

**SIMULATED FE-L EDGE XAS OF FE-PAH SANDWICH MOLECULES IN THE ISM.** Z. Gainsforth<sup>1,†</sup>, S. A. Sandford<sup>2</sup>, J. A. Tomsick<sup>1</sup>, A. J. Westphal<sup>1</sup>, <sup>1</sup>Space Sciences Laboratory, University of California, Berkeley, CA 94720, <sup>2</sup>NASA Ames Research Center, Mountain View, CA 94035, <sup>†</sup>e-mail: zackg@ssl.berkeley.edu.

**Introduction:** Fe is known to be depleted from the gas phase by an order of magnitude in the local ISM [1]. X-ray observations of the ISM using Chandra and XMM space-based X-ray telescopes show promise for identifying the phase(s) hosting Fe [2]. Here, Fe L-edge ( $\sim 710$  eV) extinction spectra of the ISM are observed using bright X-ray binaries as continuum light sources. In previous work, we compared extinction observations of Cyg X-1, the brightest such X-ray source in the sky, with extinction spectra derived via the Kramers-Kronig relation from a standards library of X-ray absorption spectra acquired by synchrotron X-ray microprobe, and the Weingartner-Draine [3] model of the ISM dust size distribution. We found that the observations are most consistent with extinction by Fe metal, as opposed to Fe sulfide, Fe oxide or Fe-bearing silicates [4]. However, the fit is imperfect, and differs from Fe metal in two important ways (see Figure 1). A) The ISM Fe-L edge is sharper than Fe metal. B) The intensity of the ISM Fe-L<sub>3</sub> line is weaker than expected for metallic Fe-L. The Fe-L<sub>3</sub> branching ratio is defined as  $B_{L_3} = L_3 / (L_2 + L_3)$  where  $L_3$  and  $L_2$  are the integrated areas under the peaks in the Fe-L spectrum after removing the edge jumps. The branching ratio is proportional to the angular component of the valence spin-orbit operator [6]. The branching ratio for the ISM spectrum is 0.7, while kamacite has a branching ratio of 0.8. These factors are the focus of our current investigation.

Recent astronomical work has suggested that Fe could be bound into carbonaceous phases such as  $\text{FeC}_2\text{H}_2$  and  $\text{FeCO}$  [7, 8]. Furthermore, the suggestion that Fe could be important to understanding interstellar polyaromatic hydrocarbons (PAH) [9] provides a launching point for our own work. Here we consider sandwich structures comprising multiple PAHs bound together by an Fe atom (e.g. Fig. 2) and compute the XAS spectra theoretically for comparison against our experimental ISM spectra (Fig. 3).

**Methods:** We use Density Functional Theory (DFT) to obtain the ground state electronic structure of each phase, then calculate absorption spectra using the Restricted Open-Shell Configuration Interaction with Singles (ROCIS) method, which has been shown to reproduce many of the experimental features in transition metal spectra [10].

We carried out our calculations using the Orca quantum chemistry package [11], the B3LYP hybrid exchange-correlation functional [12], an atom centered triple-zeta function basis set for Fe (def2-TZVP, [13]), a zeroth order regular approximation of the Dirac equation (ZORA, [14]) and the D3BJ dispersion correction [15] in order to better replicate energy splittings within the Fe-L edge.

Rather than assume a specific “oxidation” state or spin state for the Fe atom in each molecule, we repeated the calculation for several multiplicities ( $2S+1$  where  $S$  is the spin of the molecule) and chose the lowest energy configuration. We then determined the electronic structure from the number of

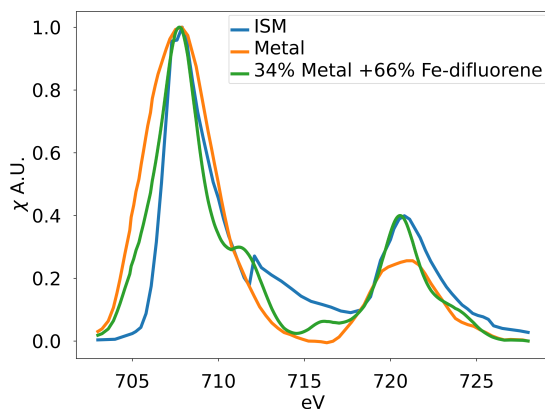


Figure 1: Fe-L of kamacite (BCC metal) compared with the ISM spectrum after removing edge jumps and real scattering assuming an WD01 particle size distribution with a 100 nm upper bound cutoff [4, 5]. A spectrum comprising metal and an Fe-PAH shows that the fit can be improved. See text.

unpaired electrons in the lowest energy configuration. We generated intrinsic bonding orbitals (IBO) [16] in order to visualize the bonding connections between the Fe atom and the PAHs and in order to calculate an oxidation state for the Fe atom. (See Figure 2.)

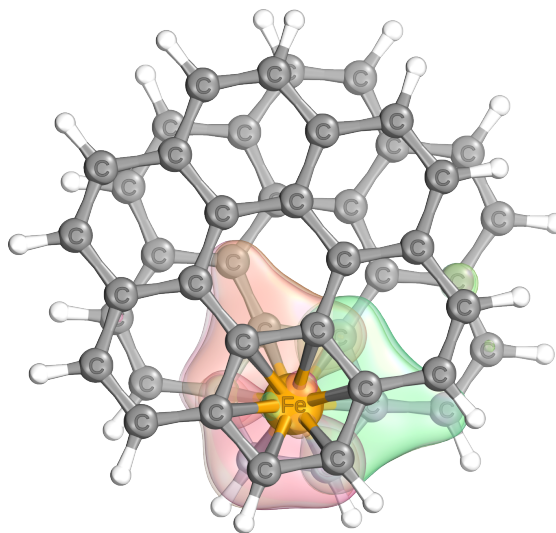


Figure 2: Calculated structure of an  $\text{Fe}(\text{C}_{24}\text{H}_{12})_2$  sandwich. Three intrinsic bonding orbitals are shown bonding the Fe to resonance  $\pi$  orbitals in the bottom  $\text{C}_{24}\text{H}_{12}$  PAH [16].

**PAH Sandwiches:** The number of possible PAH species

in the ISM is vast, so Fe can bind electronically onto and into carbonaceous material in the ISM in many ways, in principle. Since the abundance of Fe is about one order of magnitude less than C in the ISM, a carbonaceous molecule containing  $\gg 10$  C atoms might have one or more Fe atoms bonded to it. When one or more transition metals form a bond between two PAHs such that the basal plane of the PAHs are parallel, this is called a sandwich structure [17].

Posniak & Dunbar synthesized Fe-coronene ( $\text{FeC}_{24}\text{H}_{12}$ ) by combining Fe and coronene in a vacuum [18]. They also measured the reaction rate to form Fe-coronene sandwich structures:  $\text{FeC}_{24}\text{H}_{12} + \text{C}_{24}\text{H}_{12} \rightarrow \text{Fe}(\text{C}_{24}\text{H}_{12})_2$ . The forward reaction was favorable and eventually much of the  $\text{FeC}_{24}\text{H}_{12}$  was depleted in favor of the sandwich  $\text{Fe}(\text{C}_{24}\text{H}_{12})_2$ . Figure 2 shows our calculation of one possible structure for this molecule.

We calculated spectra for several sandwich molecules including Fe-difluorene ( $\text{Fe}(\text{C}_{13}\text{H}_{10})_2$ ), two configurations of Fe-dianthracene ( $\text{Fe}(\text{C}_{14}\text{H}_{10})_2$ ), and two configurations of Fe-dicoronene ( $\text{Fe}(\text{C}_{24}\text{H}_{12})_2$ ). Fluorene consists of two benzene rings and a cyclopentadienyl ring while anthracene and coronene consist only of benzene rings.

Previous work has also suggested that PAHs and PAH sandwiches may form from ionized species. The ISM is ionized to varying degrees [19], so we also considered singly and doubly ionized versions of the anthracene and coronene sandwiches as well as sandwiches missing one or two hydrogens.

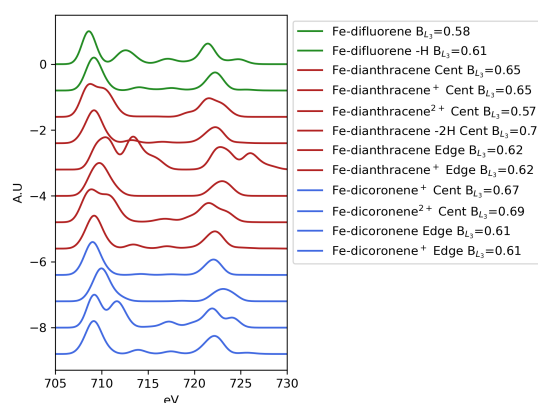


Figure 3: Some simulated sandwich spectra. *Cent* indicates two PAHs with an Fe atom joining them through the center benzene ring. *Edge* indicates two PAHs with an Fe atom joining them through an edge ring (as in Fig. 2). *-H* and *-2H* indicate removal of one or two hydrogens.

**XAS:** Figure 3 shows the variation in spectra that can be expected for different species. Fe-difluorene sandwiches are shown in green near the top, Fe-dianthracene spectra are red, and Fe-dicoronene are blue. It can be seen that branching ratios vary from 0.6 to 0.7 depending on the position of the Fe atom within the molecule, the molecule's ionization state, and whether it is missing hydrogens. Ground state saturated

sandwiches have the lowest branching ratios. Removal of hydrogens increases the branching ratio, and ionization generally (not always) increases the branching ratio. In addition, the positions of the peaks vary by  $>1$  eV, and several structures exhibit complex multiplet structure. In the ISM we may expect a diverse mix of these molecules so an aggregate spectrum would be an abundance-weighted sum over many such spectra. This would in general lead to a broadening of features, and increased intensity in the regions where multiplet features appear, e.g. 712 - 718 eV and above 722 eV. In Fig. 1 we provide a fit consisting of 2/3 Fe-difluorene and 1/3 metal to show that it can improve the fit from using metal alone. In this case, we expanded the energy axis by 10% and shifted the energy to place the primary Fe  $L_3$  peak at 708 eV. The energy shift and scale is necessary because of the DFT approximations for electron correlation and exchange. However, it is possible that the actual shift and scale values differ from those used here. It will be necessary to anchor this using a higher level of theory, or better, an experimental spectrum for a single Fe-PAH molecule, because the relative energy shifts in DFT calculations are expected to be accurate.

**Future work:** It should be possible to obtain experimental XAS spectra for some of these sandwich structures for direct comparison against the simulated spectra. We plan to simulate additional PAHs including defects such as N substitution, multiple Fe atoms, and mixed sandwiches in order to better estimate the average spectrum we should expect.

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