

EXPERIMENT V

ELECTRONIC SPECTRA OF CHARGE TRANSFER COMPLEXES

1. Purpose

In the present experiment, the *charge transfer* (CT) absorption spectra of a series of electron donor (Lewis base) mixed with a same common electron acceptor (Lewis acid) will be recorded. From these measurements, the extinction coefficient and the equilibrium constant corresponding to the CT complex can be obtained. The results will be interpreted using Mulliken's theory.

2. Pre-Lab Preparation

Be sure to work out in advance how to prepare the series of solutions needed for this experiment (see Table 1 and 2 and experimental section).

3. Safety

The samples prepared in this experiment consist of either organic solvents (benzene and substituted benzene) or solutions of organic material in heptane. Minimize inhalation of these substances by preparing the samples under the fume extractor or in a fume hood and keeping the sample containers covered during the experiment.

4. Introduction

When certain substances are mixed, although no chemical reaction occurs, an absorption band, not present in the spectra of either of the pure compound, may appear in the UV/VIS region. For example, solutions of iodine in benzene have a very strong absorption band at 297 nm. This absorption band has been interpreted as the result of a molecule of benzene acting as an electron donor and interacting strongly with the electron acceptor, iodine. In this particular case the electronic excited state can be viewed as the pair $C_6H_6^+$ and I_2^- produced by a π -electron transfer from the benzene to the iodine.

Of course, this phenomenon is not general and special energetic conditions have to be fulfilled for this type of interaction to occur between a pair of molecules. Using quantum mechanical language, for strong charge transfer interaction, the donor and acceptor molecular orbitals must be very close in energy and there must a large orbital overlap; in other words, the geometry of the two partners must allow for such an overlap. Typically, these conditions are fulfilled when high energy orbitals from a donor interact with low energy empty orbitals from the acceptor.

The experimental quantity easily obtained is the frequency of the CT absorption band, $\tilde{\nu}_{CT}$. One finds that $\tilde{\nu}_{CT}$ is correlated to the electron affinity of the acceptor molecule, E_A and to the ionisation potential of the donor molecule, I_b . Furthermore, if one looks at a series of molecular complexes (*i.e.*, varying I_b) for which the acceptor is the same (*i.e.*, E_A constant), $\tilde{\nu}_{CT}$ and ΔG^0 show each a simple dependence on I_b .

The purpose of the present experiment will be to collect and interpret the UV/VIS spectra of the molecular complexes formed between a series of methylbenzenes (electron donors) and a same common electron acceptor, tetracyanoethylene (TCNE)

5. Theory

All the details of the theoretical derivation which follows can be found in Ref. [1 – 3]. Only the main points are presented here. However, a complete grasp of the derivation is not essential in interpreting the results which can be understood with semi-intuitive arguments.

Mulliken's theory attempts to deal with the formation of molecular complexes both inorganic or organic; in general, such species would be the result of interaction between a Lewis acid A (electron acceptor) and a Lewis base B (electron donor). The formation of the weak complex AB,



is due to attractive dipole and polarization forces between the two molecules. Note that, in principle it is possible that higher order complexes be formed (more than two molecules), but only 1:1 complexes will be considered here. Also, it will be assumed that all the valence electrons are paired up in A and B and therefore not available to form a covalent bond between A and B.

Let $\psi(A,B)$ be the wave-function for the molecular structure AB arising from the weak dipole and polarization interactions. The nature of the partners in the formation of the complex (electron donor/acceptor) gives rise to an ionic contribution in the bonding which can be viewed as A^-B^+ ; let $\psi(A^-B^+)$ be the wave-function for this resonance structure*. Using the above two resonance structures as a basis set, the wave-function corresponding to the ground state of the complex is expressed as:

$$|\psi_G\rangle = a |\psi(A,B)\rangle + b |\psi(A^-B^+)\rangle \quad (2)$$

Using standard quantum mechanical formalism, E_G the ground state energy is written:

$$E_G = \langle \psi_G | H | \psi_G \rangle \quad (3)$$

where H is the exact Hamiltonian operator including nuclei and electrons for both molecules of the complex and with the extra condition that ψ_G be normalized, *i.e.*,

$$\langle \psi_G | \psi_G \rangle = 1 = a^2 + b^2 + 2abS \quad (4)$$

where S , the overlap integral is:

$$S = \langle \psi(A,B) | \psi(A^-B^+) \rangle \quad (5)$$

Simple substitution of Eq. 2 and 4 into Eq. 3 leads to one expression for E_G :

* Note that the contribution from the other resonance structure A^+B^- can be safely taken as negligible since the molecule A was chosen to have a much greater electron affinity than B.

$$E_G = \frac{a^2 E_0 + 2abH_{01} + b^2 E_1}{a^2 + 2abS + b^2} \quad (6)$$

where E_0 and E_1 are the energies corresponding to the pure states AB and A^-B^+ respectively, and H_{01} the mixing energy:

$$E_0 = \langle \psi(A,B) | H | \psi(A,B) \rangle \quad (7)$$

$$E_1 = \langle \psi(A^- B^+) | H | \psi(A^- B^+) \rangle \quad (8)$$

$$H_{01} = \langle \psi(A,B) | H | \psi(A^- B^+) \rangle \quad (9)$$

Now the aim is to express E_G and the parameters a and b as a function of these three energies which in principle can be “easily” calculated since they correspond to ideal pure states. Using the variational principle[3] which states that E_G must be a minimum with respect to variable a and b , Eq. 6 must satisfy the conditions:

$$\frac{\partial E_G}{\partial a} = \frac{\partial E_G}{\partial b} = 0 \quad (10)$$

which results in having to solve the following equations:

$$a(E_0 - E_G) + b(H_{01} - E_G S) = 0 \quad (11a)$$

$$a(H_{01} - E_G S) + b(E_1 - E_G) = 0 \quad (11b)$$

These two simultaneous linear equations can have solutions (other than the trivial solution $a = b = 0$) only if the associated determinant is zero, *i.e.*:

$$(E_0 - E_G)(E_1 - E_G) - (H_{01} - E_G S)^2 = 0 \quad (12)$$

At this stage, one should notice that the resonance form AB is the major contribution to the ground state of the molecular complex, which implies that $\psi_G \approx \psi(A,B)$ (*i.e.*, $|a| \gg |b|$ in Eq. 2) and $E_G \approx E_0$. Then, by substituting E_0 for E_G (except in $E_0 - E_G$) one obtains an approximate expression for E_G :

$$E_G \approx E_0 - \frac{(H_{01} - E_0 S)^2}{E_1 - E_0} \quad (13)$$

and from Eq. 11, a relationship between a and b

$$\frac{b}{a} \approx -\frac{H_{01} - E_0 S}{E_1 - E_0} \quad (14)$$

Now for the electronic excited state whose energy E^* will be approximately E_1 and which represents mostly the dative resonance form, A^-B^+ , using the same basis set as before, the corresponding wave-function is written as

$$|\psi^*\rangle = a^* |\psi(A,B)\rangle + b^* |\psi(A^- B^+)\rangle \quad (15)$$

where $\psi^* \approx \psi(A^- B^+)$ (or $|a^*| \ll |b^*|$).

The same derivation as for the ground state can be applied to the excited state and one gets readily:

$$E^* \approx E_1 + \frac{(H_{01} - E_1 S)^2}{E_1 - E_0} \quad (16)$$

and

$$\frac{a^*}{b^*} \approx \frac{H_{01} - E_1 S}{E_1 - E_0} \quad (17)$$

Comparing Eq. 14 and 17 and providing that the value of the overlap S is small, the following is true:

$$\frac{b}{a} \approx -\frac{a^*}{b^*} \quad (18)$$

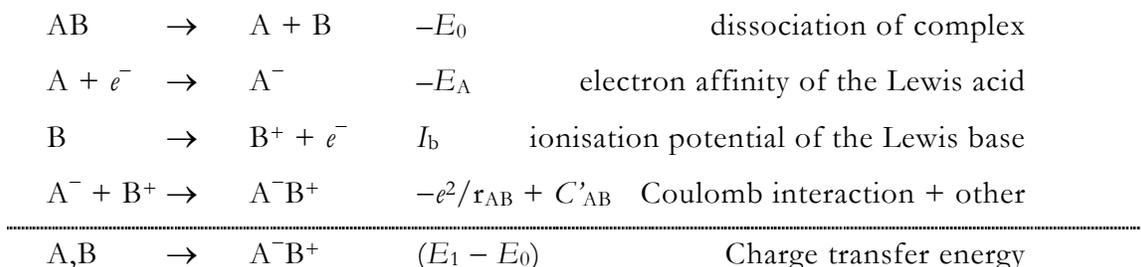
This last equation verifies that the assumptions made lead to internally consistent results; the ground state wave-function has mostly $\psi(A,B)$ character while in the excited state, the dominant term is $\psi(A^- B^+)$. In this context, it is justified to regard the transition from the ground state to the excited state as a transfer of an electron from B to A resulting in a *charge transfer spectrum*. The energy of the transition is given by (using cm^{-1} unit):

$$\tilde{\nu}_{CT} = \frac{1}{hc} (E^* - E_G) \approx \frac{1}{hc} (E_1 - E_0 + \delta) \quad (19)$$

where the small correction term δ can be explicitly written (see Eq. 13 and 16):

$$\delta = \frac{(H_{01} - E_1 S)^2 + (H_{01} - E_0 S)^2}{E_1 - E_0} \quad (20)$$

To introduce into Eq. 19 molecular parameters readily available, it is convenient to break down the charge transfer process into the following elementary steps:



Therefore:

$$(E_1 - E_0) \approx I_b - E_A - e^2/r_{AB} + C_{AB} \quad (21)$$

where $C_{AB} = C'_{AB} - E_0$ represents the difference between all additional energy terms in the dative and no-bond resonance forms. Eq. 19 and 21 allow us to relate the experimentally observable transition energy to the ionisation potential of the electron donor

$$\tilde{\nu}_{CT} \approx \frac{1}{hc}(I_b - P) \quad (22)$$

where $P = E_A + e^2/r_{AB} - C_{AB}$ is nearly constant for a series of complexes having a common acceptor since E_A is constant while the other two terms are not expected to change significantly providing there are no unusual steric effects in the series.

For condensed systems like the ones under consideration, the energy terms can be identified with enthalpy terms, which in turn, vary linearly with the standard free energy for the present set of complexes[2]. Going back to Eq. 13 and 21, and identifying ΔG^0 with E_G , one can relate ΔG^0 to I_b according to:

$$\Delta G^0 \approx M - \frac{Q}{I_b - P} \quad (23)$$

where M and Q are constants. The right-hand side of Eq. 23 represents a hyperbola which over a limited region is practically linear.

Finally, the standard free energy is related to the equilibrium constant of the complex (an experimentally accessible parameter) through the expression

$$\Delta G^0 = -RT \ln K \quad (24)$$

6. Practical considerations

The energy of the CT band due to complex formation is given by Eq. 22. The exact location of this band will depend obviously on I_b and E_A ; in particular, if the electron acceptor has a low electron affinity while the electron donor has high ionisation potential, the CT band may well be located into the UV region where it would interfere with other absorption bands making it impossible to observe. For the series of complexes used in the present experiment, the CT band shows up in the visible and is easily identified to measure the corresponding absorbance with a spectrophotometer. At the desired wavelength, Beer-Lambert's law relates the concentration to the absorbance (or optical density, OD) at wavelength λ according to:

$$OD_\lambda = \varepsilon_\lambda c l \quad (25)$$

where ε_λ is the molar extinction coefficient at the particular wavelength, c the concentration and l the path length of light through the absorbing medium. For the present solution, at the maximum of absorption in the CT band, Eq. 26 takes the form:

$$\frac{OD_{\max}}{l} = \epsilon_A [A] + \epsilon_B [B] + \epsilon_{AB} [AB] \quad (26)$$

Let $[A]_0$ and $[B]_0$ be the known nominal concentrations of A and B when the mixture is prepared. One must have:

$$[A]_0 = [A] + [AB] \quad \text{and} \quad (27)$$

$$[B]_0 = [B] + [AB] \quad (28)$$

In addition, species A, B and the CT complex AB are in equilibrium with equilibrium constant:

$$K = \frac{[AB]}{[A][B]} \quad (29)$$

in which concentrations are taken to be equal to activities.

Of all these quantities, OD_{\max} , the absorbance of the CT complex solution is measured experimentally and ϵ_A and ϵ_B can be obtained from an absorption spectrum of the pure substances[†]. An extra simplification comes from the fact that in general one of the component is in large excess – say B – such that $[B]_0 \gg [A]_0$ and therefore $[B] \approx [B]_0$. Equation 25 can be solved for $[AB]$ using this last assumption:

$$[AB] = K[A][B] \approx K([A]_0 - [AB])[B]_0 \quad (30)$$

and after re-arrangement

$$[AB] \approx \frac{K[A]_0[B]_0}{1 + K[B]_0} \quad (31)$$

Substitution of Eq. 31 into 26, neglecting ϵ_A and ϵ_B and re-arrangement leads to:

$$\frac{OD_{\max}}{l[A]_0} = \frac{\epsilon_{AB} K [B]_0}{1 + K [B]_0} \quad (32)$$

Taking the reciprocal of both sides of Eq. 32, one gets an equation of the form:

$$U = s \frac{1}{[B]_0} + i \quad (33a)$$

$$\text{where } U = \frac{l[A]_0}{OD_{\max}}, \text{ with } s = \frac{1}{\epsilon_{AB} K} \text{ and } i = \frac{1}{\epsilon_{AB}} \quad (33b)$$

[†] Actually in the present case, the various pure substances used have negligible absorption in the region of interest and one can take $\epsilon_A = \epsilon_B \approx 0$.

Eq. 33a shows that a plot of U versus $1/[B]_0$ should be linear where the slope is s and the intercept is i . Then from the definitions of s and i , the equilibrium constant and the molar extinction coefficient of the complex can be obtained:

$$K = \frac{i}{s} \quad \text{and} \quad \varepsilon_{AB} = \frac{1}{i} \quad (34)$$

7. Procedure, data collection and analysis.

The visible spectrum of complexes of benzene and methyl-substituted benzenes - toluene, *o*-xylene, mesitylene, hexamethylbenzene (HMB) - as electron donor with the same electron acceptor (TCNE) will be recorded using a HP-8453 spectrophotometer to measure the absorbance of the CT band. Then, following Eq. 33, the equilibrium constant K and ε_{AB} will be obtained for two of the methylbenzene (*the ones for which the equilibrium constant is not listed in Table 3*). Next, using Eq. 24, ΔG^0 will be calculated so that the relationship between ΔG^0 and I_b can be determined.. Relevant data are provided (see Table 3) to explore the validity of Eq. 22 and 23.

7.1. SOLUTION PREPARATION

All solutions are to be prepared in reasonably pure and water-free *n*-heptane; the HPLC grade is sufficient for the present purpose[‡].

Important!! In the following, make sure that all the volumetric flasks are dry as trace of water will invalidate the results. Rinse the flasks with some acetone, shake dry then air dry.

Table 1. Suggested amounts to prepare stock solutions of donor/acceptor complex ("B₁" solutions).

Donor ID	Volume donor	Volume sol. A	Final volume
Benzene	2 mL	8 mL	10 mL
Toluene	2 mL	8 mL	10 mL
<i>o</i> -Xylene	2 mL	8 mL	10 mL
Mesitylene	2 mL	8 mL	10 mL
HexaMethylBenzene (HMB)	20 mg	10 mL	10 mL

7.1.1 TCNE stock solution

To prepare 200 mL of a $\approx 10^{-4}$ M solution in *n*-heptane, weigh *no more than 3 mg* TCNE; use the special glass boat provided to do the weighing on the analytical balance and to transfer quantitatively this small amount into the volumetric flask. *TCNE is not very*

[‡] For very precise work, care should be taken to remove dissolved oxygen which interferes to some extent with complex formation; this can be done by bubbling dry nitrogen through all the solutions. However, for the series of complexes under study here, good results can be obtained without this extra, time-consuming manipulation.

soluble in heptane. First, pour heptane solvent into the volumetric flask only to 1/2, 3/4 full, next immerse the flask for 5 - 10 minutes in a sonicator bath (until all the TCNE has dissolved), and finally fill the flask to the mark with heptane. This is your TCNE stock solution (solution A).

7.1.2 Stock solutions of the methylbenzene/TCNE complex.

Next, five solutions (B series stock solutions), each corresponding to one of the methylbenzene/TCNE complex can be prepared as suggested in Table 1. Two 5 mL syringes are provided for volume measurements.

Please be careful to avoid cross-contaminating the compound storage bottles, and make sure that all the volumetric flasks are dry (trace of water in the solutions will invalidate the results).

Finally, for each of the two selected methyl benzene (*for this term – Spring 2013 – toluene and hexamethylbenzene*) two sets of four further dilutions (set "B₂" to "B₅" solutions) are prepared following Table 2.

In total, one should end up with thirteen donor/acceptor solutions.

Table 2. Suggested amounts necessary to prepare a series of dilutions of donor/acceptor.

Solution ID	Volume sol. B*	Volume sol. A	Final volume
Stock solution B ₁	see Table 1		10 mL
Solution B ₂	4 mL B ₁	6 mL	10 mL
Solution B ₃	2 mL B ₁	8 mL	10 mL
Solution B ₄	3 mL B ₂	7 mL	10 mL
Solution B ₅	1 mL B ₂	9 mL	10 mL

* Here, "B" stands first for the *toluene*, then for the *hexamethylbenzene* series of solutions

7.2. UV/VIS SPECTRA

All spectra will be recorded in a quartz cell with an optical path of 1 cm using the HP-8453 spectrophotometer. This instrument is driven by a PC through a proprietary interface. The instructor will demonstrate the operation of this instrument.

Once the HP software has been loaded, load the proper "Method" (File -> Load Methods -> choose CTEXPT.M in the directory C:\366). A pop-up window will come up, asking whether you want to change the light source configuration; verify that the tungsten lamp is ON and the deuterium lamp OFF; if necessary, click ON/OFF the appropriate tags, then accept the lamp configuration.

Check the scanning range (Instrument -> Setup Spectrophotometer); set a range of 300 to 750 nm, Integration time of 5 s and Interval 1 nm.

If not already set, you can alter the lamps setting (Instrument -> Lamps): select tungsten lamp ON and deuterium lamp OFF.

Under Method, click on Spectrum/Peak.

To check overall status, Instrument -> Spectrophotometer Status.

To avoid wasting valuable solution and to make sure that the cuvette is not contaminated with the previous left over solution, it is highly recommended to rinse each time the cuvette at least three times with some acetone, then air dry it. In this way, the cuvette is dry for the solution to be measured to be poured in directly without pre-rinsing and thus resulting in a minimum of waste solution.

Record first between 300 nm to 750 nm a spectrum of the pure solvent which will be used as your blank (**M**easure -> **B**lank). Next, in the same wavelength range obtain a spectrum of each of the solution B1 (**M**easure -> **S**ample), then a spectrum of each of the various donor/acceptor dilutions prepared; make sure the button "Overlay Spectra" has been activated. Save your spectra (**F**ile -> **S**ave -> **S**amples as). From each spectrum, record the λ_{\max} of the charge-transfer band and the corresponding absorbance. To clear saved spectra from display **E**dit -> **C**lear -> **S**amples. To recall saved files: **F**ile -> **L**oad -> **S**amples.

Note: be careful with the software; although the machine is supposed to find the maximum absorbance of your spectrum, for some unknown reason, it fails miserably sometimes, and reports a nonsensical maximum wavelength. Check visually if the maximum reported by the machine makes sense; if not, with the mouse pointer, point to your spectrum, and then click using the mouse **r**ight button. A black arrow pointer should appear which can be moved up and down the spectrum while the corresponding wavelength and absorbance are displayed at the bottom of the screen. In this way find the relevant maximum optical absorbance and the corresponding wavelength and record these numbers in your note book.

Obtain a printout of your spectra (**F**ile -> **P**rint -> Selected **W**indow). If the absorbance reported by the instrument is negative (which has no physical meaning), or the different spectra do not appear to have a common baseline, you will have to extract the absorbance values directly from the plot by measuring the height of the peak relative to its wings. This is illustrated in fig. 1.

Please, enter the required information into the instrument log-book before leaving the lab.

7.3. DATA ANALYSIS

For each mixture donor/acceptor, calculate the prepared concentrations $[A]_0$ and $[B]_0$. (careful with this calculation; work out first the actual number of moles of A and B which are going into the dilution). Tabulate for each complex and for each series of concentration, the λ_{\max} , the OD_{\max} and the corresponding concentrations $[A]_0$ and $[B]_0$. Convert the wavelength to cm^{-1} .

With the appropriate plot and fit, verify that Eq. 22 is satisfied (or otherwise) with the expected slope (see Table 3 for values of relevant ionisation potentials).

From the series of spectra recorded at different concentrations of the complex, obtain the formation equilibrium constant and the extinction coefficient of the CT complex following Eq. 33 and 34; perform this determination at λ_{\max} .

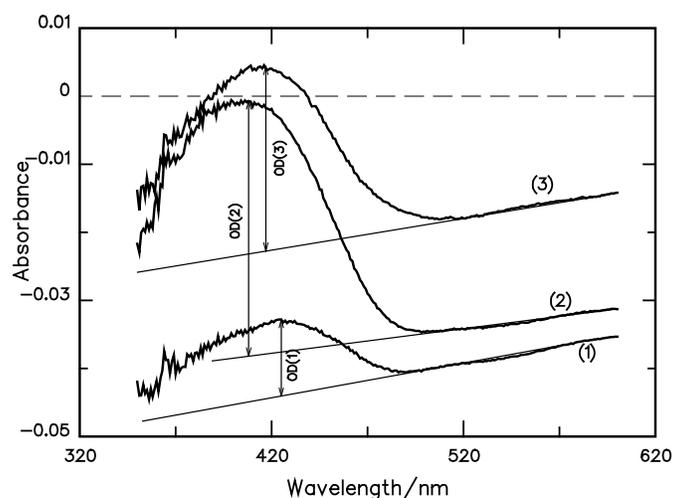


Fig. 1. Method to measure graphically the maximum absorbance relative to a reconstructed baseline when a baseline shift has occurred between successive spectra. Spectra (1), (2) and (3) were supposed to have a common baseline; the graph shows how to estimate in each case the baseline, and then to obtain the relevant absorbance, labelled OD(i) in the diagram.

Calculate ΔG^0 from the equilibrium constants obtained and check the correlation between ΔG^0 and I_b (for the equilibrium constants not measured, use the data provided in Table 3). Is the expected variation observed?

Comment on the validity of the model used to account for these data. Can you think of other systems (donor/acceptor) which would have (or could be expected to have) similar behaviour as the pair TCNE/substituted benzenes?

Table 3. Selected data for methylbenzene/TCNE complexes.

Donor ID	I_b (eV)	K (M^{-1})
Benzene	9.245	0.938
<i>Toluene</i>	8.82	-
<i>o</i> -Xylene	8.56	4.76
Mesitylene	8.40	13.6
<i>HMB</i> (<i>Hexamethylbenzene</i>)	7.85	-

8. References

- [1] R.S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).
- [2] S.P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).
- [3] W.E. Wentworth, G.W. Drake, W. Hirsch and E. Chen, *J. Chem. Ed.*, **41**, 373 (1964).
- [4] F.A. Bettelheim, *Experimental Physical Chemistry*, W.B. Saunders Co., Toronto (1971).

Chem 366W report check list

A report will not be accepted without all the items of this list checked. If a checked item is found missing in the report, the report will be automatically down-graded.

Student Name: _____

Report: Charge Transfer Complexes

Title page.

Correct title of the experiment

Student Name & student ID

Partner name (*if applicable*) _____

Date of performance of experiment

Abstract

Introduction and theory

Experimental

Changes from text description mentioned (*if applicable*)

Sample ID, ser no, stock solution ...etc recorded (*if applicable*)

Results

Results as Tables

Graphs

Size, at least ½ page

Axis labelled

Axis labels have units

Axis scales are sensible

Only significant figures

Uncertainties quoted

Raw data provided (*electronic form, if applicable*)

Calculations

Sample calculation provided

Error analysis

Sample error calculation provided

Discussion

Comments on results

Questions in text book and in manual answered

Comparison with literature value(s)

Conclusion

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