

MOLECULAR STRUCTURE REANALYSIS OF  
IRON PENTACARBONYL AND CYCLOBUTADIENE IRON TRICARBONYL  
BY GAS-PHASE ELECTRON DIFFRACTION

BY

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IRON PENTACARBONYL AND CYCLOBUTADIENE IRON TRICARBONYL  
BY GAS-PHASE ELECTRON DIFFRACTION

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Robert Ta-Po Li

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## CHAPTER I

### INTRODUCTION

The use of gas-phase electron diffraction to determine the structure of molecules has been developed for a long time. The method of the data analysis has been improved each year. An investigation has been carried out to see if the use of recently developed data-analytic techniques leads to an improvement in our knowledge of the structural details of a pair of molecules. The molecules, iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , (Fig.1) and cyclo-butadiene iron tricarbonyl,  $\text{C}_4\text{H}_4\text{Fe}(\text{CO})_3$ , (Fig.2) have been reinvestigated here.

In the case of iron pentacarbonyl, the most interesting feature is the existence of two structurally non-equivalent types of Fe-C bond. We wished to determine confidence limits for the difference between axial and equatorial Fe-C bond lengths. That is to say that we attempted to use statistics to determine the probability that the axial is the shorter. In the case of cyclo-butadiene iron tricarbonyl we wished to examine certain angular features, notably the planarity of the cyclo-butadiene moiety. In both instances we have made use of a modified least squares analysis program devised in this laboratory.

Determinations of the structures of these two molecules had been made by several people.<sup>1-8</sup> There are some differences

between their results. For the molecule iron pentacarbonyl, most of the reports showed that the bond distance Fe-C(ax.) is shorter than the Fe-C(eq.). In our studies, we wanted to find the mean value of the Fe-C bond length, and determine which of the bond types is longer. For the molecule cyclobutadiene iron tricarbonyl, we wished to find whether the Fe-C-O bond is linear or not, and whether the C-H bonds form angles with the cyclobutadiene ring.

The electron diffraction data of these two molecules were collected by Davis and coworkers.<sup>2,6</sup>

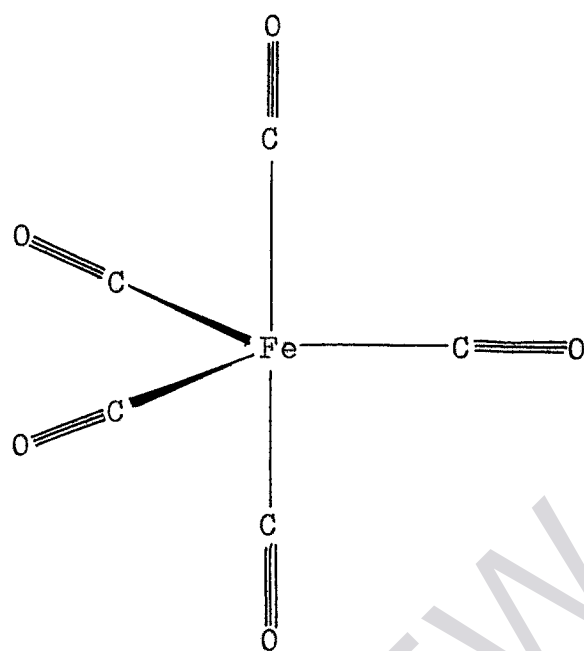


Figure 1

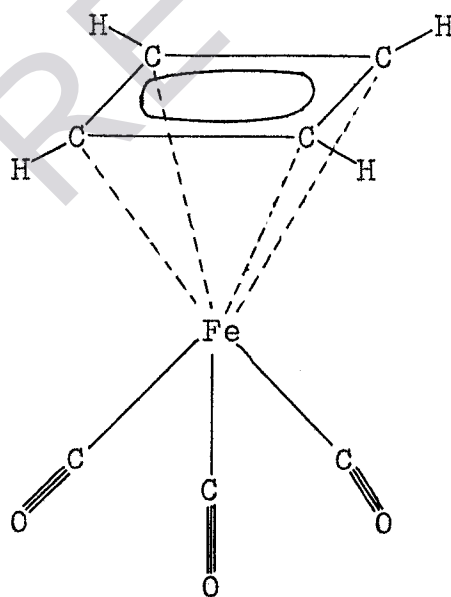


Figure 2



## CHAPTER II

### THEORY

The main area of activity of this study is data analysis. The theory of gas-phase electron diffraction which relates to this data analysis will be included in this chapter.

#### A. Atomic Scattering

This application of the theory of electron diffraction is based upon some assumptions. The most important assumption is that a given beam electron can be deflected by the force field of but one of the atoms of the molecule. Thus, we need to derive the atomic scattering expression. First, we start with the classical physical aspect to study this point.

In the case of a mobile object being deflected from its initial path by coulombic interaction with a stationary object of infinite mass, its locus will be hyperbolic. This hyperbolic path can be represented, as below (Fig.3):

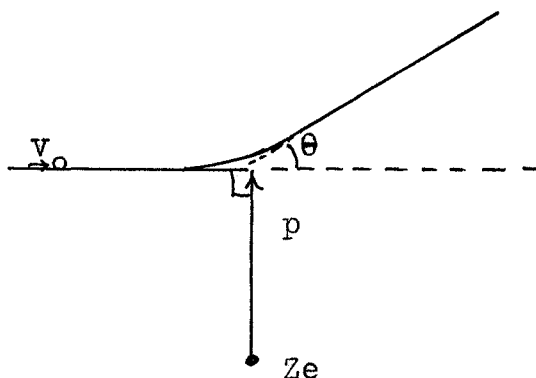


Figure 3

where  $\theta$  is the angle of scattering;  $p$  is the impact parameter, which is the perpendicular distance from the stationary object to the initial path of the projectile.

If the mobile and stationary object have charges of  $e$  and  $Ze$ , respectively, there exists a relationship which can be expressed as follows:<sup>9</sup>

$$p \cdot \tan(\theta/2) = Ze^2/(mv_0^2) \text{ -----(1)}$$

where  $m$  is the mass of the mobile particle and  $v_0$  is its initial velocity.

If instead of a single projectile electron, we have a homogeneous beam being scattered by the point charge  $Ze^-$ , there is an intensity distribution given by

$$I(s) = \frac{R^2 Z^2}{s^4}$$

where  $s = 4\pi \sin(\theta/2)/\lambda$ ,  $R$  is the collection of natural and experimental physical constants, and  $\lambda$  is the de Broglie wavelength.

The very existence of interference effects for electrons calls for a wave description of the electron beam. We can equate observed beam intensities with probability distributions, which in turn can be derived from wave functions.

Obtaining solutions to Schrodinger equation for a beam of electrons being scattered by an atom is a long and rather involved business. The Hamiltonian operator for this system is given by

$$H(r, \theta) = \left( \frac{-h^2}{8\pi^2 m} \right) \nabla^2 + V(r)$$

where  $\nabla^2$  is Laplacian Operator,<sup>10</sup> and  $V(r)$  is the atomic interaction potential which is a function of  $r$  only.

Since the system of the electron beam we are using must possess cylindrical symmetry about the axis that passes through the beam source and the atom; the wave function of the electron depends only upon the distance  $r$  and the deflection angle  $\theta$ . The wave function for the electron beam in this system is  $\Psi(r, \theta)$  which may be replaced by the product  $R(r) \cdot Y(\theta)$ . Thus, the general form of the Schrodinger equation may be written as:

$$\frac{-h^2}{8\pi^2 m} \nabla^2 R(r)Y(\theta) + V(r)R(r)Y(\theta) = ER(r)Y(\theta) \text{ -----(2)}$$

This equation can be separated into the following:

$$\frac{d}{d\theta} \frac{\sin\theta dY(\theta)}{d\theta} = -\ell(\ell+1)Y(\theta)\sin\theta \text{ -----(3)}$$

$$\frac{1}{r^2} \frac{d}{dr^2} \frac{r^2 dR_\ell(r)}{dr} + k^2 - U(r) - \frac{\ell(\ell+1)}{r^2} R_\ell(r) = 0 \text{ -----(4)}$$

where  $\ell$ , the angular momentum quantum number, is zero or some positive integer,  $k^2 = 8\pi^2 mE/h^2$  and  $U(r) = 8\pi^2 mV(r)/h^2$ . The solutions of Eq.(3) are:<sup>10</sup>

$$Y(\theta) = P_\ell(\cos\theta)$$

which are the Legendre Polynomials of  $\cos\theta$ . The wave

function can be written as the linear combination of the state functions:<sup>12</sup>

$$\psi(r, \theta) = \sum_{\ell} A_{\ell} R_{\ell}(r) P_{\ell}(\cos \theta) \text{ -----(5)}$$

where  $A_{\ell}$  are constants.

Since the incident beam is a plane wave function, the asymptotic form of the incident beam is

$$\psi(z) = \exp(ikz) \text{ -----(6)}$$

There is no atomic interaction potential for the incident beam. Thus, we can set  $U(r)$  equal to zero in Eq.(4). The solutions for this equation are<sup>12</sup>

$$R_{\ell}(r) = (kr)^{-1} \sin(kr - \frac{\ell\pi}{2}) \text{ -----(7)}$$

substituting Eq.(7) into Eq.(5) and comparing it with Eq.(6), we can find the coefficients  $A_{\ell}$ :

$$A_{\ell} = (2\ell + 1) i^{\ell}$$

The asymptotic form of the wave function for the scattered beam can be considered as:<sup>9</sup>

$$\psi(r, \theta) = \exp(ikz) + r^{-1} f(\theta) \exp(ikr) \text{ -----(8)}$$

where  $f(\theta)$  is the amplitude function.

The incident beam has been converted to the scattered beam by passing through atomic potential field. Due to potential interaction, there are phase shifts between

these two waves. The radial part of the scattered beam wave function has the following form:

$$R_\ell(r) = (kr)^{-1} \sin(kr - \frac{\ell\pi}{2} + \eta_\ell) \text{ -----(9)}$$

where the  $\eta_\ell$  is termed a partial wave phase shift.

From Eq.(5) and Eq.(8), we can obtain the equation for the scattered beam:

$$\sum_\ell A_\ell R_\ell(r) P_\ell(\cos\theta) = \exp(ikr \cdot \cos\theta) + f(\theta) r^{-1} \exp(ikr) \text{ ---(10)}$$

where  $R_\ell(r)$  is expressed in eq.(9). The coefficients  $A_\ell$  for the asymptotic form of the scattered beam can be obtained from Eq.(10):

$$A_\ell = (2\ell + 1) i^\ell \exp(i\eta_\ell) \text{ -----(11)}$$

From Eq.(5),(6),(7),(8),(9),(10), we obtain the following equation:

$$f(\theta) = (2ik)^{-1} \sum_\ell (2\ell + 1) [\exp(2i\eta_\ell) - 1] P_\ell(\cos\theta) \text{ -----(12)}$$

The only variable we have to determine in the Eq.(12) is the phase shift  $\eta_\ell$ . The phase shift  $\eta_\ell$  can be expressed in the following form:<sup>9</sup>

$$\eta_\ell = - \frac{4\pi^3 m}{h^2} \int_0^\infty V(r) \cdot [J_{\ell+1/2}(kr)]^2 dr \text{ -----(13)}$$

the potential function,  $V(r)$ , has the form