in a simultaneous increase of the positive silicon net charge (from +0.5 in $Me_4Si$ to +1.6 in $SiF_4$) and the Slater exponent for the valence orbitals 3s and 3p (from 1.44 in $Me_4Si$ to 1.57 in $SiF_4$). This increase of the Slater exponent implies a decrease of the mean radius $\langle r \rangle$ of the valence orbitals from 0.73 Å in $Me_4Si$ to 0.69 Å in $SiF_4$. This contraction of the silicon valence shell leads to a simultaneous shortening of both Si–C and Si–F bonds.

Since (p–d) $\pi$ bonding would cause shortening of the Si–F bonds only, it cannot explain the very similar behavior of Si–F and Si–C bonds. There is no evidence for major d-orbital involvement. This conclusion is supported by the interpretation of UPS[20] and XPS[21] spectra of fluorosilanes. The interpretation of ab initio calculations for fluorosilanes is ambiguous. Experimental quantities, such as bond lengths or dipole moments, are reproduced better if d functions are included in the Si basis set. It is not obvious, however, whether such functions just compensate for an inadequate s,p basis set or whether they imply actual participation of Si 3d orbitals. Breeze et al.[22] interpret these functions as polarization functions, while Roelandt et al.[23] conclude from the population of d functions in the series $SiH_4$, $SiH_3F$, and $SiH_2F_2$ (0.151, 0.235, and 0.318 au) that Si 3d orbital involvement in bonding increases with increasing fluorination. On the other hand, such an increasing population of d functions with increasing fluorination has also been reported for the fluoromethane series.[24] Ab initio calculations

for $SiF_4$[25] result in slightly better agreement with the experimental bond length (1.553 (2) Å) if Si d functions are included in the basis set (1.56 Å) than without such d functions (1.59 Å). A Mulliken population analysis, however, demonstrates, that these d functions compensate to a large extent for the inadequate s and p basis set, while (p–d) $\pi$ contributions to the overlap population are very small (0.05 au).

In di-*tert*-butyldifluorosilane both Si–F and Si–C bonds are longer than in the dimethyl compound (1.606 (4) vs. 1.586 (2) Å and 1.869 (3) vs. 1.836 (2) Å). Due to the electron-releasing property of the *tert*-butyl groups, the positive net charge of silicon will be reduced, thus reducing polar effects and contraction of the silicon valence shell. These two effects can rationalize qualitatitively the lengthening of both bonds. Of course, other effects such as hybridization—the CSiC angle increases from 116.7 (6)° to 125.5 (11)° and the FSiF angle decreases from 104.6 (4)° to 97.7 (8)°—may also be responsible for different bonding properties in the methyl and *tert*-butyl compounds. The very small distortions of the *tert*-butyl groups (tilt and twist angles) indicate that steric effects are of minor importance. The shortest H···H contact between the two *tert*-butyl groups is greater than 2 Å.

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# Particle Bombardment (FAB) Mass Spectra of Methanol at Subambient Temperatures

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**Abstract:** The spectra produced by methanol when bombarded with a mixed beam of argon ions and atoms with a nominal energy of 8 keV have been obtained at temperatures between 179 and 100 K. The spectrum of liquid methanol at 179 K consists primarily of clusters of methanol around the proton, $H(CH_3OH)_n^+$, where the maximum value of $n$ observed is 18. The spectrum of solid methanol at 169 K is very similar to that of liquid methanol. Mixed methanol–water clusters produced as a result of water impurity are also observed. The spectrum of solid methanol at 100 K is quite different, for the $H(CH_3OH)_n^+$ ions lose their prominence, and the high mass spectrum (above $m/z$ 60) is without character, consisting of ions at more or less every mass. The change in the spectrum is reversible. At an intermediate temperature (137 K) the spectrum is a mixture of the features observed at 169 and 100 K. This change in the character of the spectrum can be represented by plotting $\sum_n H(CH_3OH)_n^+/TIC$ (TIC = total ion current) as a function of $T$, and such a plot shows a sharp decrease between approximately 150 and 130 K. Evidence is presented that the phenomenon is not caused by surface melting produced by the particle bombardment or by surface charging.

Temperature effects in EI, CI, and FI/FD mass spectrometry have been the subject of investigation for approximately the past 15 years,[1–3] and work continues to the present.[4–10] In general

the amount of fragmentation occurring for a given compound increases as the temperature increases, which is the result of the larger thermal energy content of the molecule ion at higher temperatures. However, virtually no studies have been made of the

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effect of temperature on the mass spectra produced by the several bombardment ionization techniques, namely, ion bombardment, fast atom bombardment, and fission fragment bombardment. We have started a program of study of temperature effects in ion/atom bombardment with the thought that temperature might prove to be an experimental variable useful for providing some control of the degree of fragmentation produced in this type of mass spectrometry.

In conventional fast atom bombardment mass spectrometry using magnetic deflection or quadrupole mass spectrometers the ions are produced from a solution of the solute of interest in a solvent such as glycerol. The solvent contributes significantly to the total mass spectrum, and consequently our initial investigation of temperature effects was made on neat glycerol. The results obtained were puzzling, and consequently we undertook investigations of temperature effects on simpler organic hydroxylic compounds. The simplest such compound is methanol, and we here describe our results for this compound.

The volatility of methanol is high enough that to prevent the rapid evaporation of the methanol sample spectra must be taken only at temperatures appreciably below room temeprature. Consequently, in this study spectra were taken at temperatures down to 100 K. In recent years three groups of workers have made studies of the bombardment spectra of small, covalently bonded compounds at low temperatures, and the primary objective of these studies was to elucidate the mechanisms of the desorption and ionization. Michl and co-workers have studied nitrogen oxides,[11] $O_2$,[12] $CO_2$, COS, $CS_2$,[13] $N_2$ and CO,[14] rare gases,[15] and neat and argon diluted organic solids.[16] Michl has also published a paper summarizing some of his work and advancing his ideas about the mechanisms involved in bombardment mass spectrometry.[17] These studies were done for the most part in the temperature range of 15–30 K. Rabalais and co-workers have studied the secondary ion mass spectrometry of frozen water, benzene, and cyclohexane,[18] and they have discussed the ejection dynamics and electronic processes governing secondary particle emission in SIMS.[19] Barber and co-workers have obtained the argon ion bombardment spectra of several organic compounds at 77 K, namely, *n*-pentane, isopentane, neopentane, acetone, butan-2-one, pentan-2-one, 4-methylpentan-2-one, and *n*-butyl acetate.[20]

## Experimental Section

The measurements were made with the Rockefeller chemical physics mass spectrometer, modified for operation in the ion/atom bombardment mode.[21] This is a 12 in. radius of curvature, 60° sector, single-focusing mass spectrometer. The bombarding flux consisted of a mixture of argon ions and atoms produced by a Capillaritron source obtained from Phrasor Scientific Inc., Duarte, CA. The voltage applied to the Capillaritron source was 8.0 keV, and the discharge current in the source was maintained at 50 µA. The actual flux incident on the target was not measured, but the operating conditions in the Capillaritron source were similar to those used in a previous study,[21] except that in the previous study the Capillaritron voltage was 5 keV. In the previous study the flux on the target was determined to be equivalent to 5 µA, and because of the higher voltage used in the present work, we think that the flux will be
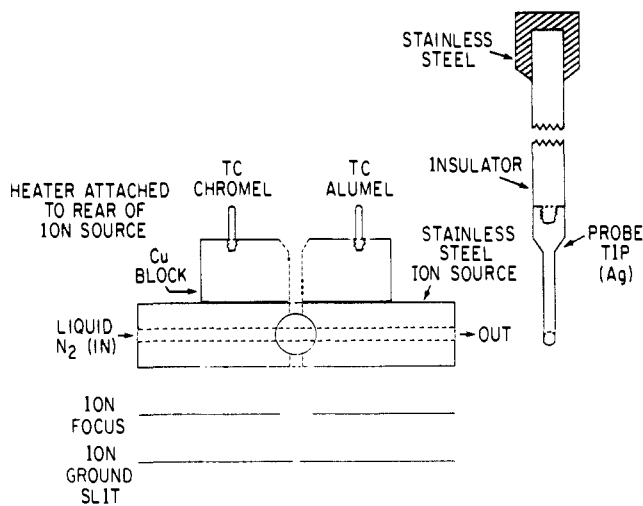
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**Figure 1.** Variable temperature ion source.

somewhat higher (perhaps equivalent to about 10 µA) but certainly of the same order of magnitude.

The sample holder consisted of a silver cylinder which could be screwed into the source insertion probe used in conventional mass spectrometry. The surface of the holder was formed by making a 45° cut with respect to the axis of the cylinder, and thus the shape of the surface of the sample holder was approximately elliptical. The surface area was approximately 0.2 $cm^2$. The bombarding beam was normal to the axis of the probe, and thus the angle of incidence of the beam to the surface was nominally 45°. However, the orientation of the surface to the ion beam was adjusted empirically to give maximum ion signal by rotating the probe about its axis, and thus the actual angle of the sample to the beam might have deviated somewhat from 45°.

The components of the ion source which pertain to temperature control of the sample are depicted in Figure 1. The bombarding argon beam is normal to the plane of the diagram and entered the ion source through a tunnel in the center of the source. Cooling was effected by flowing liquid nitrogen and liquid nitrogen off-gas through a channel in the ion source. This channel passed behind the tunnel through which the bombarding beam enters. A copper cooling block was fastened by screws to the top of the ion source, and it and the ion source are drilled so as to accept the silver sample holder represented in Figure 1. For clarity the probe assembly is drawn to the side of the ion source assembly, but in actual use it was inserted into the hole in the cooling block and ion source. The dimensions are such that the surface of the tip which holds the sample was in the center of the bombarding beam. The dimensions of the probe and the hole in which it is inserted were such as to make a reasonably tight sliding fit to ensure good thermal contact. An electrical heater was attached to the rear of the ion source for use when needed. The temperature of the copper block was measured by a thermocouple consisting of $^1/_8$ in. diameter chromel and alumel rods screwed into the cooling block. The temperature of the silver sample holder was not measured directly nor was the temperature of the sample itself.

It was assumed that the temperature of the copper block as measured by the thermocouple adequately represented the temperature of the sample holder and sample. To ensure that this was the case, in making a measurement at a given temperature, the ion source and copper block were established at the temperature of interest and then the sample holder containing the sample was inserted into the block. It was maintained in the block for a minimum of 5 min to establish temperature equilibrium before any spectra were taken. We feel that in the absence of the bombarding beam the temperature of the sample holder and sample was established with an accuracy corresponding to the resolution of the millivoltmeter used to read the voltage generated by the thermocouple, which was ±0.05 mV, corresponding to ±1.5 K. Our evidence for this statement is provided by an experiment wherein the melting of methanol was observed. The vacuum envelope of our mass spectrometer is fitted with a glass viewing window. The melting point of methanol is −97.8 °C[22] (175.4 K). The copper block was established at a temperature about 30 K below the melting point of methanol, and the sample holder loaded with solid methanol was inserted into the block. The block and source assembly were allowed to warm as a result of the small heat leak inherent in the apparatus (warming rate ~2 deg/min), and the probe

(22) *The Merck Index*; 10th ed.; Windholz, M., Ed.; Merck: Rahway, NJ, 1983.

was periodically withdrawn momentarily from the block to inspect the methanol. The pressure in the mass spectrometer at the time was approximately $10^{-6}$ torr, and perturbations of the temperature of the probe caused by this momentary withdrawal were surely negligible. The solid methanol was observed to melt at the proper temperature within the resolution of the millivoltmeter.

The question of the accuracy of the measurement of the temperature of the actual sample on the probe tip in the presence of the bombarding beam will be discussed later in the section on Results.

As mentioned above, we initially planned to determine the temperature dependence of the spectra of glycerol solutions and of glycerol itself, and the vapor pressures of such samples are low enough that the samples can be loaded on the probe and inserted into the mass spectrometer at room temperature. This, of course, is not possible with a volatile material such as methanol. The usual way of obtaining the bombardment mass spectra of volatile materials at low temperature is to condense vapor on a cooled sample stage which is already located in the mass spectrometer, but our equipment did not possess this capability, and it was impractical to attempt to install it. Consequently, we developed a technique that permitted loading the methanol outside the mass spectrometer. The probe tip was covered by a sleeve through which the off-gas from a liquid nitrogen tank was passed, and the probe was thus cooled to well below the freezing point of methanol. The probe tip was then extended slightly beyond the sleeve so that a charge of liquid methanol could be applied to the probe (it immediately froze), but the protrusion of the probe was small enough that the methanol applied to it was surrounded by a curtain of dry nitrogen off-gas from the liquid nitrogen tank. The probe was then slid out of its protective sleeve, through the sample introduction interlock, and into the mass spectrometer as rapidly as possible, with the operation being carried out in such a way as to minimize contact of the frozen methanol with the atmosphere and its moisture content. This procedure reduced, but usually did not eliminate, the condensation of some water on the methanol.

In making measurements at a series of temperatures our practice was to start at a temperature below the lowest temperature in which we were interested and then to allow the thermal leak to heat the sample up to the several temperatures of interest. At each temperature of interest two or three scans were collected, each scan requiring 15 s. In between measurements at different temperatures the bombarding beam was turned off to minimize radiation damage to the sample. No change in the methanol spectra which we could attribute to radiation damage was ever observed.

The volume of methanol used as sample for these experiments was 20 μL, and it was applied from a capillary tube. It was distributed as evenly as possible over the surface of the probe, and considerable effort was made to make sure that the probe surface was completely covered. Since the bombarding beam direction was horizontal (parallel to the surface of the earth), the plane of the surface of the probe was essentially vertical (perpendicular to the surface of the earth). This configuration was designed originally for measurements on glycerol, which has sufficient viscosity not to run off the probe. Solid methanol adhered firmly to the probe, but liquid methanol exhibited a considerable tendency to run off the probe. As a consequence our measurements on liquid methanol were limited to a relatively small temperature range above the melting point.

Electron impact measurements on gaseous methanol were made with a VG 70-250 magnetic deflection mass spectrometer. In measurements at higher source pressures the value of the pressure was measured by using a Texas Instruments quartz spiral pressure gauge. This gauge was connected to the source by a probe that replaced the solid sample introduction probe.

The methanol used in the measurements was Burdick & Jackson (Muskegon, MI) high-purity methanol.

## Results and Discussion

Figure 2 shows the spectrum of methanol at $T = 179$ K, which is 4 K above the freezing point of methanol. Thus this is a spectrum of liquid methanol. Most of the ionization occurs in the form of clusters of methanol around the proton, $H(CH_3OH)_n^+$, where $n$ varies from 1 at $m/z$ 33 to 18 at $m/z$ 577. This upper limit to the series is probably determined by the sensitivity of our mass spectrometer; with a more sensitive instrument higher clusters would probably have been observed. The maximum of the cluster distribution occurs at $n = 3$, $m/z$ 97, although the difference in intensity between this ion and that at $n = 4$, $m/z$ 129, is negligible. Above $m/z$ 129 the intensities decrease in a monotonic way except that the intensity for the ion $n = 10$, is smaller than that of the next higher cluster ion. Our intensity measurements are not accurate enough for us to decide whether this deviation from monotonicity is the result of some structural feature of the $n =$
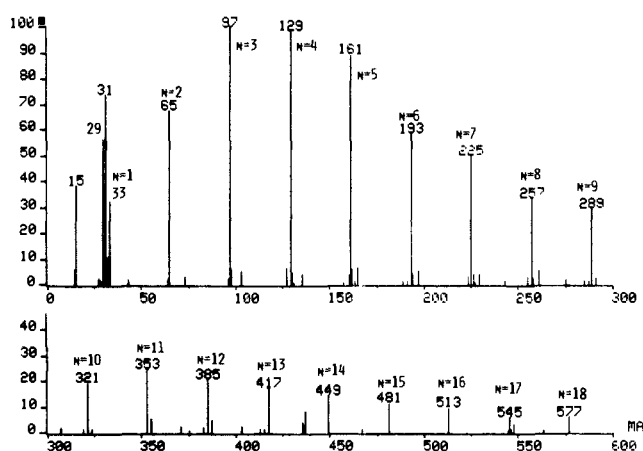


**Figure 2.** Spectrum of liquid methanol at 179 K. Peaks are annotated with the value of $n$ in $H(CH_3OH)_n^+$.

10 ion. The spectrum contains relatively intense ions at $m/z$ 31, 29, and 15, and ions with smaller intensities appear at $m/z$ 32, 30, 28, 27, and 14.

Our spectrum of methanol from $m/z$ 33 upward is quite similar in form to that of water (ice) obtained by Rabalais and co-workers[18] at 77 K. In both cases the maximum intensity occurs at clusters with $n = 3$ or 4, and intensities decline at higher cluster sizes. The clusters in both cases comprise associations with the proton of unchanged sample molecules. The studies by Michl and co-workers and Rabalais and co-workers on small covalently bonded molecules at low temperatures show some variability in behavior. In almost all cases cluster ions are produced, but oftentimes either the ion comprising the core of the cluster or the neutral entities which add to the core have different identities and/or stoichiometries from those of the sample molecules. Thus, for example, in NO the main cluster series is formed[11] by the ions $NO(N_2O_3)^+$; in $CO_2$ the cluster series $O_2^+(CO_2)_n$ dominates;[13] and in benzene and cyclohexane many different types of cluster ions are observed.[18] One forms the impression that in the low-temperature work done to date reactive clustering occurs appreciably more frequently than simple clustering. Indeed, Michl[17] suggests that chemical conversion in the damage centers caused by the particle bombardment is a standard feature of the production of secondary ions by particle bombardment. In the cases of the water clusters and the methanol clusters depicted in Figure 2 no extensive chemical reaction occurs other than the formation of protonated water and protonated methanol, which entities then probably serve as the core ions around which larger clusters are formed.

The distribution of the cluster ions in Figure 2 and the relatively intense methanol fragment ions observed at $m/z$ 31, 29, and 15 are of interest. We give in panel A of Figure 3 the electron ionization spectrum of gaseous methanol as determined in our VG 70-250 mass spectrometer under conventional electron ionization conditions. In panel B we give the spectrum of gaseous methanol at a source pressure of 0.25 torr and a temperature of 45 °C. One sees that even at this relatively low pressure all of the primary ions formed by the electron ionization of methanol are converted by rapid ion–molecule reactions to $H(CH_3OH)_n^+$ cluster ions. We point out in particular that only four cluster ions are observed, which is in sharp distinction to the very broad distribution of cluster ions produced by particle bombardment (Figure 2). Grimsrud and Kebarle[23] have investigated the equilibria of methanol over a wide temperature range (−56 to 441 °C) and at a total ion source pressure of approximately 5 torr. They observe clustering equilibria up to the $H(CH_3OH)_8^+$ ion, but even with their wider temperature range and higher total pressure, the number of methanol cluster ion species observed at any given temperature is 3–5, with which our results agree. We believe that a limited range of cluster ion formation is typical of gas-phase ionic clus-
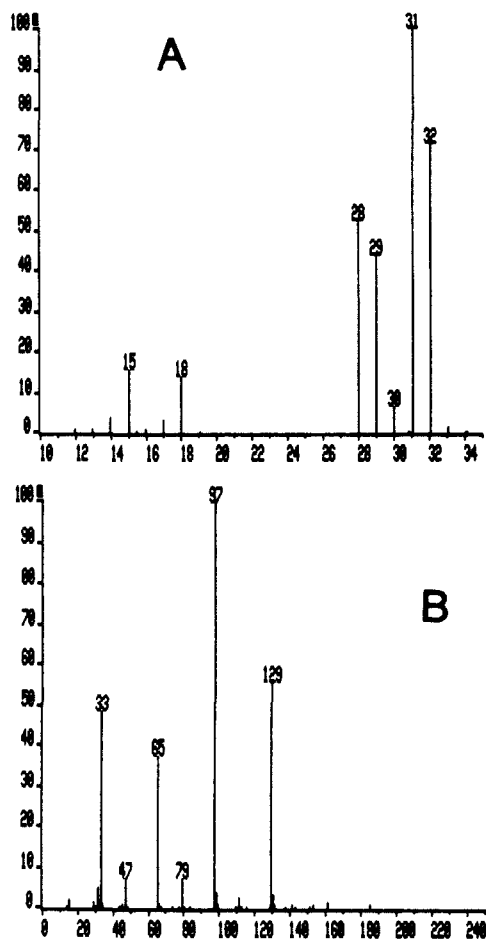
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(23) Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 7939.

**Figure 3.** Electron ionization spectra of gaseous $CH_3OH$. Panel A: $P_s$ = $10^{-5}$ torr, $t$ = 200 C. Panel B: $P_s$ = 0.25 torr, $t$ = 45 C.



**Figure 4.** Spectrum of $CH_3OH$ at 169 K. Peaks are annotated with $(x,y)$, which are the values of $x$ and $y$ in $H(CH_3OH)_x(H_2O)_y^+$.

tering processes, and the broader distribution observed as a result of particle bombardment may very tentatively be thought to indicate that the latter type of cluster ion formation does not involve gas-phase agglomeration.

Gas-phase ion–molecule reactions generally occur with rate constants on the order of $10^{-9}$ cm$^3$ mol$^{-1}$ s$^{-1}$, and the absence of significant amounts of low-mass methanol ions in the methanol spectrum at 0.25 torr (Figure 3B) is the result of the very rapid reaction of these ions with methanol molecules. The coexistence of methanol ions at $m/z$ 31, 29, and 15 in the bombardment spectrum (Figure 2) is puzzling and also suggests that the ions in the spectrum are not produced solely by conventional gas-phase clustering reactions. Michl[17] suggests that two components are present in a bombardment spectrum, namely, secondary ions produced rapidly from surface layers of the impacted condensed sample and ions produced at a later time from deeper layers in the sample. The $m/z$ 31, 29, and 15 ions observed in our methanol spectrum might well be ions ejected rapidly from the surface of the sample into the gas phase before sufficient methanol vapor was formed in the near vicinity of the surface with which the ions could react.

We give in Figure 4 the spectrum of methanol at 169 K. The sample providing the spectrum was 6 K below the freezing point of methanol and presumably was in the solid state. One observes the same envelope of $H(CH_3OH)_n^+$ peaks at $m/z$ 33, 65, 97, 129... that was observed in liquid methanol (Figure 2). However, additional ions not found in the spectrum of Figure 2 are present here, and the masses of these correspond to mixed methanol–water clusters with formula $H(CH_3OH)_x(H_2O)_y^+$, where the water is present as an impurity absorbed in the sample loading process. Two series of water clusters may be deduced from the spectrum, one with $y$ in $H(CH_3OH)_x(H_2O)_y^+$ equal to 1 and $x$ variable and the other with $y$ = 2 and $x$ variable. The monohydrate cluster exhibits its maximum intensity at $m/z$ 307, $x$ = 9, $y$ = 1 (9,1),
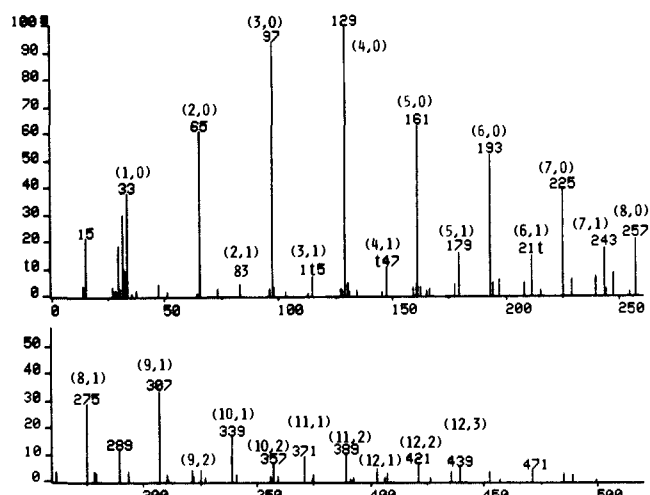
and the dihydrate exhibits its maximum intensity at $m/z$ 389 (11,2). The presence of water in the 169 K sample makes a comparison of its spectrum with that of the 179 K sample not exact. However, we doubt that the presence of what must be only a small amount of water impurity had a major effect on the methanol spectrum, and thus we draw the conclusion that the spectrum of methanol was not significantly changed by lowering the temperature below the freezing point of methanol.

The presence of water in this sample does serve the useful purpose of allowing us to compare our bombardment spectra with spectra obtained by Kebarle and co-workers[24] in a study of the competitive solvation of the proton by water and methanol molecules in the gas phase. They find that methanol is taken up preferentially in clusters of small size, but the preference for methanol decreases with the size of the cluster. Water and methanol are taken up with equal preference for the cluster for which the sum of the numbers of solvating methanol and water molecules equals 9. Water is taken up preferentially in larger clusters. The explanation given by Kebarle and co-workers for this phenomenon is that the larger polarizability of methanol results in its preferential binding in small clusters, but in larger clusters the electrostatic polarization becomes less important, and the larger size of the methanol molecule begins to militate against its inclusion in the cluster. Our spectrum at 169 K (Figure 4) is in good agreement with these findings. The maximum intensity in the pure methanol distribution occurs at $m/z$ 129 (4,0), but the maximum in the clusters containing 1 water occurs at $m/z$ 307 (9,1), and that in the clusters containing 2 waters ocurs at $m/z$ 389 (11,2). The intensities of the clusters containing no water molecules and 1 water molecule become equal when the total number of molecules clustered is approximately 8. This agreement with the value given by Kebarle and co-workers is interesting, although the good agreement with the Kebarle result is probably somewhat fortuitous because of differences which must exist in the relative amounts of methanol and water in the two experiments.

We hold the opinion that the overall agreement of our results with the equilibrium results in the gas phase has the significance that the formation of clusters by particle bombardment is governed to some degree by the same energetic considerations as those involved in chemical equilibria. This is not at all to say that the chemistry involved in particle bombardment is equilibrium chemistry, but it does seem fair to conclude that the phenomena do not involve solely random processes.

The clusters in the Kebarle gas-phase experiments are formed by agglomeration of individual molecules. We do not think that the agreement that we find with the Kebarle results can be taken to mean that clusters in our particle bombardment experiment are necessarily also formed by agglomeration. This might be the

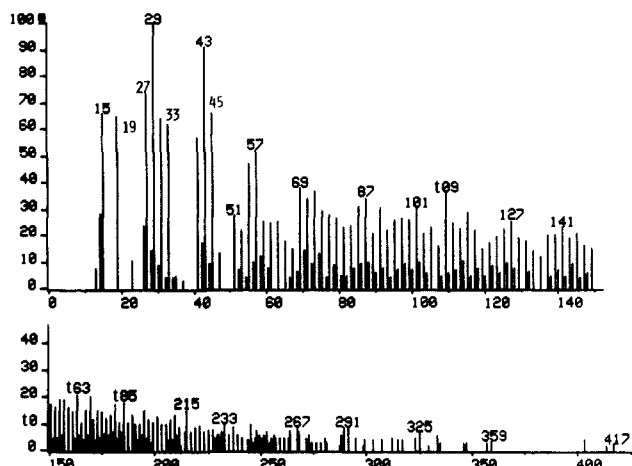(24) Kebarle, P.; Haynes, R. N.; Collins, J. G. *J. Am. Chem. Soc.* **1967**, *89*, 5753.

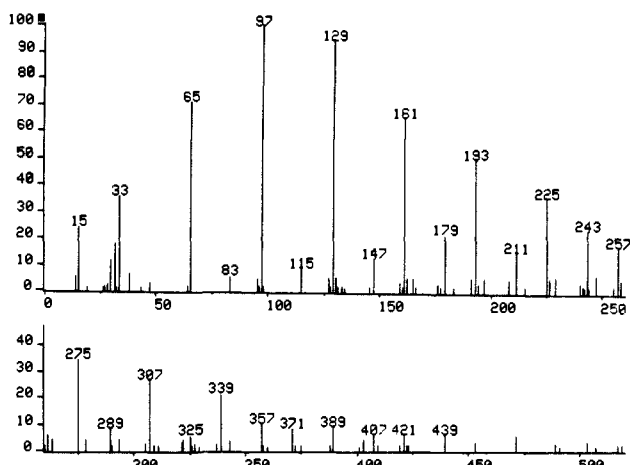**Figure 5.** Spectrum of $CH_3OH$ at 100 K. Same sample as that giving Figure 4.



**Figure 6.** Spectrum of $CH_3OH$ at 166 K. Same sample as that giving Figures 4 and 5.



**Figure 7.** Spectrum of $CH_3OH$ at 137 K.



**Figure 8.** Plot of $\sum_n H(CH_3OH)_n^+/TIC$ vs. $T$ at normal bombarding intensity. Points for duplicate runs shown.

mechanism, but it is also possible that the mechanism involves the desorption of relatively large methanol–water particles followed by ablation of some of the methanol and water molecules. The relative numbers of the two kinds of molecules ablating would be determined at least in part by energetic considerations. The dominating concept which seems to be established by our result is that whatever the mechanism, it must occur slowly enough that equilibrium energetic considerations play some role in the overall process.

The sample producing the spectrum at 169 K represented in Figure 4 was then cooled to 100 K without being removed from the mass spectrometer or otherwise disturbed in any way, and the spectrum shown in Figure 5 was taken. The spectrum at 100 K bears no resemblence to the spectra obtained at 169 or at 179 K. Above approximately $m/z$ 60 the spectrum is completely undifferentiated with no dominant ions. In particular, the methanol cluster ions which are so characteristic of the spectra at higher temperatures have vanished completely. The dominant ions occur below $m/z$ 60. The $m/z$ 33, 31, 29, and 15 ions appearing in Figure 5 also appear in the spectrum at 169 K, but the relative intensities at the $m/z$ 33, 31, and 29 ions are different. In addition new intense ions appear at $T = 100$, for example, $m/z$ 19, 27, 41–47, and 51–59. This spectrum bears very little resemblence to any of the methanol spectra that we have seen.

The absolute intensities in the spectra were not significantly changed by the change in temperature and the consequent radical change in the form of the spectrum. Thus the total ion current in the spectrum at 169 K was $2.92 \times 10^5$ arbitrary units, and that in the spectrum at 100 K was $3.22 \times 10^5$ units.

After the spectrum at $T = 100$ K was taken, the sample was allowed to warm up without any other disturbance to $T = 166$
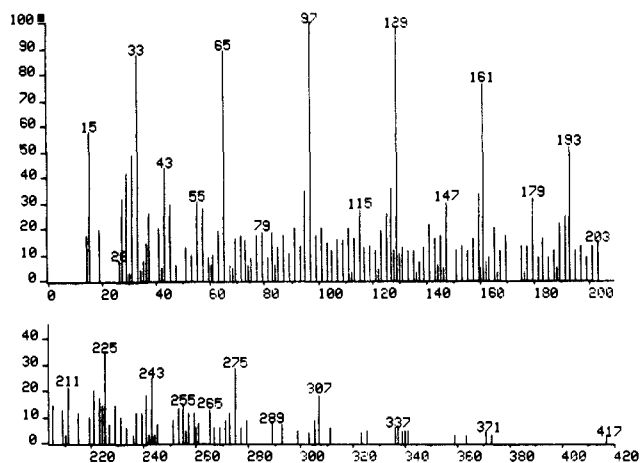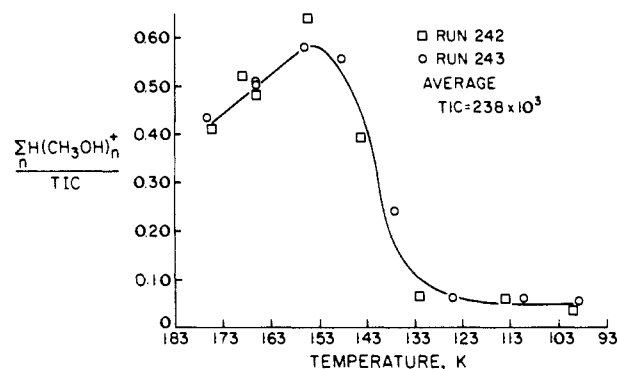
K (still below the freezing point of methanol), and the spectrum shown in Figure 6 was taken. This spectrum is identical with the spectrum at $T = 169$ K shown in Figure 4. Clearly, the phenomenon causing the changed spectrum at $T = 100$ K is reversible. The change in spectrum produced by reducing the temperature to about $T = 100$ K was observed in several replicate experiments.

To investigate the phenomenon further, we made measurements at a number of temperatures. The spectrum at $T = 137$ K is given in Figure 7. This spectrum is intermediate between the spectra obtained at $T = 100$ and 169 K. The peaks corresponding to the methanol cluster ions are still well-delineated, but the undifferentiated peaks characteristic of the spectrum at $T = 100$ K are also clearly present. It is inconvenient to show here the spectra taken at all the temperatures. Since perhaps the most important effect of lowering the temperature is to bring about the disappearance of the methanol cluster ions, we calculated the fraction of the total ion current (TIC) that these methanol cluster ions comprised, and a plot of this fraction as a function of temperature is given in Figure 8. The squares and circles which are plotted represent runs made with different samples on two different days. The fraction of methanol cluster intensity rises somewhat as the temperature decreases to approximately 150 K, after which the fraction undergoes a precipitous decrease over the course of the next 20 K decrease in temperature. This decrease corresponds, of course, to the growth of the undifferentiated spectrum depicted in Figure 4 (bottom).

In the Experimental Section we described the method of establishing and measuring the temperature of the sample, and we gave the evidence that leads us to believe that we can measure the temperature of the sample accurately in the absence of the bombarding beam. However, the actual temperature of the sample in the presence of the beam was not discussed, and we do this here. We estimated that the beam intensity was the equivalent of about 10 $\mu$A. The voltage applied to the Capillaritron gun was 8 keV, but this voltage is applied completely only to the ionic component of the beam. The atomic component has an energy somewhat
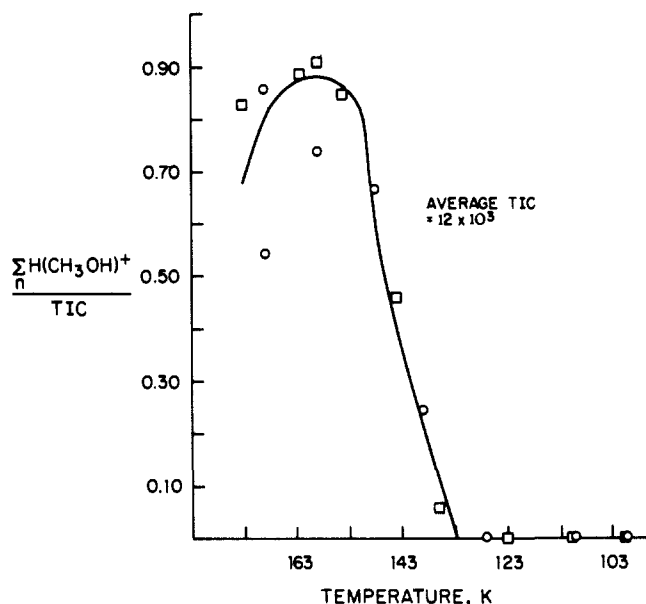
**Figure 9.** Plot of $\sum_n H(CH_3OH)_n{}^+/TIC$ vs. $T$ at low bombarding intensity. Experimental points in circles and squares represent duplicate runs done on two different days.



**Figure 10.** Plot of $\sum_n H(CH_3OH)_n{}^+/TIC$ vs. $T$ when bombarded with beam of Ar atoms. Experimental points in circles and squares represent duplicate runs done on two different days.

less than the applied energy, and we estimate that the effective energy of the total beam is on the order of 6 keV. Taking these values for the current and voltage, the power incident on the target is 0.060 W. We have made thermal conductivity calculations to try to estimate the temperature rise that this bombardment will produce. The thermal conductivity of the silver probe is high enough that we calculate that only a fraction of a degree rise would result from 0.060 W incident on the surface of the probe. To calculate the temperature rise of the layer of methanol deposited on the surface of the probe, we note that 20 $\mu$L of methanol evenly distributed over the probe area of 0.2 cm$^2$ will produce a layer of methanol with thickness 0.1 cm. The thermal conductivity of ice is given[25] as 5.7 × 10$^{-3}$ cal·cm$^{-1}$·s$^{-1}$·deg$^{-1}$. The thermal conductivity of liquid methanol is approximately one-half that of liquid water, and we assume that the same relationship applies between solid methanol and solid water. We then calculate that the temperature rise on the surface of the methanol will be on the order of 2 K. This amount of thermal rise would not be significant in our measurements. However, two experimental papers in which the temperature rise resulting from ion bombardment is measured have appeared recently. In the first[26] argon beams of 50–100 keV 0–300 mW of power were used as the heat source on a target in contact with a massive Cu holder maintained at 80 or 300 K. Beam-induced surface temperature increases as large as 270 K were found in the case of a bad thermal contact and for a beam power of 300 mW. In the second study[27] the thermal processes accompanying the formation of metal–Si microheterogeneous structures by ion-beam deposition of metal films were studied. At ion flux densities of 10–200 $\mu$A/cm$^2$ and ion energies of 40–70 eV, substrate temperature rises of 317–340 K were obtained.

A possible explanation for the sharp change in the methanol spectrum which we observed between 150 and 130 K involves the melting of the solid methanol by the bombarding beam. That is, the bombardment might keep the methanol in a liquid state until the block temperature was appreciably below the nominal freezing point of methanol. The spectrum change setting in at 150 K might then be the result of the actual freezing of the methanol. In view of the considerable discrepency between the rather trivial sample temperature rise predicted by our calculation
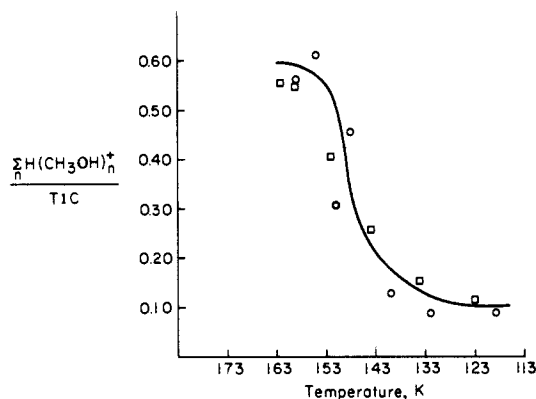
and the significant rise that one might infer from the experimental literature values, we measured the methanol spectra at several temperatures at the lowest practical bombarding beam current. The results in the form of a plot of $\sum_n H(CH_3OH)_n{}^+/TIC$ vs. $T$ are given in Figure 9, and it is obvious that the form of the plot is the same as that obtained with the higher bombarding current given in Figure 8. The average total ion current obtaining in each plot was calculated by averaging the total ion current for all the measurements in each plot, and this average value serves to represent the bombarding beam intensity in each plot. The average TIC at the higher beam intensity was 238 000 (arbitrary units), and that in the lower intensity experiment was 12 000. Thus the beam intensity and power input in the second experiment were 20 times weaker than those in the first, and any temperature rise should have been correspondingly smaller. The same sharp change in the spectrum occurred between temperatures of 150 and 130 K. Some minor differences in the form of the curve at the lower bombarding intensity may be observed, but we believe that these differences are trivial and result from the low ionic intensities resulting from the low bombardment intensity. We doubt very seriously that the change in the spectrum between 150 and 130 K is due to belated freezing of the methanol. Furthermore, we are inclined to consider as approximately correct our calculated result concerning the temperature rise caused by bombardment.

To provide information regarding the possible role of surface charging in the change in the spectrum between 130 and 150 K, we measured methanol spectra at a series of temperatures by using a bombardment beam of argon atoms rather than the mixed argon ion/atom beam used in the other experiments reported in this paper.[28] The Capillaritron gun is equipped with an electrode to which a voltage was applied to deflect charged species out of the beam. The results of this experiment are given in Figure 10, from which one sees that a drastic decrease in the fraction of protonated methanol clusters in the spectra occurs as the temperature decreases. The use of a neutral beam reduces or eliminates the amount of surface charging produced by the primary beam bombardment,[29] and the fact that the temperature profile of the spectrum is essentially the same for bombardment by both argon atoms and argon ions/atoms comprises evidence that surface charging of the sample is not involved in the phenomenon.

We can advance no definite explanation for the occurrence of the temperature-dependent change in the spectrum. We have mentioned that Michl suggests that chemical conversion in the damage centers caused by the particle bombardment occurs frequently, and perhaps the change occurring in the methanol spectrum below 150 K is a manifestation of such chemical conversion. However, the complexity of the low-temperature spectrum demands that the chemical conversions also be very complex, and we do not know the identities of a very large majority of the ions

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observed or the reactions producing them.

A question of equal interest is what change occurs in the methanol sample below 150 K to cause this change in behavior. Here also we can offer no definite hypothesis. However, we can point out that solid methanol undergoes a second-order phase transition at 157.4 K ($\lambda$ transition), wherein the orthorhombic form of methanol ($\beta$ form) undergoes a transition to a monoclinic form ($\alpha$ form).[30] Hawke and co-workers have studied this phenomenon,[31,32] and they find that some surprising chemical changes accompany this seemingly innocuous phase transition. When methanol is caused to pass through the phase transition (from higher temperatures to lower temperatures, i.e., $\beta \rightarrow \alpha$) hydrogen, carbon monoxide, and methane are produced. There are indications that other products such as formaldehyde and ethylene glycol must also be formed. The evolution of gaseous substances is accompanied by changes in the surface of the solid methanol, from an originally smooth surface to a broken, uneven surface with undulations 1 mm or more in depth. Furthermore, when the methanol transition was viewed in the dark, flashes of white light were observed to occur. The emission of light under these circumstances is referred to as triboluminescence. Triboluminescence is characterized by the fact that it is accompanied by electrical discharges, and Hawke and co-workers found that when methanol was cooled through the $\beta \rightarrow \alpha$ transition a large negative potential (roughly –100 V) was produced. In our ex-

periment to observe the melting point of methanol we observed a change in the appearance of the solid methanol at some temperature below the melting point of methanol. The initially more or less smooth surface of the solid methanol was observed to roil and become rougher. The behavior was compatible with that which would be caused by the evolution of a gas. The temperature at which this occurred was not measured nor was the phenomenon investigated further, but we think it possible that this was the same phenomenon described by Hawke and co-workers. One difference which can be mentioned however was that our phenomenon was observed in going from low to high temperature whereas those reported by Hawke and co-workers involved going from high to low temperatures.

It is quite clear that rather large amounts of energy are somehow involved in this phase transition. The temperature at which it occurs (157.4 K) is quite close to the temperature at which the change of spectrum occurs in our study, and we wonder if these two phenomena are related in some causal manner. It is not impossible to think that since the phase transition causes enough strains in the methanol molecules to effect spontaneous breaking of bonds and generation of electrical discharges and light emission, it may also entail enough strain in the solid methanol structure that the particle bombardment involved in producing our spectra may result in a very extensive bond rupture and chemical reaction. These would, of course, be manifested by a complex spectrum.

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# Relationship between the Extractability and the Rate of Transfer of Potassium Ion by Macrocyclic Carriers in Liquid Membrane Systems[1]

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**Abstract:** The relationship between the extractability and the rate of transfer of potassium ion by macrocyclic carriers was investigated in chloroform membrane systems. The rates of ion uptake, ion release, and ion transport and the liquid–liquid extraction constants were determined for a series of carriers (polynactin, dibenzo-18-crown-6, dicyclohexano-18-crown-6, and 18-crown-6). Kinetic equations for ion uptake and release are developed, and the apparent rate constants were calculated by introducing the experimentally determined extraction constants. The rate constants for the ion release and ion uptake are comparable to each other. For the four macrocyclic carriers employed, the rate of uptake was found to control the overall rate of transport through the liquid membrane. Both the rate of uptake and that of transport depend crucially on the extractability of the metal ion. A systematic analysis of each rate taking the constituent equilibria into account indicates that a macrocyclic ligand which forms a more stable complex with the metal ion and is less hydrophobic is preferable as a mobile carrier in liquid membrane systems.

Active research is recently in progress on the use of macrocyclic compounds as mobile carriers in liquid membrane systems, in view of their capability of highly selective transport of metal ions, particularly of alkali- and alkaline-earth metal ions. In most of the previous works, the ion transport mediated by neutral macrocyclic carriers was evaluated in terms of the overall rate of cation transport through liquid membranes.[2-7] The ion transport, being

actually the salt transport when a neutral carrier is employed, consists of four major steps: uptake of a cation and an anion into a membrane phase, diffusion of a metal–carrier complex associated with the anion within the membrane phase, release of the ions into an aqueous phase, and back diffusion of a free carrier. For

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