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Bilalbegović, Goranka; Maksimović, Aleksandar; Mohaček-Grošev, Vlasta

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Missing Fe: hydrogenated iron nanoparticles

G. Bilalbegović,[1]★ A. Maksimović[2] and V. Mohaček-Grošev[2]

[1]*Department of Physics, Faculty of Science, University of Zagreb, Bijenička 32, 10000 Zagreb, Croatia*
[2]*Center of Excellence for Advanced Materials and Sensing Devices, Rudjer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*

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ABSTRACT

Although it was found that the FeH lines exist in the spectra of some stars, none of the spectral features in the interstellar medium (ISM) have been assigned to this molecule. We suggest that iron atoms interact with hydrogen and produce Fe-H nanoparticles which sometimes contain many H atoms. We calculate infrared spectra of hydrogenated iron nanoparticles using density functional theory methods and find broad, overlapping bands. Desorption of H_2 could induce spinning of these small Fe-H dust grains. Some of hydrogenated iron nanoparticles possess magnetic and electric moments and should interact with electromagnetic fields in the ISM. Fe_nH_m nanoparticles could contribute to the polarization of the ISM and the anomalous microwave emission. We discuss the conditions required to form FeH and Fe_nH_m in the ISM.

Key words: astrochemistry – methods: numerical – stars: individual: IRC+10216 – ISM: lines and bands – ISM: magnetic fields – ISM: molecules.

1 INTRODUCTION

Iron is one of the most abundant chemical elements on Earth and in the Galaxy. It is proposed that more than 65 per cent of Fe is injected as gas into the interstellar medium (ISM; Dwek 2016). However, it is known that iron is strongly depleted (Savage & Bohlin 1979; Jensen & Snow 2007; Delgado Inglada et al. 2009; Jenkins 2009; Jones 2014; Dwek 2016). Therefore, it was suggested that Fe atoms hide in dust grains. Although the number of known molecules in the ISM approaches 200 (Tielens 2013), only two chemical species containing iron have been detected: FeO and FeCN (Walmsley et al. 2002; Furuya et al. 2003; Zack, Halfen & Ziurys 2011; Endres et al. 2016). Therefore, the search for additional iron species in the ISM and cosmic dust is necessary.

The most abundant element in the Universe is hydrogen. It is important to consider chemical compounds consisting of iron and hydrogen. The FeH molecule has been discussed in the astrophysical literature. It was proposed that FeH forms in the Sun and some other stars (Carroll, McCormack & O'Connor 1976). The spectrum of several stars in the ultraviolet (UV), visible and near-infrared (near-IR) region was compared with laboratory measurements of FeH, and good agreement for some lines was obtained. The near-IR Wing-Ford band at 0.99 μm was connected with the FeH spectral features in S stars, M-type giants, M and L dwarfs (Nordh, Lindgren & Wing 1977; Wing, Cohen & Brault 1977; Clegg & Lambert 1978; Jones et al. 1996; Kirkpatrick et al. 1999; McLean et al. 2000; Buenzli et al. 2015). The extensive literature about FeH is available on the ExoMol web page: http://www.exomol.com/bibliography/FeH (Tennyson & Yurchenko 2012).

Studies in materials science have shown that the Fe atom and small iron clusters could bind many hydrogen atoms (Parks et al. 1985; Richtsmeier et al. 1985; Whetten et al. 1985; Knickelbein et al. 1998; Wang & Andrews 2009; Takahashi, Isobe & Ohnuki 2013). It was suggested that hydrogen atoms chemisorb on Fe_n in the first step. Additional hydrogen atoms are attached by physisorption in the second step. Therefore, complexes and super-complexes containing one, or a few, Fe atoms and many H atoms are formed. We study hydrogenated iron nanoparticles to shed light on the missing cosmic iron problem.

2 COMPUTATIONAL METHODS

We use density functional theory (DFT) methods (Becke 2014; Jones 2015). In DFT, the total energy of a quantum system is determined by the electron density $n(\boldsymbol{r}) = \Sigma|\psi(\boldsymbol{r})|^2$ of the ground state. By using various physical and computational algorithms, DFT gives a realistic description of many physical and chemical properties of nuclei, atoms, molecules, nanoparticles and solids.

Results are obtained by the GPAW code (Enkovaara et al. 2010) and its ASE user interface (Bahn & Jacobsen 2002). The generalized gradient approximation (Perdew, Burke & Ernzerhof 1997) in its spin-polarized form is chosen, as well as the Projector Augmented Wave (PAW) pseudopotentials (Mortensen, Hansen & Jacobsen 2005). We start from Fe-H nanoparticles first optimized globally, and then using GPAW DFT methods, by Takahashi and coworkers (Takahashi et al. 2013; Takahashi 2014). However, we use the newest version of the GPAW package and reoptimize structures for the grid spacing of 0.14 Å. Takahashi and coworkers investigated structural properties and

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★ E-mail: goranka.bilalbegovic@gmail.com

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bonding of Fe-H nanoparticles. They also reported magnetic moments for a few of Fe-H clusters. We are interested in astrophysical applications. In this work, we calculate IR spectra, electric and magnetic moments of hydrogenated iron nanoparticles. IR spectra are obtained using the finite-difference approximation for a dynamical matrix and the gradient of the dipole momentum (Porezag & Pederson 1996; Frederiksen et al. 2007). The IR intensity I_i of the mode i is obtained using

$$I_i = \frac{N\pi}{3c}\left|\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}Q_i}\right|^2,$$

where N is the particle density, c is the velocity of light, μ is the electric dipole momentum and Q_i is the coordinate of the normal mode. The same DFT code and similar computational methods in calculations of IR spectra of cement (Ca-Si-O-H) nanoparticles with astrophysical applications (Bilalbegović, Maksimović & Mohaček-Grošev 2014) produced good agreement with measured IR spectra of the cement paste (Garbev et al. 2007). The IR frequencies we calculate correspond to stretching and bending modes in nanoparticles. Calculated data are absorption spectra and they are convolved with the Lorentzian band profiles to adjust them to astronomical emission spectra (Bauschlicher et al. 2010). These vibrational modes are excited when nanoparticles are heated by starlight and their main excitation mechanism is the absorption of a UV photon. Excited nanoparticles relax by IR emission. However, hydrogenated iron nanoparticles could also form or adsorb on to dust grains where they could be seen in absorption.

3 RESULTS AND DISCUSSION

3.1 IR spectra of hydrogenated iron nanoparticles

We present here IR spectra for four typical examples of hydrogenated iron nanoparticles shown in Figs 1 and 2. FeH_{10} (Fig. 1a) is the structure with the largest number of hydrogen atoms connected to the single Fe atom we investigated. Fe_9H_{56} (Fig. 1b) is the hydrogenated iron nanoparticle with the largest number of atoms we studied. Much larger Fe_nH_m nanoparticles, with n up to 130, were investigated in experiments (Parks et al. 1985). In the Supporting Information, we also show IR spectra for Fe_3H_{25} (Fig. 2a) and Fe_4H_{25} (Fig. 2b) to compare two structures with the same number of hydrogen atoms bonded to Fe_n and Fe_{n+1}. The Lorentzian profiles with a full width at half-maximum of 20 cm^{-1} are used for IR bands presented in Figs 3 and S1 in the Supporting Information. Tables of bands and their intensities for these structures are available in the Supporting Information. For some Fe-H nanoparticles the spectrum extends to the far-IR. For example, bands of Fe_4H_{25} draw out above 100μm [see Fig. S1(d) in the Supporting Information].

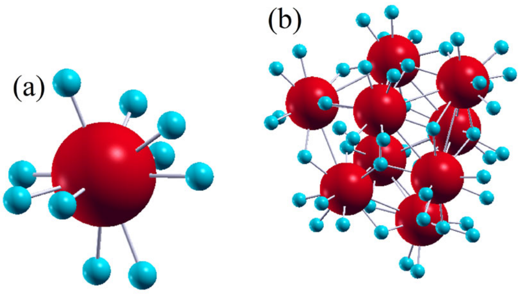

Figure 1. The optimized structures of: (a) FeH_{10}, (b) Fe_9H_{56}. Fe and H atoms are represented by the red and blue circles, respectively.

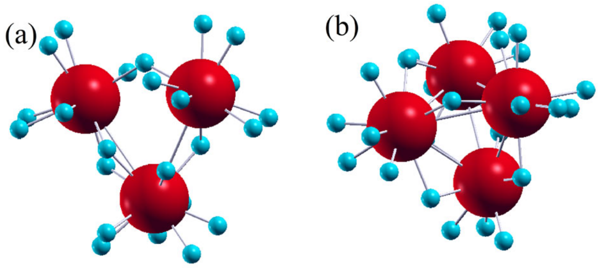

Figure 2. The optimized structures of: (a) Fe_3H_{25}, (b) Fe_4H_{25}. Fe and H atoms are represented by the red and blue circles, respectively.

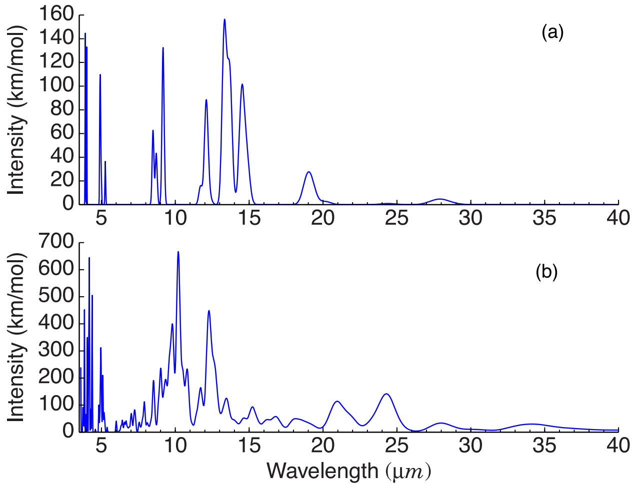

Figure 3. IR spectra of: (a) FeH_{10}, (b) Fe_9H_{56}.

Knickelbein et al. (1998) carried out an experimental study of multiplying hydrogenated iron nanoparticles, F_nH_m, $n = 9$–20. IR spectra were recorded in the 9.2–11.3 μm region. They found that bands overlap and that each band is about 20 cm^{-1} in width. They also carried DFT calculations using the local spin density approximation for only one cluster: $Fe_{13}H_{14}$. This structure was constructed to have Th symmetry of the iron core. Its theoretical IR spectrum was much simpler than measured spectra showing that real hydrogenated iron nanoparticles have low symmetry. In agreement with experimental results of Knickelbein et al. (1998), we optimize structures with low symmetry and find that their IR bands often overlap. It could be difficult to disentangle some of these IR features from those of other species in the space.

3.2 Hydrogenated iron nanoparticles and the interstellar electromagnetic fields

Some of Fe-H nanoparticles have electric and magnetic moments. For example, we calculate magnetic moments of 4 μ_B (FeH_2), 0 μ_B (FeH_{10}) and 0 μ_B (Fe_9H_{56}). Starting from FeH_2, magnetic moments for FeH_m decrease with m in the oscillatory way. For Fe_8H_{51}, we calculate 1 μ_B. For Fe_3H_{25} and Fe_4H_{25} (shown in Fig. 2), we find magnetic moments of -1 μ_B and +1 μ_B, respectively. All magnetic and electric dipole moments we calculate are shown in Table 1. The values of electric moments fluctuate between 0 and 2.6 D. The values of all magnetic moments in Table 1 are rather low. However, Knickelbein (2002) carried out magnetic measurements on Fe_n and Fe_nH_m, $n = 10$–25, nanoparticles and found that hydrogenation

Table 1. Calculated magnetic (M) and electric dipole (μ) moments for Fe-H species.

System	M (μ_B)	μ (D)
FeH_2	4	0
FeH_3	3	2.361
FeH_4	2	2.553
FeH_5	1	1.339
FeH_6	2	0.125
FeH_7	1	0.779
FeH_8	2	0.025
FeH_9	1	1.040
FeH_{10}	0	1.232
Fe_2H_{18}	0	1.510
Fe_3H_{25}	1	0.675
Fe_4H_{25}	1	1.012
Fe_5H_{28}	0	1.218
Fe_6H_{32}	0	0.611
Fe_7H_{39}	1	1.429
Fe_8H_{51}	1	2.324
Fe_9H_{56}	0	0.454

substantially increases magnetic moments of iron clusters for $n \geq 13$. The largest enhancement was measured for $n = 13$. All n values between 13 and 18 also show big enhancements. Magnetic moments of F_nH_m, n = 13–18, were 4–5 μ_B, whereas the corresponding values for Fe_n were 2–3 μ_B (Knickelbein 2002). It is possible to expect that the most pronounced interaction with the magnetic field occurs for hydrogenated iron dust grains of this size. Other intervals of enhancements for magnetic moments of F_nH_m (for $n > 25$) are also possible.

Therefore, some of Fe_nH_m nanoparticles interact with the cosmic electromagnetic field. The alignment of interstellar grains is a well-known problem (Andersson, Lazarian & Vaillancourt 2015). Various mechanisms of this alignment have been discussed for some time. Present understanding is that larger dust grains are aligned because of radiative processes, whereas alignment by a paramagnetic relaxation is feasible for small grains. The 2175 Å extinction bump was attributed to polycyclic aromatic hydrocarbon (PAH) molecules (Steglich et al. 2011). It was found that this 2175 Å feature shows polarization (Martin, Clayton & Wolff 1999). Therefore, it is important to study magnetic properties and polarization of the smallest dust grains, such as PAHs and Fe-H nanoparticles. The alignment of silicate grains with inclusions in the form of iron nanoparticles was recently investigated (Hoang & Lazarian 2016). Most of the previous studies on alignment of silicate grains with Fe were based on the model where iron atoms are distributed diffusively. It was found that iron nanoparticles inclusion in grains can enhance their alignment. The core of iron atoms is also present in the Fe_nH_m nanoparticles.

It is important to consider a possible photodestruction of Fe_nH_m. Similar problems, i.e. loss of aromatic H and side-groups, have been studied for PAHs (Tielens 2005). Reaction rates for these processes have been evaluated within several models (RRK, RRKM, RKM, QRKM). Because of the exponential dependence, small errors in the energies and entropies in unimolecular reactions produce large errors in the reaction rates. Therefore, better solutions are based on experimental data (Tielens 2005). Hydrogenated iron nanoparticles are much less studied than PAHs, for which plenty of data were accumulated for a long time in chemistry and physics, as well as over last 30 yr in astrophysics. However, Parks et al. (1987) found that multiphoton absorption for hydrogenated iron nanoparticles leads primarily to loss of hydrogen adsorbates because of the less energy which this process takes in comparison to breaking a metal–metal bond. One-photon fragmentation was also observed in a few cases.

Liu et al. (1985) found that the laser-induced multiphoton absorption on hydrogenated iron nanoparticles leads to desorption of a specific number of H_2 molecules. The desorption energy of 1.3 eV was estimated, but it was also found that this value slightly depends on the coverage. They also analysed their experimental results within the RRKM model (Liu et al. 1985). In experiments on hydrogen-saturated iron nanoparticles, Knickelbein et al. (1998) observed that the laser-induced heating below 150 K leads to a loss of some of the physisorbed H_2 molecules. UV lasers were used in experiments on photodestruction of Fe_nH_m (Liu et al. 1985; Parks et al. 1987; Knickelbein et al. 1998). The strength of the far-UV interstellar field is 1.7 (Draine 1978), or 1.6 (Parravano, Hollenbach & McKee 2003), times greater than the Habing field of 1.6 $\times\ 10^{-3}$ erg cm^{-2} s^{-1}. Therefore, desorption, induced by radiation and heating, could occur in the ISM. It was suggested that the H_2 desorption from small dust grains could induce their spinning (Mathis 1986).

The anomalous microwave emission (AME) is the excess emission observed in the 10–60 GHz frequency range (Kogut et al. 1996; Leitch et al. 1997; Dickinson, Paladini & Verstraete 2013). Electric dipole emission from spinning small dust grains (Draine & Lazarian 1998) and magnetic dipole emission from magnetic nanoparticles (Draine & Lazarian 1999) were proposed as the source of the AME. PAHs are often studied as very small grains. By analysing full-sky observations in the IR and microwave region from the Planck Collaboration XV (2014), Hensley, Draine & Meisner (2016) found that there is no correlation between fluctuations of the AME intensity and fluctuations in the emission of PAHs. Other carriers, such as nanosilicates (Hoang, Vinh & Lan 2016), were recently proposed for a possible origin of the AME. Fe-H nanoparticles could also be present in the ISM and their spinning, electric and magnetic emissions could be one of the sources of the AME.

3.3 Astrophysical origin

FeH molecules have been seen in brown dwarfs, S stars and M-type giants till now. Brown dwarfs do not have typical stellar winds and the amount of FeH molecules they could inject to the ISM is small. However, S stars and M giants do have pronounced winds (Kudritzki & Reimers 1978; Ferrarotti & Gail 2002; Ramstedt, Schöier & Olofsson 2009) and could inject FeH to the ISM. The presence of FeH in S stars and M giants is discussed in Wing (1972), Nordh et al. (1977), Clegg & Lambert (1978), Lambert (1988) and Hirai & Chinami (1992). Mould & Wyckoff (1978) calculated column densities of FeH for several models of stellar atmospheres for S and M stars. This calculation was updated by Lambert & Clegg (1980). The values at 3000 K are: log $N = 15.3$ for the M giant (C/O = 0.6), log $N = 15.8$ for the S star (C/O = 0.98) and log $N = 15.9$ for the S star (C/O = 1).

It is known that PAHs are destroyed in the ISM by shocks (Micelotta, Jones & Tielens 2010a), and in a hot post-shock gas (Micelotta, Jones & Tielens 2010b) by cosmic rays (Micelotta, Jones & Tielens 2011). The PAHs injection time to the ISM is longer than a time-scale for their destruction. The same problem exists for interstellar dust grains (Jones et al. 1994). It was suggested that PAHs and grains reform in the ISM. An efficient process is condensation on already existing grains (Jones et al. 1994;

Dwek 2016). Similar mechanisms play a role in the destruction and replenishment of hydrogenated iron nanoparticles.

Bar-Nun, Pasternak & Barrett (1980) suggested that FeH and FeH_2 may form on grain surfaces in very cold interstellar clouds. After performing and analysing laboratory astrophysical experiments, they proposed that H atoms diffuse and react with Fe atoms adsorbed on the graphite, silicate or icy grains at low temperatures. The energy of 1.7 eV released in the chemical reaction Fe + H → FeH is absorbed by a grain. The ejection of FeH and FeH_2 from grains by cosmic rays and sputtering during cloud collisions was proposed. Hydrogenated iron species could also be ejected from very small grains by the energy released from chemical reactions during the bond formation (Bar-Nun et al. 1980). Recent DFT and experimental studies have shown that hydrogenation of Fe nanoparticles is preserved on a single layer graphene supported by the Cu substrate (Takahashi et al. 2014). Iron nanoparticles were deposited by vacuum deposition, and hydrogenation was done with hydrogen gas under 1 atm and at the liquid nitrogen temperature. The copper substrate (on which a graphene layer is physisorbed) was chosen because of commercial applications (Takahashi et al. 2014). We expect that some other substrates, including cosmic dust grains, show similar properties, i.e. support and preserve hydrogenation of iron nanoparticles under suitable conditions. For example, Navarro-Ruiz et al. (2016) studied the formation of H_2 on Fe-containing olivine-based interstellar grains using DFT methods. They found that H adsorption on Fe sites is much stronger than on Mg ones. Because of the strong chemisorbed Fe-H bond, Fe-containing olivines can capture hydrogen atoms on an astronomical time-scale. Using computational methods Fioroni & DeYonker (2016) studied the H_2 formation on siliceous surfaces grafted with Fe^+. It was found that Fe-H and Fe-H_2 formation is always thermodynamically favoured. The H atom remains on the Fe-H centre increasing the probability for a second atom to react. Therefore, hydrogenated iron nanoparticles could form at S stars, M giants and on dust grains in the ISM.

IRC+10216 (CW Leo) is the nearby, asymptotic giant branch evolved carbon star known as one of the brightest mid-IR sources outside the Solar system. More than 80 molecular species, as well as many unidentified lines, have been detected in IRC+10216 (Cernicharo et al. 1996, 2013; Monnier et al. 2000; Mauron & Huggins 2010; Tenenbaum et al. 2010; Agúndez et al. 2012; Gong et al. 2015). Gas-phase iron in significant abundance was detected in the circumstellar envelope of IRC+10216 with the UVES spectrograph (Mauron & Huggins 2010). Observed column densities of refractory metals indicated that iron and other such elements are not completely removed from the gas phase by dust condensation. The FeCN molecule was detected in IRC+10216 (Zack et al. 2011), as well as several other molecules containing metals. Therefore, we suggest that IRC+10216 is one of the astrophysical environments where hydrogenated iron nanoparticles may form. The upper limit of 10^{-9} (relative to H_2) to the FeH abundance in IRC+10216 was proposed under the assumption that the emitting region has an average kinetic temperature of 300 K (Cernicharo et al. 2010). Ozin & McCaffrey (1984), as well as Rubinovitz & Nixon (1986), found that UV radiation promotes the formation of FeH_2. We expect that the formation of hydrogenated iron nanoparticles is efficient in astrophysical environments with UV radiation.

4 CONCLUSIONS

It is very important to study iron and its compounds in order to understand the properties of cosmic dust and molecules in the ISM. While pure iron, its oxides and sulfides, were discussed as components of cosmic dust grains, Fe-H nanoparticles were not studied in the astrophysical literature, to the best of our knowledge. We studied hydrogenated iron nanoparticles to point out their possible role in the balance of iron and hydrogen in the ISM. Fe atoms are sometimes surrounded by many hydrogen atoms. Therefore, it is difficult for iron atoms in the core to interact with non-hydrogen atoms. This could explain why only two molecules containing iron atoms were detected in the space till now. We use DFT methods and calculate IR spectra of Fe-H nanoparticles, their electric and magnetic moments. The IR spectrum of hydrogenated iron nanoparticles consists of broad, overlapping bands that could be difficult to separate from those of other species in the ISM. We propose observations in the radio, optical and UV spectral regions as additional, and perhaps better, tests for detection of hydrogenated iron nanoparticles in the ISM. Hydrogenated iron nanoparticles with electric and magnetic moments interact with cosmic electromagnetic fields. In addition, H_2 molecules could desorb from highly hydrogenated nanoparticles yielding to their spinning. Therefore, hydrogenated nanoparticles are good candidates for the analysis of processes such as the alignment of interstellar grains and the AME. We suggest S stars and M giants, as well as IRC+10216, as astrophysical sources where the search for hydrogenated iron nanoparticles could start. New experimental, theoretical and observational studies are needed to reveal a role of hydrogenated iron nanoparticles in the ISM.

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SUPPORTING INFORMATION

Supplementary data are available at *MNRASL* online.

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