

**Figure 1.** Temperature-integrated mass spectrum for 58-68 amu. The gray area shows the baseline, these are counts recorded due to electrical noise on the amplifier and dark current of the MCP. This kind of noise is unavoidable. The blue region are 61 amu ions that are produced during the extraction pulse, and are therefore not mass-focused into a peak on the detector.



**Figure 2.** These are the 0.25 integrated mass channels for 61 and 64 amu. 61 is much more intense, and production of ions during extraction into the ToF-MS results in ions of 61 amu being continuously extracted for ~1.5 us after the onset of the extraction pulse. These ions arrive with a nearly uniform distribution in over 1.5 us, which results in ‘contamination’ of mass channels 62-64.



**Figure 3.** The TPD profile at 61 amu is normalized to the intensity of the contamination peak it produces. The exact match confirms this assignment of the origin of the peak at 170K, and demonstrates that there is a simple linear dependence on the intensity of any peak and the contamination of mass channels at +1, +2, and +3 amu.



**Figure 4.** Comparison of signal for 64 amu and 47 amu (target). While the peak position is clearly not a match, the small variations in intensity appear to correlate to those of 64 amu. Because the mass is an odd number, 47 must be a fragment, though it is likely a fragment produced by dissociation of several . Note the onset of signal at 156 K which is due to the change in chopper timing at this temperature.



**Figure 5.**  Comparison of TPD profiles at 64 and 31 amu. Unlike the TPD profile at 47 amu, 31 amu (*O*- or *C*-protonated formaldehyde) must be the result of fragmentation of the molecule at 64 amu, and in particular of the isomer responsible for the peak at 195K rather than the peak at 205K. The difference between these profiles at 205K indicates that the 64 amu TPD profile is the result of sublimation of two different isomers.



**Figure 6.** For the sake of comparison to a mass channel that clearly does not represent a dissociation product of 64, I have included the 34 amu TPD profile. This small changes in intensity during the 195K and 205K peaks are not replicated by the 34 amu profile, showing that these changes cannot correspond to variations in TPD power or other experimental parameters, but are mass-specific, and therefore correspond to dissociation processes specific to observed molecules. The dotted line indicates the temperature at which the chopper timing was off-set to improve signal intensity.

Despite what appears here, careful analysis of the intensity of the methanol signal shows that the change in this timing results in a 7- to 8-fold increase in signal intensity, at the cost of a reduced S/N. The analysis demonstrated in Figures 1-3 show that this loss in S/N can be corrected for in *this* experiment. The presence of this noise between the mass focused peaks, e.g. in the range 63.25-63.75 amu, its linear dependence on peak intensity, and predictable nature means that in *most* circumstances it can be subtracted from the TPD profiles. I want to emphasize that this appears not to be the result of any mistake or problem with the instrument, but is the result of the interface of an intense and highly localized ion source to a pulsed mass spectrometer. It’s a bit late now, but if the money were available, I would recommend the use of a Mattauch-Herzog geometry magnetic sector mass spectrometer rather than a ToF because of its CW rather than pulsed detection while maintaining the ability to detect ions across a similarly large mass range. These are common in SIMS applications specifically because of these properties, but I assume it would cost a few hundred thousand dollars. In theory, this would increase the maximum signal to ½ that of the Keck to 5 times larger, without the complications due to noise.

