Metastable Dissociation of CH_5^+ Ions in the Methane Mass Spectrum

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(Z. Naturforsch. **24 a**, 1959—1963 [1969]; received 19 August 1969)

The main dissociation channels of the CH_5^+ ion, i. e.

$$\uparrow CH_5^+ \begin{array}{l} \xrightarrow{\quad 1 \quad} CH_4^+ + (H) \qquad (m_0^* = 14{,}90) \\ \xrightarrow{\quad 2 \quad} CH_3^+ + (2\,H) \qquad (m_0^* = 13{,}26) \end{array}$$

have been investigated by a mass spectrometric method. The pressure dependences of the ratios $I_{14,90}/I_{17}$ and $I_{13,26}/I_{17}$, in the range from $4{,}4 \cdot 10^{-4}$ to $1 \cdot 10^{-4}$ Torr, were plotted. The two ratios depend linearly on the pressure in the mass spectrometer analyzer. Since the two straight lines do not pass through the origine the conclusion is drawn that, for both dissociation channels of the CH_5^+ ion, besides the collision-induced transitions, spontaneous transitions, i. e. pure metastable transitions, take place.

The spontaneous dissociations constants ($\lambda_1 = 7{,}5 \cdot 10^5$ sec^{-1}, $\lambda_2 = 5{,}2 \cdot 10^4$ sec^{-1}) and collision-induced dissociation cross-sections ($\sigma_1 = 5{,}25 \cdot 10^{-16}$ cm^2, $\sigma_2 = 3{,}2 \cdot 10^{-16}$ cm^2) have been estimated. These results are discussed and compared with those reported by other authors.

The often investigated [1−11] reaction

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \qquad (1)$$

is not the only possible one between the parent CH_4^+ ion and the neutral methane molecule, many others, leading to the formation of heavier ions, being known, but it is generally accepted that it has the largest cross-section. Reaction (1) takes place at low energies, especially in the mass spectrometer ion source. At larger energies, corresponding to the whole accelerating voltage of conventional mass spectrometers, dissociation reactions of the parent ion take place [11].

As to the stability of the CH_5^+ ion, **Field** et al. [5] investigated the dissociation channels of the CH_5^+ ion in a mass spectrometer at a pressure of 320 mTorr. The relative cross-sections for the different dissociation processes were identified. From their results it follows that the dissociation processes

$$CH_5^+ \rightarrow CH_4^+ + (H) \qquad (m_0^* = 14{,}90) \qquad (2)$$

$$\rightarrow CH_3^+ + (2\,H) \qquad (m_0^* = 13{,}26) \qquad (3)$$

have by far the largest cross-sections. It is specified by them that for the transition (2) the ratio $I_{14,90}/I_{17}$ increases approximately linearly with the pressure in the mass spectrometer analyzer. The conclusion is drawn that this process in collision-induced. The absolute value of the cross-section of process (2) is $2 \cdot 10^{-16}$ cm^2.

The dissociation processes of CD_5^+, CH_5^+ and CD_4^+ were studied by **Kuprianov** [12] with two mass spectrometers in tandem. Between the two a collision chamber was inserted [13], in which there was a controlled low pressure atmosphere of neon or air. From the obtained results the author drew the conclusion that in all cases the dissociation of these ions takes place as a result of their collisions with the gas molecules. He concluded that the CD_5^+, CH_5^+ and CD_4^+ ions are stable with regard to spontaneous dissociation (i. e. pure metastable transitions), for all the studied reaction channels.

In the present paper the CH_5^+ ion transitions (2) and (3) were again studied.

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1. Apparatus

A Dempster type mass spectrometer with electrical scanning of the masses was used. The schematic representation of the apparatus is given in Fig. 1.

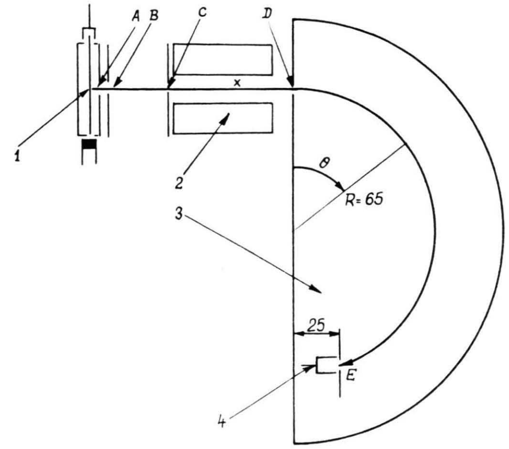

Fig. 1. Schematic representation of the mass spectrometer. 1 — beam of ionizing electrons, 2 — deflector, 3 — analyzer, 4 — collector.

A detailed description of the apparatus is given in [14]. Some characteristics which are of interest in the present paper, will be given. The voltages on the slits are: (A)→1—5% of V; (B)→25% of V and (C, D)→100% of V, V being the whole accelerating voltage of the ions (from 360 to 3000 volts). On the deflector plates (corresponding to the trajectory CD) a potential ~80% of V is applied. Thus, in the deflector the ions will practically keep the energy gained at point C of the trajectory.

The shape of the metastable "peak" depends on the mass spectrometer characteristics. We give some specifications concerning the shape of our metastable "peaks" in [14].

The following metastable transitions are considered

$$m^+ \rightarrow m_1^+ + \Delta m\,.$$

The apparent masses m^* at which the m_1^+ ions will be collected depend on the trajectory points at which the dissociation took place.

If dissociation takes place at A (cf. Fig. 1), then $m^* = m_1$ and if dissociation takes place at C, then $m_0^* = m_1^2/m$. The other apparent masses are in between these limiting values.

Since the slits C and D are at the same potential all ions dissociating on the trajectory portion CD will be practically collected at the same apparent mass $m_0^* = m_1^2/m$. *At this apparent mass they will form a metastable peak similar to the normal peaks of the mass spectrum. This apparent mass,* $m_0^* = m_1^2/m$, *corresponds to the maximum height of the metastable "peak".*

The ions which are dissociated on the trajectory portion DE will be collected at masses ranging from $m_0^* = m_1^2/m$ (if dissociation takes place in the neighbourhood of D), to $m^* = m$ (if dissociation takes place at the collector).

The superposition of the contributions corresponding to the trajectory portions AC, CD and DE will give the shape of the metastable "peak". Thus, metastable "peaks" in our mass spectrometer are asymmetrical and very diffuse.

The measurements were performed in a range of pressures in the mass spectrometer analyzer from $4{,}4 \cdot 10^{-4}$ to $1 \cdot 10^{-4}$ Torr. The mass spectrometer ion source is of the Nier type. The energy of the ionizing electrons is constant and equal to 85 eV.

2. Experimental Data

In a previous paper [14] the methane mass spectrum obtained in our mass spectrometer with a relatively high pressure in the analyzer and the ion source was studied. An approximate estimation of the shapes of the main collision-induced metastable transition "peaks" was given. Using these results we have studied the most important channels of the CH_5^+ ion dissociation as indicated in (2) and (3). For this purpose we have investigated the pressure dependence of the ratios $I_{14,90}/I_{17}$ and $I_{13,26}/I_{17}$. The obtained results are given in Fig. 2.

The two ratios depend linearly on the pressure in the mass spectrometer analyzer. From the fact that the two straight lines do not pass through the origine we conclude that besides the collision-induced transitions, spontaneous transitions, i. e. pure metastable transitions, take place.

It is likely that for the energy of 85 eV of the ionizing electrons the CH_4^+ ions have a large internal energy. Hence, a part of the CH_5^+ ions can have sufficiently large internal energies to undergo spontaneous dissociation on their way from the source to the collector. From Fig. 2 it can be seen that in the spontaneous dissociation of the CH_5^+ ion the forma-

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[14] I. MASTAN and V. MERCEA, to be published.

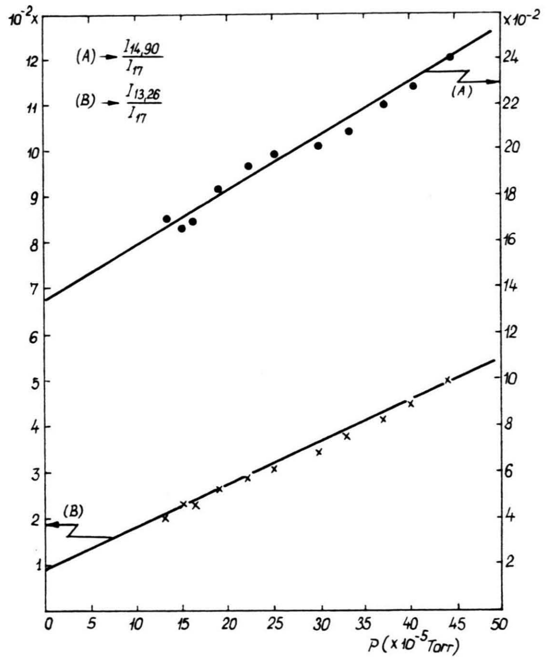

Fig. 2. Pressure dependences of the ratios $I_{14,90}/I_{17}$ and $I_{13,26}/I_{17}$. (I_{17}, $I_{14,90}$ and $I_{13,26}$ represent the "peak" heights corresponding to the given masses.)

tion of CH_4^+ is about 10 times more probable than that of CH_3^+.

With these results the diagram of the main dissociation channels of the CH_5^+ ion may be written in the form

$$\begin{array}{ll} CH_5^+ \xrightarrow{\lambda_1} & CH_4^+ + (H) \\ \quad\ \ \xrightarrow{\sigma_1} & CH_4^+ + (H) \\ \quad\ \ \xrightarrow{\lambda_2} & CH_3^+ + (2\,H) \\ \quad\ \ \xrightarrow{\sigma_2} & CH_3^+ + (2\,H) \end{array}$$

Here λ represents *the constant of the spontaneous dissociation,* while σ corresponds to the collision-induced dissociation and represents *the cross-section of the process.*

The wole metastable "peak" is formed by superposition of the ionic currents corresponding to the spontaneous and collision-induced metastable transitions. If I_{m^*} is the height of the metastable "peak", corresponding to the apparent mass m^*, one can write

$$I_{m^*} = I_{m^*}^{*} + (I_{m^*})_{\mathrm{c.i}}\,. \tag{4}$$

Here, I^{*}_{*} represents the contribution of the spontaneous dissociations (pure metastable transitions) and $(I_{\mathrm{m}^*})_{\mathrm{c.i}}$ represents the contribution of the collision-induced dissociations.

3. Estimation of the Parameters σ_1, σ_2, λ_1, λ_2 and of $(I_0)_{17}$

3.1. *The system of equations for these quantities*

To estimate these quantities we shall follow a way analogous to that presented in the paper[14]. For this, each point of the trajectory (Fig. 1), from the source to the collector, is associated with a coordinate x ($x_{\mathrm{A}} = 0$) and a corresponding time t ($t_{\mathrm{A}} = 0$).

Knowing the main dissociation channels of the CH_5^+ ion the following differential equation can be written

$$\mathrm{d}I_{17} = -(\lambda_1 + \lambda_2)\, I_{17}\, \mathrm{d}t - (\sigma_1 N + \sigma_2 N)\, I_{17}\, v\, \mathrm{d}t. \tag{5}$$

On the trajectory portion AC the ion is accelerated up to the maximum energy. For simplification we will put, for the ion on the trajectory portion AC, an average velocity k_{a}. If $k = \sqrt{2\,e\,V/m}$ is the ion velocity at C one can write $k_{\mathrm{a}} = k/2$. For the trajectory portion CE the ion velocity is constant and equal to k.

Introducing

$$Q = \exp\{-[(\sigma_1 N + \sigma_2 N)\,(k\, t_{\mathrm{E}} - (k/2)\, t_{\mathrm{C}})]\}. \tag{6}$$

Eq. (5) is integrated to give

$$I_{17} = I_0\, Q \exp\{-(\lambda_1 + \lambda_2)\, t_{\mathrm{E}}\}\,. \tag{7}$$

Eq. (7) gives the CH_5^+ ion current intensity at the collector in terms of $(I_0)_{17}$ (for $x_{\mathrm{A}} = 0$) and of the dissociation parameters. The CH_5^+ ions which undergo spontaneous dissociation in the spectrometer deflector (the CD trajectory portion — cf. Fig. 1) will give just the heights of the pure metastable "peaks" corresponding to the apparent masses 14,90 and 13,26. For these heights the notations $I_{14,90}^*$ and $I_{13,26}^*$ are introduced.

If the CH_5^+ ions would only dissociate spontaneously then (for the transition $CH_5^+ \rightarrow CH_4^+ + (H)$) we could write

$$I_{14,90}^* = I_0 \exp\{-\lambda_1 t_{\mathrm{C}}\} - I_0 \exp\{-\lambda_1 t_{\mathrm{D}}\}\,. \tag{8}$$

But in the ionic beam the spontaneous and the collision-induced metastable transitions take place simultaneously. Thus, a better approximation for $I_{14,90}^*$ can be obtained if in Eq. (8) I_0 values are replaced by average values of the CH_5^+ ionic currents which remain after collision-induced metastable transitions have taken place on each of the trajectory portions AC and CD. If these average values are denoted by $(I_{\mathrm{a}})_{\mathrm{AC}}$ and $(I_{\mathrm{a}})_{\mathrm{CD}}$ Eq. (8) can be written in the form

$$I^*_{14,90} = (I_a)_{AC} \exp\{-\lambda_1 t_C\} - (I_a)_{CD} \exp\{-\lambda_1 t_D\}. \tag{9}$$

For $(I_a)_{AC}$ and $(I_a)_{CD}$ one can write

$$(I_a)_{AC} = (I_0/2)\,(1+\Psi_1), \tag{10}$$

$$(I_a)_{CD} = (I_0/2)\;\Psi_1(1+\Psi_2) \tag{11}$$

with

$$\Psi_1 = \exp\{-(\sigma_1 N + \sigma_2 N)\,(k/2)\,t_C\},$$
$$\Psi_2 = \exp\{-(\sigma_1 N + \sigma_2 N)\,k(t_D - t_C)\}.$$

Using (10) and (11) Eq. (9) can be written in the form

$$I^*_{14,90} = (I_0/2)\,[(1+\Psi_1)\exp\{-\lambda_1 t_C\} - \Psi_1(1+\Psi_2)\exp\{-\lambda_1 t_D\}]. \tag{12}$$

Similarly, for $I^*_{13,26}$ one can write

$$I^*_{13,26} = (I_0/2)\,[(1+\Psi_1)\exp\{-\lambda_2 t_C\} - \Psi_1(1+\Psi_2)\exp\{-\lambda_2 t_D\}]. \tag{13}$$

The following notations will be introduced

$$(I^*_{14,90}/I_{17}) = A_1, \quad (I^*_{13,26}/I_{17}) = A_2,$$
$$A_1 Q \exp\{-\lambda_1 t_E\} = R, \; \sqrt{\tfrac{1}{2}}\,[(1+\Psi_1)\exp\{-\lambda_1 t_C\} - \Psi_1(1+\Psi_2)\exp\{-\lambda_1 t_D\}] = P$$

and

$$\lambda_2 = \ln(R/P)/t_E. \tag{14}$$

With these notations the exponential Eqs (7), (12), (13), and (14) lead to the transcendental Equation

$$A_2 Q \exp\{-\lambda_1 t_E\} = \frac{\tfrac{1}{2}[(1+\Psi_1)\exp\{-\lambda_2 t_C\} - \Psi_1(1+\Psi_2)\exp\{-\lambda_2 t_D\}]}{\exp\{-\lambda_2 t_E\}}. \tag{15}$$

If Q is known (it implies the knowledge of the values σ_1 and σ_2), λ_1 and λ_2 can be computed with the help of Eqs (15) and (14).

3.2. *Estimation of the cross-sections σ_1 and σ_2*

For that pressure range in which the ratios $I_{14,90}/I_{17}$ and $I_{13,26}/I_{17}$ depend linearly on the pressure (cf. Fig. 2), one can write

$$(I_{14,90}/I_{17}) = \sigma_1\,p\,\Delta x + K_1,$$
$$(I_{13,26}/I_{17}) = \sigma_2\,p\,\Delta x + K_2\,^{15}. \tag{16}$$

We specify that by I_{17}, $I_{14,90}$ and $I_{13,26}$ the whole heights of the peaks are denoted. On the basis of the Eq. (4) one can write

$$(I^*_{14,90}/I_{17}) = K_1 = A_1, \quad (I^*_{13,26}/I_{17}) = A_2 = K_2. \tag{17}$$

Hence

$$[(I_{14,90})_{\text{c.i}}/I_{17}] = \sigma_1\,p\,\Delta x, \; [(I_{13,26})_{\text{c.i}}/I_{17}] = \sigma_2\,p\,\Delta x. \tag{18}$$

If in (18) one puts $\Delta x = x_E$ then it is necessary to replace, on the left hand side of these relations, the ratio of the heights with the ratio of the peak areas. We recall that metastable "peaks" given by our mass spectrometer are asymmetrical and very diffuse [14]. For example, the "tail" of the metastable "peak" $m_0{}^* = 14{,}90$ is practically extended up to $m^* = 17$. We have approximated with triangles the "peaks" 14,90, 13,26 and 17. By γ_1 and γ_2 we have denoted the ratios of the bases of these triangles for the peaks 14,90 and 17, and 13,26 and 17 respectively. As a result of these specifications the relations (18) can be written

$$\gamma_1[(I_{14,90})_{\text{c.i}}/I_{17}] = \sigma_1\,p\,x_E,$$
$$\gamma_2[(I_{13,26})_{\text{c.i}}/I_{17}] = \sigma_2\,p\,x_E. \tag{19}$$

For the pressure range in which these ratios are given (cf. Fig. 2) one can write

$$\gamma_1 \cdot \Delta[(I_{14,90})_{\text{c.i}}/I_{17}]/(\Delta p \cdot x_E) = \sigma_1,$$
$$\gamma_2 \cdot \Delta[(I_{13,26})_{\text{c.i}}/I_{17}]/(\Delta p \cdot x_E) = \sigma_2. \tag{20}$$

With the numerical values $\gamma_1 = 1{,}7$, $\gamma_2 = 2{,}65$ and $x_E = 21{,}4$ cm one obtains

$$\sigma_1 = 5{,}25 \cdot 10^{-16}\ \text{cm}^2, \quad \sigma_2 = 3{,}20 \cdot 10^{-16}\ \text{cm}^2.$$

On the basis of the mass spectrometer features (geometry, accelerating voltage, etc.) one gets for the $CH_5{}^+$ ion

$$t_C = 2 \cdot 10^{-7}\ \text{sec}, \qquad t_E = 1{,}58 \cdot 10^{-6}\ \text{sec},$$
$$t_D = 4 \cdot 10^{-7}\ \text{sec}, \qquad k = 1{,}4 \cdot 10^7\ \text{cm/sec}.$$

Using these numerical values, for $p = 4{,}4 \cdot 10^{-4}$ Torr, one obtains $Q = 7{,}6 \cdot 10^{-1}$.

3.3. *Estimation of the constants λ_1, λ_2 and of the $(I_0)_{17}$*

Equation (15), where λ_2 is given by Eq. (14), is solved using the following known values ($p = 4{,}4 \cdot 10^{-4}$ Torr)

$$t_C = 2 \cdot 10^{-7}\ \text{sec}, \qquad Q = 7{,}6 \cdot 10^{-1},$$
$$t_D = 4 \cdot 10^{-7}\ \text{sec}, \qquad A_1 = 13{,}6 \cdot 10^{-2},$$
$$t_E = 1{,}58 \cdot 10^{-6}\ \text{sec}, \qquad A_2 = 9 \cdot 10^{-3},$$

One obtains

$$\lambda_1 = 7{,}5 \cdot 10^5\ \text{sec}^{-1}, \quad \lambda_2 = 5{,}2 \cdot 10^4\ \text{sec}^{-1}.$$

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[15] In order to avoid any confusions we specify that N is the concentration expressed in molecules/cm^3, while p is the pressure expressed in Torr.

With the help of λ_1 and λ_2 the lifetimes and half-lives for both spontaneous dissociations may be computed

$$\tau_1 = (1/\lambda_1) = 1{,}33 \cdot 10^{-6}\ \text{sec},$$
$$\tau_2 = (1/\lambda_2) = 1{,}93 \cdot 10^{-5}\ \text{sec},$$
$$(T_{1/2})_1 = (\ln 2/\lambda_1) = 0{,}93 \cdot 10^{-6}\ \text{sec},$$
$$(T_{1/2})_2 = (\ln 2/\lambda_2) = 1{,}33 \cdot 10^{-5}\ \text{sec}.$$

From Eq. (7), using the values obtained here, $(I_0)_{17}$ can be computed. For $p = 4{,}4 \cdot 10^{-4}$ Torr, knowing that $(I_{17})_E = 32$, one obtains $(I_0)_{17} = 142$ (in arbitrary units).

4. Discussion of the Results

A value of $\sigma_1 = 5{,}25 \cdot 10^{-16}\ \text{cm}^2$ was estimated by us for the cross-section of the collision-induced dissociation corresponding to the reaction

$$CH_5^+ \rightarrow CH_4^+ + (H).$$

Field et al.[5] reported, for the same dissociation process, a cross-section of $2 \cdot 10^{-16}\ \text{cm}^2$. The agreement between the two values is acceptable if it is taken into account that our determination is only approximative.

In his paper Kuprianov[12] specifies that the time necessary for the ions to cross the first mass spectrometer analyzer is of the order of $6 \cdot 10^{-6}$ sec. Under these conditions the fact that one does not observe spontaneous dissociation of the CH_5^+ ions in the tandem collision chamber[13], becomes explicable.

For the spontaneous dissociation

$$CH_5^+ \rightarrow CH_4^+ + (H),$$

which is much more probable than that into CH_3^+, we have obtained $(T_{1/2})_1 = 0{,}93 \cdot 10^{-6}$ sec. If one compares this value with the time of $6 \cdot 10^{-6}$ sec necessary for the ions to reach the collision chamber, it becomes clear that the spontaneous dissociations which occure in the chamber, will be masked by the collision-induced ones.

For the spontaneous dissociation

$$CH_5^+ \rightarrow CH_3^+ + (2\,H),$$

which is more than 10 times less probable than the first one, we have obtained $(T_{1/2})_2 = 1{,}33 \cdot 10^{-5}$ sec. Having in view the smallness of this transition probability and the fact that $(T_{1/2})_2$ is comparable with $6 \cdot 10^{-6}$ sec, it will be difficult to observe it in the collision chamber.