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Secondary Ion Mass Spectrometry of Small Molecules Held at Cryogenic Temperatures

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In recent years more emphasis has been placed on the analytical potential of Secondary Ion Mass Spectrometry (SIMS) for the study of organic materials [1, 2, 3]. We wish to report on static SIMS experiments on a few simple molecules condensed on a copper substrate held at low temperatures. For the experiments we used an Extranuclear Inc., quadrupole massfilter equipped with a Bessel box type energy filter. The bandwidth of the ions accepted in the massfilter was set at 1 eV. Our ion gun is differential pumped and during the experiments a pressure in the 10^{-9} torr range could easily be maintained in the main chamber. Our primary ion beam current density was between 1 and 10 nA/cm² and the beam energy was varied between 500 and 5000 eV. As primary

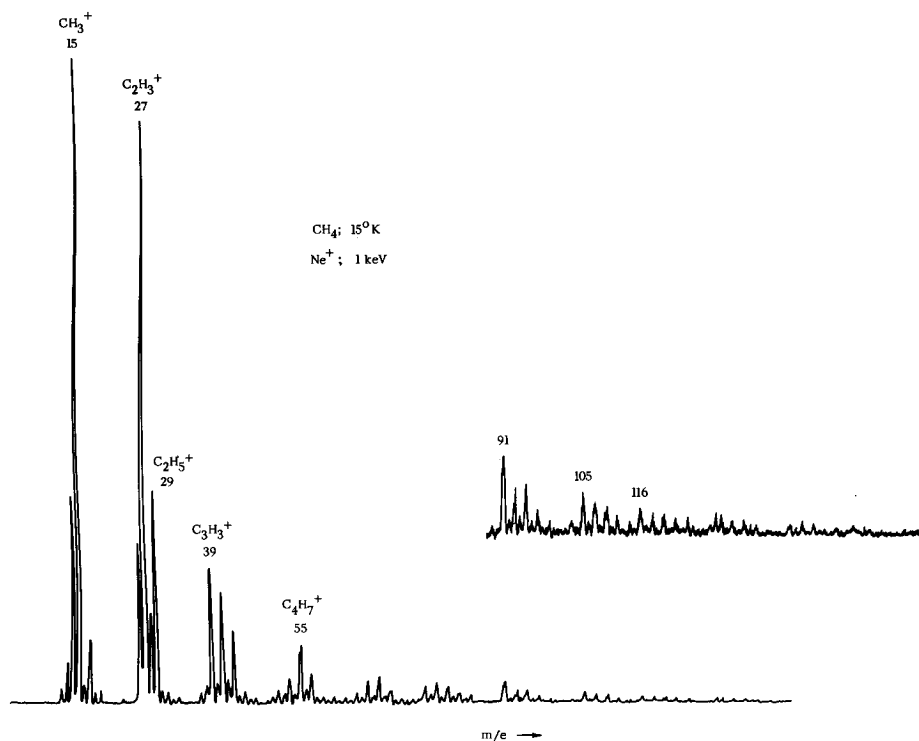


Fig. 1 SIMS spectrum of neat methane at 15°K using 1 keV Ne⁺ ions

ion we used He^+ , Ne^+ , Ar^+ , Kr^+ , and Xe^+ . The nature of our samples made it necessary to use an electron floodgun to compensate for charge buildup on the sample. The energy of the flooding electrons was kept below 7 eV. In all the experiments the temperature of the sample was held at 15°K. In Fig.1 the positive SIMS spectrum of neat methane using a 1 keV Ne^+ beam shows fragments up to C_{11} .

The spectrum looks very similar to the ones of propane and pentane reported before [2]. The type of fragments observed are independent of the type of primary ion used and its kinetic energy, although higher beam energies and/or heavier type ions give rise to a higher abundance of the larger fragments. Fig. 2 shows a SIMS spectrum of methane diluted in an argon matrix [1:500].

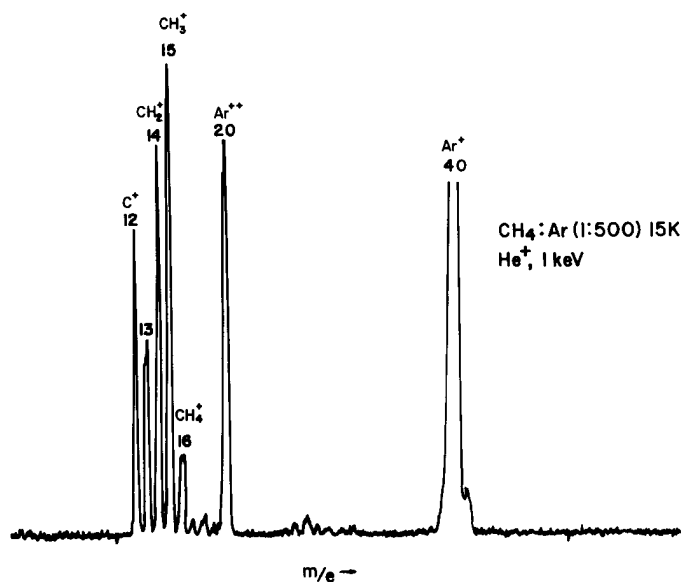


Fig. 2 SIMS spectrum of methane diluted in an argon matrix [1:500] at 15°K using 1 keV He^+ ions

In this spectrum there is no evidence of ion-molecule reaction or cluster formation and only the C_1 group is visible. It is important to observe that the fragment distribution in this case is different from that of the C_1 group in neat methane. Fig.3 shows the SIMS spectrum of N_2 with a 4 keV Ar^+ beam. Here we observe N^+ , N_2^+ , N_3^+ , and a large number of clusters with an odd and even number of nitrogen atoms up to the limit of the mass range of our spectrometer. These clusters can be considered as consisting of N^+ or N_3^+ ions for the odd ones and N_2^+ ions for the even ones, solvated in clusters of neutral N_2 molecules. The existence of these clusters and their stability of at least several milliseconds, which is their estimated flight time through the mass spectrometer, suggests that they must be extremely cold since they can only be held together by weak induced dipole and Van Der Waals forces. This suggests a rapid cooling of the clusters upon expansion in the vacuum.

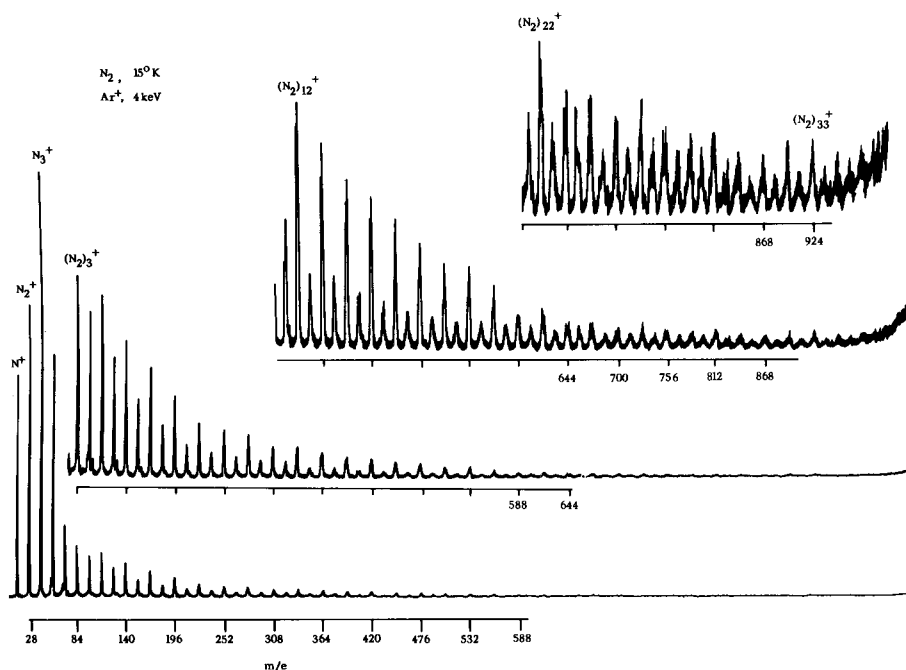


Fig. 3 SIMS spectrum of neat N_2 at $15^\circ K$ using $4 \text{ keV } Ar^+$ ions

Figure 4 shows the SIMS spectra of N_2 obtained with a $4 \text{ keV } He^+$ beam. Here only N^+ , N_2^+ , N_3^+ , and N_4^+ fragments are visible. This can be attributed to the fact that because of their low mass, most He^+ ions are scattered and are less able to penetrate deep into the solid and consequently give less rise to ion molecule reactions and cluster formation. For N_2 we recorded the secondary ion energy distribution for the different fragments. The N^+ and N_2^+ fragments have a much wider distribution [$\pm 20 \text{ eV}$] than the higher clusters [$\pm 7 \text{ eV}$]. It was observed that heavier fragments came off with smaller average kinetic energies than lighter ones. It is impossible to measure absolute energies because of the interaction between the emission current setting of the floodgun (slightly under or over charge compensation) and the center band-pass setting of the prefilter. This contradicts observations in [3]. The fact that the lower fragments came off with a wide energy distribution causes their underrepresentation in the recorded spectra because of the relatively small bandwidth admitted to the massfilter. In addition to the molecules mentioned before, we investigated a series of two and three atomic systems. These results will be reported elsewhere.

In general, we believe that the first step upon ion impact is ionization and dissociation by charge transfer and kinetic processes followed by ion molecule reactions and cluster formation in the solid. The clusters then expand in the vacuum accompanied by a rapid cooling, which gives these clusters their remarkable stability.

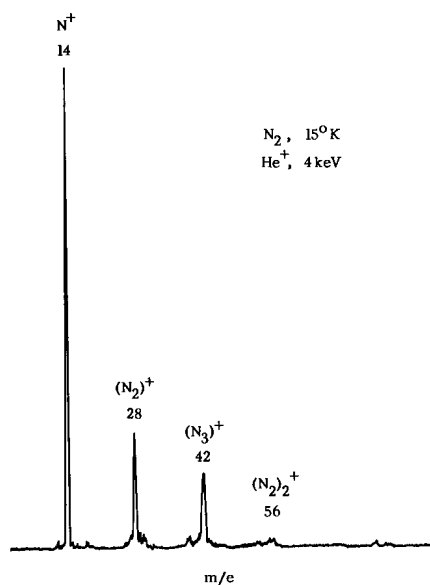


Fig. 4 SIMS spectrum of neat N_2 at $15^\circ K$ using 4 keV He^+ ions

Acknowledgement

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