NOTIZ

Photoelectron Spectroscopy and Molecular Complexes Having Multiple Charge Transfer Bands

S. Pignataro and G. Aloisi

Istituto chimico „G. Ciamician“, 40126 Università di Bologna
Italy
and Istituto di Chimica Fisica, Università di Perugia
06100 Italy

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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 acceptor[1].

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 postulated[2] to explain the charge transfer (CT) systems.

An alternative explanation of the multiple CT bands is that transitions are ocurring 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 basis[3].

The photoelectron spectroscopy[4] 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 $\nu_{\max}$ of the CT band and the first ionization potential (IP) of the donor[5] it is possible to evaluate this IP. Assuming that the $\nu_{\max}$ at higher frequency are due to donation from inner valence orbitals of the donor, the same correlation should also give the IP's corresponding to ionization from these penultimate orbitals.

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

Making use of the following ones:

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

the various IP's corresponding to the various $\nu_{\max}$ 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 coments 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 $1e_{1g}$ orbital[18]. 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 degenerancy 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

Reprint requests to Prof. S. Pignataro, Istituto „G. Ciamician“, Università di Bologna, Via Selmi 2, *40126-Bologna*, Italia.

Table 1. Comparison between the difference of the two first I.P.'s as obtained from Photoelectron Spectroscopy (PES) and Multiple Charge-Transfer Bands (CT).

Donor	Acceptor *	Solvent	ΔI.P. (eV) CT	ΔI.P. (eV) ** PES	Ref.†
Benzene, chloro	TCNE	CH_2Cl_2	0.55 [a]	0.40	16
Benzene, bromo	TCNE	CH_2Cl_2	0.59 [a]	0.53	16
Benzene, 1,4-dibromo	TCNE	CH_2Cl_2	0.98 [a]	0.98	16
Benzene, 1,4-dichloro	TCNE	CH_2Cl_2	0.83 [a]	0.84	16
Benzene, iodo	TCNE	CH_2Cl_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_2Cl_2	0.40 [a]	0.50	2
Benzene, methoxy	TCNE	CH_2Cl_2	1.0 [a]	0.83	16
Benzene, 1-bromo-4-methoxy	TCNE	CH_2Cl_2	1.42 [a]	1.16	16
Benzene, 1,4-dimethoxy	TCNE	CH_2Cl_2	1.7 [a]	1.29	2
Biphenyl	TCNE	CH_2Cl_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_3Cl	0.50 [e]	0.62 [++++]	17
Thiophene	TCNE	CH_2Cl_2	0.60 [a]	0.62 [++++]	6
Pyrrole	TCNE	CH_3Cl	0.97 [e]	0.94 [++++]	17
Furan	TCNE	CH_3Cl	1.65 [e]	1.42 [++++]	17

* 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 $\nu_{\max}$ value.

a–e 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 $\nu_{\max}$ 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 recomended for obtaining a deeper insight into the charge-transfer phenomenon.

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