SIMULATED FE-L EDGE XAS OF MOLECULAR SPECIES IN THE ISM. Z. Gainsforth[1,†], A. L. Butterworth[1], J. Tomsick[1], A. J. Westphal[1], [1]Space Sciences Laboratory, University of California, Berkeley, CA 94720, [†]e-mail: zackg@ssl.berkeley.edu.

Introduction: X-ray absorption spectra (XAS) of the interstellar medium (ISM) can tell us about what phases are present in the ISM including atomic species, chemical species, and dust. Bright extraterrestrial X-ray sources generate continuum X-ray energy which can be absorbed on its path to Earth orbit where the Chandra (NASA) or XMM-Newton (ESA) X-ray telescopes can record the absorption spectrum of several edges. The focus of our recent research has been the Fe-L absorption edge at ~710 eV [1]. However, to interpret the spectra, we need to compare them against experimental spectra of sensible phases measured at synchrotron facilities. An issue arises in that many possible interstellar phases (e.g. FeH or Fe_2) are difficult to prepare or measure in a terrestrial environment. Therefore, we are using theoretical chemistry to simulate spectra as a complement to our existing synchrotron measurements.

What is Observable in ISM Spectra? Interstellar X-ray spectra are noisier and have a lower energy resolution compared to spectra acquired at terrestrial synchrotrons. In addition they can have systematics caused by physics occurring at the X-ray origin (in our case, typically a black-hole/neutron star accretion disk and/or jet). Black hole binary systems generate X-rays from their accretion disks, from a corona of energetic electrons near the disk or at the base of the jet. This can lead to different continuum components, fluorescence lines from ionized atoms, and absorption features. We can use machine learning to select only observations that contain the minimum confounding factors [2], but even then we should expect a spectrum with an energy resolution of ≥ 1 eV, considering uncertainty caused by noise in the signal. With this in mind, we are interested in simulating primarily the positions of the Fe-L_3 peak, the Fe-L_2 peak, and the amplitude ratio between the two (branching ratio). As our models gain sophistication, we may evolve to consider factors such as peak width or skew.

Our present work has indicated that the ISM spectra are closest to Fe metal but differ in two important ways. 1) The Fe-L edge seems to be shifted to lower energies than expected for Fe metal. 2) The intensity of the Fe-L_3 line is weaker than expected for typical Fe-L branching ratios. These factors are a current focus of our investigation. We present more detail on this in a sister abstract [3].

Methods: We want to simulate a range of phases including atomic Fe, simple Fe-bearing molecules (e.g. FeH), larger species such as polycyclic aromatic hydrocarbons (PAHs) containing Fe, Fe clusters (e.g. Fe_2) and other species. Exact quantum mechanical approaches such as multiplet theory become computationally intractable for large molecules and nanoparticles. As such, we are willing to sacrifice some spectral quality for speed so long as the resulting spectra still contain the information necessary to discriminate phases in the ISM.

We use Density Functional Theory (DFT) to obtain the ground state electronic structure of each phase, and then we
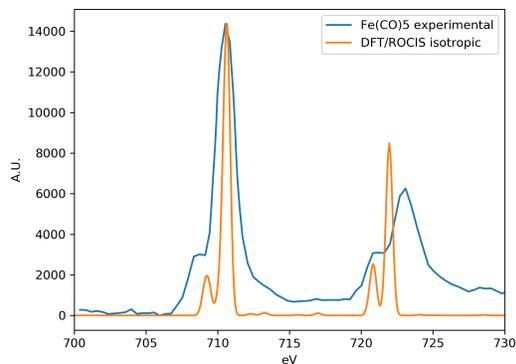

Figure 1: Experimental $Fe(CO)_5$(g) spectrum taken from [11] compared to a theoretical spectrum computed using DFT/ROCIS (see text). The L_3:L_2 branching ratio of the theoretical spectrum is 1.7 whereas the L_3:L_2 branching ratio of the experimental spectrum is 1.8. Note that the theoretical spectrum has been convolved with a 0.5 eV gaussian, and dual sigmoids were removed from the experimental spectrum before integrating the peak areas.

calculate X-ray Absorption Spectroscopy (XAS) spectra using the Restricted Open-Shell Configuration Interaction with Singles (ROCIS) method which can reproduce many of the features seen in transition metal spectra [4].

We carried out our calculations using the Orca quantum chemistry package [5]. We used the BHLYP hybrid exchange-correlation functional [6], an atom centered triple-zeta function basis set (def2-TZVPP, [7]), and a zeroth order regular approximation of the Dirac equation (ZORA, [8]) in order to better replicate energy splittings within the Fe-L edge.

Predictive Power of Theoretical Spectra: A theoretical spectrum of $Fe(CO)_5$ is shown in Figure 1. We don't necessarily expect $Fe(CO)_5$ to exist in the ISM, but we do have a synchrotron measurement that enables us to evaluate how accurate our theoretical spectrum is. Note that one typically would convolve theoretical spectra with a Gaussian to match empirical spectra, but in the interests of communicating spectral differences we plot theoretical spectra in this abstract using only a small convolution ≤ 0.5 eV. The energy splittings in the theoretical spectrum of $Fe(CO)_5$ underestimate the Fe $2p_{3/2}$ - $2p_{1/2}$ splitting by about 2 eV, and the multiplet splitting within the L_3 and L_2 edges are underestimated by an eV as well. This is a common occurrence in DFT, and not largely a cause for concern. Typically, when using theoretical XAS spectra, absolute differences in edge positions, splittings, etc. can exist due to shortcomings in the approximations used to make the calculations tractable. However, relative differences between two simulated spectra do not include systematic errors present

ISM simulation: Z. Gainsforth *et al.*

in both spectra – assuming they were simulated in the same fashion. For example, the edge position of a theoretical spectrum of Fe metal cannot be compared against the edge position of an experimental Fe metal spectrum. However, the edge position delta between Fe metal and FeO from theoretical spectra will more closely match the delta between experimental spectra. Of importance for our application, the integrated L_3:L_2 branching ratio of the theoretical spectrum is 1.7 while the integrated L_3:L_2 branching ratio of the experimental spectrum is 1.8, in good agreement.
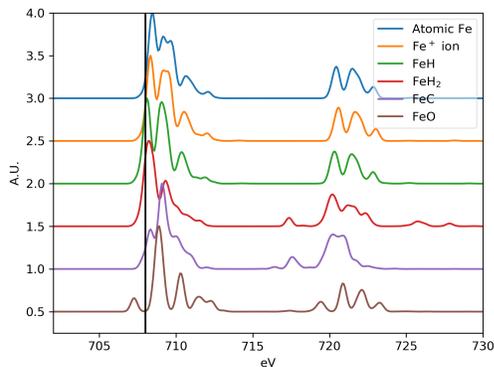

Figure 2: Selected spectra showing a variety of edge shifts and peak intensities of gaseous species. The spectra have been convolved with a Gaussian (σ=0.5 eV). A vertical line is at 708 eV.

Species	L_3:L_2 branching ratio
Atomic Fe	2.0
Fe^+ ion	2.1
FeH	2.2
FeH_2	1.6
FeC	1.5
FeO	1.4

Table 1: Table showing calculated ratios for the integrated intensity between the Fe-L_3 and Fe-L_2 peaks.

Results: In Figure 2 we show a selection of spectra simulated for molecules in vacuum, convolved with a Gaussian (σ = 0.5 eV). The onset of the spectra vary by 1-2 eV. These shifts should be clearly recognizable in XMM-Newton and Chandra data. In addition, Table 1 shows that the L_3:L_2 branching ratio for each of these molecular species varies. It can be seen that both atomic Fe and singly ionized Fe are similar, varying

primarily in the intensity of the multiplets. This matches other theoretical calculations and measurements of ionized Fe [9].

The spectrum for FeO gas is very different from the spectrum of FeO (wüstite). In wüstite, Fe is 6-fold coordinated with oxygen while in FeO gas Fe is only one-fold coordinated with oxygen. Therefore, despite having the same stoichiometry, the spectroscopic nature of the two species is very different.

Fe-H bonds appear to draw the onset to lower energies and can vary the branching ratio depending on the number of hydrogens. FeC seems to move the edge to higher energies, and the L_3 intensity is reduced.

Discussion: The experimental spectra we see in the ISM is both shifted to lower eV relative to bulk metal, and has a lower L_3 peak intensity relative to metal. If we assume that the edge position of Fe metal and atomic Fe are similar, we see that FeH_2 meets both these criteria, while other molecular species meet one or the other. For example, the L_3 branching ratio is significantly less in the FeO gas molecule but the edge position is slightly higher than atomic Fe.

Another experimental phase which is promising is amorphous iron carbide [10]. We intend to calculate larger Fe_xC_y molecules for comparison.

We have begun to investigate metal clusters (Fe_2 and Fe_3) but the number of spin configurations increases rapidly with the cluster size.

We would also like to examine the effect of passivation surfaces. For example, one expected phase for Fe in the ISM is small nm-sized metal grains embedded in silicate. However, the surface area of e.g. a 2 nm metal grain is substantial and the spectra of the Fe-Si or Fe-O bonded atoms at the surface could significantly influence the aggregate spectrum of the nanoparticle.

References: [1] Westphal A. J. et al. (2019) *Ap. J.* 872, 66. [2] Gainsforth Z et al. (2019) *M&M* 25(S2), 258-259. [3] Westphal Abstract. [4] Roemelt, M., et al. (2013) *J. Chem. Phys.* 138, 204101. [5] Nesse, F. (2017) *WIREs Comput. Mol. Sci.* e1327. [6] A.D. Becke, (1993) *J. Chem. Phys.* 98, 1372. [7] F. Weigend and R. Ahlrichs, (2005) *Phys. Chem. Chem. Phys.* 7(18) 3297-3305. [8] Pantazis, D. A., et al. (2008) *J. Chem. Theory Comput.* 4(6) 908-919. [9] Schippers, S. et al. (2017) . *Ap. J.* 849, 5. [10] Furlan, A., et al. (2015) *J. Phys.: Condens. Matter* 27, 045002. [11] Godehusen, K. et al. (2017) *J. Phys. Chem. A* 121, 66-72