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Mass-Resolved Nanosecond Laser Spectroscopy of Jet-Cooled Ferrocene in the Region of the $3d_{z^2} \rightarrow R4p_{x,y}$ One-Photon Rydberg Transition

Sergey Yu. Ketkov,*,†,‡ Heinrich L. Selzle,† Edward W. Schlag,† and Georgy A. Domrachev‡

Institut für Physikalische und Theoretische Chemie der Technischen Universität München, Lichtenbergstrasse 4, D-85748 Garching, Germany, and G. A. Razuvaev Institute of Organometallic Chemistry RAS, Tropinin st. 49, 603600 Nizhny Novgorod, Russian Federation

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The wavelength-dependent mass-selected ion signals produced by supersonic-cooled ferrocene irradiated with nanosecond laser pulses in the region of the $3d_{z^2} \rightarrow R4p_{x,y}$ transition (40 000−42 000 cm^{-1}) have been investigated. Surprisingly, in a one-color multiphoton experiment, conditions have been found for the formation of intact molecular ions $(C_5H_5)_2Fe^+$ as the only ionic product. Neutral iron atoms are generated, however, in large amounts under these conditions by the photodissociation of the ferrocene molecules. Multiphoton ionization of the Fe atoms by the second UV laser makes it possible to reveal a resolved vibronic structure of the ferrocene Rydberg transition. The two-color multiphoton dissociation/multiphoton ionization spectrum shows a 0_0^0 peak at 41 090 cm^{-1} and a 4_0^1 component at 41 410 cm^{-1} demonstrating better resolution than the one-photon absorption spectrum measured in a static cell at elevated temperature. The distance between the vibronic components corresponds to the symmetric metal−ligand stretch in the Rydberg state. The two-color mass spectrum is changed dramatically when the second laser operates in the 17 500-cm^{-1} region. In this case, the excited states populated by the first laser are ionized efficiently by the second one, and the intensity of the molecular ion signal increases significantly. The REMPI excitation spectra measured at the masses of $(C_5H_5)_2Fe^+$ and fragment ions agree very well with that derived from the ionization of neutral iron atoms and reveal the same vibronic structure of the $3d_{z^2} \rightarrow R4p_{x,y}$ transition in the ferrocene molecule.

1. Introduction

Ferrocene, Cp_2Fe ($Cp = \eta^5$-C_5H_5), occupies a specific position among other metallocenes that represent one of the most important and interesting classes of organometallics.[1,2] Since its discovery in 1951,[3] this iron complex has played a key role in both fundamental and application-oriented organometallic chemistry.[4] Owing to its high molecular symmetry (the D_{5h} point group[5,6]) and a stable closed "18-electron" shell with the ...$[Cp(e_1)]^4[3d_{z^2}(a_1)]^2[3d_{xy,x^2-y^2}(e_2)]^4$ configuration,[7] ferrocene serves as a model compound in theoretical and experimental studies of organometallic systems.

In recent years, multiphoton dissociation/multiphoton ionization (MPD/MPI) processes accompanying laser irradiation of ferrocene in the gas phase have been a subject of considerable interest. The first experiments with microsecond and nanosecond laser pulses in the visible and near-UV regions[8−10] have shown that dissociation, preceding ionization, occurs for ferrocene. Mass spectroscopic ion detection[10] revealed that ion production at all resonant atomic iron lines yielded the metal ions exclusively. Ion formation through the continuous nonresonant background regions was also almost wholly due to the bare Fe^+ ions. Two dissociation mechanisms, one involving the vibrationally excited ground electronic state[11,12] the other via direct fragmentation in excited electronic states,[13,14] were suggested to explain the experimental results.

Recent studies of ferrocene cooled in a supersonic jet with the use of nanosecond tunable laser pulses in the 235−285 nm range[15−17] have also revealed only iron ions in the mass spectra. Under optimal conditions, very small amounts of $CpFe^+$ (m/z = 121) and Cp_2Fe^+ (m/z = 186) with intensities of less than 1% relative to that of the base peak Fe^+ (m/z = 56) have been found.[15] It has been concluded, therefore, that "soft ionization of ferrocene in a two-photon process with nanosecond laser pulses is not possible because of its fast dissociation in the intermediate state".[16] From femtosecond experiments in the 237−272 nm region,[18] the lifetimes of the Cp_2Fe electronic excited states were estimated to be about 200 fs.

To obtain information on the ferrocene molecule by employing high-resolution laser spectroscopic techniques such as resonance-enhanced multiphoton ionization (REMPI) spectroscopy[19,20] and zero-kinetic energy (ZEKE)[21] spectroscopy, it would be necessary to find conditions for the multiphoton ionization of jet-cooled Cp_2Fe by tunable narrow-line laser irradiation. The Cp_2Fe^+ molecular ions have been produced in higher yield by the excitation of room-temperature gas-phase ferrocene with nanosecond eximer lasers at 351 and 193 nm[22,23] as well as by the irradiation of ferrocene in a supersonic jet with femtosecond laser pulses.[15,16,18] These types of excitation cannot be used, however, in the high-resolution spectroscopic methods based on wide-range frequency tuning. It would be preferable, therefore, to employ narrow-line nanosecond tunable dye lasers for the multiphoton ionization of ferrocene when trying to overcome the difficulties arising from the short lifetimes of its excited states.

On one hand, the efficiency of ion production can be increased by the use of two lasers with overlapping pulses, the frequency of the second laser being appropriate for the ionization of the excited-state ferrocene. On the other hand, electronic

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* Corresponding author. E-mail: sketkov@imoc.sinn.ru.
† Technischen Universität München.
‡ G. A. Razuvaev Institute of Organometallic Chemistry RAS.

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transitions from the nonbonding iron 3d$_{z^2}$ orbital to the lowest molecular Rydberg p levels have recently been revealed in the one-photon gas-phase absorption spectrum of Cp_2Fe.[24,25] The ion yield can be higher if a Rydberg transition is chosen as the initial step in multiphoton ionization because of lower interconversion rates for the first molecular Rydberg states as compared to the rates of the intravalency excited states.[26−28] In this work, one- and two-color nanosecond laser spectroscopic studies of jet-cooled ferrocene in the region of the Rydberg R4p$_{x,y}$ absorption band (40 000−42 000 cm^{-1}) have been undertaken.

2. Experimental Section

The experiments are carried out with use of an apparatus described elsewhere.[29−32] Ferrocene (Strem Chemicals, purified by vacuum sublimation) at 130 °C seeded in Ar at 1.4 bar is expanded through a heated pulsed nozzle (orifice: 200 μm) into the vacuum. A skimmer with a 1-mm opening is placed 35 mm downstream from the nozzle to select the center part of the molecular beam. The ferrocene molecules are excited and ionized by the laser beams at a distance of 170 mm from the nozzle.

In the two-color experiments, the beams of two dye lasers (Quanta Ray PDL-1) pumped simultaneously by a Nd:YAG laser (Quanta Ray DCR1-A) are focused onto the molecular beam. The frequency-doubled first dye laser L1 is scanned in the region of the 3d$_{z^2}$ → R4p$_{x,y}$ transition of ferrocene (40 000−42 000 cm^{-1}). In one type of experiment, the frequency of the second laser L2 is chosen to be high enough to ionize ferrocene by the detachment of the Rydberg electron. Because according to the one-photon spectroscopic measurements[24,25] the binding energy of the R4p$_{x,y}$ electron in Cp_2Fe is ~17 550 cm^{-1}, laser L2 operates at 17 400−17 700 cm^{-1}. Ferrocene has a very low extinction coefficient at this frequency;[33,34] therefore, laser L2 does not contribute to the multiphoton excitation of ground-state Cp_2Fe. By defocusing laser L1, it appears to be possible to detect a pure two-color ion signal from Cp_2Fe^+, $CpFe^+$, and Fe^+. In another type of two-color experiment, the doubled frequency of laser L2 is fixed at the intense $a^5D_4 \rightarrow z^5P^0_3$ iron transition[35,36] ($\nu_{vac} = 29\,056.35$ cm^{-1}, $\lambda_{air} = 344.0606$ nm). Then the wavelength dependence of the ion signal from Fe^+ produced by the multiphoton dissociation of ferrocene with the subsequent ionization of neutral iron atoms can be analyzed.

The laser frequencies are controlled by a Burleigh WA-4500 pulsed wavemeter. The laser resolution is 0.5 cm^{-1}. The energies for L1 and L2 are 0.7 and 2.5−4.2 mJ/pulse, respectively. The pulse duration is 8 ns. The pathways for the beams of lasers L1 and L2 are adjusted to provide maximal overlapping in time of the two pulses in the point of crossing the molecular beam. In the one-color experiments, laser L2 is switched off.

The ions formed in the ionization chamber are extracted into a reflectron time-of-flight mass spectrometer (RETOF) with a resolution of 2000 M/ΔM and are detected with a multichannel detector. The mass and excitation spectra are then recorded with a transient recorder (Tektronix RTD 710) and after averaging are stored in a FORCE computer. The mass spectra are calibrated by adding a small amount of benzene vapor to the carrier gas. The ion yield spectra are compared with the gas-phase one-photon electronic absorption spectrum of ferrocene measured with a Specord UV−vis (Carl Zeiss, Jena) spectrometer at 100 °C in an evacuated static quartz cell. The resolution of the spectrometer is 30 cm^{-1}. Calibration is carried out by recording the absorption spectrum of the benzene vapor.

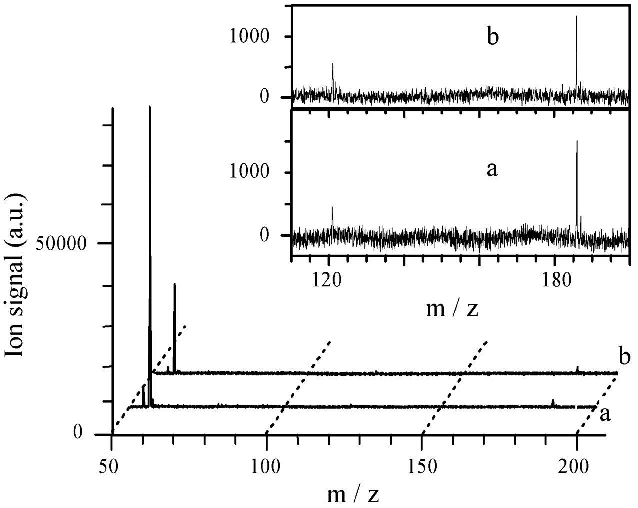

Figure 1. One-color multiphoton ionization mass spectra of ferrocene at 40 426 cm^{-1} (a) and 40 329 cm^{-1} (b). The inset shows magnified portions of the spectra in the region corresponding to the Cp_2Fe^+ (m/z = 186) and $CpFe^+$ (m/z = 121) ions.

3. Results

3.1. One-Color Laser Spectroscopy. Mass-resolved analyses of ionic products formed under irradiation of jet-cooled[16] or room-temperature[22,23] ferrocene at 248.3 nm (this wavelength is very close to that of the intense $a^5D_4 \rightarrow x^5F^0_5$ one-photon absorption line of the iron atom[35,37]) have shown a strong metal ion peak and the absence or vanishing amounts of the intact molecular ions. The mass spectra of ferrocene in a supersonic molecular beam measured in this work using shorter wavelengths corresponding to the intense resonance lines of neutral Fe also reveal a strong Fe^+ peak. For example, the spectrum measured at 40 426 cm^{-1} ($\lambda_{air} = 247.3$ nm; the $a^5D_3 \rightarrow x^5F^0_3$ transition[35,37]) demonstrates a Cp_2Fe^+/Fe^+ intensity ratio of about 0.014 (Figure 1a). However, despite the low relative intensity, the molecular ion peak is clearly seen in this mass spectrum, in contrast to the results obtained earlier for jet-cooled Cp_2Fe excited at 260 or 248 nm.[15,16] The spectrum also shows a very weak $CpFe^+$ fragment peak at m/z = 121 (Figure 1a).

Laser irradiation of ferrocene in the 40 316−40 400 cm^{-1} region ($\lambda_{air} = 247.97 - 247.45$ nm) containing no intense one-photon transitions of the iron atom[36,37] leads, nevertheless, to mass spectra dominated also by the Fe^+ peak. The spectrum measured at 40 329 cm^{-1} is given in Figure 1b as an example. The Cp_2Fe^+/Fe^+ intensity ratio increases to ~0.05 in this case, the molecular ion $Cp_2Fe^+$and fragment ion $CpFe^+$ signals being close in intensity to those at 40 426 cm^{-1} (Figure 1). A similar picture is observed for the shorter-wavelength nonresonant regions up to ~40 700 cm^{-1}.

When going to higher photon energies, the efficiency of Fe^+ ion production decreases significantly. The mass spectra recorded at 41 198 and 42 184 cm^{-1} are given in Figure 2a and b. The Cp_2Fe^+/Fe^+ intensity ratios are 0.17 and 0.45, respectively. Moreover, by defocusing the beam of laser L1, it appears to be possible to produce intact molecular ions exclusively in the one-photon experiment (Figure 2c). The ionization of the Cp_2Fe molecules in the one-color nanosecond experiment is of fundamental importance because this result indicates that the spectroscopic methods based on molecular MPI can be employed to study ferrocene. The one-color Cp_2Fe^+ peak, however, remains very weak (the signal/noise ratio is ~10); therefore, we were not able to find any features corresponding to the one-photon gas-phase absorption spectrum of ferrocene when

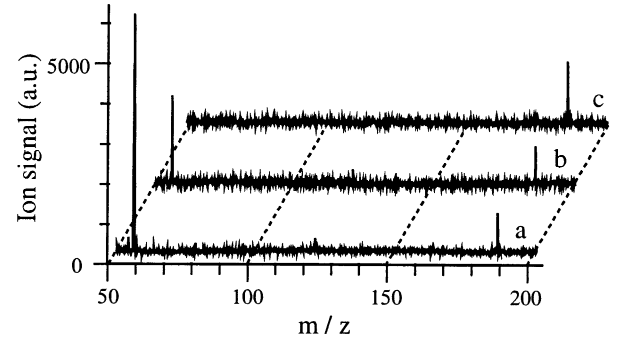

Figure 2. One-color multiphoton ionization mass spectra of ferrocene irradiated by a focused laser beam at 41 198 cm^{-1} (a) and 42 184 cm^{-1} (b) and by a slightly defocused beam at 42 184 cm^{-1} (c).

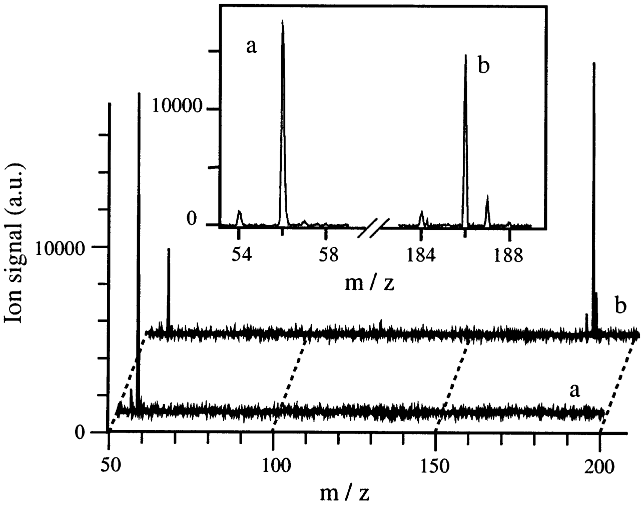

Figure 3. Two-color ionization mass spectra of ferrocene at ν_{L1} = 41 090 cm^{-1}, ν_{L2} = 29 056 cm^{-1} (a) and ν_{L1} = 41 090 cm^{-1}, ν_{L2} = 17 417 cm^{-1} (b). The intensity of laser L1 and the position of the focusing lens are the same as those in the one-color experiment (Figure 2c). The inset shows the isotopic structures of the Fe$^+$ signal in the former spectrum (a) and of the Cp_2Fe^+ signal in the latter spectrum (b).

measuring the wavelength dependence of the Cp_2Fe^+ signal. Such features appear in the two-color spectra obtained in this work.

3.2. Two-Color Laser Spectroscopy. When laser L2 operates alone in the 29 000-cm^{-1} region corresponding to a very low absorption of ferrocene,[33,34] it produces no ions under our conditions. However, when laser L2 fixed at a one-photon iron transition (e.g., $a^5D_4 \rightarrow z^5P^0_3$ excitation[35,36] at ν_{vac} = 29 056.35 cm^{-1}) is used together with laser L1 working in the 41 000-cm^{-1} region, a substantial increase in the Fe$^+$ yield is observed. At the same time, the intensity of the Cp_2Fe^+ peak decreases. By defocusing beam L1, the conditions can be found for the production of iron ions exclusively as a result of the ionization of neutral Fe atoms by laser L2 (Figure 3a). In that case, the dependence of the Fe$^+$ signal on the L1 frequency reveals two clearly defined peaks at 41 090 and 41 410 cm^{-1} (Figure 4a).

For comparison, the one-photon absorption spectrum of gas-phase ferrocene measured at 100 °C in the region of the $3d_{z^2} \rightarrow R4p_{x,y}$ transition is given in Figure 4 b. This spectrum agrees very well with the previously reported data[24,25,34] and shows a peak at 40 950 cm^{-1} accompanied by a shoulder at ~41 200 cm^{-1}. The absorption features are less resolved and shifted to the red as compared to the peaks revealed by the Fe$^+$ ion yield spectrum (Figure 4a).

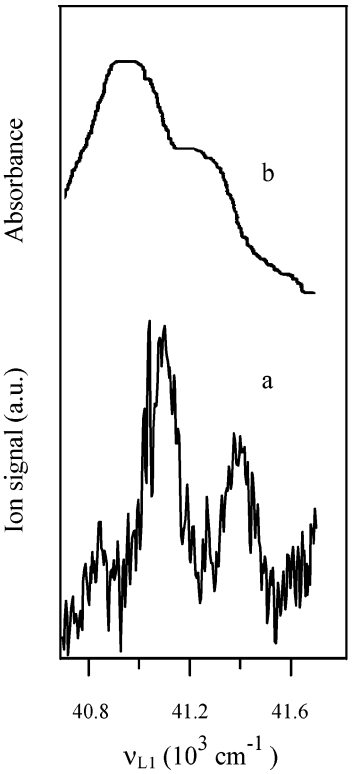

Figure 4. Two-color multiphoton dissociation/multiphoton ionization spectrum of jet-cooled ferrocene at ν_{L2} = 29 056 cm^{-1} (a) compared with the one-photon gas-phase absorption spectrum (b).

A quite different mass spectrum is observed when laser L2 operates in the 17 500-cm^{-1} region. The extinction coefficient of ferrocene at these frequencies is also very low;[33,34] therefore, laser L2 itself produces no measurable amounts of ions. Adding the L2 radiation to L1 leads, however, to a significant increase in the yield of intact molecular ions (Figure 3b). This experiment demonstrates the possibility of two-color ionization of ferrocene by nanosecond laser pulses. The peaks corresponding to the Fe$^+$ and CpFe$^+$ ions also appear in the mass spectrum (Figure 3b).

The isotopic structures of the Fe$^+$ signal resulting from the ionization of neutral iron atoms at ν_{L1} = 41 090 cm^{-1}, ν_{L2} = 29 056 cm^{-1} and the Cp_2Fe^+ signal produced by the ionization of ferrocene at ν_{L1} = 41090 cm^{-1}, ν_{L2} = 17417 cm^{-1} are compared in the inset of Figure 3. The ^{56}Fe peak is accompanied by the smaller ^{54}Fe and ^{57}Fe components. The relative intensities agree with the natural abundance of the iron isotopes (91.7, 5.8, and 2.1%, respectively[36]). The Cp_2Fe^+ signal shows an intense peak at m/z = 186 and accompanying components at m/z = 184 and 187 that correspond to the molecular ions containing iron isotopes. The signal of the heavier component is more intense than that for Fe$^+$ because of the contribution of the molecular ions bearing one ^{13}C atom in the organic ligands.

Efficient two-color multiphoton ionization of ferrocene with nanosecond tunable dye lasers makes it possible to employ “classical” REMPI spectroscopy in studying jet-cooled Cp_2Fe molecules. As an example, the wavelength dependence of the ion yield has been measured in this work for the ions observed in the mass spectrum (Figure 3b). The REMPI spectrum recorded in the region of the $3d_{z^2} \rightarrow R4p_{x,y}$ transition (Figure 5) reveals the same features as those found in the first two-color experiment (Figure 4a). The peaks at 41 090 and 41 410 cm^{-1} are clearly seen in the spectra measured at the masses of Cp_2Fe^+ and Fe$^+$ (Figure 5a and c). For the fragment CpFe$^+$

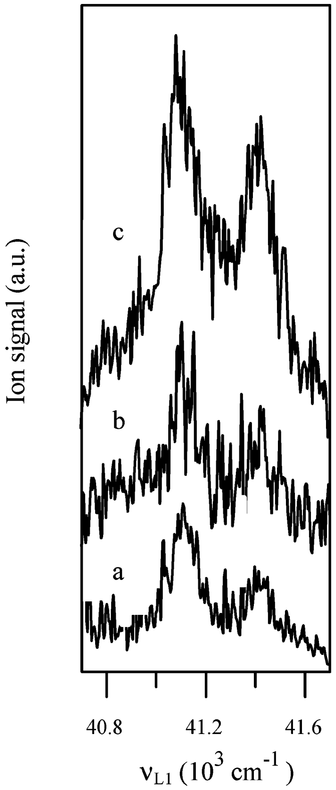

Figure 5. Two-color REMPI spectra of jet-cooled ferrocene measured for the Fe^+ (a), $CpFe^+$, (b) and Cp_2Fe^+ (c) ions at $\nu_{L2} = 17\,417$ cm^{-1}.

ions, the signal/noise ratio is lower, but the two vibronic components are also revealed (Figure 5b).

4. Discussion

The nanosecond mass spectra measured in this work at laser frequencies above 40 700 cm^{-1} (Figure 2) are completely different from the spectra reported earlier,[15−17] which revealed only the Fe^+ peak. However, comparing the mass spectra recorded in the lower-energy and higher-energy regions (Figures 1 and 2) shows that the intensity of the Cp_2Fe^+ ion signal remains practically unchanged. The increase in the Cp_2Fe^+/Fe^+ intensity ratio arises, therefore, from a decrease in the ionization efficiency of iron atoms on going to the higher frequencies. Indeed, the one-color MPD/MPI spectrum of ferrocene recorded at the Fe^+ mass (Figure 6) reveals, together with the peaks corresponding to one-photon Fe(I) transitions,[35,37] a nonresonant background signal with the intensity decreasing strongly when one goes from 40 000 to 41 000 cm^{-1}. This nonresonant ionization character explains the appearance of a strong Fe^+ peak in the 40 350-cm^{-1} region (Figure 1b) and the comparable intensity of the Fe^+ and Cp_2Fe^+ signals at frequencies above 40 700 cm^{-1} (Figure 2a and b). The observed ionization background can be attributed to saturated multiphoton processes involving excited-state iron atoms generated in the process of ferrocene photodissociation.[13]

The results of the one-color experiments show that nanosecond laser irradiation of ferrocene in the high-energy part of the $3d_{z^2} \rightarrow R4p_{x,y}$ region, in contrast to that at lower UV frequencies, leads to the formation of neutral iron atoms rather than iron ions. It is possible, therefore, to obtain the Fe atoms in high concentration without ionization. The efficient production of the iron atoms is confirmed by the two-color experiment with laser L2 fixed at the frequency of a one-photon Fe(I) atomic transition (Figure 3a). The decrease in the Cp_2Fe^+ signal can be caused by the photodissociation of the molecular ion on absorbing an L2 photon. The most interesting result of this experiment is the structure of the $3d_{z^2} \rightarrow R4p_{x,y}$ transition revealed by tuning laser L1 (Figure 4a). The separation of the peaks at 41 090 and 41 410 cm^{-1} (320 cm^{-1}) correlates very well with the frequency of a symmetric metal−ligand stretching vibration in the ferrocene neutral molecule[38] (301 cm^{-1}) and cation[39] (311 cm^{-1}). According to the notation system of the normal vibrations in ferrocene,[38] this stretching mode is designated as ν_4. The peaks at 41 090 and 41 410 cm^{-1} should be assigned, therefore, to the 0_0^0 and 4_0^1 vibronic components of the Rydberg transition, respectively. The third member of the ν_4 vibrational progression is predicted to lie at 41 730 cm^{-1}, but the corresponding feature cannot be clearly revealed because of its low relative intensity.

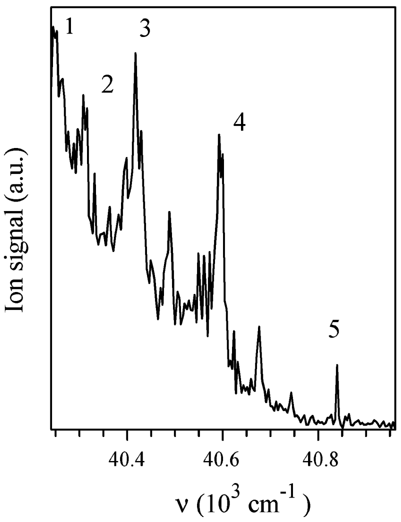

Figure 6. One-color multiphoton dissociation/multiphoton ionization spectrum of jet-cooled ferrocene in the 40 200−41 000 cm^{-1} region. The one-photon Fe(I) transitions[37] are denoted as 1 − $a^5D_4 \rightarrow x^5F^0_5$; 2 − $a^5D_2 \rightarrow x^5F^0_2$; 3 − $a^5D_3 \rightarrow x^5F^0_3$; 4 − $a^5D_4 \rightarrow z^5F^0_4$; 5 − $a^5D_4 \rightarrow z^5F^0_3$.

The peaks in the MPD/MPI spectrum (Figure 4a) correspond to the features observed in the one-photon absorption spectrum of Cp_2Fe (Figure 4b). Cooling of the ferrocene molecules in the supersonic jet results in better resolution of the vibronic components in the ionization spectrum. The shift to higher frequencies of the peaks in this spectrum as compared with the absorption features observed at elevated temperature (Figure 4) can also be a result of strong rotational and vibrational cooling of Cp_2Fe in the jet. A similar shift has been observed for Rydberg transitions in isoelectronic bis(η^6-benzene)chromium.[40,41]

The peak positions in the REMPI spectrum (Figure 5c) coincide with those observed in the MPD/MPI spectrum (Figure 4a). The spectra measured at the masses of Fe^+ and $CpFe^+$ reveal similar features (Figure 5a and b). The $CpFe^+$ fragment results from the dissociation of Cp_2Fe^+ after the absorption of an additional 17 417-cm^{-1} photon. Because laser L1 produces no iron ions in this experiment and the L2 frequency is far from the intense one-photon transitions in the iron atom,[36] the photodissociaton of Cp_2Fe^+ also seems to be the main source of the observed Fe^+ ions (Figure 3b). The ion signal remains, however, rather intense when the L1 frequency is outside the Rydberg peaks. This indicates that other excitations, which lie in the investigated region and correspond to very broad structureless bands in the absorption spectrum,[24,25] also take part in the observed MPD and MPI processes.

5. Conclusions

One-color nanosecond laser irradiation of jet-cooled ferrocene in the 40 700−42 000 cm^{-1} region results in the formation of neutral iron atoms, but the efficiency of the Fe multiphoton ionization is comparatively low. Surprisingly, an intact molecular ion signal close to the intensity of that of Fe^+ has been observed. This is explained by the absence of intense one-photon Fe(I) transitions and a strong decrease in the background from nonresonant iron ionization at these frequencies.

When the UV laser is tuned in the $3d_{z^2} \rightarrow R4p_{x,y}$ region, ionization of the iron atoms by the second laser gives an MPD/MPI spectrum revealing the vibronic structure of the Rydberg transition. The distance between the vibronic components corresponds to the symmetric metal−ligand stretching vibration. To our knowledge, this is the first example of features arising from a molecular electronic transition in the multiphoton spectrum of Cp_2Fe. Comparison with the one-photon absorption spectrum of ferrocene demonstrates better resolution achieved under the conditions of a jet-cooled molecular beam.

The most exciting result of this work consists of two-color molecular ionization of jet-cooled Cp_2Fe. The high relative intensity of the Cp_2Fe^+ signal demonstrates that the ionization channel can be efficiently activated by employing two spatially and temporarily overlapping nanosecond laser pulses. The obtained REMPI spectrum reveals the same vibronic components of the $3d_{z^2} \rightarrow R4p_{x,y}$ excitation as the MPD/MPI spectrum. The Rydberg transition “works”, therefore, in both the processes of multiphoton dissociation and multiphoton ionization of ferrocene.

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