Study of Dissociative Excitation Processes of Fe(CO)$_5$

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Abstract. Dissociative excitation and dissociative ionisation with excitation processes of organometallic molecule, iron pentacarbonyl Fe(CO)$_5$, were studied using the Electron Induced Fluorescence Apparatus. The emission spectrum of Fe(CO)$_5$ induced by electron impact (electron energy 50 eV) was recorded in spectral range between 220 nm and 450 nm. The emission spectrum was dominated by radiative transitions of Fe I, Fe II, CO and CO$^+$. Photon efficiency curves as function of the electron energy were recorded for several dissociative excitation channels originating from this molecule and dissociative excitation thresholds have been determined.

Introduction

In recent years, study of interaction between organometallic molecules and electrons has gained an importance, since these processes play an important role in the processes associated with FEBID (Focused Electron Beam Induced Deposition) [Huth et al., 2012] and have influence on the purity of structures. Low energy electrons are found in the proximity of the surfaces in the form of secondary electrons. They later interact with the surrounding gas molecules and have a major role in chemistry of this medium. Iron pentacarbonyl is a molecule widely used in these technologies [Lukasczyk et al., 2012]. The carbonyl ligands are easily removed from the iron atom and make this molecule suitable for deposition on the surfaces.

Fe(CO)$_5$ has been studied widely in the past, mostly by electron ionisation, [Norwood et al., 1990, Engelking et al., 1979, Distefano et al., 1970] electronic structure [Daniel et al., 1984], absorption and emission spectra, [Marquez et al., 1992] both in theory and experiment [Horák et al., 1983]. Metal carbonyls and simple organometalics are claimed to not fluoresce in general [Whetten et al., 1983], however emission spectra have been reported in UV, VIS and NIR region [Hale, 1983].

Interaction between low energy electrons and molecules in general can lead to (i) electron induced fluorescence (EIF) (ii) dissociative excitation (DE) and (iii) dissociative ionisation with excitation (DIE). As a product of these processes, one can detect photons emitted and obtain emission spectra and/or emission cross-sections for parent molecule (1) or fragment (2) produced by dissociative excitation.

\[ \text{EIF: } e^- (\varepsilon_1) + M (X) \rightarrow M^* (B) + e^- (\varepsilon_2) \rightarrow M^* (A) + h\nu + e^- (\varepsilon_2) \]  

\[ \text{DE: } e^- (\varepsilon_1) + M (X) \rightarrow M^* (B) + e^- (\varepsilon_2) \rightarrow Y^* (A) + [M - Y] + h\nu + e^- (\varepsilon_2) \]  

\[ \text{DIE: } e^- (\varepsilon_1) + M (X) \rightarrow M^* (B) + e^- (\varepsilon_2) \rightarrow Y'^* (A) + [M - Y] + h\nu + e^- (\varepsilon_2) \]

Where M denotes the molecules in different states (ground X, excited B, A) and Y represents a fragment dissociated of molecule.

Our group studies these processes by means of electron induced fluorescence apparatus (EIFA). The cross-beam apparatus allows to detect photons formed in reactions (1), (2) and (3). The electrons in the vacuum chamber collide with molecules and photons are detected. Fe(CO)$_5$ is in liquid state at room temperature, however, the high vapour pressure makes it suitable for examination by EIFA. In contrast to photon sources, the electron impact can excite optically forbidden states of the molecule and its fragments so the rich spectrum is expected. The emission spectra, the photon efficiency curves as function of the electron energy and the threshold energies for these processes can be determined from the measurements which represents valuable information for the understanding of the molecule’s behaviour in presence of low energy electrons.

Experimental setup

Experiment was performed on apparatus schematically presented in the Figure 1 [Danko et al., 1996].
The beam of electrons thermally emitted from a tungsten hairpin filament (Agar Scientific A054) is driven by electromagnetic field through electron gun (EG). A magnetic field of $5 \times 10^{-3}$ T is aligned in the direction of the electron beam (blue arrow on the Figure 1). The electron energy resolution of about 1000 meV Full Width at Half Maximum (FWHM) was achieved. Electron current is typically in the range of several µA and it is measured by picoammeter Keithley 6485. The effusive beam of molecules is crossed perpendicularly with the electron beam. The effusive molecular beam is formed in a capillary with dimensions of 0.5 mm diameter and 10 mm length. The capacitive pressure gauge, Pfeiffer Vacuum CMR 362, is used to measure the pressure inside the capillary, which is constant during the measurement. Working pressure ($1 \times 10^{-4}$ mbar) and the background pressure ($5 \times 10^{-8}$ mbar) in the chamber is measured by Pfeiffer Vacuum PBR 260 vacuum gauge.

The photons emitted by the molecules after the collisions with the electrons in the reaction chamber are passing through a bi-convex optical lens made of UV fused silica located 51 mm distance from the collision center, which corresponds to its focal length. Between the Czerny–Turner optical monochromator and the vacuum chamber a MgF$_2$ vacuum window is placed, after which the photons pass plano-convex lens (fused silica of 159 mm focal length). Photon collection efficiency is increased using a spherical mirror. The resolution of optical monochromator is regulated by slit width (for 200 µm slit resolution of 0.8 nm FWHM, or 100 µm slit width for resolution 0.4 nm FWHM as measured at 588 nm Ar line). Photomultiplier on the exit of the optical monochromator is Hamamatsu H4220P, which is cooled down to –25 °C and its working region is between 185–710 nm.

The surface of the electrodes of EG and the inner wall of the vacuum system is covered with colloidal graphite. This, and design of electrodes in which the filament is located, reduce the reflection of black-body radiation from the hot filament.

We have calibrated the electron energy at 14.1 eV using the peak of emission cross section of the (0,0) band of the 2$^{nd}$ positive system of N$_2$ (C$^3\Pi_u \rightarrow B^3\Pi_g$) at 337 nm emission line.

Regimes used for EIF of hydrogen molecule are (i) fluorescence spectra recording at fixed electron energies and (ii) the electron energy dependence of a specific transition measured by setting the optical monochromator to transmit the corresponding wavelength. The photon efficiency curves and the threshold energies from energy scan measurements can be determined.

**Results and discussion**

Iron pentacarbonyl investigation by EIFA consists of two types of measurements: (i) emission spectrum measurement (Fig.2) and (ii) photon efficiency curves measurement with determination of the thresholds (Figs. 4–5). We have measured the emission spectrum in wavelength range of 220–450 nm and identified many Fe I, Fe II atomic lines, as well as CO and CO$^+$ bands in this region.

![Figure 1. A schematic view of Electron Induced Fluorescence Apparatus (EIFA). Green arrow represents molecular beam, the blue arrow represents electron beam. In red the path of the photons is represented.](image)
The spectrum is very rich, as it can be seen on Fig. 2. All the lines detected in the spectrum are due to DE and DIE processes. The strong appearance of the DE and DIE processes in the emission spectra is due to both high efficiency of the dissociation processes in this molecule (due to relatively weak Fe–CO bond energies) and due to high probability of excitation of the Fe atom because of high density of exited states in Fe. Unfortunately we were not able to determine absolute cross sections for above mentioned reactions, but we believe that the DE processes in this molecule could play an important role in the FEBID, as they probably exceed the magnitude of the cross sections for electron ionisation and electron attachment processes. The most intense radiation comes from quintet and septet states of Fe I, which has been reported by previous authors [Hale, 1983]. The bands of CO and CO+ are overlapping and due to the limited spectral resolution of optical spectrometer, we cannot resolve vibrational transitions separated by less than 0.8 or 0.4 nm from each from other and from iron atom lines. There are several lines of Fe I and Fe II that are strong and relatively isolated (Fig. 3) so we were able to perform the analysis of the photon efficiency curves (Figs. 4–5) obtained at wavelengths corresponding to the peak intensities of the emission spectrum.

Observation of dissociative excitation is done by the means of photon efficiency curves as function of electron energy. We have recorded the efficiency curves at wavelengths corresponding to particular atomic lines and radiative transitions within the bands of CO and CO+. At 372 nm (Fig. 3) within the resolution of the optical monochromator (for the photon efficiency curve measurements the resolution of the optical monochromator was 0.8 nm) following radiative transitions of Fe I have the highest intensity: a $^5D(4) ← z^5F°(5)$ at 371.99 nm; a $^5P(3) ← w^5F°(4)$ at 372.13 nm; a $^5D(2) ← z^5F°(2)$ at 372.26 nm [NIST]. We have estimated the threshold for the efficiency curve at 372 nm of 11.4 ± 0.5 eV. The thermodynamic thresholds for the above mentioned transition are according to [NIST] 9.5 eV, 11.7 eV and 9.6 eV respectively. The results indicate the most probably at the threshold region the a $^5P(3) ← w^5F°(4)$ at 372.13 nm plays the most important role.

The second efficiency curve was obtained at 373.7 nm wavelength (Fig. 4). According to the NIST database, the most intense lines within the resolution of the monochromator are at 373.49 nm (a $^5F(5) ← y^5F°(5)$); 373.53 nm (z $^3P°(4) ← c^3P(4)$); 373.71 nm (a $^5D(3) ← z^5F°(4)$); and 373.83 nm (b $^3H(5) ← 1^1I°(6)$) with thermodynamic thresholds for observation from Fe(CO)$_5$ of 10.39 eV; 12.47 eV; 9.58 eV; 12.79 eV respectively [NIST]. We have evaluated the first threshold at 11.3 ± 0.5 eV, which is difficult to associate directly to the Fe I states.
**Figure 3.** Emission spectrum detail in region further investigated by measuring the Photon efficiency curves as function of the electron energy and determining the thresholds (at 372 nm, 373.7 nm and 260 nm).

**Figure 4.** Photon efficiency curves as function of the electron energy recorded at 372 nm (left) and 373.7 nm (right).

**Figure 5.** Photon efficiency curves as function of the electron energy recorded at 260 nm (black) compared with 372 nm measurement (red) subsequently subtracted from the 260 nm measurement.
Further investigation involved Fe II transition analysis. Based on the NIST atomic database, Fe II lines in the spectral region around 260 nm are more intense than Fe I lines. We have performed the photon efficiency curves measurement at 260 nm and observed several structures on the curve which indicates mixing of the Fe I and Fe II emissions (Figure 5.). The first threshold was observed at 12.8 ± 0.5 eV and it corresponds to Fe I transition at 259.96 nm $a^5F(4) \leftrightarrow x^5G^5(4)$ (thermodynamic calculations give a threshold of 11.89 eV for observation of this line originating from Fe(CO)$_5$). The second threshold is at 23 ± 0.5 eV and was obtained by subtraction of the Fe I line (we have taken the experimental 372 nm curve with intensity adjusted to match the first structure on the 260 nm efficiency curve). The most intense Fe II transition in close proximity to 260 nm is the $a^5D(9/2) \leftrightarrow z^5D^o(9/2)$ at 259.94 nm, whose upper state is at 4.77 eV above the ground state of the iron positive ion, which gives a thermodynamic prediction for the dissociative ionisation threshold of 18.87 eV for Fe(CO)$_5$. There are several more Fe II transitions with lower intensity than 259.94 nm line which are due to limited resolution of the optical spectrometer mixed to the main line and can influence the value of the threshold. The energy needed to induce Fe II emission is in range between 18.86–29 eV.

Conclusion

The investigation of the fluorescence induced by electron impact to iron pentacarbonyl was done using the EIFA apparatus in two modes: electron impact emission spectrum measurement in UV-VIS region and photon efficiency curves measurements with electrons in range between 0–100eV. Rich electron impact emission spectrum was obtained mainly due to dissociative excitation and dissociative ionisation processes. The spectrum was dominated by emission from iron atoms (Fe I), positive iron ions (Fe II) and weak molecular bands of carbonyl ion and neutral carbonyl fragments were detected as well. The photon efficiency curves at three different wavelengths for Fe I and Fe II were measured and the corresponding thresholds have been determined. We have recorded photon efficiency curves for two Fe I lines at 372 nm and 373.7 nm, however, within the resolution of the optical monochromator mixing of different atomic emission lines was observed. Similarly, at 260 nm wavelength, we have recorded Fe II line mixed with Fe I which we are able to separate in the data analysis and determine the threshold for both of the fragments.

The present study of the emission spectra of Fe(CO)$_5$ molecule was motivated mainly by the FEBID community, where this molecule is widely applied for preparation of Fe containing structures. The knowledge arising from present study could help to improve the understanding of the processes of secondary electrons with the Fe(CO)$_5$ and as well could result in establishment of a new diagnostic method for monitoring FEBID process.

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References


