The structure and formation mechanism of ions in the field ionization of methanol and ethanol have been studied by isotopic labeling with O and deuterium, and mass spectrometric analysis. It is shown that these alcohols give identical mass spectra in the molecular ion region, these consisting of four lines: M + 1, M, M - 1, and M - 2. The M + 2 ions have the structure ROH-H+, while the M - 1 ions are (R-H)-OH-. For methanol the M - 2 ions have the structure of formaldehyde, and for ethanol they have those of both an aldehyde and a vinyl alcohol. It is also shown that field ionization may be used to study the catalytic oxidation of alcohols over platinum by free oxygen.

Investigating the possibilities of autoionization mass-spectrometry to study the isotopic composition and structure of organic compounds, we found that all the aliphatic alcohols we studied give identical mass spectra in the molecular ion region, and these consist of four lines: M + 1, M, M - 1, and M - 2. Naturally, it was supposed that the (M + 1)- ion contains a hydrogen atom which is split off from the alcohol molecule to form the (M - 1)+ ion, but we did not succeed in establishing a correlation in the behavior of the ions to confirm this point of view.

The autoionization mass-spectrum of methanol absorbed on the tungsten tip of a Mueller field-emission microscope has already been studied by Ingram and Gomer [1, 2] who first introduced autoionization mass-spectrometry. In these papers they reported that for clean conditions and a pressure of 10^-5 mm Hg in the field-emission microscope the mass spectrum of methanol in the molecular ion region consisted of two lines differing by one mass unit. They assigned these lines to the CH3OH+ and CH3O+ ions. With an increase in the field strength the first peak became unsymmetrical, extending toward lower mass numbers (lower energies), while the second always remained sharp. The broadening of a line in the field mass-spectrum is caused by ionization of the molecules in the volume, since ions being produced at a certain distance from the surface of the tip do not pass through all the differences in potential between the point and the collector, and have a lower energy than ions being desorbed from the surface of the tip. Therefore, the position in the shape of the lines of the autoionization mass-spectrum contains information on the point of ionization, the ionization coordinate possibly being established with an accuracy down to Å units for ionizing fields on the order of 10^6 V/cm. In various ways the authors succeeded in varying the ratio of the intensities of these lines over very wide limits, the line assigned to CH3OH+ always remaining sharp. This made possible the conclusion that the CH3OH+ ion is a product from the dissociative adsorption of methanol on tungsten. Beckey [3, 4] showed that a higher pressure the autoionization mass-spectrum of methanol on tungsten consists of three lines which he assigned to the ions CH3OH+, CH3OH+ and CH3O+ (M + 1, M, M-1). He also observed lines which were assigned to polymers of the alcohol and water, the most intensive being found to be the 2M + 1 ion, which was greater than the intensity of the line from the molecular ion by a factor of two. Recently Beckey and Schulze [5] investigated the field ionization of aliphatic alcohols on a platinum tip and filament. They described the mass-spectra obtained and found a number of quantitative relationships in their changes with respect to the strength of the ionizing field and the molecular weight of the alcohol. However, the structure and formation mechanism of the ions comprising the field mass-spectra of the alcohols remained unexplained. This aspect of the problem is considered in the present investigation.

Measurements were made with an MI-1301 mass spectrometer reconstructed and supplemented with an autoionization source, similar to that described in [6]. The autoionization spectra of methanol and ethanol were studied in greatest detail.

**Methanol.** Using a tungsten tip we repeated the results of Beckey [3, 4]. New among these results was the discovery of the M - 2 line, whose intensity was about 1% of that of the line from the molecular ion. The experiments with the tungsten tip were terminated owing to its disintegration when the field was increased. A rapid change in the dimensions of the point occurred even at 10^-5 mm Hg. Schmidt [7] described a similar effect. Subsequent investigations were carried out on a platinum tip.

Qualitatively, the mass spectrum of methanol on platinum is the same as on tungsten, the only difference being in the intensity of the individual lines. Figure 1a shows the mass spectrum of methanol on a platinum tip for a high ionizing field strength. This spectrogram shows that with an increase in the field only the M - 1 line expanded, and not M, as in the experiments of Ingram and Gomer using tungsten [1]. Figure 2a shows the relationship between the relative intensities of the lines 2M + 1, M + 1, and M - 1 and the tip potential. It follows from the graphs that the ion-associates 2M + 1 disappear rapidly with an increase in the field, and the intensity of the line from M + 1 ion decreases appreciably, while the intensity of the line from ion fragment M - 1 is increased.

To establish the structure of the ions whose lines comprise the mass spectrum of methanol, we analyzed the alcohol having the isotopic composition CD3-OH. Figure 1b shows the mass spectrogram of heavy methanol, and Fig. 2b the relationships between the
intensities of the corresponding ions and the field. It follows from a comparison of the data for heavy and normal methanols that the \((M - 1)^+\) ion has the form \(\text{CH}_2\text{OH(\text{CD}_2\text{OH})}\) and the \((M + 1)^+\) ion has the form \(\text{CH}_3\text{OH}_2(\text{CD}_2\text{OH}_2)\). Even if the \(\text{CH}_3\text{O}^+(\text{CD}_2\text{O})^+\) ions are also formed, it is in an amount less than 0.5% of the molecular ion concentration. This means that the \(\text{CH}_3\text{OH}_2\) ion contains hydrogen from the \(\text{OH}\) group of the alcohol molecule, whereas for the \((M - 1)^+\) ion to be formed, the alcohol ion loses hydrogen from the \(\text{CI},\text{I}\) group.

A similar situation occurs in the field ionization of water, the mass spectrum of which contains an intensive line from the oxonium ion \(\text{H}_3\text{O}^+\), but does not have the \(\text{OH}^+\) line.

Schmidt [7] explained the absence of this line by the greater probability of recombination and disproportionation of the \(\text{OH}\) radicals, than their field ionization. He considers this view confirmed by the presence of lines in the spectrum of water from oxygen and hydrogen peroxide, which are products of such reactions.

![Fig. 1. Mass spectrum of methanol: a) CH\(_3\)OH; b) CD\(_3\)OH.](image)

In the case of alcohol the most probable reactions between the \(\text{CH}_3\text{O}^+\) radicals will evidently be 2CH\(_3\)O → CH\(_2\)O + CH\(_3\)OH, which should lead to formaldehyde CD\(_2\)O and the alcohol CD\(_3\)OD for the alcohol CD\(_3\)OH. In fact, for the normal alcohol there is the CH\(_3\)O line and for the deuterated alcohol that of CD\(_2\)O. If these ions were formed from radicals of the CH\(_2\)O type then it may be assumed that a similarity will be observed between the behavior of formaldehyde ions and ion-associates containing a proton. However, such a similarity could not be established with certainty because all the data relative to the lines of formaldehyde showed appreciably poorer reproducibility from one analysis to another than the data for the other lines in the mass-spectrum of methanol. This led us to the conclusion that there is yet another path by which formaldehyde may be formed, whose conditions we had not checked. It was also found that the line for deuterated water appears in the spectrum of deuterated methanol.

The spectrum of water in the field ionization of methanol was studied in detail for different tip potentials and residual pressures of water vapor in the mass-spectrometer chamber. The alcohols themselves were carefully dehydrated. These investigations established a correlation between the behavior of water having the form HDO and formaldehyde CD\(_2\)O. We assumed that the aldehyde is formed from the oxidation of alcohol by free oxygen adsorbed on the platinum point.

![Fig. 2. Relationship between the relative intensity of the mass spectral lines of methanol and the tip potential: a) CH\(_3\)OH; b) CD\(_3\)OH.](image)

This conclusion was tested by introducing into the mass spectrometer elementary oxygen enriched in the isotope O\(^{18}\) during the analysis of the alcohol. This did not alter the mass spectra of the alcohol qualitatively. No isotopic lines corresponding to oxygen O\(^{18}\) appeared in them, while the lines of the isotopic varieties of water containing O\(^{18}\) appeared in the spectrum of water. These spectra are presented in Fig. 3.

![Fig. 3. Mass spectrum of water, measured in the field ionization of methanol: a) CH\(_3\)OH; b) CD\(_3\)OH; c) CD\(_2\)OH + O\(^{16}\)O\(^{18}\).](image)

The appreciable lag in the appearance of the HDO\(^{18}\) line after adding the heavy oxygen indicates that the oxygen reaching the tip is not from the volume. It is apparently sorbed uniformly on the surface of the needle in comparison with which the surface of the tip itself is negligibly small. The concentration gradient, which is maintained by the removal of oxygen from the point into the composition of the water ions, causes a surface migration of the adsorbed oxygen to the reaction sphere. It may therefore be assumed that alde-