*Published in: Bulletin de la Classe des Sciences. Académie Royale de Belgique (1972), vol. LVIII, pp. 821-840*
*Status: Postprint (Author's version)*

# About the use of the empirical relations $h\nu_{CT}^{max} = f(I_D)$ for the interpretation of ionization potentials

by R. LOCHT, R. CAHAY, J. MOMIGNY et L. D'OR

*Institut de Chimie, Sart Tilman par 4000 Liège I, Belgium*

## Abstract

The UV absorption spectra of the charge transfer (CT) complexes formed by iodine with ethylenimine, ethylene oxide and ethylene sulfide were studied in order to interpret the first ionization potential of these organic molecules by using the empirical relationships $h\nu_{CT}^{max} = f(I_D)$. Taking into account the basical specificity of these relations, the trend of the CT data shows ethylenimine and ethylene oxide to be *n*-donors towards iodine and the first ionization potential of the same donors could be ascribed to the removal of an electron from a non-bonding orbital localized on the heteroatom. Theoretical calculations however do not support this interpretation in the case of ethylenimine.

For ethylene sulfide, the *n* and π-ionization potentials deduced from the proper empirical relations are too close to allow the ascription of the electron transfer and the first ionization potential to a π-electron or to an electron from a non-bonding orbital.

Furthermore, a re-examination has been made of some previous CT data.

## Résumé

Les spectres d'absorption dans l'ultra-violet des complexes par transfert de charge formes par l'iode d'une part et l'éthylènimine, l'oxyde d'éthylène et le sulfure d'éthylène d'autre part, ont été examinés en vue d'interpréter le premier potentiel d'ionisation de ces dernières molecules. Sur la base du caractère spécifique des relations empiriques $h\nu_{CT}^{max} = f(I_D)$, les résultats obtenus montrent que l'éthylènimine et l'oxyde d'éthylène se comportent comme des donneurs *n* vis-à-vis de l'iode et, par suite, leur premier potentiel d'ionisation doit être attribué à l'arrachement d'un électron d'une orbitale non liante localisée sur l'hétéroatome. Dans le cas de l'éthylèninime, cette interprétation n'est pas en accord avec les résultats des travaux théoriques.

Le faible écart entre la valeur des potentiels d'ionisation *n* et π , obtenus pour le sulfure d'éthylène et déduits des relations empiriques relatives aux donneurs *n* et *π,* ne permet pas d'interpréter le premier potentiel d'ionisation.

Nous avons étendu notre étude au réexamen de certaines données de la littérature relatives au même problème.

## INTRODUCTION

The photoionization efficiency curves and the photoelectron spectra of cyclopropane, ethylenimine and ethylene oxide have recently been studied [1-2].

While it is commonly accepted that the first ionization potential of cyclopropane has to be ascribed to the removal of an electron from a "pseudo π" orbital [1,3-4], conflicting interpretations, based both on theoretical and experimental work, have been given for the assignment to the first ionization potentials of ethylenimine and ethylene oxide [1-4].

The purpose of this paper is to contribute to the interpretation of the first ionization potentials of ethylenimine, ethylene oxide and ethylene sulfide by the examination of the ultraviolet absorption spectra of the charge transfer complexes formed between these compounds and iodine. This will be done by using empirical relations between the position of the maxima of the U.V. absorption band ($h\nu_{CT}^{max}$) and the ionization potential of the donor ($I_D$).

The data relative to the charge transfer spectra of furane, pyrrole and thiophene obtained by Lang [5], and those concerned with pyridine, pyrimidine and pyrazine obtained by Krishna and Chowdhury [6], will also be re-examined in the frame of this work.

## I. EXPERIMENTAL

a. *Experimental procedure.* — The spectra between 650 $m\mu$ and 200 $m\mu$ were recorded with the Carl Zeiss RPQ 20A spectrophoto-meter (double beam, double path). The solutions containing the complexes under investigation were introduced in quartz cells of 10 mm path, sealed with a teflon stopper, allowing the study of volatile compounds.

Special care was taken to prevent moisture contamination of the compounds and vessels used, in order to avoid the formation of $I_3^-$ ions characterized by intense absorption bands at 360 $m\mu$ and 290 $m\mu$ [7-8].

The investigated solutions were prepared by dilution of standard solutions made of weighed quantities of donor and iodine in dry *n*-heptane.

b. *Chemicals.* — Bisublimated iodine pro analysis purchased from Merck A. G. was preserved under dry atmosphere on phosphoric oxide.

— *n*-heptane, UV spectroscopic quality, purchased from Merck A. G. was dried on sodium.

— ethylenimine, ethylene oxide and ethylene sulfide were purchased from Fluka A. G. The commercial products were purified by distillation under vacuum and the purity of the distillate was controlled by mass spectrometry and was preserved on an adequate drying compound [9], except for ethylene oxide which was preserved in solid carbon dioxide.

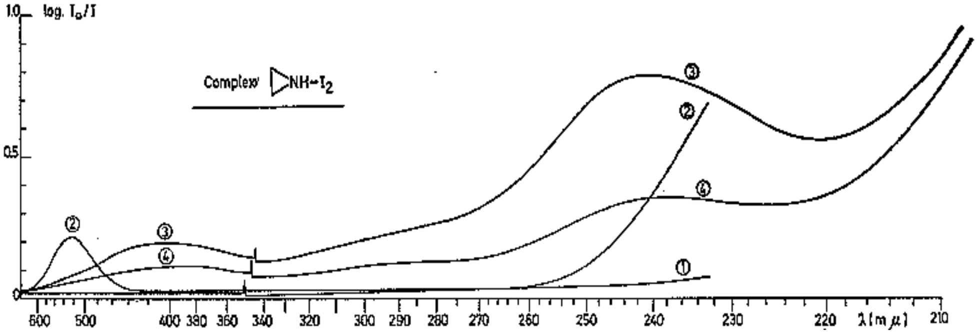
Evidence for no moisture contamination of the solutions is found in the absence of absorption bands at 360 $m\mu$ and 290 $m\mu$, due to $I_3^-$ species [7-8] (see figures 1 to 3).

## II. EXPERIMENTAL RESULTS AND DISCUSSION

### 1. RESULTS

a. *Ethylenimine.* — The absorption spectra obtained for the solutions at different concentrations of iodine and ethylenimine, and at room temperature, are shown in figure (1).

***FIG. 1.*** *— Visible-UV absorption spectrum of the CT complex ethylenimine-iodine in solution in n-heptane*



1. Solution of 3.5 x $10^{-3}$ mol. $l^{-1}$ of $C_2H_4NH$
2. Solution of 1.0 x $10^{-4}$ mol. $l^{-1}$ of $I_2$
3. Solution of 3.5 x $10^{-3}$ mol. $l^{-1}$ of $C_2H_4NH$ and 3.5 x $10^{-5}$ mol. $l^{-11}$ of $I_2$
4. Solution of 3.2 x $10^{-3}$ mol. $l^{-1}$ of $C_2H_4NH$ and 1.7 x $10^{-5}$ mol. $l^{-1}$ of $I_2$.

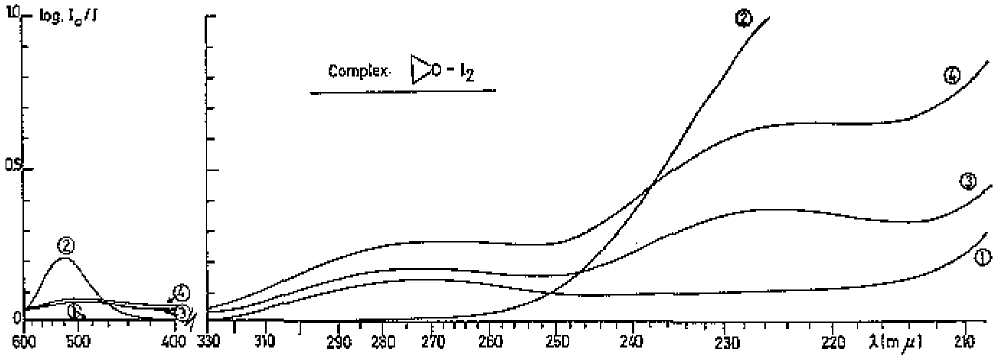
It appears an absorption band, characteristic of the charge transfer complex, showing its maximum of absorption at a mean value of $\lambda_{CT}^{max} = (239 \pm 3)$ $m\mu$, corresponding to a photon energy of $h\nu_{CT}^{max} = (5.17 \pm 0.05)$ eV. The position of the maximum of the CT absorption band is not shifted significantly by the iodine absorption band, the stability constant K for amines-iodine complexes being usually high and the initial concentration of iodine having been chosen low with respect to the donor's concentration.

The iodine's visible band is shifted by 120 *mμ* to shorter wavelength ($\lambda_{vis}^{max} \cong 400$ *mμ)* as it has been observed for amines [7].

The complex seems to be involved in a slow side reaction. The band at 239 *mμ* disappears, in place of which a band at 250 *mμ* is observed and likely characterizes a reaction product. In our experimental conditions, the velocity of this phenomenon is negligible.

b. *Ethylene oxide.* — The absorption spectrum of ethylene oxide and its charge transfer complex with iodine, taken at laboratory temperature, is given in figure (2).

***FIG. 2.** — Visible-UV absorption spectrum of the CT complex ethylene oxide-iodine in solution in n-heptane*



1. Solution of $C_2H_4O$ (*)
2. Solution of 5.4 X $10^{-5}$ mol. $l^{-1}$ of $I_2$
3. Solution of 2.0 x $10^{-5}$ mol. $l^{-1}$ of $I_2$ and $C_2H_4O$ (*)
4. Solution of 3.6 x $10^{-5}$ mol. $l^{-1}$ of $I_2$ and $C_2H_4O$ (*).

(*) Unknown concentrations of $C_2H_4O$ (see text section II, l,b).

Because of the low boiling point of ethylene oxide, it was not possible to record the spectra for well defined initial concentrations of the donor.

The spectra reveal a slight blue shift of the iodine visible absorption band and the appearance of a new absorption band at a mean value of $\lambda_{CT}^{max}$ = (225 ± 3) *mμ* corresponding to an energy of $h\nu_{CT}^{max}$ = (5.50 ± 0.05) eV. Because of the experimental difficulties, it was not possible to take into account the contribution of iodine absorption to the position of the maximum of the CT band. It has to be observed, however, that the measured $h\nu_{CT}^{max}$ is close to that obtained by Tamres and Brandon (ref. see caption of figure 4) for propylene oxide (232 *mμ).* Moreover, substracting the iodine absorption from the CT spectrum, our conclusions will not be modified significantly.

c. *Ethylene sulfide.* — Figure (3) reproduces the absorption spectra of ethylene sulfide with iodine at room temperature, showing an intense absorption band at a mean value of $\lambda_{CT}^{max}$ = (291 ± 2) *mμ* [$h\nu_{CT}^{max}$ = (4.27 ± 0.05) eV].

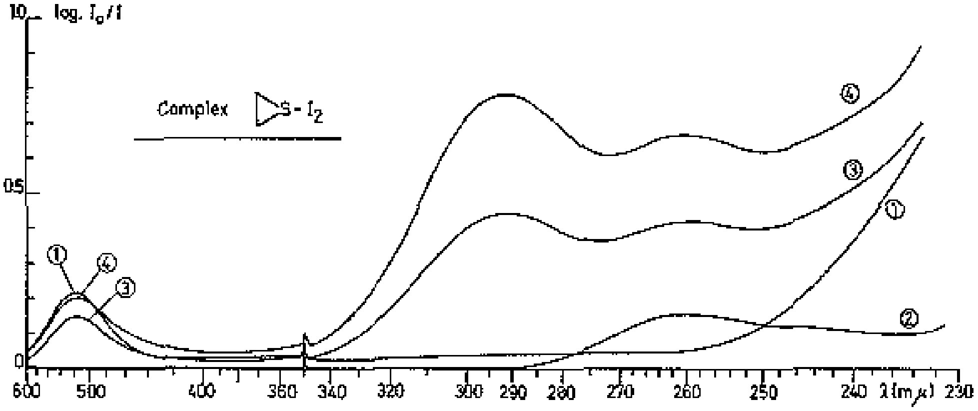
The spectrum recorded after 18 hours still shows the absorption band at 291 *mμ,* but with weakened intensity.

## 2. DISCUSSION

### A. *Preliminary discussion about the empirical relations between* $h\nu_{CT}^{max}$ *and* $I_D$

Before interpreting the experimental results, it may be useful to recall and discuss certain aspects of the relationship between the position of the maximum of the charge transfer absorption band ($h\nu_{CT}^{max}$) and the ionization potential of the donor ($I_D$) involved in the charge transfer (CT) complex.

***FIG. 3***. *— Visible-UV absorption spectrum of the CT complex ethylene sulfide-iodine in solution in n-heptane*



1. Solution of 1.1 x $10^{-5}$ mol. $l^{-l}$ of $I_2$
2. Solution of 5.0 x $10^{-3}$ mol. $l^{-l}$ of $C_2H_4S$
3. Solution of 0.9 x $10^{-5}$ mol. $l^{-l}$ of $I_2$ and 5.0 x $10^{-3}$ mol. $l^{-l}$ of $C_2H_4S$
4. Solu'ion of 1.1 x $10^{-5}$ mol. $l^{-l}$ of $I_2$ and 7.4 x $10^{-3}$ mol. $l^{-l}$ of $C_2H_4S$.

a. *Specificity of the empirical relations* $h\nu_{CT}^{max} = f(I_D)$. — On the basis of Mulliken's simplified theory of charge transfer complexes' spectra [10-11], essentially two different empirical relations between $h\nu_{CT}^{max}$ and $I_D$ have been proposed for the complexes involving iodine : (i) a linear dependence of $h\nu_{CT}^{max}$ and $I_D$ (McConnell *and al.* [13]), and (ii) a parabolic relationship (Hastings *and coll.* [12]). These studies are principally concerned with *bπ-aσ* complexes.

Briegleb [14] attempted to fit all the available CT data, concerning *bπ* as well as *nσ* donors, with only one relationship.

Yada *and his coll.* [7] for amines-iodine complexes, and Foster [15] for amines-1,3,5 triπitrobenzene complexes, first shew the specificity of the $h\nu_{CT}^{max} = f(I_D)$ relations not only for a given acceptor, but also for primary-, secondary- and tertiary-amines

This *basically specific* character of the relations

$$h\nu_{CT}^{max} = aI_D + b \qquad (1)$$

recently confirmed by Mulliken and Person [11] has been ignored by several authors [6,16] (see section II,2,0,6). For a given acceptor the values of the coefficients *a* and *b* depend upon the nature of the donor. Mulliken and Person [11] showed furthermore that the linear function (1) satisfactorily fits the experimental results concerned with donors of the same nature. This is illustrated in figure (4) where the relations $h\nu_{CT}^{max} = f(I_D)$ relative to the amines and oxygen containing compounds have been drawn taking the coefficients given by Mulliken and Person [11], For the unsaturated hydrocarbons, the coefficients given by McConnell [13] have been adopted.

b. *Selection of the ionization potentials' value.* — First, Collin [17] interpreted the deviation of his experimental results ($h\nu_{CT}^{max}$,$I_D$) from the experimental linear relation proposed by McConnell [13], as to be ascribed to the difference between the vertical ([1]) and the adia-batic ([1]) values of the ionization potential. This author concluded that $h\nu_{CT}^{max}$ has to be related with the adiabatic value of the donor's ionization potential.

Recently, Mulliken [11] establishing a general equation $h\nu_{CT}^{max} = f(1_D)$, explicitly related however the position of the maximum of the charge transfer band to the vertical ionization potential of the donor

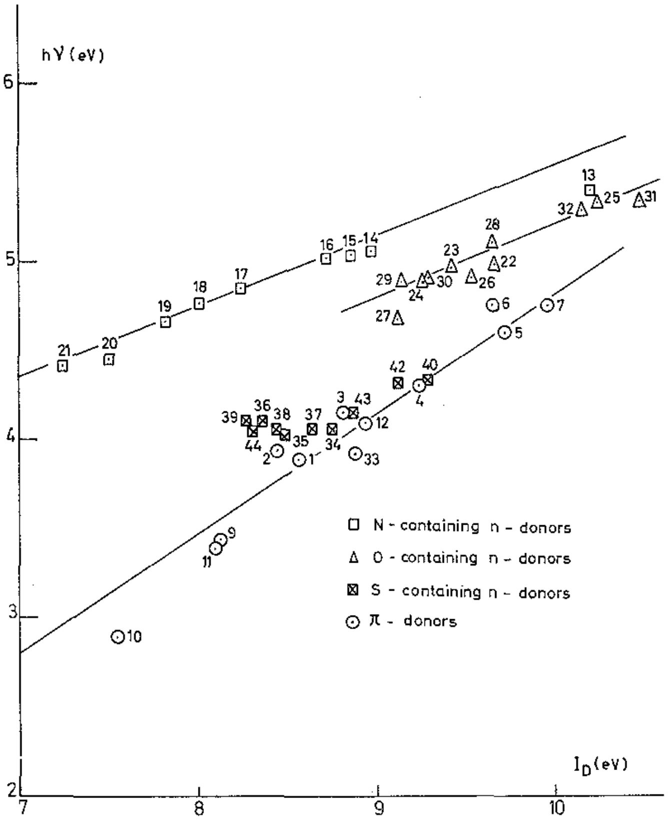
In figure (5) the ionization potential of *π* donors, determined by electron impact (vertical $I_D$) ([1]) and by

---

[1] By the comparison of the IP values obtained by electron impact and by photo-ionization, it has frequently been observed that the former method gives higher IP values than the last one. This difference has partially to be ascribed to detection sensitivity differences, to the broad energy spreading of electron beams and to the empirical methods, used in electron impact work, for the determination of IP which could correspond to the most probable transition (vertical IP values), mostly not coinciding with the lowest (or adiabatic) ionization potential.

photoionization (adiabatic ID) (1) has been plotted against the corresponding $h\nu_{CT}^{max}$ values. The electron impact values are affected by a standard error of ± 0.1 eV. It is seen from figure (5), that the validity of McConnell's relation is not significantly affected by the kind of value selected for the ionization potential of the donor.

***FIG. 4.** — $h\nu_{CT}^{max} = f(I_D)$ plots showing the basical specificity of the coefficient's values of MULLINKEN'S relation*



***Caption fig. 4.***

1. o-xylene (a.6)- 2. p-xylene (a,b) - 3. toluene (a,b) ~ 4. benzene (a,b) - 5. propene (a,b) -6. cis-dichloroethylene(a,b) - 7. trans-dichloroethylene (a,b) - 8. cyclopropene (a,b) -9. naphtalene (a,b) - 10. anthracene (a,b) - 11. phenanthrene (a,b) - 12. cyclohexene (a,b) -13. ammonia(c,b)- 14. methylamine(c,b) - 15. ethylamine (c,b) - 16. n-butylamine (c,b) - 17. dimethylamine (c,b) - 18. diethylamine (c,b) - 19. trimethylamine (c,b) - 20. triethy-lamine (c,b) - 21. tripropylamine (c,b) - 22. trimethylene oxide (d,b) - 23. tetrahydrofu-rane (d,b) - 24. tetrahydropyrane (d,b) - 25. propylene oxide (d,b) - 26. ethyl ethsr (d,b) - 27. 1,4-dioxane (e,b) - 28. acetone (e,b) - 29. cyclohexanone (e,b) - 30. cyclopenta-none(e,b) - 31. ethanol (a,b) - 32. propanol-2 (a,b) - 33. furane (f,b) - 34. thiacyclobu-tane (g,b) - 35. thiacyclopentane (g,b) - 36. thiacyclohexane (g,b) - 37. 1,4-dithiane (i,h) - 38. diethylsulfide (g,b) - 39. diethyldisulfide(i,b)-40. ethanthiol (i,b)-41. propanthiol (i,b) - 42. n-butanthiol (i,b) - 43. thiophene (f,b) - 44. di-n-propylsulfide (i,b).

(a) see ref. 14 - (b) see ref. 35 - (c) see ref. 18 - (d) M. TAMRES, M. BRANDON, J. Am. Chem. Soc. 82 (1960) 2134 - (e) D. WABSCHALL, D. A. HORTON, J. Am. Chem. Soc. 87 (1965) 3559 - (f) see ref. 5 - (g) M. TAMRES, S, SEARLES, J. Phys. Chem. 66 (1962) 1099 -(h) G. CONDE-CAPRACE, J. E. COLLIN, Org. Mass Spectrom. 2 (1969) 1277 - (i) M. GOOD, A. MAJOR, J. CHOWDHURI, S. P. MCGLYNN, J. Am. Chem. Soc. 83 (1961) 4329.

### B. *Discussion of the experimental results*

a. *Ethylenimine* ($C_2H_4NH$). — When the position of the maximum of the CT complex absorption band $h\nu_{CT}^{max}$ = (5.17 ± 0.05) eV is plotted in the $h\nu_{CT}^{max} = f(I_D)$ diagram shown in figure (6), the ionization potentials

$I_D$ = 9.1 eV and $I_D$ = 10.6 eV are evaluated for ethylenimine by using curve (1) (relative to amines) and curve (3) (relative to $\pi$-donors) respectively.

Prouveur [1] determinated 9.5 eV by photoelectron spectroscopy and 9.11 eV by photoionization. Turner [2,18] found the first ionization potential at 9.32 eV by photoelectron spectroscopy. The second ionization potential is measured at 11.45 eV [1,18].

The good agreement between the first ionization potential determined by photoionization and photoelectron spectroscopy and the I.P. inferred from the CT data, by using curve (1) in figure (6), allows to conclude that ethylenimine is *n*-donor toward iodine and consequently the first ionization potential has to be ascribed to the removal of an electron from a non bonding orbital localized on the nitrogen atom.

An argument which favours the interpretation given above is the comparable behaviour of ethylenimine on one hand and ammonia and aliphatic amines on the other hand. The last were studied recently by Hubin-Franskin [19] by electron impact, photoelectron spectro-scopy and photoionization. The main features of the experimental data for ammonia and the amines are (i) the very slow increase in the photoionization efficiency-versus photon energy curves, (ii) the similarity of the photoelectron spectra : a first well defined band precedes unresolved bands, and (iii) the similarity of the energy loss spectra of incident electrons.

Furthermore the amines show an absorption band starting at 40.000 cm$^{-1}$ (4.96eV) to 47.000 cm$^{-1}$ (5.83 eV) frequency range [20,22]. Herzberg [23] interpreted this similarity by the excitation of an electron belonging to a non-bonding orbital localized on the nitrogen atom.

Finally, table I shows that a slight variation of the first ionization potential is observed from methylamine to *n*-butylamine. The second ionization potential, showing a much larger variation, is close to those of the corresponding hydrocarbons.

Together these arguments appear to favour the interpretation of the first ionization potential of ammonia and the amines as being due to the removal of an electron from a non-bonding orbital of the nitrogen atom.

**TABLE I**

| Compound | 1st I.P. (eV) | 2nd I.P. (eV) | Compound | I.P. (eV) |
|---|---|---|---|---|
| Methylamine | 9.18 | 12. 16 | Methane | 12.99 |
| Ethylaraine | 9.19 | 11.86 | Ethane | 11.49 |
| Ethylenimine | 9.11 | 11.45 | (Ethylene) | (10.45) |
| *i*-propylamine | 8.86 | 11.23 | *i*-propane | 11.07 |
| *n*-butylamme | 8.75 | 10.75 | *n*-butane | 10.50 |

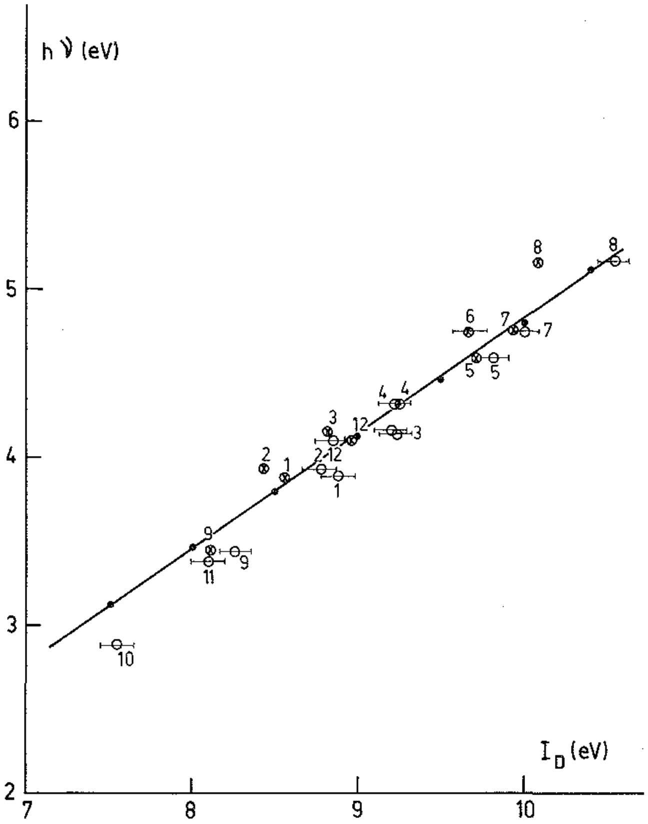
For ethylenimine a first diffuse U.V. absorption band starting at 46.000 cm$^{-1}$ is followed by a more intense band starting at 52.000 cm$^{-1}$ [2]. Moreover the photoelectron spectrum [1,2] and the photoionization efficiency curve [1] are very similar to those observed for $NH_3$ and the amines [19]. Finally, ethylenimine and ethylamine are characterized by very close ionization potentials (see table I). It has also to be underlined that the second ionization potential of ethylenimine is closer to the ionization potential of ethane than to those of ethylene.

The comparison of ethylenimine and the aliphatic amines in both the ionization phenomena and the charge transfer processes, favours the interpretation of the first ionization potential of ethylenimine by the removal of an electron of a non-bonding orbital localized on the nitrogen atom.

This conclusion however disagrees with the quantum mechanical calculations performed on ethylenimine. In agreement with Walsh [3] and Clark [4], Basch *and coll.* [2] attribute the first ionization potential to a $\pi$-ionization, the highest occupied orbital having a $\pi$-character and localized on the $C_2H_4NH$ ring.

b. *Ethylene oxide* ($C_2H_4O$). — In figure (6), the straight lines (2) and (3) represent respectively Mulliken's [11] relation $h\nu_{CT}^{max} = f(I_D)$ relative to the oxygen containing compounds and McConnell's[13] equation relative to unsaturated hydrocarbons. The ionization potentials obtained by plotting the values of the position of the maximum of the CT absorption band of the ethylene oxide-iodine complex, i.e. $h\nu_{CT}^{max} = 5.50$ eV, on both diagrams, are $(I_D)_2 = 10.7$ eV and $(I_D)_3 = 11.1$eV.

***FIG. 5.*** *— Electron impact and photoionizatiort IP of π-donors plotted against their corresponding* $h\nu_{CT}^{max}$ *values.*



For the compound's numbering, see caption of figure 4. ⊗ photoionization values of ref. 35 ○ electron-impact ("semi-log plot" method) values of ref. 35. The error bars give the standard deviation of 0.1 eV of IP values measured by electron impact. ● the straight line corresponds to the equation proposed by McConnel and al.

By photoelectron spectroscopy and by photoionization, the first two ionization potentials are measured at 10.5 eV and 11.6 eV [1,2].

The ionization potential of 10.7 eV, inferred from CT data, by using the specific relation proposed by Mulliken[11], is in good agreement with the first ionization potential measured by photoelectron spectroscopy and photoionization.

It appears to be well established that the alcohols, the etheroxides [14] and the ketones [26] are *n*-donors toward iodine.

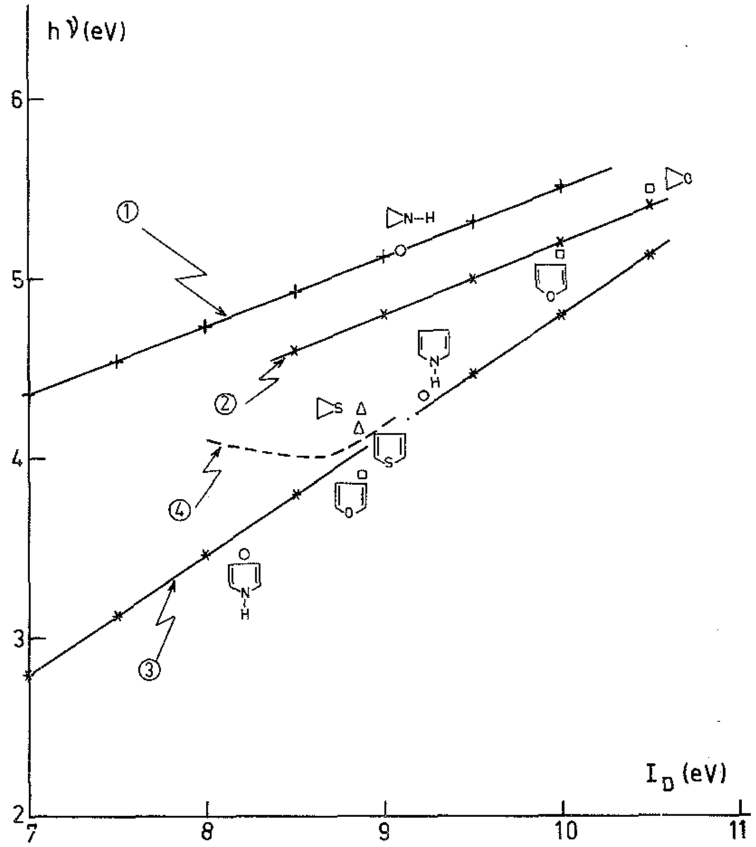
Lowrey and Watanabe [27] showed that the Rydberg series converging to the first ionization potential of ethylene oxide are very similar to those observed in dimethyl-ketone where the first ionization potential has to be ascribed to the removal of an electron from a non-bonding orbital localized on the oxygen atom.

Consequently it is likely that (i) in the charge transfer complex of ethylene oxide with iodine, an electron of the non-bonding orbital localized on oxygen is transferred to iodine, and (ii) the same electron is involved in the first ionization process.

Quantum mechanical calculations were performed on the ethylene oxide molecule. Walsh [3] and Clark

[4] have ascribed the first ionization to the removal of an electron from the highest occupied π orbital, localized on the ring system of $C_2H_4O$. But Basch *and coll.* [2] concluded that the $26_2(\pi)$ orbital of ethylene oxide is localized for 76 % on the oxygen atom and has an important non-bonding character.

***Fig. 6.*** *— Relations* $h\nu_{CT}^{max}=f(I_D)$ *for N-containing n-donors (curve 1), for O-containing n-donors (curve 2), for π-donors (curve 3), for S-containing n-donors (curve 4) (see ref. 10).*



The experimental data points ($h\nu_{CT}^{max}$, $I_D$) for $C_2H_4NH$-$C_4H_4NH$(0),for $C_2H_4O$-$C_4H_4O$ (□) and for $C_2H_4S$-$C_4H_4S$ (Δ) are shown.

c. *Ethylene sulfide* ($C_2H_4S$). — When the position of the maximum of the ethylene sulfide-iodine complex's absorption band, $h\nu_{CT}^{max}$ = 4.27 eV is plotted in the $h\nu_{CT}^{max} = f(I_D)$ diagram given in figure (6), ionization potentials at 9.1 eV and 9.2 eV are determined taking respectively the curve (4) drawn through the experimental points relative to the sulfur containing compounds and the straight line (3) related with the unsaturated hydrocarbons.

The single value available at the present time for the first ionization potential is measured by electron impact at (8.9 ± 0.2) eV [28]. Both values, i.e. 9.1 eV and 9.2 eV inferred from CT data, are in good agreement with this value. The *n*-and π-ionization potentials deduced from the proper empirical relations are too close to allow the attribution of the electron transfer and the first ionization potential to a π-electron or to an electron from a non-bonding orbital localized on the sulfur atom.

## C. *Re-examination of certain previous charge transfer data*

a. *Pyrrole, furane and thiophene. — The pyrrole-iodine* charge transfer complex is characterized by two absorption bands having their maximum successively at $h\nu_{CT}^{max}$ = 3.44 eV and $h\nu_{CT}^{max}$ = 4.35 eV, as determined by Lang [5]. Watanabe [29] measured the first ionization potential at 8.2 eV by photoionization. Recently Derrick [30] studied the pyrrole molecule by photoelectron spectroscopy. The second ionization potential of

$C_4H_4NH$ was determined at 9.2 eV.

As shown in figure (6), taking $h\nu_{CT}^{max}$ = 3.44 eV and $h\nu_{CT}^{max}$ = 4.35 eV and referring to curve (3), ionization potentials at 8.0 eV and 9.3 eV are obtained respectively .This leads to interpret the first ionization potential as well as the second one of pyrrole as due to π-ionization. This interpretation is confirmed by the quantum mechanical calculation of Clementi [31], by Watanabe's experimental work [29] and by the analysis of Rydberg series in pyrrole made by Derrick *and coll* [30].

*For the furane-iodine* complex, Lang [5] measured two maxima in the UV absorption spectrum i.e. at 317 *mµ* ($h\nu_{CT}^{max}$ = 3.91 eV) and at 240 *mµ* ($h\nu_{CT}^{max}$ =5.12eV). This author attributed these two bands to two CT transitions involving the two highest occupied π orbitals [5];

An alternative interpretation of Lang's results is to correlate the first band at 3.91 eV with the transfer of a π-electron and the second one at 5.12 eV with the transfer involving a lone-pair electron. For that purpose, the two measured values of $h\nu_{CT}^{max}$ have been plotted on the straight line (2) and (3) in figure (6). By this way two ionization potentials are determined at 8.7 eV and 9.9 eV corresponding respectively to the maxima observed at 317 *mµ* and 240 *mµ*.

These two values of the ionization potentials are in good agreement with the experimental values, i.e. 8.89 eV [29, 32] and 10.1 eV [32] determined by photoionization and photoelectron spectroscopy. Watanabe [29] ascribed the first ionization potential to π-ionization. On the basis of the study of Rydberg series in furane, Derrick [30] ascribed the first as well as the second ionization potential to the removal of a π-electron.

*In the UV absorption spectrum of the thiophene-iodine* complex, Lang [5] determined only one maximum of a band at $h\nu_{CT}^{max}$ = 4.16 *mµ*. Plotting this value in the diagram of figure (6), an ionization potential of 9.0 eV is obtained referring to curve (3) as well as to curve (4). This value is close to the experimental ionization potential of 8.86 eV [29].

Price and Walsh [33] observed Rydberg series converging to the first ionization potential ascribed to the removal of a π-electron. Herzberg [34] showed the similarity between the UV absorption spectra of benzene and thiophene. On the other hand, Watanabe [29] noticed that the first ionization potentials of thiophene and furane are very close, i.e. 8.86 eV and 8.89 eV [32] and are due to the removal of a π-electron.

By the UV absorption spectroscopy of CT complexes, however, it is not allowed, in the case of organic sulfides, to infer unambiguously the nature of the electron involved in the ionization phenomena by using the CT data.

b. *Pyridine, pyrimidine, and pyrazine.* — During the last few years, a large number of experimental work as well as theoretical calculations have been devoted to the azines, i.e. pyridine, pyrimidine and pyrazine, in order to determine the nature of the electrons implied in the ionization phenomena. In the frame of this work, it should be of interest to make a critical examination of two C.T. investigations devoted to the azines [6, 16].

These compounds are characterized by a first ionization potential around 9 eV and a second one near 10 eV (table II). One of these ionization potentials could be ascribed to the ionization of the aromatic ring and the other could be due to the removal of a lone-pair electron of the N-atom.

**TABLE II**

| **Compound** | **$I_D$(eV) ($^a$)** | **$\lambda_{max}$($^{m\mu}$) ($^a$)** | **$h\nu$(eV)** |
|---|---|---|---|
| pyridine | 9.26; 10.5 | 235 | 5.27 |
| pyrimidine | 9.36; 10.2 | 237-246 | 5.23-5.03 |
| pyrazine | 9.29; 10.4 | 242 (*) | 5.12 |

($^a$) see reference 35; ($^a$) see reference 6.
(*) this is a mean value of λ (see reference 6).

Krishna and Chowdhury [6] studied the charge transfer spectra of the complexes involving monocyclic azines and iodine, with the aim to interpret the first ionization potential of the azines.

Showing that the K values of the complexes follow the trend of the $pK_a$ values of the donors, the authors conclude that azines are n-donors towards iodine.

The trend of their ionization potential data, however, differs from that of *n*-ionization potentials inferred from CT spectra, using the relations of Mc Connell [13] and Hastings [12]. Consequently, they have ascribed the first ionization potential to π-ionization.

El-Bayoumi and Khalil [16] studied the CT spectra of acridine and phenazine using iodine and chloranil as acceptor. For both compounds the first ionization potential was attributed to the removal of a π-electron of the ring system, using the relations of Hastings [12] for the iodine complexes, and of Peticolas [37] for chloranil complexes.

Recently, Mulliken [38] ascribed the asymmetry of the CT band of the pyridine-iodine complex, to the absorption on the low frequency side of the maximum, to the π-electron transfer, the main CT band transition being due to the *n-σ* electron transfer.

Watanabe *and coll.* [29], investigating pyridine by photoionization, concluded that the first ionization potential arises from the removal of a non-bonding electron, El-Sayed *and coll.* [39-40], using the same technique, ascribed the first ionization potential of pyridine and diazines to π-ionization and the second ionization potential to the removal of a lone-pair electron. This interpretation is confirmed, for pyridine, by (i) the convergence limit of two Rydberg series, one at 9.25 eV and one at 10.25 eV [40], (ii) the observation of the same vibrational frequencies in the Rydberg series of benzene and pyridine converging to 9.25 eV [40].

Goffart *and al.* [41] determined by photoionization and photo-electron spectroscopy two close ionization potentials, at 9.10 eV and 9.56 eV, and ascribed this splitting to the removal of the degeneracy of the $e_{1g}(\pi)$ orbital of benzene. Dewar and Worley [36, 42] and Baker and Turner [32] interpreted their photoelectron spectroscopic results in the same way.

By quantum mechanical calculations, Clementi [24, 31] and Del Bene [24, 43, 44] showed the π-electron to be responsible for the first ionization potential of pyridine. Bloor and Breen [45] and Mustafa [46, 47], however, concluded that the highest orbital is a non-bonding orbital.

Except for Del Bene [43-44], the calculations show that for pyrazine the highest filled orbital is a non-bonding one [31, 45-47].

The main criticism which has to be inferred against the conclusions drawn from CT data, is the use of the relationship proposed by McConnell [13], Hastings [12] and Peticolas [37] which are valid for the π-donors only (see section II, 2, A, a).

Taking into account the specificity of the relations of Mulliken [11] (relative to *n*-donors) and of McConnell [13] (relative to π-donors) and taking the values of $h\nu_{CT}^{max}$ as given by Krishna [6] the main features of figure (7) and Table III are (i) the satisfactory agreement between the experimental and predicted positions of the maxima of CT bands, and (ii) the theoretical maxima separation decrease from pyrimidine ($\Delta\lambda = 16\ m\mu$) to pyrazine ($\Delta\lambda = 9\ m\mu$) and to pyridine ($\Delta\lambda = 5\ m\mu$). The observed separation $\Delta\lambda$ for pyrimidine is 9 $m\mu$ [6]. At $\lambda_{CT}^{max} = 242\ m\mu$, Krishna [6] observed a broad absorption band, the position of which he interpreted as being the mean position of the maximum of two unresolved bands. Our predicted "mean position" of 241 $m\mu$ ($\lambda_{CT}^{max}$ being 237 $m\mu$ and 246 $m\mu$) is in good agreement with the experimental value.

The examination of the three monocyclic azines suggests that the first ionization potentials, near 9 eV and 10 eV, have to be ascribed to *n*- and π-ionization respectively. The conclusions, however, disagree with some theoretical investigations where we notice discrepancies.

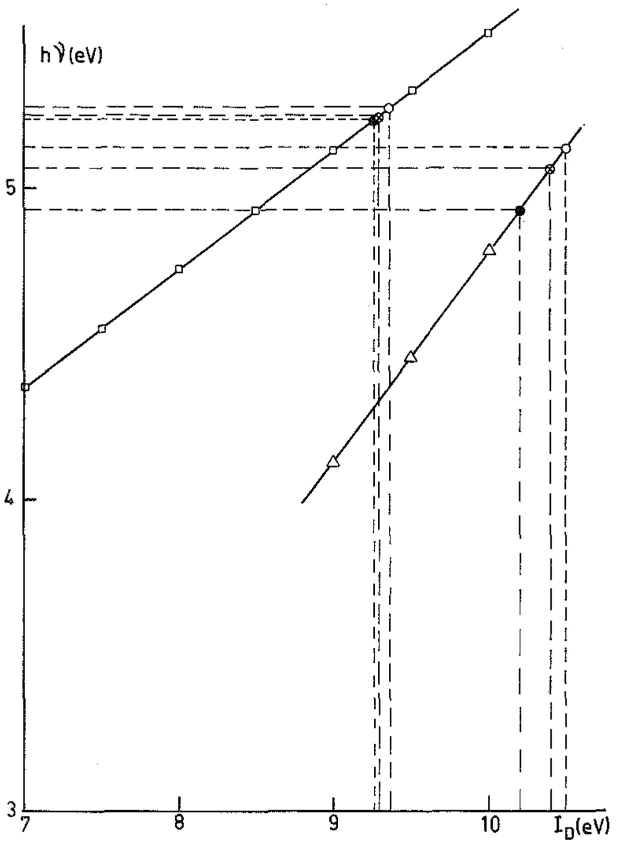
**TABLE III**

| Compounds | IP(eV) | $hv_{th}$(eV) | $\lambda_{th}$($m\mu$) | $\lambda_{exp}$($m\mu$) | IP(eV) | $h\nu_{th}$(eV | $\lambda_{th}$($m\mu$) | $\lambda_{exp}$($m\mu$) |
|---|---|---|---|---|---|---|---|---|
| pyridine | 9.26 | 5.23 | 237 | 235 | 10.5 | 5.12 | 242 | ** |
| pyrazine | 9.29 | 5.25 | 236 | 242* | 10.4 | 5.06 | 245 | 242* |
| pyrimidine | 9.36 | 5.27 | 235 | 237 | 10.2 | 4.94 | 251 | 246 |

(*) for pyrazine, 242 $m\mu$ is a mean value of $\lambda_{max}$ (see ref. 6).
(**) for pyridine, the asymmetry is observed on the low frequency side (see ref. 38).

The no longer negligible interactions between the lone-pair electrons and the delocalized π-electrons in some types of molecules could be the major difficulty in the attempts to decide about the nature of the transferred or removed electron in CT and ionization processes.

***FIG. 7.** — Determination of the magnitude of $h\nu_{CT}^{max}$ for the monoazines by using the specific relations given by reference (10) □ Nitrogen containing n-donors, Δ π-donors, ○ pyridine, ⊗ pyrazine, ● pyrimidine).*



## CONCLUSION

By the study of the UV absorption spectra of the CT complexes involving iodine as acceptor and ethylenimine, ethylene oxide and ethylene sulfide as donors, we had the opportunity to point out the basical specificity of the empirical relationships between the position of the maximum of CT band $h\nu_{CT}^{max}$ and the ionization potential of the donor $I_D$. It has also be shown that within the experimental accuracy, the validity of the empirical relations is not affected by the selection of the adiabatic or vertical value of the ionization potentials.

While the study of the UV absorption spectra of the C.T. complexes involving ethylenimine, ethylene oxide, pyrrole and furane, appears to contribute to the interpretation of the first ionization potentials of the donors, we have shown that for some molecules, the conclusions inferred from CT data have to be considered *cautiously*. This could namely be the case for monocyclic azines where the interaction strength between the lone-pair and π-electrons can no longer be neglected. Concerning the organic sulfides, with the CT data available up-to now, no conclusions can be drawn.

It would be desirable, however, that more improved experimental techniques as well as more accurate theoretical calculations could bring their contribution to the solution of the problem of the interpretation of ionization potentials.

## ACKNOWLEDGEMENT

We wish to thank Professor J. Collin for helpful discussion.

*Published in: Bulletin de la Classe des Sciences. Académie Royale de Belgique (1972), vol. LVIII, pp. 821-840*
*Status: Postprint (Author's version)*

## REFERENCES

[1] F. PROUVEUR, *Mémoire de licence,* Université de Liège (1968).

[2] H. BASCH, M. B. ROBIN, N. A. KUEBLER, C. BAKER, D. W. TURNER, *J. Chem. Phys.* 51 (1969) 52.

[3] A. D. WALSCH, *Trans. Farad. Soc.* 45 (1949) 179.

[4] D.T. CLARK, *Theor. Chun. Ada* (Berlin) 10 (1968) 111.

[5] R. P. LANG, *J. Am. Chem. Soc.* 84 (1962) 4438.

[6] V. G. KRISHNA, M. CHOWDHURY, *J. Phys. Chem.* 67 (1963) 1067.

[7] H. YADA, J. TANAKA, S. NAGAKURA, *Bull. Chem. Soc. Japan* 33 (1960) 1660.

[8] J. CANTACUZENE, *J. Chim. Phys.* (1961) 475.

[9] A. I. VOGEL, *Practical organic chemistry,* Longmans Green & Co. (London) 1957, 139-145.

[10] R. S. MULLIKEN, *J. Am. Chem. Soc.* 74 (1952) 811.

[11] R. S. MULLKEN, W. B. PERSON, *Molecular complexes,* Wiley-Intersc. New York (1969).

[12] S. H. HASTINGS, J. L. FRANKLIN, J. C. SCHILLER, F. A. MATSEN, *J. Am. Chem. Soc.* 75 (1953) 2900.

[13] H. MCCONNELL, J.S. HAM, J. R. PLATT, *J. Chem. Phys.* 21 (1953) *66.*

[14] G. BRIEGLEB, *Elektronen-Donator-Acceptor Komplexe,* Springer Verlag, Berlin (1961).

[15] R. FOSTER, R. K. MACKIE, *J. Chem. Soc.* (1962) 3843.

[16] M. A. EL-BAYOUMI, O. S. KHALIL, *J. Chem. Phys.* 47 (1967) 4863.

[17] J. E. COLLIN, *Z. Elektrochem.* 64 (1960) 936.

[18] D. W. TURNER, C. BAKER, A. D. BAKER, C. R. BRUNDLE, *Molecular photo-electron spectroscopy,* Wiley-Intersc. (London) 1970.

[19] M. J. HUBIN-FRANSKIN, *Thèse de doctorat,* Université de Liège (1971).

[20] J. E. COLLIN, *Extr. Mém. Soc. Roy. Sc. Liège,* XIV, 1 (1967).

[21] V. HENRI, W. LAZAREFF, *Comptes-Rendus* 200 (1935) 829.

[22] E. TANNENBAUM, E. M. GOFFIN, A. J. HARRISON, *J. Chem. Phys.* 21 (1953) 311.

[23] G. HERZBERG, R. KÖLSCH, *Z. Elektrochem.* 39 (1933) 572.

[24] E. CLEMEN-IT, *Chem, Rev.* 68 (1968) 341.

[25] J. DEL BENE, H. H. JAFFE, *J. Chem. Phys.* 48 (1968) 1807.

[26] J. FOSTER, M. GOLDSTEIN, *Spectrochim. Acta* 24A (1968) 807.

[27] A. LOWREY, K. WATANABE, *J. Chem. Phys.* 28 (1958) 208.

[28] E. GALLEGOS, R. W. KISER, *J. Chem. Phys. 65* (1961) 1177.

[29] K. WATANABE, T. NAKAYAMA, J. MOTTL, *J. Quant. Spectr. Rad. Transf. 2* (1962) 369.

[30] P. J. DERRICK, L. ÅSBRINK, O. EDQVIST, B. O. JONSSON, E. LINDHOLM, *Intern. J. Mass Spectwm. Ion Phys.* 6 (1971) 161, 191.

[31] E. CLEMENTI, H. CLEMENTI, D. R. DAVIS, *J. Chem. Phys.* 46 (1967) 4725.

[32] A. D. BAKER, D. W. TURNER, *Phil. Trans. Farad. Soc.* (London) A268 (1970) 131.

[33] W. C. PRICE, A. D. WALSH, *Proc. Roy. Soc.* A179 (1941) 201.

[34] G. HERZBERG, *Electronic spectra and electronic structure of polyatomic molecules,* Van Nostrand, Princeton (1969).

[35] J. L. FRANKLIN, J. G. DILLARD, H. M. ROSENSTOCK, J. T. HERRON, K. DRAXL, *Ionization potentials, appearance potentials, and heats of formation of gaseous positive ions,* NSRDS 26 (1968).

[36] S. D. WORLEY, *Chem. Rev.* 71 (1971) 295.

[37] W. L. PETICOLAS, *J. Chem. Phys.* 26 (1957) 429.

[38] R. S. MULLIKEN, *J. Am. Chem. Soc.* 91 (1969) 1237.

[39] A. J. YENCHA, M. A. EL-SAYED, *J. Chem. Phys.* 48 (1968) 3469.

[40] M. A. EL-SAYED, M. KASHA, Y. TANAKA, *J. Chem. Phys.* 34 (1961) 334.

[41] G. GOFFART, J. MOMIGNY, P. NATALIS, *Intern. Mass Spectrom. Ion Phys.* 3 (1969) 371.

[42] M. J. S. DEWAR, S. D. WORLEY, *J. Chem. Phys.* 51 (1969) 263.

[43] J. DEL BENE, H. H. JAFFE, *J. Chem. Phys.* 50 (1969) 563.

[44] J. DEL BENE, H. H. JAFFE, *J. Chem. Phys.* 48 (1968) 4050.

[45] J. E. BLOOR, D. L. BREEN, *J. Am. Chem. Soc.* 89 (1967) 6875.

[46] M. R. MUSTAFA, *Pakistan J. Sc.* 23 (1971) 53.

[47] M. R. MUSTAFA, *Mol. Phys.* 21 (1971) 359.