

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

Yasuhiro Yamada\*

Department of Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Received: June 22, 2000; In Final Form: October 31, 2000

The reaction products of laser-evaporated iron atoms and methyl iodide  $\text{CH}_3\text{I}$  are isolated in low-temperature Ar matrices and their Mössbauer spectra are obtained. The yields of the products vary depending on the concentration of  $\text{CH}_3\text{I}$  in the Ar matrix-gas. The Mössbauer parameters suggest that these species that are isolated in matrices are monomeric  $\text{FeI}_2$  and dimeric  $\text{Fe}_2\text{I}_4$ , 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 oxygen<sup>1</sup> and nitrogen.<sup>2</sup> We have also reported a study into the reaction of laser-evaporated iron atoms with  $\text{SF}_6$  gas, in which  $\text{FeF}_3$ ,  $\text{Fe}_2\text{F}_6$ , and  $\text{Fe}_2\text{F}_4$  were investigated.<sup>3</sup> 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  $\delta$  and quadrupole splitting  $\Delta E_Q$  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  $\text{CH}_3\text{I}$ .

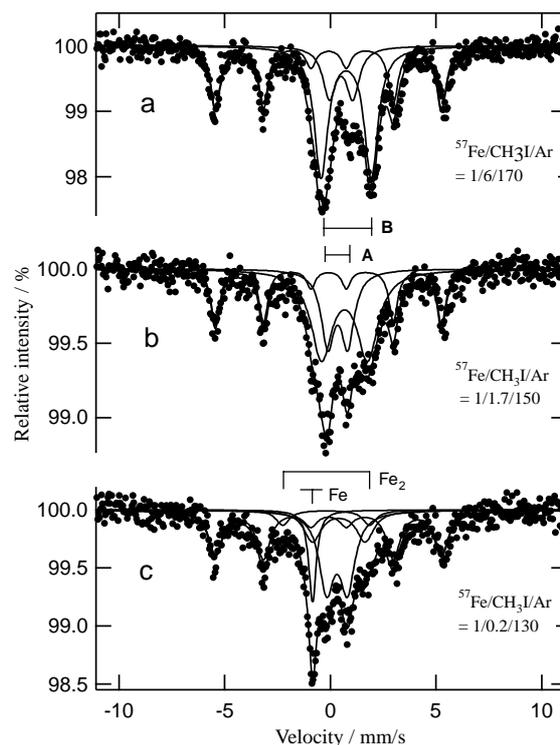
The photochemistry of  $\text{CH}_3\text{I}$  itself has been studied extensively, and it has been reported that the photolysis of  $\text{CH}_3\text{I}$  produces a methyl radical and an iodine atom.<sup>4</sup> Laser-evaporated iron atoms may break  $\text{CH}_3\text{I}$  molecules and release iodine atoms for the production of iron iodide species. The vaporization of solid  $\text{FeI}_2$  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.<sup>5</sup> Although the infrared spectra of gaseous  $\text{FeI}_2$  has been reported,<sup>6</sup> the Mössbauer spectra of matrix-isolated  $\text{FeI}_2$  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  $^{57}\text{Fe}$  iron, and iron atoms were produced by laser-evaporation. The gas mixture of  $\text{CH}_3\text{I}$  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  $\text{CH}_3\text{I}$  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  $\alpha$ -iron appeared, which is attributed to larger iron particles produced directly by the laser-ablation of iron metal.<sup>1</sup> At the lowest  $\text{CH}_3\text{I}$  concentrations (Figure 1c), Fe atoms,  $\text{Fe}_2$  dimers and two sets of doublets (species A and B) were observed. Their Mössbauer parameters are summarized in Table 1. With increasing  $\text{CH}_3\text{I}$  concentration (Figure 1b), Fe atoms and  $\text{Fe}_2$  dimers disappear and the intensity of species B increases. At the highest  $\text{CH}_3\text{I}$  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  $\text{CH}_3\text{I}$  in Ar matrices. Molar ratios are indicated in the figure.

\*Corresponding author. E-mail: yasu@ch.kagu.sut.ac.jp. FAX: +81-3-3235-2214.

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

Species	Isomer shift / mm/s	Quadrupole splitting / mm/s
Fe atom	$-0.77 \pm 0.03$	
Fe <sub>2</sub>	$-0.12 \pm 0.03$	$4.05 \pm 0.10$
<b>A</b> FeI <sub>2</sub>	$0.48 \pm 0.11$	$1.01 \pm 0.10$
<b>B</b> Fe <sub>2</sub> I <sub>4</sub>	$0.80 \pm 0.04$	$2.28 \pm 0.10$

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

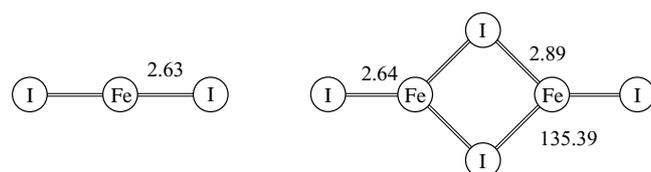
Species	electronic properties / au	
	$\rho(0)$ -15000	EFG
FeI <sub>2</sub>	92.09	-1.28
Fe <sub>2</sub> I <sub>4</sub>	91.68	-2.85

Fe atoms and Fe<sub>2</sub> dimers only appear at the lowest CH<sub>3</sub>I concentration, while large iron particles are always present, independent of CH<sub>3</sub>I concentration. Fe atoms and Fe<sub>2</sub> dimers react easily to produce iron iodide species, more so than larger particles. The excited iron atoms encounter CH<sub>3</sub>I molecules and produce methyl radicals and iodine atoms in the gas phase. Species **A** is produced at lower CH<sub>3</sub>I concentrations and is assigned to monomeric FeI<sub>2</sub>. The  $\delta$  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 CH<sub>3</sub>I concentrations; monomeric FeI<sub>2</sub> further reacts with other FeI<sub>2</sub> to produce Fe<sub>2</sub>I<sub>4</sub> in the gas phase.

Species **B** is obtained at the highest CH<sub>3</sub>I concentration as major species. This species may be a stable form of iron iodide. It has been reported that solid FeI<sub>2</sub> exhibits a CdI<sub>2</sub> structure, and that it has  $\delta=0.993$  mm/s and  $\Delta E_Q=0.802$  mm/s at 78 K.<sup>7</sup> The quadrupole splitting  $\Delta E_Q$  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 Fe<sub>2</sub>X<sub>4</sub> (X = F, Cl, and Br) species are stable and have large  $\Delta E_Q$  values.<sup>3,8</sup> Therefore, species **B** is assigned to dimeric Fe<sub>2</sub>I<sub>4</sub>.

We have reported the reaction of laser-evaporated Fe atoms with SF<sub>6</sub> and found that FeF<sub>3</sub> and Fe<sub>2</sub>F<sub>6</sub> were produced.<sup>3</sup> In this study, trivalent iron species such as FeI<sub>3</sub> or Fe<sub>2</sub>I<sub>6</sub> were not found. Neither of these are obtained in the solid phase because of the reductive properties of I<sub>2</sub>, which forms I<sub>2</sub>. The interplay between the oxidizing properties of Fe and the reducing properties of I also prevents the formation of FeI<sub>3</sub> or Fe<sub>2</sub>I<sub>6</sub> 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 FeI<sub>2</sub> and Fe<sub>2</sub>I<sub>4</sub> were performed using Gaussian 98<sup>9</sup> with HF/6-311G<sup>10</sup> to confirm the assignments. The procedure of performing molecular orbital calculations in this study is the same as that reported previously.<sup>11</sup> The calculated electronic properties ( $\rho(0)$  and EFG) and their optimized geometries are indicated in Table 2 and Figure 2, respectively. Monomeric FeI<sub>2</sub> has a linear struc-

**Figure 2.** Calculated structures of FeI<sub>2</sub> and Fe<sub>2</sub>I<sub>4</sub> using HF/6-311G.

ture with S=2 and dimeric Fe<sub>2</sub>I<sub>4</sub> has a bridged structure with S=4, similar to that of FeX<sub>2</sub> and Fe<sub>2</sub>X<sub>4</sub> (X=F, Cl, and Br). The calculated electronic properties are in agreement with the assignment of species **A** and **B** to FeI<sub>2</sub> and Fe<sub>2</sub>I<sub>4</sub>, respectively. Further molecular orbital calculations were performed for species containing methyl group, and only FeI<sub>2</sub> and Fe<sub>2</sub>I<sub>4</sub> 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 FeX<sub>2</sub> and Fe<sub>2</sub>X<sub>4</sub> (X=F, Cl, and Br) have been estimated using HF/6-311G and have been reported previously.<sup>3</sup> The calculated electronic properties of FeI<sub>2</sub> and Fe<sub>2</sub>I<sub>4</sub> is in agreement with other halide species. The small  $\delta$  value and large  $\rho(0)$  value for FeI<sub>2</sub> and Fe<sub>2</sub>I<sub>4</sub> in the FeX<sub>2</sub> and Fe<sub>2</sub>X<sub>4</sub> series are obtained because of the larger covalency of the iodide series. The energy of formation of Fe<sub>2</sub>I<sub>4</sub> from two FeI<sub>2</sub> molecules is estimated to be 15.75 kcal/mol on the basis of ground state energies; dimeric Fe<sub>2</sub>I<sub>4</sub> was found to be more stable than monomeric FeI<sub>2</sub>, which is in agreement with the experimental results.

## Conclusion

The reactions of laser-evaporated iron atoms with CH<sub>3</sub>I were investigated, and the Mössbauer spectra of FeI<sub>2</sub> and Fe<sub>2</sub>I<sub>4</sub> trapped in low-temperature Ar matrices were obtained. Monomeric FeI<sub>2</sub> was produced at lower CH<sub>3</sub>I concentrations, and dimeric Fe<sub>2</sub>I<sub>4</sub> was produced at higher CH<sub>3</sub>I concentrations. Molecular orbital calculations proved that monomeric FeI<sub>2</sub> and dimeric Fe<sub>2</sub>I<sub>4</sub> have linear and bridged structure, respectively.

## References

- (1) Y. Yamada, H. Sumino, Y. Okamura, H. Shimasaki, and T. Tominaga, *Applied Radiation and Isotopes* **52**, 49 (2000).
- (2) Y. Yamada, H. Shimasaki, Y. Okamura, Y. Ono, and K. Katsumata, *ibid.* **54**, 21 (2001).
- (3) Y. Yamada and K. Katsumata, *Chem. Lett.* **2000**, 746 (2000).
- (4) T. Monose, M. Miki, M. Uchida, T. Shimizu, I. Yoshizawa, and T. Shida, *J. Chem. Phys.* **103**, 22 (1995).
- (5) S. Scarozza and V. Piacente, *J. Alloys and Compounds* **235**, 48 (1996).
- (6) R. J. M. Konings and A. S. Booiij, *J. Molecular Structure* **269**, 39 (1992).
- (7) E. Pfletschinger, *Z. Physik* **209**, 119 (1968).
- (8) F. J. Litterst, A. Schichl, and G. M. Kalvius, *Chem. Phys.* **28**, 89 (1978).
- (9) Gaussian 98, A.6. (Gaussian Inc., Pittsburg PA, U. S. A., 1998).
- (10) 6-311G basis set for I: M.N. Glukhovtsev, A. Pross, M.P. McGrath, and L. Radom, *J. Chem. Phys.* **103**, 1878 (1995); Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.
- (11) Y. Yamada and T. Tominaga, *Radiochim. Acta* **80**, 163 (1998).