

Sub-millimeter Spectroscopy of Astrophysically Interesting Metal-Containing Molecules

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Abstract

With the advent of SOFIA and Herschel, new spectral windows will be opened for spectroscopy in the sub-millimeter region. To conduct science in this band, laboratory measurements must be carried out to provide accurate transition frequencies for molecular identification and physical interpretation. We are presently conducting such measurements using gas-phase submm direct absorption techniques. Of particular interest are simple molecules containing iron-peak elements, including carbides, and metal hydride ions (MH^+), both which possess favorable transitions at submm wavelengths.

1. Introduction

Various wavelength regions exist that are inaccessible by ground-based astronomy, but may contain important spectral information. For example, there are large gaps in the atmospheric windows from $\sim 525 - 575$ GHz, $725 - 775$ GHz, and upwards of 950 GHz. NASA has been developing SOFIA and Herschel for operation within these frequency ranges. The detector systems currently being constructed for these projects will have the necessary heterodyne capability for high resolution molecular spectroscopy. It is naturally assumed that new molecular discoveries will be made with these instruments; however, only with the necessary laboratory measurements will these expectations be realized.

The Ziurys group has been pursuing the measurements of rest frequencies for potentially new interstellar molecules for many years, in particular those containing a cosmically abundant metallic element (in the chemist's sense). Such species are relevant for astrophysical studies because many of them have relatively high cosmic abundances. Also, to date, eight metal-bearing molecules have been detected in the circumstellar gas of AGB stars such as IRC+10216, CRL2688 and CRL618. The species detected include AlNC (Ziurys *et al.* 2002), MgCN (Ziurys *et al.* 1995), MgNC (Kawaguchi *et al.* 1993; Highberger *et al.* 2001), NaCl, KCl, and AlF (Cernicharo & Guelin 1987; Ziurys, Apponi, & Phillips 1994; Highberger *et al.* 2001). Their appearance in these objects make them potential tracers of nucleosynthetic processes, as studies of the magnesium isotopes of MgNC have demonstrated (Guelin *et al.* 1995).

Interestingly, thus far such compounds have not been observed towards molecular clouds. Metallic elements are important components of the ISM, where they contribute to the electron density and hence the ionization balance, and where they are likely to form dust grains. On the other hand, they could also be contained in molecular form. The metal-bearing species AlNC, MgNC and MgCN, for example, are located in the outer circumstellar envelope of IRC+10216, where the gas is cold and dense. If there is a cold gas-phase refractory component in AGB shells, why not in molecular clouds?

2. Laboratory Molecular Spectroscopy

Submillimeter direct absorption spectroscopy is a relatively straightforward process in which radiation from a tunable source is focused through a reaction chamber and changes in power level due to absorption by molecules are measured with a detector. Currently, there are three operational systems in the Ziurys lab. The millimeter wave radiation sources used are Gunn oscillator/Schottky multiplier combinations that cover the range of 65 – 810 GHz. The gas cells are free-space chambers designed quasioptically, and the detectors are InSb hot electron bolometers. These systems are not commercially available.

Creation of metal-bearing molecules in the gas phase is not simple; these are highly reactive species whose physical properties are largely unknown. The technique used to synthesize these molecules is exotic: metal vapor is produced in a Broida-type oven and an appropriate precursor material is added, usually in the presence of a d.c. discharge. There is no guarantee that this method will work for any given molecule. Furthermore, large frequency ranges (30 – 60 GHz) must be scanned to identify the spectrum of a particular species.

Recently, metal bearing nitrides and carbides have been investigated in the Ziurys group. Metal nitrides are of interest because nitrogen is abundant, and molecules such as SiN and CN have been detected in the ISM. One of the radicals studied is CrN, which was produced by the reaction of chromium vapor and ammonia in a d.c. discharge. Nine rotational transitions were recorded in the frequency range 294 – 636 GHz, each consisting of four fine structure lines that compose an irregular quartet, consistent with a $^4\Sigma^-$ ground state. These data have been subsequently analyzed and rotational, spin-spin, and spin-rotation constants accurately determined (Sheridan, Brewster, & Ziurys 2002). The pure rotational spectrum of FeN ($X^2\Delta_i$) has also been recorded using a similar synthetic method. Eight transitions were measured for the lowest spin-orbit component, $\Omega = 5/2$, where no evidence of Λ -doubling was found. Again, highly accurate spectroscopic parameters were established from these data.

Metal carbides with the general formula MC are of interest because all metal-bearing molecules to date have been observed in circumstellar shells of carbon-rich stars. During the past two years, the Ziurys group has recorded the pure rotational spectrum of NiC and CoC, and very recently CaC. Each species was created by the reaction of the appropriate metal with CH₄ in a d.c. discharge. Four rotational transitions of CoC were measured, each consisting of 16 hyperfine components, while multiple transitions were obtained for both ⁶⁰NiC and ⁵⁸NiC (Brewster & Ziurys 2001). Highly accurate spectroscopic constants have been established for both species. In the case of CaC, eleven rotational transitions were recorded in which three fine structure components were resolved, as shown in Figure 1. Rotational, spin-spin, and spin-rotation parameters have been obtained from these measurements (Halfen, Apponi, & Ziurys 2002). This study is the first measurement of an alkaline earth carbide by any spectroscopic technique. The laboratory detection of CaC is thus a landmark experiment.

The work on CaC will hopefully lead to the discovery of other carbon-metal rings and chains, such as CaC₂, CaC₃, CaC₄, etc., in analogy to known silicon-carbon species. The magnesium and aluminum counterparts of these metal-carbon complexes are additionally of interest.

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