# ELECTRONIC EXCITATION OF GAS PHASE $[Fe(CO)_5]$ IN THE 2 TO 22 eV ENERGY RANGE

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## ABSTRACT

The electronic excitation of gas phase iron pentacarbonyl has been studied by variable-angle, low resolution (0.5 eV), high energy (1 eV) electron energy-loss technique.

Two new strong bands have been observed above the first ionization potential, at 11.5 and 13 eV. Based on the angular behavior of the energy-loss spectra, the latter band can probably be associated to a non-dipole, quadrupole allowed electronic transition.

## 1. INTRODUCTION

The valence electronic structure of metal carbonyls has been studied in a number of experimental and theoretical papers[1-5], due to the general interest in the coordenative bond in this type of complex.

In the case of $[Fe(CO)_5]$, its electronic structure has been the subject of several theoretical works[7-10].

From the experimental point of view, however, although the photoelectron spectrum of this molecule has been obtained by different authors[6,7], until the present time only one measurement of the photoabsorption spectrum has been published[2], limited to the energy range of 3 to 6 eV. Furthermore, this measurement was done on solution, which could make difficult a comparison between experiment and theoretical calculations.

In the present work the electronic spectrum of gas phase $[Fe(CO)_5]$ has been measured in the energy range between 2 and 22 eV.

In the ground state, the $[Fe(CO)_5]$ molecule belongs to the $D_{3h}$ symmetry point group and has the following valence electronic configuration[5]:

$(10a_1')^2$, $(6e')^4$, $(11a_1')^2$, $(6a_2'')^2$, $(1e'')^4$, $(12a_1')^2$, $(13a_1')^2$, $(7e')^4$, $(7a_2'')^2$, $(8e')^4$, $(9e')^4$, $(1a_2')^2$, $(2e'')^4$, $(8a_2'')^2$, $(3e'')^4$, $(10e')^4$, $(9a_2'')^0$.

## 2. EXPERIMENTAL

The excitation spectra were obtained by electron impact technique[8]. As it is well known, the measurement of electron energy-loss spectra at different scattering angles allows for the observation of both allowed and non-allowed electronic transitions[9].

The general characteristics of the spectrometer and of the experimental method utilized in the present work have been previously described[10,11]. In summary, a 1 keV electron beam collides at 90$^o$ with a molecular beam (sample) inside a high vacuum chamber (background pressure, $1.5 \times 10^{-6}$ torr). Electrons scattered at different angles are energy-analyzed and then detected by an electron multiplier. The spectrometer is controlled by a microcomputer, as described recently[12].

The $[Fe(CO)_5]$ sample was produced by Aldrich Chemical Company, Inc. and used without any further purification.

Because of the high photochemical reactivity of this compound, care was taken to avoid exposition of the sample to the sunlight. Before data acquisition the $[Fe(CO)_5]$ sample was submitted to repeated freeze-thaw cycles.

The spectra were obtained at $2 \times 10^{-5}$ torr. The incident energy was 1 keV and the energy resolution was 0.5 eV.

## 3. RESULTS AND DISCUSSION

In figure 1, we present electronic excitation spectra for the $[Fe(CO)_5]$ molecule, obtained at scattering angles of 1.75, 2.25 and 2.75 degrees. Three principal bands can be observed. The firts one (band A), with a maximum of intensity at 6.2 eV, shows a discernible "shoulder" at 5.3 eV, in excellent agreement with the photoabsorption spectrum measured by Dartiguenave et al[2].

The masimum at 6.2 eV has been assigned to dipole-allowed transitions from $^1A_1$ to $A_2''$ and from $^1A_1$ to E', by Guenzburger et al[5], and from $^1A_1$ to E' by Dick et al[4]. Two dipole allowed transitions, from $^1A_1$ to E' and from $^1A_1$ to $A_2''$, have been assigned to the peak at 5.3 eV by both groups[4,5].

The two other bands, at 11.5 eV (B) and 13 eV (C), are situated above the first

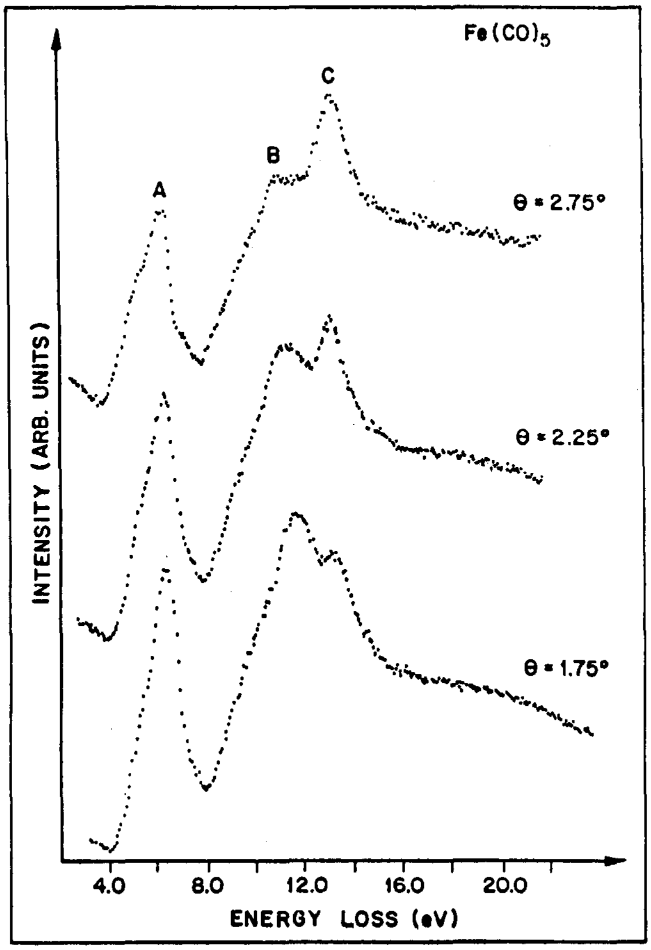

FIG. 1 - ELECTRONIC EXCITATION OF $Fe(CO)_5$ AT DIFFERENT SCATTERING ANGLES.

ionization potential of the molecule (8.6 eV)[6,7] and are here presented for the first time.

The non-availability of theoretical calculations involving the excited states of $[Fe(CO)_5]$ above 7 eV makes difficult a rigorous assignment of the electronic states associated to bands B and C. These bands are located above the 3e" ionization potential[6,7] and could energetically be associated to the valence and Rydberg transitions starting from the $8a_2$", 2e", $1a_2$', 9e', 8e', $7a_2$", 7e', $13a_1$', $12a_1$', 1e", $6a_2$", $11a_1$' and 6e' states.

The interesting angular behavior of band C, whose relative intensity with respect to A seems to increase with increasing angle, reflects, in our opinion, a non-dipole, quadrupolar character (main contributions to A arise from dipole-allowed processes). This angular behavior could also, in principle, be explained by a much faster decrease in intensity with angle of bands A and B with respect to C. It is well known, on the other hand, that small angle, fast electron beam scattering is quite well suited for exciting quadrupole-allowed electronic transitions[13] and we consider this to be the most probable possibility in the present case.

The broadness of band C (roughly 1 eV fwhm) could be related to our limited energy resolution (0.5 eV). We point out, though, that broad bands above the first ionization potential have already been observed in the electronic excitation of $C_2H_2$[14,15], this broadness being associated to a molecular geometry change in the excited state[13]. For a quadrupole-allowed transition the large fwhm can also be associated to the short lifetime of the excited state.

## 4. CONCLUSIONS

The valence electronic excitation spectrum of $[Fe(CO)_5]$ has been measured for the first time, using variable angle, high-energy electron energy-loss technique. The experimental conditions (1 keV incident electron beam, 1 to 7 degrees scattering angle) are ideally suited to the observation of allowed (dipole) and non-allowed (quadrupole) electronic transitions.

Besides the known dipolar transitions located at 5.1 and 6.2 eV, two well defined bands are observed at 11.5 and 13 eV. To the latter, a quadrupole character has been proposed, on the basis of the angular behavior of the energy-loss spectra.

A detailed study of the cross sections associated to the elastic and inelastic scattering of 1 keV electrons by the $[Fe(CO)_5]$ molecule as well as a more precise assignment for the observed bands will be presented in a forthcoming paper.

## 5. ACKNOWLEDGMENTS

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