

NOTIZ

**Photoelectron Spectroscopy
and Molecular Complexes
Having Multiple Charge Transfer Bands**

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The ultra violet spectral data for molecular complexes showing multiple charge-transfer bands are compared with the photoelectron energy spectra of the free donors.

The energy separation between the first two photoelectron bands of the free donor is shown to correspond to the energy separation between the absorption maxima of the charge-transfer band for a number of complexes involving aromatic compounds as donors.

This indicates that in the cases considered the multiple charge-transfer maxima are due to transitions from two different occupied orbitals of the donor to the same vacant orbital of the acceptor.

In 1955 ORGEL published a paper in which the multiple charge-transfer bands were interpreted as due to transitions involving two occupied orbitals of the donor and the same vacant orbital of the acceptor¹.

The criterion normally used to establish that the multiple maxima are due to this phenomenon is to prove that the energy difference between the components of these bands is independent of the particular acceptor. In some cases different isomeric complexes have been postulated² to explain the charge transfer (CT) systems.

An alternative explanation of the multiple CT bands is that transitions are occurring from the last occupied orbital of the donor to two vacant orbitals in the acceptor. The multiple CT maxima of hexamethylbenzene was, for instance, interpreted on this basis³.

The photoelectron spectroscopy⁴ gives now the opportunity of testing in a direct and simple way the possibility that a given multiple CT band could be due to Orgel's hypotheses.

In the past years a number of multiple CT bands were found by different authors for various systems. Most of the frequency values of the maxima are summarized in Ref. 2.

By using the usual correlation between the ν_{\max} of the CT band and the first ionization potential (IP) of the donor⁵ it is possible to evaluate this IP. Assuming that the ν_{\max} at higher frequency are due to donation from inner valence orbitals of the donor, the same cor-

relation should also give the IP's corresponding to ionization from these penultimate orbitals.

Several correlation equations between the IP of the donor and the ν_{\max} of the CT complex are available in the literature.

Making use of the following ones:

- 1) IP (eV) = $5.21 + 1.65 \times 10^{-4} \nu_{\text{TCNE}} (\text{cm}^{-1})$
(solvent = CH_2Cl_2)⁶,
- 2) IP (eV) = $5.13 + 1.39 \times 10^{-4} \nu_{\text{CHLOR}} (\text{cm}^{-1})$
(solvent = CCl_4)⁷,
- 3) IP (eV) = $3.91 + h \nu_{\text{PMDA}} / 0.87 (\text{eV})$
(solvent = CCl_4)⁸,
- 4) $h \nu_{\text{TCNE}} (\text{eV}) = \text{IP} (\text{eV}) - 6.1 + 0.54 / \text{IP} - 6.1$
(solvent = CCl_4)⁹,
- 5) IP (eV) = $4.28 + h \nu_{\text{TCNE}} (\text{eV}) / 0.82$
(solvent = CH_3Cl)¹⁰,

the various IP's corresponding to the various ν_{\max} of a given multiple CT band were evaluated. Table 1 summarizes the energy differences between the IP's so obtained. The fifth column of the Table gives the energy differences between the first two photoelectron bands of the various donors. This value is just the difference between the IP's involving the last two occupied orbitals.

The agreement of the figures reported in the columns four and five of the Table is very good considering also the approximations involved in the evaluation of the IP's from the CT bands. This is therefore demonstrating in a quantitative way that in the cases considered here the molecular complexes involve two occupied orbitals of the donor and the same orbital of the acceptor. Few more comments are needed to better show the importance of the PES-CT data comparison.

The first photoelectron band of benzene is caused by electrons coming from the last degenerate $1e_{1g}$ orbital¹⁸. The second one falls at 11.5 eV and is therefore separated from the first by more than 2 eV. This energy difference is much too high to allow the formation of an isomeric complex involving this inner orbital; this even assuming a weak donor-acceptor interaction, since also in this case the difference in interaction energy should remain very high.

On the other hand the substituted benzenes show below the 11.5 eV band two other bands. These two bands are due to the substitution which removes the degeneracy of the last orbital of the benzene system. According to this, the separation between these two bands increases with the interaction energy of the substituent with the benzene π system. In correspondence the substituted benzenes show multiple CT bands having $\Delta\nu_{\max}$ increasing again with the interaction energy between substituent(s) and benzene π system (see Table).

In the five-membered heteroaromatic compounds the heteroatom causes a splitting of the benzene type π

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Donor	Acceptor *	Solvent	$\Delta I.P.$ (eV) CT	$\Delta I.P.$ (eV) ** PES	Ref. †
Benzene, chloro	TCNE	CH ₂ Cl ₂	0.55 ^a	0.40	16
Benzene, bromo	TCNE	CH ₂ Cl ₂	0.59 ^a	0.53	16
Benzene, 1,4-dibromo	TCNE	CH ₂ Cl ₂	0.98 ^a	0.98	16
Benzene, 1,4-dichloro	TCNE	CH ₂ Cl ₂	0.83 ^a	0.84	16
Benzene, iodo	TCNE	CH ₂ Cl ₂	0.93 ^a	0.97	16
Toluene	PMDA	CCl ₄	0.53 ^b	≈ 0.2	2
Benzene, 1,4-dimethyl	PMDA	CCl ₄	0.62 ^b	0.50	2
Benzene, 1,4-dimethyl	TCNE	CH ₂ Cl ₂	0.40 ^a	0.50	2
Benzene, methoxy	TCNE	CH ₂ Cl ₂	1.0 ^a	0.83	16
Benzene, 1-bromo-4-methoxy	TCNE	CH ₂ Cl ₂	1.42 ^a	1.16	16
Benzene, 1,4-dimethoxy	TCNE	CH ₂ Cl ₂	1.7 ^a	1.29	2
Biphenyl	TCNE	CH ₂ Cl ₂	0.94 ^a	0.80 ⁺	16
Biphenyl	CHLOR	CCl ₄	0.91 ^c	0.80 ⁺	2
Naphthalene	CHLOR	CCl ₄	0.72 ^c	0.78 ⁺⁺	2
Naphthalene	TCNE	CCl ₄	0.71 ^d	0.78 ⁺⁺	2
Fluorene	TCNE	CCl ₄	0.83 ^d	0.81 ⁺⁺⁺	2
Acenaphthene	TCNE	CCl ₄	1.06 ^d	0.93 ⁺⁺⁺	2
Phenanthrene	TCNE	CCl ₄	1.23 ^d	1.27 ⁺⁺⁺	2
Thiophene	TCNE	CH ₃ Cl	0.50 ^e	0.62 ⁺⁺⁺⁺	17
Thiophene	TCNE	CH ₂ Cl ₂	0.60 ^a	0.62 ⁺⁺⁺⁺	6
Pyrrrole	TCNE	CH ₃ Cl	0.97 ^e	0.94 ⁺⁺⁺⁺	17
Furan	TCNE	CH ₃ Cl	1.65 ^e	1.42 ⁺⁺⁺⁺	17

Table I. Comparison between the difference of the two first I.P.'s as obtained from Photoelectron Spectroscopy (PES) and Multiple Charge-Transfer Bands (CT).

* TCNE=Tetracyanoethylene;
CHLOR=Chloranyl (1,4-Benzoquinone, tetrachloro);
PMDA=Pyromellitic dianhydride (1,2,4,5-Benzene-tetracarboxylic dianhydride).
** The I.P.(PES) were taken from Ref. ¹¹ unless otherwise indicated:
⁺ Ref. ¹²; ⁺⁺ Ref. ¹³; ⁺⁺⁺ Ref. ¹⁴;
⁺⁺⁺⁺ Ref. ¹⁵.
† Number of the reference used to get the ν_{\max} value.
^{a-c} These figures were evaluated from the equations: $a=1$; $b=3$; $c=2$; $d=4$; $e=5$.

orbital. Such splitting is larger for furan because of its larger electronegativity. This trend is found also in the ν_{\max} separation of the multiple CT bands of their molecular complexes.

It is therefore evident that the comparison of the photoelectron spectra of the donor with the CT data gives very interesting information and is recommended

for obtaining a deeper insight into the charge-transfer phenomenon.

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