ has been generated by electron ionization and by charge exchange ionization to vary its internal energy content. It has been found that the collision-induced dissociation (CID) via electronic excitation becomes more efficient at higher incident energy, while the efficiency of the vibrational excitation is hardly affected by the incident energy. Most importantly, it has been found that the electronic excitation is the main mechanism in CID at kiloelectronvolt incident energy. Vibrational excitation also occurs but supplies only a few vibrational quanta and hence is important for the least endoergic process only.

Introduction

Collision-induced dissociation (CID) of polyatomic ions has been known for a long time in the field of mass spectrometry. A tremendous research effort has been made over the years mainly to develop this as a useful analytical technique. At the moment, it is regarded as one of the most important methods for ion dissociation in tandem mass spectrometry, which is widely applied to molecular structure determination and mixture analysis. In spite of its widespread use, however, the fundamental understanding of this process is not satisfactory yet, mainly due to the inherent experimental and theoretical difficulties. Overview of the current understanding of CID of polyatomic ions at kiloelectronvolt translational energy is available from several articles.

It is widely accepted that CID at kiloelectronvolt occurs in two successive steps, collisional activation and subsequent unimolecular dissociation of activated ions.

$$m_1^+ + N \rightarrow m_3^+ + m_3$$  \(1\)

$$m_1^+ \rightarrow m_2^+ + m_3$$  \(2\)

Here, $m_1^+$ and $N$ represent the parent ion and the collision gas, respectively. $m_3^+$ and $m_3$ are the daughter ion and neutral, respectively. Validity of the above “two step model” has its basis on the large disparity in time scale between the collision and dissociation steps.

One of the most important subjects in the study of CID is the excitation mechanism in the collision step. Previously, it was generally thought that purely electronic excitation via the Franck-Condon process was the dominant excitation mechanism at kiloelectronvolt translational energy and that vibrational excitation via momentum transfer became important at lower energy. However, recent investigations on the collision dynamics in CID by Futrell and co-workers utilizing angle- and energy-resolved cross-beam tandem mass spectrometry have shown that the electronic excitation is much more prevalent even at modest collision energy than was previously thought. This means that the previous dichotomy of the collisional excitation mechanism, i.e., vibrational excitation dominating at low collision energy and electronic excitation at high collision energy, is not generally applicable. Another important finding reported by the above investigators is that the energy-transfer collision is impulsive in nature, resulting in significant angular scattering. Namely, purely electronic excitation via the Franck-Condon process is no longer an acceptable model at intermediate energy. Rather, the electronic transition observed in CID is non-Franck-Condon in nature, which was referred to as the vibronic transition by the above investigators.

In our previous study on the scattering angular distribution in CID of polyatomic ions, the impulsive nature of the collisions contributing to CID was confirmed. Specifically, the scattering became more backward or the impact parameter got smaller to satisfy the energetics requirement as the center-of-
mass translational energy decreased. It was suggested that either vibrational excitation via momentum transfer or vibronic excitation via nonadiabatic interaction is compatible with the experimental data. Contributions from each of the two processes could not be separated in the experimental data, however, and the relative importance of each could not be evaluated.

It is known that the loss of hydrogen from methane molecular ion in CID occurs via two different channels, one presumably via electronic (or vibronic) and the other via vibrational excitation.  

\[
\text{CH}_4^{+} \rightarrow \text{CH}_3^{+} + \text{H}^+ \quad (3)
\]

Contributions from the two CID channels are easily separable by analyzing the kinetic energy release distribution (KERD) derived from a mass-analyzed ion kinetic energy profile. This makes it an ideal system for the study of the relative importance of the two excitation processes under various experimental conditions. Results from such a study are presented in this paper.

Experimental Section

A double-focusing mass spectrometer with reversed geometry (VG Analytical, Model ZAB-E) was used in this work. Methane was introduced via a septum inlet into the ion source maintained at 170 °C. Ions were generated either by electron ionization at 70 or 15 eV electron energy (termed 70 eV/EI or 15 eV/EI) or by charge exchange ionization using Kr or Xe as reagent gas (termed Kr/CE or Xe/CE). Ion source temperature was 140 °C under the charge exchange ionization condition. Ions thus generated were accelerated to 1–8 keV and the molecular ions were selected by the magnetic sector.

He collision gas was introduced to the collision cell located near the intermediate focal point of the instrument. Its pressure was adjusted to 10% attenuation of the parent ion beam such that the effect of multiple collision was not important. Under this condition, the efficiency of double collision relative to single collision is 5% as estimated by equations in ref 16. Experimentally, it was found that the CID profile was hardly affected by the collision gas pressure at low attenuation. The translation energy spectra of daughter ions generated by CID in the cell were obtained by scanning the electric sector voltage. This is so-called the mass-analyzed ion kinetic energy spectrometry (MIKES).

Even though the intensity of CH$_3^+$ generated by CID was much stronger than the background signal measured in the absence of the collision gas, contribution from the latter was removed by numerical subtraction. The purity of the collision gas was better than 99.995% and gas purifier was used to remove water as much as possible.

Results and Discussion

Before getting into details of the present results, let us first summarize the energetic data pertinent to reaction 3. The best literature value for the ionization energy of CH$_4$ seems to be 12.61 eV, which was reported by Chupka and Berkowitz in 1971 and confirmed in 1987. Taking the result of the appearance energy measurement reported by the same group sets the critical energy for reaction 3 at 1.71 eV. According to ref 21, the first and second electronic states of CH$_4^{+}$ are thought to lie 1.66 and 2.39 eV above the ground state, respectively. A schematic energy level diagram is shown in Figure 1.

![Energy level diagram relevant to reaction 3.](image)
which is usually the case, band broadening of a MIKE profile is proportional to $K^{1/2}$. Hence, to compare MIKE profiles obtained at different translational energies, it is convenient to adjust the x-scales such that they are inversely proportional to $K^{1/2}$. Such an adjustment has been made in Figure 2 and in subsequent MIKE profiles. Comparing parts a and c of Figure 2, it is seen that CID/MIKE profiles are affected by the parent ion translational energy unlike most cases. As the electron energy used for generating CH$_4^+$ is reduced from 70 to 15 eV, the CID/MIKE profile gets broader as is seen in Figure 2b. This is also against the conventional wisdom that a CID/MIKE profile is essentially invariant with the ionization method as far as the parent ion structure remains the same.

The CID/MIKE profiles in Figure 2 were corrected for the energy-transfer effect according to the method in ref 22. Then, KERDs were evaluated from the corrected profiles following the method developed by Yeh and Kim. The results are shown in Figure 3, in which the bimodal nature of KERD is apparent.

To separate each experimental KERD into two components, the surprisal analysis$^{29}$ was adopted as in the previous work. The surprisal, $I$, for KERD is defined as

$$I(T) = -\ln[n(T)/n_0(T)] \quad (6)$$

Here, $n(T)$ is the experimental KERD and $n_0(T)$ is the prior distribution. Since the unimolecular dissociation of methane molecular ion proceeds via a loose transition state, the phase space theory$^{30,32,33}$ can be used here to evaluate $n_0(T)$. The molecular parameters needed for the calculation are available in ref 14. In our previous work$^{14}$ the main purpose of which was to relate the CID/MIKE peak shape with the collision energetics, the internal energy distribution was estimated from previous knowledge on collisional excitation energetics. Since $n_0(T)$ was evaluated here mainly to separate the two components, the internal energy distribution was modeled simply as a Gaussian form. Then the parameters in the Gaussian function were adjusted such that the surprisal became a straight line with zero slope at large KER region. A sample of the surprisal plots obtained is shown in Figure 4. The small (open circles) and large (filled circles) KER components separated by surprisal analysis are also shown.

![Figure 2](image)

**Figure 2.** CID/MIKE profiles for reaction 3 with He collision gas. (a) and (b) were recorded at 8-keV incident energy for CH$_4^+$ generated by 70 eV and 15 eV/EI, respectively. (c) was recorded at 1 keV for CH$_4^+$ generated by 70 eV/EI. Origin of x-scale is the corresponding position for the unimolecular dissociation (metastable ion decomposition). x-scales have been adjusted to be inversely proportional to $K^{1/2}$.

![Figure 3](image)

**Figure 3.** Solid curves in (a), (b), and (c) are KERDs derived from CID/MIKE profiles in (a), (b), and (c) of Figure 2, respectively. The small (open circles) and large (filled circles) KER components separated by surprisal analysis are also shown.

![Figure 4](image)

**Figure 4.** Surprisal plots for the KERD shown in Figure 3a. Circles denote the surprisal, $I(T)$, and the best-fit line for the B component is also shown. $n_0(T)$ was calculated with the phase space theory using the internal energy distribution $f = 0.2688 \exp(-0.1323(E - 3.6214)^2)$.
TABLE 1: Percent Fraction and Average Kinetic Energy Release (KER) in Hydrogen Loss from CH$_4$* Generated by 70 eV/EI

<table>
<thead>
<tr>
<th>$K_1$, keV</th>
<th>small KER component</th>
<th>large KER component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$w_{A_1}$, %</td>
<td>$T_E$, meV</td>
</tr>
<tr>
<td>8</td>
<td>20 ± 2</td>
<td>56 ± 3</td>
</tr>
<tr>
<td>6</td>
<td>21 ± 2</td>
<td>55 ± 3</td>
</tr>
<tr>
<td>4</td>
<td>26 ± 3</td>
<td>53 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>28 ± 3</td>
<td>53 ± 3</td>
</tr>
<tr>
<td>2</td>
<td>35 ± 3</td>
<td>58 ± 3</td>
</tr>
<tr>
<td>1</td>
<td>48 ± 3</td>
<td>56 ± 3</td>
</tr>
</tbody>
</table>

a Percent fractions. b Average KER. c Average excess energy obtained from surprisal analysis.

in the surprisal analysis. $E_B$ can be considered as a rough estimate of the average postcollision internal energy of the parent ion contributing to the B component referred to the product ground level. Percent fraction, the average KER, and the average excess energy ($E_B$) of the B component all increase with $K_1$. The final column in the table lists the ratio $T_B/E_B$ which is essentially invariant with the incident energy. This means that the average KER of the B component increases with $K_1$ simply because a collision deposits larger internal energy at higher incident energy. The average KER of this component is in good agreement with the ones measured at the similar energy range by Stockbauer using the threshold photoelectron–photoion coincidence spectrometry. This, together with the fact that the fraction of B increases with $K_1$, indicates that this component arises from collisional excitation to some excited electronic states(s). Then, the fact that the statistical calculation provides a decent fit to this component means that the molecular ions excited to upper electronic states undergo efficient internal conversion to the ground state and that the intramolecular vibrational relaxation is also efficient.

The average kinetic energy release in the A component is only about 10% of that in the B component. Also, not only the average of KER but also its distribution remains nearly the same with the change in the incident energy. Two interpretations are possible on its origin; dissociation from a certain isolated electronic state and dissociation from the ground state at internal energy slightly above the threshold. The former is not likely in view of the fact that the percent fraction of this component decreases with the incident energy. Assuming that dissociation contributing to this component occurs statistically also, the average internal energy may be estimated by fitting with a phase space theory calculation. The average internal energy thus estimated is 0.13 eV, corresponding to one or at the most two vibrational quanta above the threshold.

In the scattering contour diagram determined for the same reaction by Futrell and co-workers using the angle- and energy-resolved cross-beam tandem mass spectrometry, a very sharp feature was observed in the forward direction with very little inelastic energy loss. Similar features were observed for other reactions such as CH$_3$NO$_2$* + → CH$_3$* + NO$_2$* and C$_2$H$_4$* + → C$_2$H$_4$* + CH$_4$* which are the least endoergic dissociation channels from the respective parents. It was suggested that these features are due to dissociations of parents with internal energies very near the reaction thresholds after gaining a few vibrational quanta at the most in a collision. Namely, molecular ions produced by electron ionization possess a wide range of internal energy all the way up to or even higher than the threshold for the least endoergic channel. Then, the ions with internal energy near the threshold may gain a few vibrational quanta via momentum-transfer collision and dissociate. In the case of CH$_3$*+, it is known that even the parents with internal energy immediately below the threshold dissociate via quantum mechanical tunneling through a centrifugal barrier. Hence, CH$_3$*+ ions arriving at the collision cell must possess internal energy less than the threshold energy. Among these ions, those with internal energy slightly below the threshold may gain a few vibrational quanta via momentum-transfer collisions and dissociate. This model is entirely compatible with the observation made for the A component. Validity of this interpretation will become clearer below.

If the A component is generated by vibrational excitation of the parent slightly below the threshold, its contribution to the CID/MIKE profile can be reduced by decreasing the population of such parents. As an initial attempt, we decreased the electron beam energy used for ionization in the source to 15 eV. The CID/MIKE profile obtained from CH$_4$*+ generated by 15 eV/EI is shown in Figure 2b. As was mentioned earlier, this is broader than the one from CH$_4$*+ generated by 70 eV/EI, Figure 2a, against the conventional wisdom. KERD calculated from the profile is shown in Figure 3b. Comparing parts a and b of Figure 3, it is clear that percent fraction of the A component decreases as the electron energy used for generating the molecular ion is reduced. Namely, as the relative population of parents with internal energy near the threshold decreases, the relative contribution from the A component decreases. This supports that the A component is generated by vibrational excitation of parents near the threshold (see also the following results for CH$_3$*+ generated by charge exchange).

Simultaneous appearance of product ions induced by the electronic and vibrational excitations provides a rare opportunity to investigate the nature of these processes. In this regard, we attempted to study the relative efficiency of the vibrational excitation as a function of the initial energy deficit, namely, the difference between the threshold energy and the precollision internal energy of the parent ion. For this purpose, we used the charge exchange with rare gas ions such as Kr$^+$ and Xe$^+$. The internal energy of CH$_3$*+ generated by charge exchange, ignoring the thermal energy, is well approximated by

$$E = \text{RE}(X^+)^{-} - \text{IE}(\text{CH}_4)$$

Here, RE is the recombination energy of X$^+$ and IE is the ionization energy of CH$_4$, which is 12.61 eV. In case of charge exchange with Kr$^+$, or Kr/CE, Kr$^+$ both in the $\text{P}_3/2$ and $\text{P}_1/2$ states with REs of 14.0 and 14.7 eV, respectively, will contribute to formation of CH$_3$*+. Charge exchange with Kr$^+$ in the $\text{P}_1/2$ state will generate CH$_3$* with 2.1 eV internal energy. Since this energy is well above the threshold energy for reaction 3, all the CH$_3$*+ ions generated by this process will dissociate within the ion source. Hence, only the CH$_3$*+ ions generated by charge exchange with Kr$^+$ in the $\text{P}_3/2$ will survive and arrive at the collision cell with 1.4 eV internal energy. In Xe/CE, atomic ions in the $\text{P}_3/2$ and $\text{P}_1/2$ states with RE of 12.1 and 13.4 eV are useful for charge exchange in general. However, RE of Xe$^+$ in the $\text{P}_3/2$ does not possess sufficient energy to generate CH$_3$*+. So, CH$_3$*+ ions produced by Xe/CE possess 0.8 eV internal energy. In addition, CH$_3$*+ ions generated by charge exchange possess thermal energy. The thermal internal energy distribution can be calculated with the molecular parameters in ref 14. The average thermal energy calculated is 0.06 eV and the probability to possess thermal energy larger than 0.3 eV is negligible. The estimated internal energies of...
the molecular ions generated by Kr/CE and Xe/CE are shown in Figure 1. Shaded areas in the figure represent uncertainties due to thermal energy distribution.

Figure 5 shows the CID/MIKE profile obtained with CH$_4$$^+$ generated by Kr/CE. KERD determined from the profile is also shown together with A and B components separated by surprisal analysis. The results of the CID/MIKE profile analysis are summarized in Table 2. The property of the B component, namely, the average KER and excess energy, is essentially the same as the one obtained with CH$_3$$^+$ generated by 70 eV/EI, as is expected for dissociation induced by electronic excitation. The average KER of the A component is a little bit larger than for 70 eV/EI. Its contribution to the overall KERD is only half that in 70 eV/EI. Considering that only a fraction of CH$_4$$^+$ generated by 70 eV/EI has internal energy near the threshold, the above observation is all the more remarkable. The minimum energy needed in the collision for the dissociation of CH$_4$$^+$ generated by Kr/CE, namely, the energy deficit, is 0.2 eV on the average. Hence, it is obvious that transfer of more than a few tenths of an electronvolt by vibrational excitation is not an efficient process.

To confirm the above conclusion, we also recorded and analyzed the CID/MIKE profile obtained with CH$_4$$^+$ generated by Xe/CE. The results are shown in Figure 6 and the average KERs evaluated from the results are listed in Table 2. In this case, the A component is essentially absent and the average KER of the overall distribution is essentially the same as that of B component in 70 eV/EI. Hence vibrational excitation is not efficient enough to provide the 0.8 eV average energy deficit needed here. On the other hand, transfer of 1–4 eV internal energy via electronic excitation, namely, the process leading to the B component, occurs efficiently regardless of the slight change in the parent ion internal energy.

So far, we have compared the contributions from the vibrational and electronic excitation processes in relative sense only. To investigate the changes in the efficiencies (cross sections) with the incident energy, we measured the intensities of each component normalized to the parent ion beam intensity in the absence of the collision gas. The results for the A and B components are drawn separately in Figure 7. Since the contribution from the A component was negligible in CID of CH$_4$$^+$ generated by Xe/CE, the whole signal was taken as the B component. It is to be noted that the normalized intensity of the A component, whether it is from CH$_4$$^+$ generated by 70 eV/EI or by Kr/CE, is insensitive to the incident energy. On the other hand, the normalized intensity of the B component increases with the incident energy. Also, the normalized intensities are nearly the same for the parent ions generated by 70 eV/EI, Kr/CE, and Xe/CE. Namely, efficiency of electronic excitation is not influenced much by the parent internal energy.

We have argued that the vibrational excitation in reaction 3 can supply only a few vibrational quanta at the most. This means that this excitation mechanism is not useful for inducing dissociation via other channels which are more endoergic. In this regard, we also measured the CID/MIKE profiles for the daughter ions CH$_3$$^+$, CH$_2$$^+$, and C$^+$ and their normalized intensities. KERDs evaluated from the profiles look to consist of one component only. Also, the normalized intensities of these ions, shown in Figure 7c, increase monotonically with the incident energy just as for the B component of CH$_4$$^+$. This suggests that electronic excitation is the main mechanism for energy transfer in CID except for the least endoergic channel.

In the previous investigations utilizing angle-resolved mass spectrometry, it was reported that larger angle scattering resulted from more endoergic collisions. Since an electronic excitation via a Franck–Condon process would not lead to substantial deflection in a collision, the above was often taken as evidence for the excitation via momentum transfer, namely, vibrational excitation. The angle- and energy-resolved cross-beam tandem mass spectrometric studies by Futrell and co-
workers\textsuperscript{11,12} and the scattering angular distributions obtained in this laboratory\textsuperscript{13} also showed substantial deflections in collisions leading to dissociations. It was recognized, however, that an electronic transition due to a nonadiabatic interaction in the neighborhood of avoided crossings and conical intersections as had been suggested by Lorquet and co-workers\textsuperscript{47} was compatible with experimental data. Hence, either vibrational excitation via momentum transfer or electronic excitation via nonadiabatic interaction was taken as responsible for the inelastic energy transfer in a collision. The results from the present investigation show that electronic excitation is the main mechanism in CID of CH$_2^+$ at kiloelectronvolt incident energy. Vibrational excitation also occurs but supplies only a few vibrational quanta and hence is important for the least endoergic process only.

In the usual approach to formulating vibrational excitation via momentum transfer on an adiabatic potential energy surface, a polyatomic projectile is divided into two parts, the impact and spectator portions. The simplest of these models is the so-called binary collision model.\textsuperscript{48,49} More elaborate models which can address various aspects of the collision event such as the relation between the scattering angle and the endoergicity have been developed also.\textsuperscript{40–52} All these models predict substantial vibrational excitation via momentum transfer in contrast with the present results. If the projectile ion which has undergone a severe momentum-transfer collision is deflected substantially, its dissociation product may not be detected by the conventional apparatus used in the present work. However, it is well-known in angle-resolved mass spectrometry that the product ion yield decreases rapidly as the deflection angle increases.\textsuperscript{43,46} Namely, deposition of several electronvolts of internal energy via momentum transfer, if it occurs, is much less efficient than the electronic excitation at kiloelectronvolt incident energy. Since the relative cross sections for the electronic processes decrease gradually as the incident energy decreases, the vibrational process may become important in a relative sense at low incident energy ($<1$ keV). In particular, it will be of interest to see if transfer of more than a few electronvolts via momentum transfer becomes practical at low incident energy in relation to the tandem mass spectrometry at low translational energy.\textsuperscript{15,33} Such an investigation is being planned together with the extension to other polyatomic ion systems.

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References and Notes
