Introduction: Comets retain relatively primitive icy material remaining from the epoch of Solar System formation, however the extent to which their ices are modified remains a key question in cometary science. One way to address this is to measure the relative abundances of primary (parent) volatiles in comets (i.e., those ices native to the nucleus).

High-resolution ($\lambda/\Delta\lambda > 10^5$) infrared spectroscopy is a powerful tool for measuring parent volatiles in comets through their vibrational emissions in the $\sim 3$–$5$ $\mu$m region. With modern instrumentation on world-class telescopes, we can quantify a multitude of species (e.g., H$_2$O, C$_2$H$_2$, CH$_4$, C$_2$H$_6$, CO, H$_2$CO, CH$_2$OH, HCN, NH$_3$), even in comets with modest gas production. In space environments, compounds of keen interest to astrophysics could originate from HCN and NH$_3$ (leading to amino acids), H$_2$CO (leading to sugars), or C$_2$H$_6$ and CH$_4$ (suggested precursors of ethyl- and methylamine). Measuring the abundances of these precursor molecules and their variability among comets contributes to understanding the synthesis of the more complex prebiotic compounds.

Observations: Results will be presented from pre-perihelion spectra of C/2009 P1 (Garradd), a moderately bright comet from the Oort cloud, using three world-class facilities (with UT 2011 dates and $R_0$): Keck/NIRSPEC (Sep 09, 2.1AU[1]; Oct 13, 1.8AU[2]), VLT/CRIRES (Aug 07, 2.4AU; Sep 17–21, 2.0AU[3]), and NASA-IRTF/CSHELL (Sep 08, 2.1AU [1]). Compared with the majority of Oort cloud comets, our observations of C/2009 P1 reveal enriched CO, severely depleted C$_3$H$_2$, normal C$_2$H$_6$, and normal to somewhat enriched CH$_2$OH.

Implications for Surface Chemistry: The importance of H-atom addition to C$_2$H$_2$ on the surfaces of interstellar grains to produce C$_3$H$_4$ and then C$_2$H$_6$ was validated astronomically by the discovery of abundant ethane in comet C/1996 B2 (Hyakutake), with C$_2$H$_6$/CH$_4$ well above that achievable by gas-phase chemistry [4], and subsequently in irradiation experiments on laboratory ice samples in the range $\sim 10$–$50$ K [5]. The large abundance ratios C$_2$H$_6$/CH$_4$ observed universally in comets since Hyakutake establish H-atom addition as an important and likely ubiquitous process. Comparing C$_2$H$_6$/C$_2$H$_2$ among comets can provide information on the efficiency of this process, and the infrared spectral region is uniquely capable in this regard since symmetric hydrocarbons (e.g., C$_2$H$_2$, CH$_4$, C$_2$H$_6$) have no electric dipole moment and so have no allowed pure rotational transitions.

CO is also hydrogenated on grain surfaces. Laboratory irradiation experiments on interstellar ice analogs have shown this to require very low temperatures, the resulting yields of H$_2$CO and CH$_3$OH being highly dependent both on hydrogen density (i.e., fluence) and on temperature in the range $\sim 10$–$25$ K [6]. The relative abundances of these chemically-related molecules in comets provide one measure of the efficiency of H-atom addition to CO on pre-cometary grains.

Oxidation of CO is also important on grain mantles, as evidenced by the widespread presence of CO$_2$ ice towards interstellar sources observed with ISO [7] and also in a survey of seventeen comets observed with AKARI [8]. H-atom addition to C$_2$H$_2$ produces the vinyl radical (CH$_2$CH), which through subsequent oxidation/reduction reactions can lead to the three C$_2$H$_4$ isomers: ethylene oxide (c-C$_2$H$_2$O), vinyl alcohol (CH$_2$CHOH), and acetaldehyde (CH$_2$CHO) [9, 10]. This may have implications for interpreting observed abundance ratios for parent volatiles initially condensed onto grains (in particular CO/C$_2$H$_2$). For example, the depleted C$_2$H$_2$ we measure in C/2009 P1 may result from its conversion not only to ethane but also to these C$_2$H$_4$ isomers and (possibly) also to ethanol (CH$_3$CH$_2$OH).


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