

Mössbauer Study of Iron Iodide Produced by a Reaction of Laser-Evaporated Iron Atoms and Methyl Iodide

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The reaction products of laser-evaporated iron atoms and methyl iodide CH_3I are isolated in low-temperature Ar matrices and their Mössbauer spectra are obtained. The yields of the products vary depending on the concentration of CH_3I in the Ar matrix-gas. The Mössbauer parameters suggest that these species that are isolated in matrices are monomeric FeI_2 and dimeric Fe_2I_4 , which is confirmed by molecular orbital calculations.

Introduction

Laser-evaporated iron atoms have high-energy and thus can react with a variety of molecules to produce novel species. These kinds of novel species are generally unstable and can only be trapped in low-temperature matrices. The author has previously reported the production of a variety of novel iron oxide and iron nitride species by reactions of laser-evaporated iron atoms with oxygen¹ and nitrogen.² We have also reported a study into the reaction of laser-evaporated iron atoms with SF_6 gas, in which FeF_3 , Fe_2F_6 , and Fe_2F_4 were investigated.³ Mössbauer spectra provide direct information of the electronic properties of novel iron species that are trapped in low-temperature matrices, from which the structures of the species are derived with the assistance of molecular orbital calculations. In the case of halide species, the isomer shift δ and quadrupole splitting ΔE_Q are strongly influenced by the number of halide atoms and structure of a molecule. In this study, we investigate the novel iron iodide products of the reaction of laser-evaporated iron atoms with methyl iodide CH_3I .

The photochemistry of CH_3I itself has been studied extensively, and it has been reported that the photolysis of CH_3I produces a methyl radical and an iodine atom.⁴ Laser-evaporated iron atoms may break CH_3I molecules and release iodine atoms for the production of iron iodide species. The vaporization of solid FeI_2 produces the monomer as the major species while the dimeric species was found as a minor species. The vapor pressures of the two species have been measured and the standard sublimation enthalpy has been reported.⁵ Although the infrared spectra of gaseous FeI_2 has been reported,⁶ the Mössbauer spectra of matrix-isolated FeI_2 species has not.

Experimental

Pulsed laser light (248 nm, 200 mJ/pulse, 20 ns) from a KrF excimer laser (Lambda Physik EMG101MSC) was focussed on a block of ^{57}Fe iron, and iron atoms were produced by laser-evaporation. The gas mixture of CH_3I and Ar gas was introduced by a magnetic pulse valve synchronized with the laser pulse. Laser-evaporated iron atoms were mixed with the gas and the reaction products were condensed onto an aluminum plate cooled to 18 K using a closed cycle helium refrigerator. The gas and laser pulses were repeated 5000 times at 0.2 Hz. Mössbauer spectra were measured at 18 K in a transmission geometry using a $^{57}\text{Co}/\text{Rh}$ source.

Results and Discussion

Laser-evaporated iron atoms were condensed in an Ar matrix with CH_3I in various mixture ratios. The Mössbauer spectra at 18 K are shown in Figure 1. In all the spectra, sextet absorption that has the same Mössbauer parameters as those of α -iron appeared, which is attributed to larger iron particles produced directly by the laser-ablation of iron metal.¹ At the lowest CH_3I concentrations (Figure 1c), Fe atoms, Fe_2 dimers and two sets of doublets (species A and B) were observed. Their Mössbauer parameters are summarized in Table 1. With increasing CH_3I concentration (Figure 1b), Fe atoms and Fe_2 dimers disappear and the intensity of species B increases. At the highest CH_3I concentration (Figure 1a), species B occurs as a major product. The temperature of the samples was increased to 32 K for a 48 h period, and then the Mössbauer spectra were taken again at 18 K in order to examine the effects of annealing. No change was observed in the shape of the spectra, indicating that the species are stable enough not to undergo further reactions on migration at 32 K.

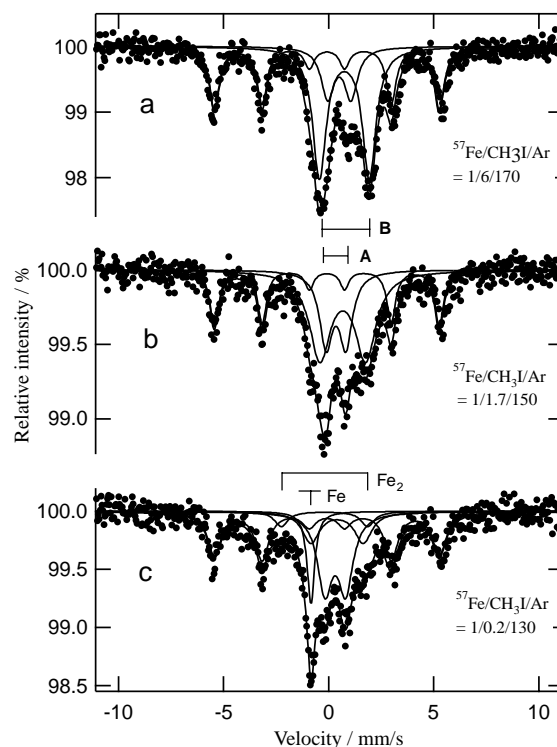


Figure 1. Mössbauer spectra at 18 K of laser-evaporated iron atoms condensed with CH_3I in Ar matrices. Molar ratios are indicated in the figure.

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TABLE 1: Mössbauer Parameters of the Species Isolated in Low-Temperature Matrices

Species	Isomer shift / mm/s	Quadrupole splitting / mm/s
Fe atom	-0.77 ± 0.03	
Fe ₂	-0.12 ± 0.03	4.05 ± 0.10
A FeI ₂	0.48 ± 0.11	1.01 ± 0.10
B Fe ₂ I ₄	0.80 ± 0.04	2.28 ± 0.10

TABLE 2: Calculated Electronic Properties Using HF/6-311G

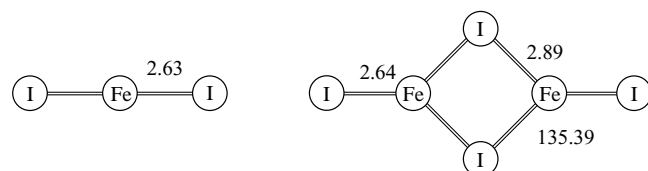
Species	electronic properties / au	
	$\rho(0)$ -15000	EFG
FeI ₂	92.09	-1.28
Fe ₂ I ₄	91.68	-2.85

Fe atoms and Fe₂ dimers only appear at the lowest CH₃I concentration, while large iron particles are always present, independent of CH₃I concentration. Fe atoms and Fe₂ dimers react easily to produce iron iodide species, more so than larger particles. The excited iron atoms encounter CH₃I molecules and produce methyl radicals and iodine atoms in the gas phase. Species **A** is produced at lower CH₃I concentrations and is assigned to monomeric FeI₂. The δ value of species **A** is too small to be a regular high-spin divalent species, which may reflect the high covalency of Fe-I bonds compared to other halide species. The intensity of species **A** decreases at higher CH₃I concentrations; monomeric FeI₂ further reacts with other FeI₂ to produce Fe₂I₄ in the gas phase.

Species **B** is obtained at the highest CH₃I concentration as major species. This species may be a stable form of iron iodide. It has been reported that solid FeI₂ exhibits a CdI₂ structure, and that it has $\delta=0.993$ mm/s and $\Delta E_Q=0.802$ mm/s at 78 K.⁷ The quadrupole splitting ΔE_Q of species **B** is larger than that of solid. Species **B** is not amorphous or a combination of clusters in various sizes because it has relatively sharp absorption peaks. Generally, dimeric Fe₂X₄ (X = F, Cl, and Br) species are stable and have large ΔE_Q values.^{3,8} Therefore, species **B** is assigned to dimeric Fe₂I₄.

We have reported the reaction of laser-evaporated Fe atoms with SF₆ and found that FeF₃ and Fe₂F₆ were produced.³ In this study, trivalent iron species such as FeI₃ or Fe₂I₆ were not found. Neither of these are obtained in the solid phase because of the reductive properties of I⁻, which forms I₂. The interplay between the oxidizing properties of Fe and the reducing properties of I also prevents the formation of FeI₃ or Fe₂I₆ in the gas phase. In a similar manner, the matrix-isolation system used in this study was not able to produce trivalent iron iodide species.

Molecular orbital calculations of FeI₂ and Fe₂I₄ were performed using Gaussian 98⁹ with HF/6-311G¹⁰ to confirm the assignments. The procedure of performing molecular orbital calculations in this study is the same as that reported previously.¹¹ The calculated electronic properties ($\rho(0)$ and EFG) and their optimized geometries are indicated in Table 2 and Figure 2, respectively. Monomeric FeI₂ has a linear struc-

**Figure 2.** Calculated structures of FeI₂ and Fe₂I₄ using HF/6-311G.

ture with S=2 and dimeric Fe₂I₄ has a bridged structure with S=4, similar to that of FeX₂ and Fe₂X₄ (X=F, Cl, and Br). The calculated electronic properties are in agreement with the assignment of species **A** and **B** to FeI₂ and Fe₂I₄, respectively. Further molecular orbital calculations were performed for species containing methyl group, and only FeI₂ and Fe₂I₄ were adequate to interpret the observed Mössbauer parameters. The reactivity of an iodine atom is higher than that of a methyl radical, and the only reaction products of laser-evaporated iron atoms obtained in this study were the iron iodide species.

The electron densities $\rho(0)$ of the related species FeX₂ and Fe₂X₄ (X=F, Cl, and Br) have been estimated using HF/6-311G and have been reported previously.³ The calculated electronic properties of FeI₂ and Fe₂I₄ is in agreement with other halide species. The small δ value and large $\rho(0)$ value for FeI₂ and Fe₂I₄ in the FeX₂ and Fe₂X₄ series are obtained because of the larger covalency of the iodide series. The energy of formation of Fe₂I₄ from two FeI₂ molecules is estimated to be 15.75 kcal/mol on the basis of ground state energies; dimeric Fe₂I₄ was found to be more stable than monomeric FeI₂, which is in agreement with the experimental results.

Conclusion

The reactions of laser-evaporated iron atoms with CH₃I were investigated, and the Mössbauer spectra of FeI₂ and Fe₂I₄ trapped in low-temperature Ar matrices were obtained. Monomeric FeI₂ was produced at lower CH₃I concentrations, and dimeric Fe₂I₄ was produced at higher CH₃I concentrations. Molecular orbital calculations proved that monomeric FeI₂ and dimeric Fe₂I₄ have linear and bridged structure, respectively.

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