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Sub-millimeter Spectroscopy of Astrophysically Important Molecules and Ions: Metal Hydrides, Halides, and Cyanides

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ABSTRACT

With the advent of SOFIA, Herschel, and SAFIR, new wavelength regions will become routinely accessible for astronomical spectroscopy, particularly at sub-mm frequencies (0.5-1.1 THz). Molecular emission dominates the spectra of dense interstellar gas at these wavelengths. Because heterodyne detectors are major instruments of these missions, accurate knowledge of transition frequencies is crucial for their success. The Ziurys spectroscopy laboratory has been focusing on the measurement of the pure rotational transitions of astrophysically important molecules in the sub-mm regime. Of particular interest have been metal hydride species and their ions, as well as metal halides and cyanides. A new avenue of study has included metal bearing molecular ions.

1. Introduction

Over 130 molecular species have been identified in the interstellar medium in a variery of regions, such as circumstellar envelopes, dense clouds, and diffuse gas. These molecules range from diatomics to complex organic species. While much has been learned about the composition of the ISM, a great many spectral features remain unidentified. In order to determine the origin of these emission lines, high resolution, pure rotational laboratory spectroscopy of new metal species has been conducted.

2. Experimental

Three direct absorption, millimeter/sub-mm instruments have been used in the studies of metal containing species, including molecular ions, and they are described in detail elsewhere (Ziurys et al. 1994, Savage & Ziurys 2005). These instruments are all quasi-optical systems employing lenses, grids, and mirrors to propagate the radiation. The radiation sources are combinations of Gunn oscillators with Schottky diode multipliers, and the detectors used are He-cooled, InSb bolometers. Two systems contain Broida-type ovens for metal vapor production and are employed for studies of neutral molecules, while the third utilizes an ion-selective technique called velocity modulation. Molecules are created *in situ* by reacting specific precursors, often metal vapor and a reactant gas. Organometallic precursors are also used. As molecular constants are generally not available for the species of interest, large regions in frequency space usually need to be searched to identify spectral features.

3. Results and Discussion

The spectra of several small metal-containing molecules of astrophysical interest have been recently measured. A new avenue of research has also been initiated concerning the study of metal-contining molecular ions.

Hydrides - The pure rotational spectra of AlH and CrH have been measured (Halfen & Ziurys 2004, Halfen & Ziurys 2004, Harrison et al. 2006). For AlH, the quadrupole hyperfine structure was accurately determined for the first time in the N = 1 ← 0 transition. Rest frequencies are now available for CrH (X $^6\Sigma^+$). Because of the presence of five unpaired electrons and two nuclear spins, this molecule exhibits complicated fine and hyperfine splittings, as shown in Figure 1. Future laboratory studies are planned for TiH, MnH, and MgH^+.

Halides - Halides are common carriers of metals in the interstellar medium. Therefore, the spectra of several metal halides, including MnCl (X $^7\Sigma^+$) and ZnF (X $^2\Sigma^+$), have been recorded (Halfen & Ziurys 2005, Flory et al. 2006). The work on ZnF represents the first spectroscopic study of this radical in the gas phase. Given the presence of KCl in IRC+10216, ZnF (and ZnCl) may also be present in circumstellar gas.

Cyanides - The rotational spectrum of CrCN (X $^6\Sigma^+$) has been measured. Spectra of three isotopomers of CrCN ($^{52}Cr^{12}C^{14}N$, $^{53}Cr^{12}C^{14}N$, and $^{52}Cr^{13}C^{14}N$) have been recorded in order to determine the ground state structure, which has been established to be the linear metal cyanide rather than the isocyanide. Spectroscopic constants for CrCN are presented in Table 1. Currently, studies of FeNC are being pursued.

Ions - Several metal-containing ions have been studied with the ion-selective spectrometer. The spectra of VCl^+ (X $^4\Sigma^-$), $TiCl^+$ (X $^3\Phi_r$) (Halfen & Ziurys 2005), TiF^+ (X $^3\Phi_r$), and $FeCO^+$ (X $^4\Sigma^-$) have all been observed. $FeCO^+$ has never been studied previously in the gas phase, and it has been found to exhibit a complex spectral pattern, as shown in Figure 2. Plans for future studies include metal hydride ions, such as TiH^+ and CrH^+.

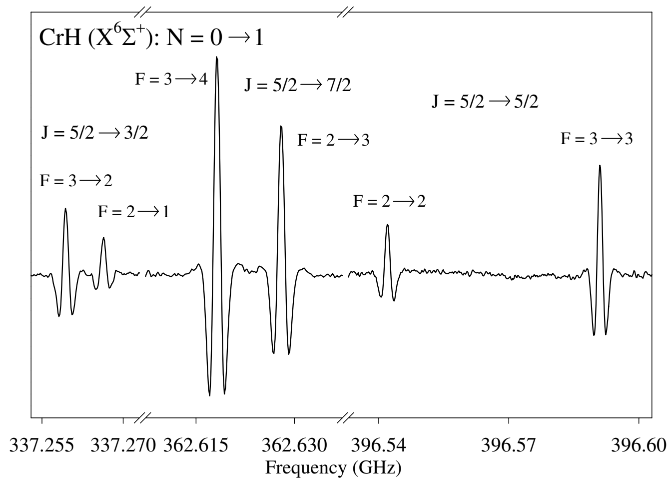

Fig. 1.— Spectrum of CrH N = 0 → 1 showing the fine structure components and proton hyperfine splittings.

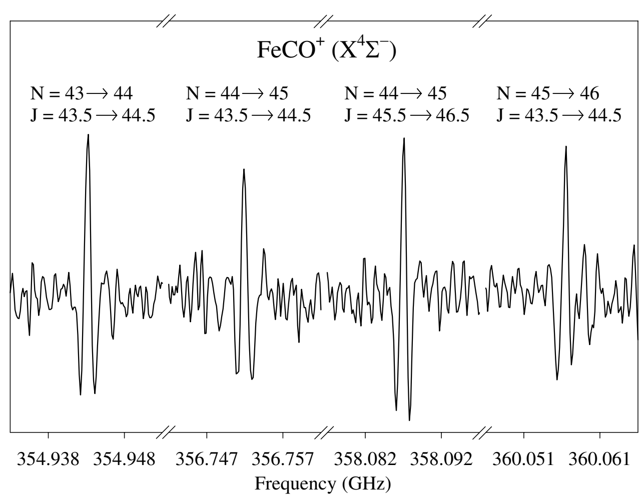

Fig. 2.— The spectrum of $FeCO^+$ near 357 GHz. Four spin components are shown, originating from three rotational transitions. The spin splitting is very large for this ion, resulting in the fine structure overlapping the rotational structure.

Table 1: Spectroscopic Constants for CrCN (X $^6\Sigma^+$) in MHz[a].

Constant	Value	Constant	Value
B	3895.6410(19)	D	0.00144627(26)
γ	36.41(13)	γ_D	-0.000016(11)
λ	633(37)	λ_D	-0.00662(75)
λ_H	0.00000021(10)	rms	0.125

[a]Values in parentheses are 3σ errors.

4. Conclusion

The pure rotational spectra of several metal containing molecules (radicals and ions) have been measured in the laboratory in the millimeter/sub-mm regime. Transition frequencies and molecular constants with accuracy better than 1 in 10^7 are now available for astronomical searches. Such laboratory work is clearly necessary in order to evaluate interstellar spectra, particularly the rich data sets that will be avilable at sub-mm wavelengths.

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