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Mössbauer and Infrared Studies of Reactions of Laser-Evaporated Iron Atoms with Methane

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The reaction of laser-evaporated iron atoms with methane gas was studied using a matrix-isolation technique, and the reaction products were observed by Mössbauer and infrared spectroscopy. The reaction produced CH_3FeH in a CH_4/Ar mixture, whereas $Fe_2H_2(CH_3)_4$ was also obtained in addition in a pure CH_4 matrix. Molecular orbital calculations were performed in order to confirm the assignments.

Laser-ablation is a very useful technique for surface treatment and for the vaporization of compounds with low vapor pressure. Laser-evaporated iron has high translational and electronic energy, and reacts with various reactant gases to produce novel compounds. Very few matrix-isolation studies have been reported in spectroscopic studies of the novel compounds produced by laser-evaporation, and a Mössbauer study of this kind had never been reported. We have developed a new system to observe Mössbauer and infrared spectra of matrix-isolated novel species produced by the laser-evaporated iron atoms, and have studied the reactions of laser-evaporated iron atoms with O_2,[1] N_2,[2] N_2O, SF_6,[3] and CH_3I.[4] The reactions with O_2, N_2, or N_2O produced simple iron oxide or nitride species following the decomposition of molecules to produce O or N atoms. The reaction with SF_6 or CH_3I produced simple halide species because of the high reactivity of F or I atoms produced by decomposition of molecules. No methyliron species was produced with the reactions with CH_3I. The reaction of iron atoms with alkanes may provide a simple model of reactions on iron metal surface, catalytic reactions or chemisorption of organic compounds, which also provide basic information on the bonding nature of organometallic compounds or complexes. Furthermore, the reactions of laser-evaporated iron atoms may have new reaction pathways because of the high energy available to decompose reactant molecules, and novel organometallic compounds may be synthesized. Mössbauer spectroscopy provides useful information regarding the electronic properties of iron atoms, particularly valence and spin-state, and infrared spectroscopy provides direct information on the bonding structures of species trapped in matrices. In this study we applied both techniques in order to characterize the species produced by the reaction of laser-evaporated iron atoms with methane. As this kind of novel species is unstable and conventional references for spectral data are not available, the assignments are made with the aid of molecular orbital calculations.

Iron atoms were vaporized resistively and trapped in a pure CH_4 matrix. CH_4 does not react with iron atoms in the ground electronic state at low temperature, providing results similar to those achieved using an inert gas matrix such as Ar.[5,6,7] Ultraviolet irradiation of iron atoms and methane at 15 K induces a photoreaction to produce CH_3FeH with the oxidative cleavage of a carbon-hydrogen bond.[8] This reaction was found to be a photoreversible reaction; irradiation of CH_3FeH with 420-nm light produces Fe and CH_4.[9] Similar photoreactions for Ni atoms with methane to form CH_3NiH have been reported.[10] Metal atoms, Zn, Cd or Hg, can be excited by microwave discharge and reacted with methane to form CH_3MH species.[11] Such excitation of the metal atoms is necessary for reaction with methane. Though we have previously reported that laser-evaporated iron atoms are highly excited and can react with various molecules, reactions of laser-evaporated iron atoms with CH_4 are yet to be studied. In this study, we investigate the reaction of laser-evaporated iron atoms with methane in order to identify novel species that are produced exclusively by the high excitation energy.

Experimental

Laser light from a KrF-excimer laser (Lambda Physik EMG-101MAC, 248 nm, 200 mJ/pulse, 20 ns) or a YAG-laser (Continuum Surelite I-10, 532 nm, 200 mJ/pulse, 6 ns) was focused by a convex lens onto a block of iron metal in a reaction chamber. A ^{57}Fe-enriched iron sample was used for Mössbauer measurements. The reactant gas (pure CH_4 or CH_4/Ar mixture) was introduced by a magnetic pulse valve, synchronized with the laser pulses. Iron atoms were laser-evaporated in an atmosphere of the reactant gas, and the reaction took place in the gas phase. The products were condensed on an aluminum plate that had been cooled to 17 K by a closed-cycle helium refrigerator (Iwatani Cryo-Mini D). The pulsed gas introduction and laser-evaporation was repeated 5000 times at 0.2 Hz. The total amount of iron in the sample was approximately 0.3 mg. Mössbauer spectra (Wissel MDU1200) were measured at 17 K in transmission geometry with a ^{57}Co/Rh source. Infrared spectra (Perkin Elmer System 2000) were measured using a CsI plate as a low-temperature substrate instead of an aluminum plate.

Results

Mössbauer Spectra. Mössbauer spectra obtained at 17 K are shown in Fig. 1 for a range of CH_4 concentrations. In all spectra, sextet absorption peaks are observed. These have identical Mössbauer parameters to α-iron metal and are assigned to large iron particles produced by the laser-ablation of the iron block. At the lowest CH_4 concentrations (Fig. 1a), unreacted iron atoms Fe and iron dimers Fe_2 are observed. Besides the pure iron species (Fe atom, dimer, bulk iron), a new species **A** is observed. Although the Mössbauer parameters of species **A** are very close to those of Fe_n ($n = 3$ or 4) as reported previously[1] ($\delta = 0.54 \pm 0.05$ mm/s, $\Delta E_Q = 1.36 \pm 0.10$ mm/s), species **A** has a conspicuously larger ΔE_Q than that of Fe_n. The Mössbauer parameters of species **A** indicate that it is a high-spin Fe(II) species. High-spin Fe(II) species with the large covalency such as FeI_2 have similar Mössbauer parameters.[4] At higher CH_4 concentration (Fig. 1b), species **A** is observed as a major product, whereas Fe and Fe_2 are not observed. Therefore, species **A** is not a pure iron species, and it is assigned to CH_3FeH produced by the reaction of laser-evaporated Fe atoms and CH_4 in the gas phase. The laser-evaporated iron has high energy and induces the cleavage of a C–H bond of CH_4 to form CH_3FeH. When the laser-evaporated iron atom is trapped in a pure CH_4 matrix (Fig. 1c), another species **B** is obtained, along with species **A** and bulk iron. Mössbauer parameters of species **A** and **B** are summarized in Table 1. Although the δ value of species **B** is negative, the species is not a pure iron atom. It has been reported that iron atoms vaporized by resistive heating can be trapped in a pure CH_4 matrix, and that an iron atom in a pure CH_4 matrix does not have quadruple splitting.[6] The species is considered to be an iron species produced by the reaction of CH_4 and has excess H or CH_3.

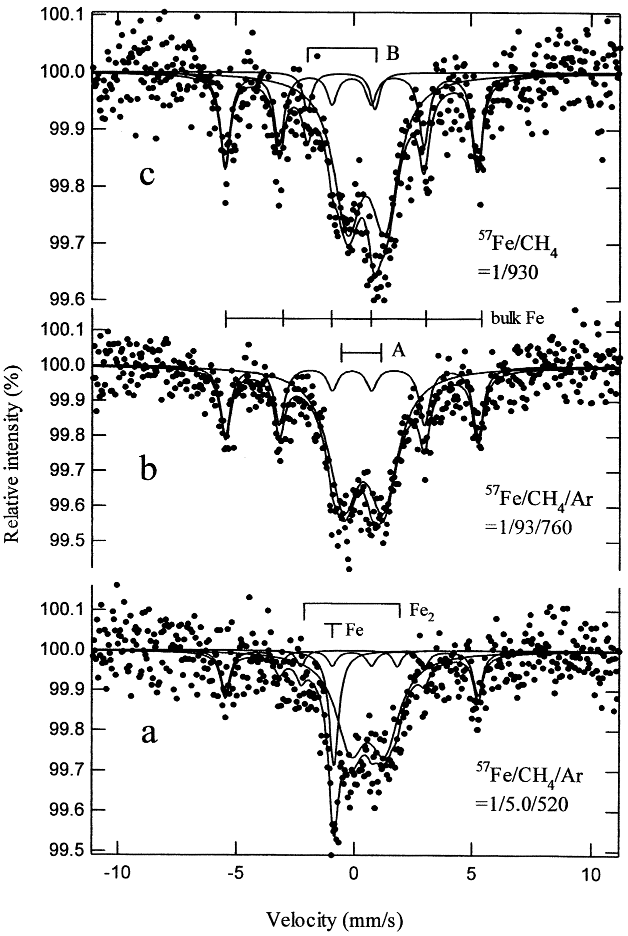


Fig. 1. Mössbauer spectra at 17 K of laser-evaporated ^{57}Fe atoms cocondensed with CH_4 in Ar matrices (a and b) and isolated in pure CH_4 (c). Molar ratios are indicated in the figure.

The temperature of the samples was increased to 30 K for 24 h and cooled again to observe the effects of annealing. According to the Mössbauer spectra, the sample of $^{57}Fe/CH_4/Ar = 1/5.0/520$ (Fig. 1a) exhibits a significant change on annealing (Fig. 2); the absorption of Fe disappears and the intensity of the species **A** absorption increases. Fe is expected to be unable to react with stable CH_4 at 30 K. The fragments produced by the decomposition of CH_4, such as CH_3 and H, are trapped in a matrix and reacted with iron atoms on annealing, forming CH_3FeH (species **A**).

No changes in the spectral shape on annealing at 30 K were observed for either $^{57}Fe/CH_4/Ar = 1/93/760$ (Fig. 1b) or $^{57}Fe/CH_4 = 1/930$ (Fig. 1c), indicating that CH_3FeH is stable on annealing at 30 K. Species **B** is not formed by aggregation of CH_3FeH.

Infrared Spectra. Typical infrared spectra of matrix isolated samples obtained at 17 K are shown in Fig. 3. The matrices were CH_4 in Ar ($Fe/CH_4/Ar = 1/330/330$) and pure CH_4 ($Fe/CH_4 = 1/910$). Absorption bands at 2903 and 1151 cm^{-1} are observed (Fig. 3a), which are assigned to $^{\nu}CH$ and $^{\nu}CH_3$ of

Table 1. Mössbauer Parameters of the Species Isolated in Low-Temperature Matrices (17 K)

	Species	δ (mm/s)	ΔE_q (mm/s)
	Fe atom	-0.77 ± 0.03	
	Fe dimer	-0.12 ± 0.03	4.05 ± 0.10
A	CH_3FeH	0.56 ± 0.10	1.57 ± 0.09
B	$Fe_2H_2(CH_3)_4$	-0.46 ± 0.05	2.85 ± 0.10

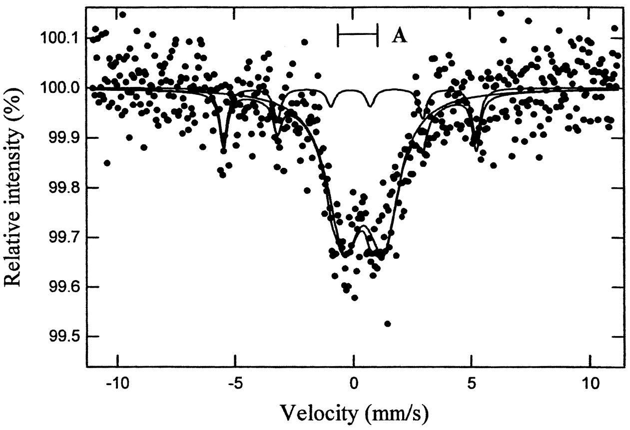


Fig. 2. Mössbauer spectrum (17 K) of $^{57}Fe/CH_4/Ar = 1/5.0/520$ (Fig. 1a) obtained after annealing at 30 K for 24 h.

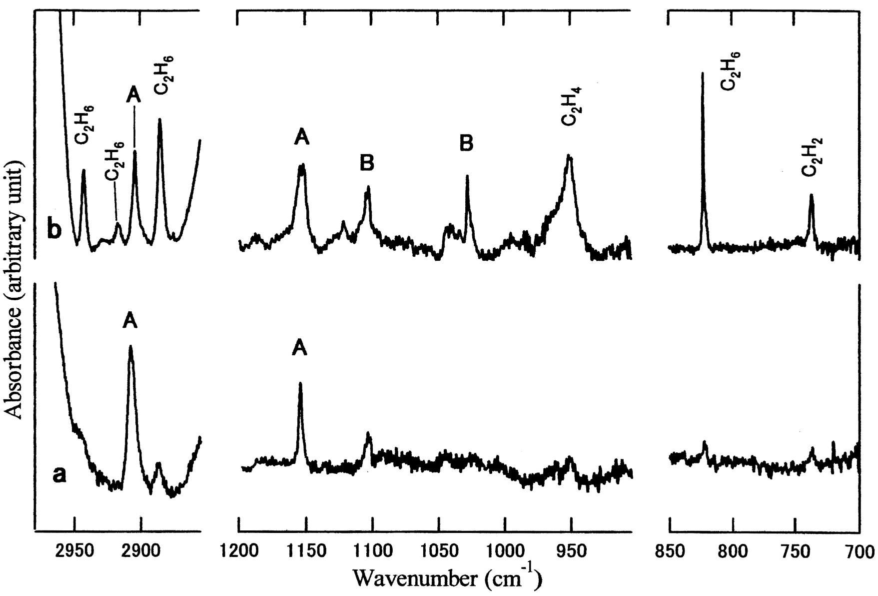
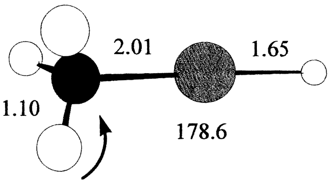


Fig. 3. Infrared spectra for reactions of laser-evaporated iron with methane at 17 K. (a) $Fe/CH_4/Ar$ = 1/330/330; (b) Fe/CH_4 = 1/910.

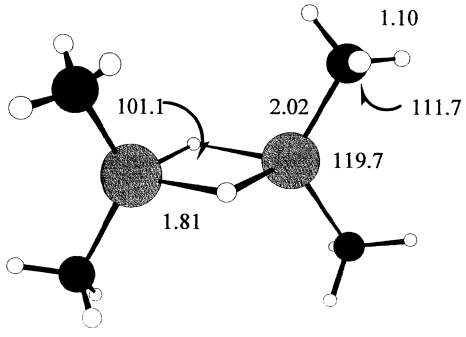
CH_3FeH, respectively. In a pure CH_4 matrix (Fig. 3b), additional absorption bands appear, most of which are attributed to stable hydrocarbon compounds: C_2H_6 (2943, 2917, 2885, and 823 cm^{-1}), C_2H_4 (951 cm^{-1}), and C_2H_2 (737 cm^{-1}). Unassigned bands at 1103 and 1028 cm^{-1}, which do not correspond to stable hydrocarbon compounds, are attributable to iron species produced in the pure CH_4 matrix. It has been reported that Ga reacts with H_2 to form $Ga_2(b\text{-}H_2)$ with bridging H atoms of Ga_2, with absorption bands at 1002.1 or 1022.3 cm^{-1} in Ar or Kr matrices.[12] Therefore, the absorption band at 1028 cm^{-1} in this study is assigned to the bridging H atom of Fe dimer atoms. As species **B** is obtained only in pure CH_4, the species contains more CH_3 or H.

Molecular Orbital Calculations. We performed molecular orbital calculations in order to predict the structure of the species obtained in the experiments and to confirm the assignments. The Gaussian 98 software program[13] with HF/6-311G and B3LYP/6-311G* basis sets was employed to interpret the Mössbauer and infrared spectroscopy results. The electronic properties of the species were estimated according to HF/6-311G in order to provide a comparison with the observed Mössbauer parameters. The structures of the species optimized using HF/6-311G and B3LYP/6-311G* were almost identical, and frequency calculations were performed using B3LYP/6-311G*. The Mössbauer isomer shift δ and ΔE_q are related to the electron density $\rho(0)$ and electric field gradient EFG at an iron nucleus, respectively. These Mössbauer parameters were estimated using the procedure reported previously.[14] We obtained good correlations between δ and $\rho(0)$, and between ΔE_Q and EFG for the species isolated in low-temperature matrices: iron carbonyl species,[14] iron oxide species,[1] iron nitride species,[2] and iron halide species,[3,4] though the correlation factors are dependent on the valence states of iron because of Sternheimer shielding or antishielding effects.

We performed molecular orbital calculations for CH_3FeH (species **A**) with a variety of spin states and found that S = 2 is the most stable state. For species **B**, we performed calculations for a variety of compounds having the Fe–H–Fe bridging bond, such as $Fe_2H_2(CH_3)_2$, $Fe_2H_4(CH_3)_4$, and $Fe_2H_2(CH_3)_4$ with various spin states, and found that $Fe_2H_2(CH_3)_4$ with S = 5 gives the most stable results. The optimized geometries for CH_3FeH (S = 2) and $Fe_2H_2(CH_3)_4$ (S = 5) are shown in Fig. 4. Estimated electronic properties and Mössbauer parameters are listed in Table 2. Although the ΔE_Q estimated for CH_3FeH is



CH_3FeH



$Fe_2H_2(CH_3)_4$

Fig. 4. Optimized geometry using B3LYP/6-311G*. Bond lengths are given in angstroms and angles in degrees.

smaller than the observed value of the species **A**, the discrepancy of the values is acceptable; such a difference was also observed for other species reported previously[1,2,3,4,14]. The other estimated Mössbauer parameters are in good agreement with the observed Mössbauer parameters. The large ΔE_Q value for $Fe_2H_2(CH_3)_4$ is attributed to the dimeric structure of the species, and the negative δ value is due to the high valence of iron atoms. Vibrational frequencies for CH_3FeH (S = 2) and $Fe_2H_2(CH_3)_4$ (S = 5) calculated using B3LYP/6-311G* are listed in Table 3. Frequency calculations were also performed for observed hydrocarbons: CH_4, C_2H_6, C_2H_4, and C_2H_2; frequencies calculated were in good agreement with the IR absorption bands observed in this experiment. The scaling factor was estimated to be 0.95 from the comparison of calculated and observed absorption bands of CH_4, C_2H_6, C_2H_4, and C_2H_2. In order to compare the calculated results with observed spectra, estimated IR spectra are shown in Fig. 5 with a 0.95 scaling factor. The intense absorption of CH_3FeH (species **A**), 2903 and 1151 cm^{-1}, is in good agreement with the calculated results. The absorption at 1103 and 1028 cm^{-1} attributed to the Fe–H–Fe bridging bond is also in good agreement with the calculated frequencies of $Fe_2H_2(CH_3)_4$.

Discussion

The reaction of laser-evaporated Fe atoms with diluted CH_4 gas in Ar matrices produces CH_3FeH. An excited Fe atom produced by laser ablation decomposes a CH_4 molecule to produce CH_3 and H; then it produces CH_3FeH in a reaction similar to that of the CH_3MH (M = Zn, Cd, Hg) species. Electronic configurations of metals play an important role in the reactions when the metals are excited using photolysis or microwave discharge. However, kinetic energy of the atoms may also

Table 2. Calculated Electronic Properties Using HF/6-311G and Estimated Mössbauer Parameters

		Electronic properties		Estimated Mössbauer parameters	
Species	S	$\rho^{MO}(0)$ −15000 (au)	EFG (au)	δ (mm/s)[a]	ΔE_Q (mm/s)
CH_3FeH	2	91.72	0.66	0.37	0.73
$Fe_2H_2(CH_3)_4$	5	94.16	2.21	−0.35	2.44

a) α-Fe standard.

Table 3. Calculated Vibrational Frequencies and IR Intensities Using B3LYP/6-311G*

Species	Frequency[a] (IR intensity[b])/cm^{-1} (KM/mol)
CH_3FeH (S = 2)	220(273) 221(273) 540(54) 577(66) 578(66) 1245(6) 1466(6) 1471(5) 1722(606) 2994(18) 3052(37) 3055(37)
$Fe_2H_2(CH_3)_4$ (S = 5)	11(0) 16(0) 25(0) 27(0) 30(0) 70(0) 80(0) 98(7) 109(0) 125(0) 143(4) 199(0) 491(9) 491(13) 502(15) 506(0) 526(0) 529(41) 560(0) 567(0) 578(1) 583(50) 639(32) 650(0) 675(0) 678(63) 1077(416) 1127(0) 1146(0) 1165(69) 1181(192) 1193(0) 1320(0) 1369(2058) 1439(9) 1441(1) 1442(104) 1442(0) 1449(2) 1450(25) 1450(2) 1451(0) 3005(0) 3005(39) 3006(11) 3006(0) 3083(0) 3083(5) 3083(1) 3083(63) 3094(3) 3094(5) 3096(67) 3096(0)

a) Both IR and Raman active frequencies are listed without scaling factor.

b) Intensities less than 0.5 KM/mol are indicated as "(0)".

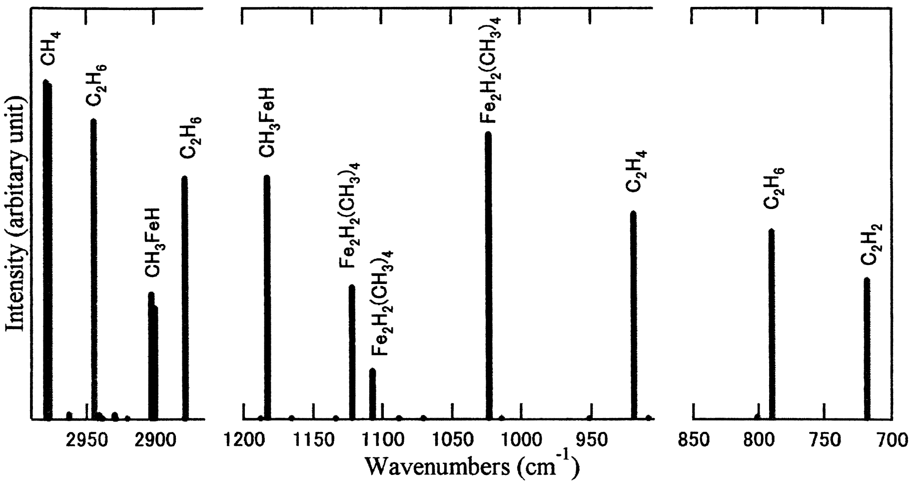


Fig. 5. Calculated frequencies using B3LYP/6-311G*. The scaling factor 0.95 was applied.

have an effect in this reaction to form CH_3FeH because laser-evaporated iron atoms have higher kinetic energies. The reaction of laser-evaporated iron atoms is not a simple oxidative addition, and it is accompanied by the dissociation of CH_4. This fact is supported by the formations of stable hydrocarbon compounds C_2H_6, C_2H_4, and C_2H_2. The CH_3FeH species is the major species produced by the reaction of Fe atoms with CH_4 molecules, independent of the CH_4 concentration. This is also a very stable species, as evidenced by the facts that it is the main product independent of CH_4 concentration and that there is no intensity change on annealing. The reaction between a ground state iron atom and a CH_4 molecule to form CH_3FeH is slightly endothermic, based on the ground sates energies estimated by molecular orbital calculation (B3LYP/6-311G*).

$$\begin{aligned}&\mathrm{Fe}\ (S = 2) + \mathrm{CH_4}\ (S = 0) \rightarrow\\&\mathrm{CH_3FeH}\ (S = 2)\ \Delta H = +19\ \mathrm{kJ/mol}\end{aligned}$$

The isomer shift of this species is $\delta = 0.56$ mm/s, which corresponds to the parameters of a high-spin divalent iron atom. Molecular orbital calculations also suggest that the most stable spin state of CH_3FeH is high spin S = 2. The arrangement of C–Fe–H is almost linear. The results of frequency analysis of CH_3FeH are in agreement with the observed infrared spectra. Absorption bands at 2903 and 1151 cm^{-1} are attributed to $^{\mathrm{v}}\mathrm{CH}$ and $^{\mathrm{v}}\mathrm{CH_3}$ of CH_3FeH, respectively.

On annealing of the sample, Fe disappeared to form CH_3FeH. The isolated iron atom in the ground state may not react with the CH_4 molecule to form CH_3FeH without further excitation because this reaction is endothermic and the activation energy of the reaction is high. CH_3 and H radicals produced by the decomposition of CH_4 on laser ablation of the iron sample are trapped in the matrix and react with isolated Fe atoms on annealing, consuming Fe to produce CH_3FeH.

In a pure CH_4 matrix, the most abundant product is also CH_3FeH. An additional species **B**, assigned to $Fe_2H_2(CH_3)_4$ (S = 5), is produced as a minor product. In infrared spectra, absorption bands due to stable hydrocarbon molecules (C_2H_6, C_2H_4, and C_2H_2) are observed, these are not observed in the sample reacted with the diluted CH_4 in Ar matrix. Therefore, a large number of CH_4 molecules are decomposed into hydrocarbon radicals (CH_3, CH_2, CH, and H) by excitation through collision with laser-evaporated iron atoms. These unstable species, which exist in high concentration, may react to form stable hydrocarbon molecules in the gas phase. As species **B** is also produced in such conditions, the species is expected to contain some more CH_3 or H. Species **B** is not produced on annealing of the CH_3FeH sample, indicating that it is not an aggregate of the form $(CH_3FeH)_n$. The results of molecular orbital calculations for $Fe_2H_2(CH_3)_4$ (S = 5) are in agreement with experimentally observed Mössbauer and infrared spectra of species **B**. Although the reaction mechanism to form $Fe_2H_2(CH_3)_4$ in the gas phase is complicated, the bulk reaction, governed only by the reaction of energetic laser-evaporated iron atoms with excess CH_4 molecules, is thought to be highly endothermic ($\Delta H = +241$ kJ/mol) on the basis of ground state energy calculations. To the author's knowledge, this is the first report of $Fe_2H_2(CH_3)_4$ (S = 5).

Conclusion

According to Mössbauer spectra, the major species produced by the reaction of laser-evaporated iron atoms with methane molecules in low-temperature matrices is CH_3FeH, in which the iron atom exists in a C–Fe–H bond. The species $Fe_2H_2(CH_3)_4$, which has a bridging Fe–H–Fe bond, was an additional product in a pure methane matrix. Infrared spectra of CH_3FeH and $Fe_2H_2(CH_3)_4$ were also observed. The assignments were confirmed by ab-initio molecular orbital calculations.

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