# *Mass Spectrometric Study on Adsorption of Water Vapor on a Graphite Surface*

By Hokotomo INOUYE

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Although it is of interest in connection with the study of the adsorption of gas on a solid surface to know what sorts of ions are formed by electron bombardment at the surface, there are few mass spectrometric studies on the subject.

By electron bombardment at surface, ions are formed both on the surface and in the gas phase. Therefore, it is important to distinguish the ions which are formed from adsorbed molecules on the surface from those formed simultaneously in the space adjacent to the surface. For this purpose the author has devised a method to know places of formation of ions by analyzing their peak shapes obtained by means of a single focusing mass spectrometer with a modified ionization chamber.

Plumlee and Smith[1] found that $O^+$ was

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[1] R. H. Plumlee and L. P. Smith, *J. Appl. Phys.*, **21**, 811 (1950).

emitted from an electron-bombarded molybdenum surface by means of a mass spectrometer with the ionization chamber of special structure. However, the author's method may be simpler and give more precise results than Plumlee's method.

The results obtained by application of the author's method to the ions formed by electron bombardment at a graphite surface covered with adsorbed water vapor are described below.

## Experimental

In Fig. 1 is shown the schematic diagram of the mass spectrometer used in the present work. The repeller is replaced by a solid surface, S, to be studied. A hot filament, W, for an electron source is placed between S and the drawing-out electrode, A. Thermoelectrons emitted from W are accelerated by a potential difference $V_{SW}$ and strike S, forming ions on the surface and also in the space between the surface and the place where the potential corresponds to the ionization potential of a gas molecule. A part of these ions is drawn out of the slit $S_1$ of A by a definite potential difference $V_{SA}$ and is accelerated by the variable potential difference $V_{AB}$ for voltage scanning. Ions formed at different places in the ionization chamber, even if they have the same $m/e$, acquire different energies from $V_{SA}$, and hence, for scanning all of them, $V_{AB}$ should be varied over a certain range. Thus the peak shape of the ions will be determined by their distribution in the ionization chamber.

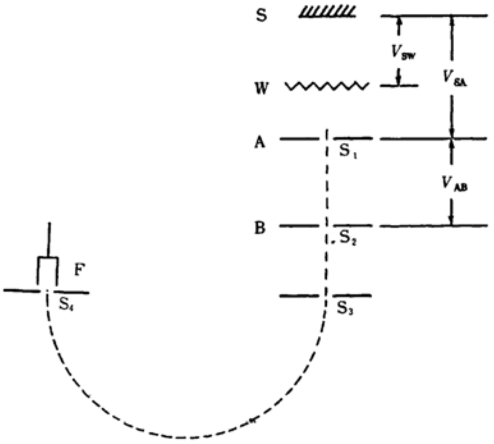

Fig. 1. Schematic diagram of the mass spectrometer.

**Peak Shape of the Ions Formed on the Surface.**—If all the ions of one kind are emitted from the surface with zero initial kinetic energy, the only value, ${}_SV_{AB}$, of $V_{AB}$ will be sufficient to bring the ions to the exit slit, $S_4$, of the analyzer. The peak shape will be a symmetrical one characteristic of the instrument (Peak 1). Now, let $V_s$ be the total accelerating potential ($V_{SA}+{}_SV_{AB}$) for the apex of this peak.

If the ion has a certain initial kinetic energy $V_0$ and the angle between its direction and the normal to the surface is $\theta$, $V_{AB}$ bringing the ion to $S_4$ is ${}_SV_{AB}-V_0\cos\theta$, since it has the energy of $V_{SA}+V_0\cos\theta$ at $S_1$. As the directional divergency of the ion beam at $S_3$ is small owing to the geometry of the instrument, the position of the peak apex can be determined only by the energy divergency, or the distribution of $\theta$, among the ions passing through $S_3$. Some ions formed even with great values of $\theta$ are able to enter the analyzer through $S_3$. The value of $\theta$ of the most abundant ions in this distribution is assumed to be $\theta_m$. Then the peak apex will move from $V_s$ by $V_0\cos\theta_m$ towards the lower potential side on the potential axis representing $V_{SA}+V_{AB}$. The peak shape also depends on the directional distribution of the ions at formation and on the geometry of the instrument. Generally, the peak width is broader than that of the ions with zero initial kinetic energy (Peak 2).

If the magnitude of the initial kinetic energy extends over a certain range, this distribution will also affect the position and shape of the peak.

**Peak Shape of the Ions Formed in the Gas Phase.**—If the energy of an electron emitted from W becomes equal to the ionization potential $J$ of a gas molecule at P on the way to S, the molecule in the space between P and S will be ionized by a collision with the electron. The number of ions formed per unit volume, the unit electronic current and the unit time is given by the product of the ionization probability and the density of the gas molecules. Ionization probability increases with the increasing energy of the incident electron and decreases after reaching the maximum. Therefore, the number of the ions formed along the electron path increases from zero at P up to the maximum at S, provided that the applied accelerating potential $V_{SW}$ of the electron is higher than $J$ and lower than the value corresponding to the maximum probability.

Even if the ions thus formed are supposed to have zero initial kinetic energy, they acquire different energies from $V_{SA}$ according to the places of their formation; thus, a wide range of $V_{AB}$ is necessary for scanning all of them. When $V_{AB}$ is equal to ${}_SV_{AB}$ the ions formed just before S can arrive at $S_4$, and at greater values of $V_{AB}$ those formed at places distant from S arrive at $S_4$. The amount of the ions formed just before S is maximum, and it decreases as the distance of the place of the

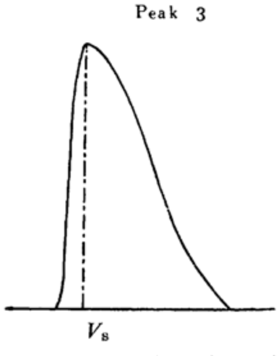

Fig. 2. Peak of the ions formed in the gas phase.

ion formation from S increases. Therefore, the peak has its apex at $V_s$, and its slope at the higher potential side is more gentle than that at the lower potential side as shown in Fig. 2 (Peak 3).

If $V_{SW}$ is higher than the value corresponding to the maximum probability, the place of the maximum ion formation moves from the surface toward P. So the apex moves from $V_s$ toward the higher potential side (Peak 4 in Fig. 3).

If the ions have some initial energies, the peak will be broadened also toward the lower potential side similarly to Peak 2, provided that any ion striking upon the surface underwent an elastic reflection. It may, however, be difficult to distinguish this peak from Peak 3.

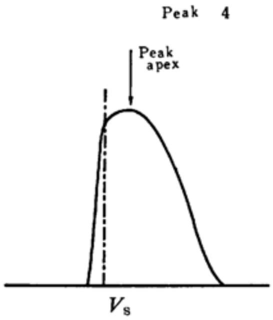

Fig. 3. Peak of the ions formed in the gas phase at $V_{SW}$ exceeding the value corresponding to the maximum ionization probability.

**Peaks of the Ions Formed Both on the Surface and in the Gas Phase.**—If an adsorbed gas is ionized in the gas phase after desorption as neutral molecules or atoms, the peak of the ions will have a shape quite similar to Peak 3. However, it is able to be distimguished from the peak of the ions due to the molecules originally present in the gas phase, because for the former peak the height is proportional to the square of the electronic current but for the latter it is directly proportional to the electronic current[2].

If the adsorbed gas is removed not only directly as ions from the surface but also as neutral molecules or atoms giving the ions of the same $m/e$ afterwards, two kinds of peaks will result either from superposition of Peaks 1 and 3, or from that of Peaks 2 and 3.

(A) All the ions of the same $m/e$ formed on the surface and in the gas phase are supposed to have no initial kinetic energy. Since Peak 1 is obtained for the former and Peak 3 for the latter, the observed peak will be one that results from superposition of both peaks as shown in Fig. 4 (Peak 5).

If $V_{SW}$ higher than the value corresponding to the maximum ionization probability is applied, the observed peak has a shape such as is shown in Fig. 5 (Peak 6), since Peak 4 takes the place of Peak 3 in Fig. 4. Thus, detection of the ions formed on the surface will become easier.

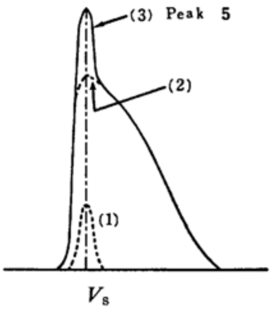

Fig. 4. Peaks of the ions of the same $m/e$ formed simultaneously on the surface and in the gas phase with no initial kinetic energy. (1): peak of the ions formed on the surface, (2): peak of the ions formed in the gas phase, (3): the compounded peak of 1 and 2.

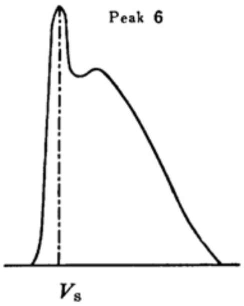

Fig. 5. Peak of the ions of the same $m/e$ formed simultaneously on the surface and in the gas phase by application of $V_{SW}$ higher than the value corresponding to the maximum ionization probability.

(B) If the ions formed on the surface have a fairly high initial kinetic energy but those formed in the gas phase have little, Peak 2 is obtained for the former and Peak 3 for the latter. The compounded peak is such as is shown in Fig. 6 (Peak 7). However, in some cases this peak may be indistinguishable from Peak 2 or Peak 5.

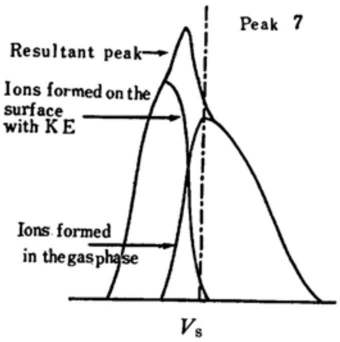

Fig. 6. Peak of the ions formed simultaneously on the surface with an initial kinetic energy and in the gas phase without initial kinetic energy

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[2] Y. Ohta, *J. Chem. Soc. Japan*, (*Nippon Kwagaku Kwaisi*), **64**, 849, 986 (1943).

As described above, the shapes of ion peaks are different from one another according to the places of their formation and to the presence of the initial kinetic energy. From the shape of the peak one may be able to know the place of formation of the ions and also, though not so exactly, to estimate their initial kinetic energy.

## Experimental Results

Ions found in the present work have *m/e* of 1($H^+$), 2($H_2^+$), 17($HO^+$), 18($H_2O^+$), 28($CO^+$), and 183∼186. The peaks of these ions are shown in Figs. 7—12. Besides them a group of ions which is supposed to be formed from grease vapor is found.

1) **$H_2O^+$ and $HO^+$.**—As the peak of $H_2O^+$ has a similar shape to Peak 3 in Fig. 2, this ion is supposed to be formed in the gas phase.

The peak shape of $HO^+$ appears to be similar to Peak 7 rather than to Peak 3. Thus, some of them may be formed on the surface with kinetic energy. However, for the present, $HO^+$ is supposed to be formed only from water molecules in the gas phase, owing to the fact that the observed relative intensity of $HO^+$ to $H_2O^+$ is not greatly different from the result, i.e., 1:4 which Tate and others[3] have obtained on water vapor by voltage scanning, and that it is difficult because of their low intensity to judge certainly whether the peak is similar to Peak 7 or not.

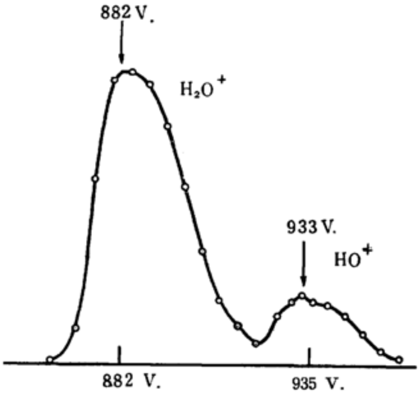

Fig. 7. $H_2O^+$ and $HO^+$. Figures on the potential axis indicate the normal position of the peak apex of the ion.

No measurement has yet been carried out to certify whether these ions are due to residual water vapor or due to the molecules desorbed by electron bombardment.

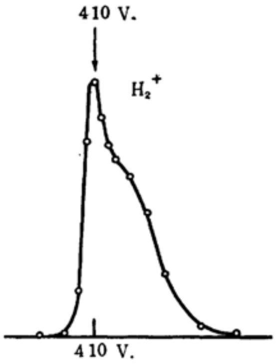

Fig. 8. $H_2^+$ when $V_{SW}$ is 50 V.

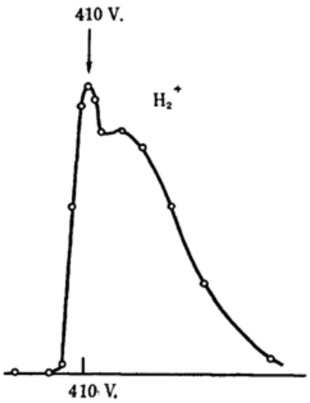

Fig. 9. $H_2^+$ when $V_{SW}$ is 100 V.

2) **$H_2^+$.**—As shown in Figs. 8 and 9, the peak shape is similar to Peak 5 in Fig. 4 when $V_{SW}$ is 50 V. and to Peak 6 in Fig. 5 when it is 100 V. The ions are supposed to be formed both on the surface and in the gas phase and neither of them is supposed to have any initial kinetic energy.

3) **$H^+$.**—As the peak has a similar shape, as shown in Fig. 10, to that of Peak 7, the ions are formed both on the surface and in the gas phase, and, at least, those formed on the surface seem to have a certain initial kinetic energy.

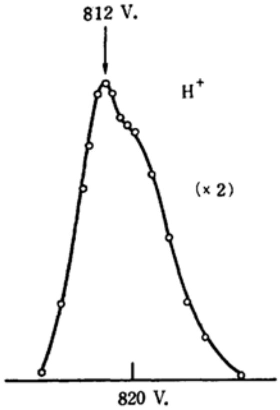

Fig. 10. $H^+$.

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[3] M. M. Mann, A. Hustrulid and J. T. Tate, *Phys. Rev.*, 58, 340 (1940).

The position of the peak apex of Fig. 8 corresponds to the total accelerating potential of $H_2^+$ leaving the surface without initial kinetic energy. From the value, 410 V., for the apex of $H_2^+$, the position of the apex of $H^+$, peak is calculated to be 820 V., whereas the observed value is 812. Hence, it is shifted by 8 V. towards the lower potential side. This shift will be due to the initial kinetic energy of $H^+$ from the surface.

Now, if the peak of the ions formed in the gas phase is assumed to be curve 1*[1] of Fig. 11 and is deducted from the observed curve 3, then curve 2 will result. This curve corresponds to the peak of the ions leaving the surface with initial kinetic energy, the value of which is calculated*[2] from the position of the apex to be 10 V.*[3]

**4) $CO^+$.**—Ions of *m/e* 28 correspond to $CO^+$ or $N_2^+$, but they are concluded to be $CO^+$ and not $N_2^+$, since $N^+$ (*m/e* 14) has not been found.

From the peak shape these ions are considered to consist of those formed in the gas phase and of those leaving the surface with kinetic energy, the value of which, however, would be small.

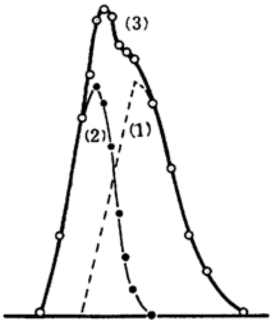

Fig. 11. $H^+$ peak divided into the component peaks.

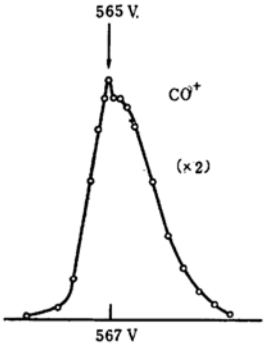

Fig. 12. $CO^+$.

**5) Ions of *m/e* 183～186.**—The behavior of this group of ions is very different from that of any other ion, and hence they are not supposed to be grease vapor ions but possibly $W^+$ which is produced by electron impact on tungsten vapor evaporating from the heated tungsten filament for the electron source. However, they have not yet been confirmed as such, because the resolving power of the instrument is not sufficient to determine exactly of what *m/e* of ions they consist.

## Consideration

Despite the fact that hydrogen and carbon monoxide were not introduced into the apparatus on purpose, it was found that $H_2^+$, $H^+$ and $CO^+$ were formed both on the surface and in the gas phase. Therefore, these ions must be formed from the water vapor adsorbed on graphite.

According to the results obtained by the thermal method on adsorption of water vapor on a carbon surface[4,5], $H_2$ will be desorbed from the surface even at room temperatures, and the gas removed from the surface at lower temperatures containing $CO_2$ and a smaller quantity of CO. At higher temperatures CO is increased. These facts are considered to suggest that the reaction of water with carbon gives adsorbed $H_2$ and two types of surface oxides of carbon; one that readily decomposes even by evacuation at room temperatures to give $CO_2$ and the other that is more stable and decomposes at higher temperatures with evolution of CO.

Thus, formation of $H_2^+$ and other ions both on the surface and in the gas phase may be interpreted as follows:

By electron bombardment upon the graphite surface covered with adsorbed water vapor, some of the adsorbed $H_2$ molecules may leave the surface directly as $H_2^+$, and others give $H_2^+$ in the gas phase by successive electron impact after desorption as neutral gaseous molecules. $H_2^+$ formed in the gas phase does not possess initial kinetic energy. Also $H_2^+$ directly leaving the surface will not have initial kinetic energy if the potential curves of the adsorbed $H_2$ molecules are not very different from those of gaseous $H_2$ molecules.

If the more stable surface oxide is assumed to take a configuration such that CO rather

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*[1] In the curve (1) the peak width due to the instrument is taken into consideration.

*[2] As the $\theta$ distribution of the amount of the ions passing through $S_3$ is unknown, the amount of the ions emitted along the axis of the slit system is assumed to be maximum ($\theta_m = 0$).

*[3] Several possible peaks were tried as curve (1), but always 10 V. was obtained.

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4) R. N. Smith, C. Pierce and C. D. Joel, *J. Phys. Chem.*, **58**, 298 (1954).

5) P. H. Emmett, *Chem. Revs.*, **43**, 69 (1948).

than O is adsorbed on the surface after the apparatus is sufficiently evacuated, it can be removed as CO or $CO^+$ by electron bombardment.

$H^+$ formed in the gas phase may originate from $H_2$ or H leaving the surface by electron bombardment and, in addition, from gaseous water molecules and grease vapor. However, most of them are probably due to dissociative ionization of $H_2$ or ionization of H, since the contribution of $H^+$ from the last two origins to the total $H^+$ current is small.

$H^+$ from the surface may also be due to the adsorbed $H_2$ which resulted from water adsorbed on the graphite surface.

According to the potential curves of higher energy states of $H_2$ molecules, there is the state of unstable $H_2^{2+}$ at 46 V. higher than the normal state, and this $H_2^{2+}$ gives two $H^+$'s, each with kinetic energy of about 7 V., after spontaneous dissociation. Also at 28 V. higher, there is the unstable $^2\Sigma_u$ state of $H_2^+$. It is dissociated into H and $H^+$, each with kinetic energy of about 5 V. Increased energy of the incident electrons can increase this energy up to about 7 V.[6]

If the electronic states of the adsorbed $H_2$ are not greatly different from those of the gaseous molecule, there is sufficient possibility of transition of the adsorbed $H_2$ to unstable $H_2^+$ or $H_2^{2+}$, because the energy $V_{SW}$ of the incident electrons is at least 50 V. When these unstable molecular ions are dissociated, if it is assumed that only one $H^+$ leaves the surface and the other $H^+$ or H is bound to the surface, the leaving $H^+$ will carry all of the initial energy of 10∼15 V. for two particles.

Such being the case, and taking into consideration the presence of the directional distribution at formation, the presence of $H^+$ leaving the surface with kinetic energy of about 10 V. will, at least qualitatively, be explainable.

It has also been supposed that some of surface oxides formed from adsorbed water on a graphite surface might have OH-radicals[4]. If that is the case, formation of $HO^+$ on the surface will be possible. However, it was not confirmed in this work as mentioned in Experimental Results 1).

## Summary

Peak shapes in mass spectra obtained by voltage scanning using a mass spectrometer with such a modified ionization chamber as that described above are characterized by the places of formation and the initial kinetic energy of the ions. Thus, from the shape of the peak, one may be able to decide the place of formation of the ions and, though not so precisely, to estimate their initial kinetic energy.

When the method was applied to the ions formed by electron bombardment at a graphite surface covered with adsorbed water vapor, it was found that (1) $H_2O^+$ and $HO^+$ were formed from residual or desorbed $H_2O$ only in the gas phase, (2) $H_2^+$, $H^+$ and $CO^+$ were formed both on the surface and in the gas phase, and (3) $H^+$ which formed on the surface had the initial kinetic energy of about 10 V. These results will confirm the fact that the adsorbed water molecule is dissociated into adsorbed $H_2$ and surface oxide of carbon that probably takes a configuration such that CO is adsorbed on the surface.

The author wishes to express his hearty thanks to Professor Nobuji Sasaki of Kyoto University for his guidance throughout the course of this work.

*Department of Chemistry*
*Faculty of Literature and Sciences*
*Kochi University*
*Kochi*

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6) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena", Oxford University Press (1952), p. 231.