

Interstellar Inorganic Chemistry

Margaret E. Kosal

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The vast expanses between stars were once thought to be vacuous space devoid of any significant chemistry. The variety of molecules detected in interstellar space, however, shows such regions to be rich in an active and diverse chemistry.¹

The interstellar medium, the area between stars, is characterized by extreme physical conditions: densities lower than mechanically possible in a terrestrial laboratory and temperature ranges from 10-10⁶ K. The total gas and dust content of these regions is estimated to compose 3-10% of the total galactic mass. In the cooler regions of the interstellar medium, thermodynamic equilibrium is rarely, if ever, obtained. In order for reactions to proceed at appreciable rates activation energies must be negligible. In the more tenuous regions of the ISM, the kinetic temperature is so low that all reactions considered must be exothermic, and three-body collisions are ignored since densities are too low.²

Collisions between chemical species and photons or other energetic particles occur infrequently; molecules typically are in ground or low excitation states, except in hot coronal gas and H II (H⁺) regions. Electronic transitions, in the visible and ultraviolet, can only be observed as absorption bands in the spectra of background starlight passing through the interstellar medium. Measurable emission spectra may be produced from pure rotational transitions, seen in the far infrared and microwave regions, and hyperfine interactions observed at longer radio frequencies.³

Inorganic ions are observed as ultraviolet absorption lines (Figure 1). Most of the first transition row elements, along with a few heavier species, have been detected as singly ionized species in the interstellar medium.⁴

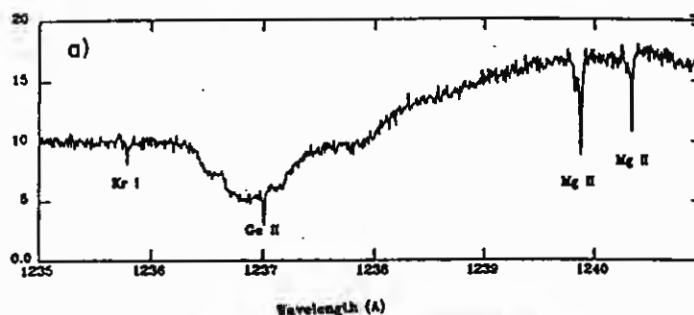


Figure 1. Spectrum from ζ Oph showing interstellar Kr λ 1235.83 Å, Ge⁺¹ λ 1237.059 Å, and Mg⁺¹ $\lambda\lambda$ 1239.925 and 1240.395 Å from the Goddard High Resolution Spectrograph.

Some of the most interesting interstellar inorganic molecules have been detected in the circumstellar shell that surrounds the red-giant star Mira IRC+10°216. Thermodynamics dominate the chemistry of the inner circumstellar shell where the first sodium-containing molecule, NaCl,^{1c,5} was observed via millimeter emission spectroscopy. The aluminum monohalides, AlF and AlCl, were also detected in the inner shell.^{5a,6} In the kinetically-controlled outer circumstellar shell, NaCN was identified and its geometry predicted based on spectroscopic constants.⁷ Despite extensive searches for MgO, MgS and MgH, the only detected magnesium-containing molecules are the isotopomers MgNC and MgCN.⁸ Initially discovered in the outer circumstellar shell, MgNC was subsequently synthesized terrestrially:



Using similar experimental technique, MgCN was first synthesized in the laboratory and later identified in the interstellar medium. Both species were determined to be linear molecules with a free radical isolated on the magnesium atom based on the observed (Figure 2) and terrestrially-generated millimeter emission spectra.

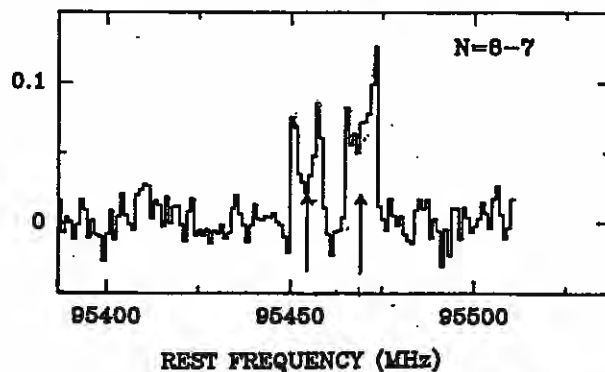


Figure 2. MgNC from IRC+10°216 with the IRAM 30-m telescope.

The theory of organometallic complexes in the interstellar medium was proposed as a possible explanation for three issues perplexing astronomers and astrochemists: the diffuse interstellar bands (DIBs), the unidentified infrared bands (UIBs) and the apparent depletion of certain heavier elements in the ISM relative to the standard cosmic abundance. The diffuse interstellar bands⁹ and the unidentified infrared bands¹⁰ are unaccountable features observed in galactic and extra-galactic spectra. A number of different possible molecular sources have been suggested to account for these features in the past, including fullerenes. Current theory attributes the DIBs and UIBs to large polycyclic aromatic hydrocarbon molecules (PAHs).¹¹ Combining this concept with the observed heavy metal depletion¹² in the interstellar medium of elements that exhibit strong bonding interactions, organometallic compounds have been hypothesized as an explanation.¹³ Iron-PAH moieties have been produced in the laboratory under conditions attempting to simulate the interstellar medium, and the Fe-PAH cationic complexes have been shown to participate in the formation of new species when reacted with interstellarly significant ligands (Figure 3).¹⁴

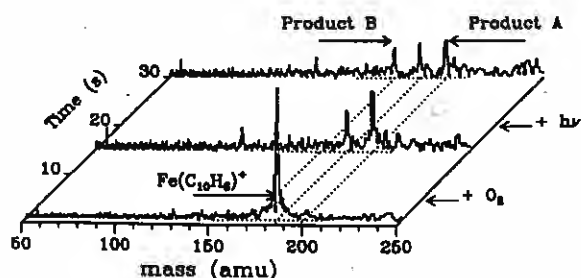
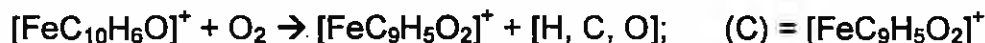
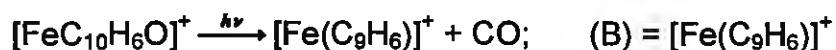


Figure 3. Oxidation of $[\text{Fe}(\text{C}_{10}\text{H}_8)]^+$ and irradiation of the reaction product.

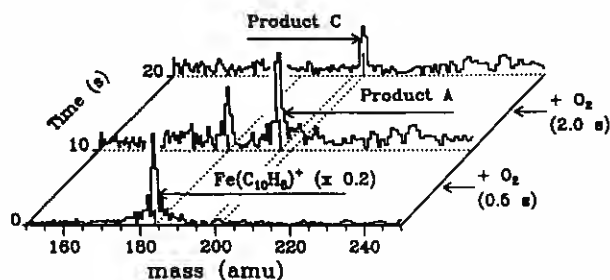


Figure 4. Oxidation of product A.

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