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M. Dell'Ariceia, A. Gargano, C. R. Natoli and A. Bianconi :
A CALCULATION OF C K-SHELL X-RAY ABSORPTION
SPECTRA OF C_2H_n ($n = 2, 4, 6$) ORIENTED MOLECULES:
CORRELATION BETWEEN POSITION OF THE MULTIPLE
SCATTERING RESONANCE IN THE CONTINUUM AND THE
C-C BOND LENGTH

A calculation of C K-shell X-Ray Absorption Spectra of C_2H_n ($n = 2, 4, 6$)
oriented molecules: correlation between position of the multiple
scattering resonance in the continuum and the C-C bond length.

M. Dell' Ariccia*, A. Gargano[†], C.R. Natoli, A. Bianconi*

Laboratori Nazionali di Frascati dell' INFN, P.O. Box 13, 00044 Frascati, Italy

ABSTRACT

In order to elucidate the connection between coordination geometry and X-Ray Absorption Near Edge Structure (XANES), we have undertaken the study of simple molecular systems (C_2H_n series for $n = 2, 4, 6$). In the framework of the multiple scattering (m.s.) theory approach to the calculation of the photoabsorption cross section, we use the condition $DetM = 0$, where M is the multiple scattering matrix equ.(2.4) of the text, to obtain an implicit relation between energy position of the only m.s. resonance in the continuum, (referred to the muffin-tin zero), and C-C bond length. We discuss the conditions under which such a relation is applicable and compare with available experimental data. Moreover, by using the fact that a similar relation for the T -matrix gives the position of the valence bound states, we derive the same relation between bond length R and energy position of the m.s. first continuum resonance E_r , now referred to a pre-edge absorption feature representing a transition to an empty valence bound state at energy E_b . Such a relation takes the simple form $(E_r - E_b) \cdot R^2 = const.$ As a consequence, the assumptions of the theory are subject to experimental verification, since all the quantities appearing in the relation are independently measurable. Generalization of the relation to clusters is given, and application to a series of Mn -oxides is discussed. In such a way a strong final state effect on the position of the rising edge in core photoabsorption spectra is displayed.

[†] On leave from ENEA, Centro Ricerche Energia Casaccia, Casella Postale 2400, Casaccia, 00100 Roma, Italy.

* Dipartimento di Fisica, Universita' di Roma " La Sapienza ", 00185 Roma, Italy.

1. INTRODUCTION

The possibility of using X-Ray Absorption Near Edge Structure (XANES) from deep core states as a tool for determining coordination geometry, symmetry of the unoccupied valence electronic states and effective charge on the absorbing atom has been suggested by several authors¹⁻⁴ and is receiving more and more attention as a complementary aid to EXAFS techniques for local structure determination.

This rising interest is due to the experimental evidence that information on coordination geometry and bonding angles, not given by EXAFS, which is only sensitive to interatomic distances, can indeed be extracted from XANES.

The importance of this correlation has been stressed by Bianconi et al in ref(3b) where the effects on the near edge absorption features induced by bond changes and distortion of the coordination geometry in the $Fe(CN)_6^{3(4)}$ clusters have been investigated.

In this paper we want to point out that XANES too is very sensitive to interatomic distances. As a matter of fact, in some cases distances can be determined to a few percent accuracy (5% or less). This aspect of XANES is particularly useful whenever EXAFS modulations are too weak to be measured, as in the case of low Z backscatterers.

For this reason we have undertaken here the study of the X-Ray Absorption Spectra in oriented simple molecules, of the type C_2H_n ($n = 2, 4, 6$). These latter seem to be suitable systems to study in this connection. In fact, due to the limited scattering power of the hydrogen atoms, these molecules can be considered as C-C diatomic molecules with variable bond length, as far as C K-shell absorption is concerned. Hence there is only one relevant distance in the system and the correlation between absorption resonances and bond length can be elucidated more efficiently. Moreover by assuming the C-C bond oriented in some way, one can study the variation of the absorption cross section with polarization direction of the incident X-ray and in this way assess its influence on the near edge structure.

The study has also been motivated by the empirical observation that a correlation exist between bond length of the first coordination shell around the photoabsorbing atom, and the peak energy of the first strong absorption maximum (continuum p-like multiple scattering (m.s.) resonance in case of K-shell absorption due to the caging effect of the first shell).

Indeed in the case of MoO_4^{--} and CrO_4^{--} , it was noted that the observed pre-edge peak to continuum peak separation increases by 13.6 % (going from 38 eV in molybdate to 44 eV in

chromate²), a variation which is in keeping with a simple minded " molecular cage " picture which would predict a peak energy increase as the inverse of the square of the bond length in going from MoO_4^{--} ($R = 1.744 \text{ \AA}$) to CrO_4^{--} ($R = 1.615 \text{ \AA}$), $\left(\frac{44}{38} \simeq \left(\frac{1.744}{1.615}\right)^2\right)$. The same relation was seen to hold in the case of C_2H_2 and C_2H_4 C K-shell absorption spectra^{3a}, where a bond length increase from $R = 1.204 \text{ \AA}$ in C_2H_2 to $R = 1.334 \text{ \AA}$ in C_2H_4 leads to a peak energy decrease (from 25.0 to 21.1 respectively) $[(1.334/1.204)^2 = 1.22 ; 25/21 = 1.19]$. Previously, in another study, Gupta⁵ had observed that for a series of strontium salts a linear correlation exists between the strontium K-edge shift (relative to a reference compound) and the distance to the first coordination shell. Again this result can be understood in terms of the differential relation $\frac{\Delta E_r}{2E_{ref}} = -\frac{\Delta R}{R_{ref}}$ obtained by differentiating the relation $E_r R^2 = const^{3a,4}$. This finding is confirmed by an analogous observation of a series of *Mn* compounds (MnO , Mn_2O_3 , MnO_2 , $KMnO_4$)⁶, where the same trend is observed, although the correlation between peak position of the main m.s. resonance and bond length of the first coordination shell is an averaged one, since the oxygen atoms around *Mn* lie at slightly different distances from the metal atom (cf. Table VI).

Clearly there must be a profound reason underlying this correlation which seems to be of such general nature.

In the course of the following sections we shall try to elucidate this connection in the framework of the multiple scattering model. This latter, in our opinion, provides the natural setting in which to frame our understanding of the final state effects in a photoabsorption process which give rise to the near edge structures.

2. THEORETICAL ASPECTS OF PHOTOABSORPTION IN THE FRAMEWORK OF THE MULTIPLE SCATTERING MODEL (MSM).

For the calculation of the molecular photoionization cross section we used an extension of the bound state molecular scattered wave $X\alpha$ method of Johnson and coworkers⁷ already used for similar calculations^{1,2} to determine the one-electron wave function for continuum states. The extension of the method, formulated by Dehmer and Dill⁸, to whose paper we shall refer for notations, is one in which the continuum wave function is matched to the proper asymptotic solution of the Coulomb scattering states. The essence of the method is the representation of

the molecular potential as a cluster of non-overlapping spherical potentials centered on the atomic sites.

The $X\alpha$ potential, with α in the range $0.7 \div 0.75$, was generated by superposition of atomic charge densities of neutral atoms and spherical averaging inside each muffin-tin sphere (Mattheis method). No self-consistent determination of the charge density was attempted. Relaxation of the photoionized atom was taken into account via the usual $Z + 1$ rule, whereas complete screening was assumed by promoting the inner shell photoelectron to the first empty outer shell state (2p in the case of Carbon).

As will be clearer from the following argumentation, a better determination of the potential was not deemed necessary to the plausibility of the arguments we want to put forward in order to correlate bond length and continuum peak resonances on one side, and assess the influence of the varying polarization direction of the incident light with respect to the molecular bond in oriented molecules on the other.

Certainly the self consistency of the charge density and consequently of the potential is necessary if one is interested either in the absolute calibration of the ionization energy or in the relative position of the peaks corresponding to transitions from inner shells to empty bound valence states or in the details of the various peak widths and intensities.

However the kind of questions we are addressing depends on the geometrical structure of the potential, i.e. by the fact that it consists of a collection of scattering centers located at the atomic sites. This is what determines the gross qualitative features of the photoabsorption spectrum whereas the details (at least in the continuum part of the spectrum) are sensitive to the actual distribution of the charge density near the atomic sites and in the interstitial region.

Indeed a calculation for N_2 continuum photoabsorption spectrum based on a not self-consistent potential along the lines discussed above (fig.4) compares very favourably with a similar calculation by Dehmer and Dill⁹ based on a self-consistent calculation of the molecular potential, apart from a rescaling of the muffin-tin constant which shifts the spectrum with respect to the ionization threshold. This result is in line with our personal experience on other cases¹, where use of the non self-consistent potential in the case of $GeCl_4$ led to essentially the same results as far as the gross features of the spectrum were concerned.

Based on these facts, we have chosen not to spend much computing time in getting self-consistent potentials, in favour of a more detailed analysis of the influence of their structural characteristics on the continuum spectral resonances. The basis of our argumentation is the form of

the photoabsorption cross section for oriented molecules in the framework of the multiple scattering model. With reference to Dill and Dehmer⁸, Siegel and Dehmer¹⁰ papers and using the same notations we have

$$\sigma(E) = 4\pi^2\alpha h\nu \sum_{\underline{L}} |D_{\underline{L}}^-(E; \vec{\epsilon})|^2 \quad (2.1)$$

where $\vec{\epsilon}$ is the polarization vector, L stands for l, m and

$$D_{\underline{L}}^-(E; \vec{\epsilon}) = \frac{[j_{l_r}, n_{l_r}]_{Ij_0}}{[j_{l_r}, f_{l_r}^j]_{Ij_0}} \sum_{L''} [(I + iK)^{-1}]_{L, L''} \frac{[f_{l''}^{III}, g_{l''}^{III}]_{III}}{[j_{l''}, g_{l''}^{III}]_{III}} \sum_{iL'} J_{L'L''}^o [M^{-1}]_{L'L''}^i (f_{L'}^j, |\vec{\epsilon} \cdot \vec{r}| \psi_{in}) \quad (2.2)$$

$$K_{LL} = \frac{-1}{[j_l, g_l^{III}]_{III}} \left(\delta_{LL} [j_l, f_l^{III}]_{III} - \frac{[f_l^{III}, g_l^{III}]_{III}}{[j_l, g_l^{III}]_{III}} \sum_{iL'} \sum_{jL''} J_{LL'}^o [M^{-1}]_{L'L''}^i J_{L''L}^j [j_l, n_l]_{III} \right) \quad (2.3)$$

$$M_{LL}^i j_L = \left[\cot g \delta_l^j - \sum_{L''} J_{LL''}^j \cot g \delta_{l''}^j J_{L''L}^o j_L \right] \delta_{ij} \delta_{LL'} + (1 - \delta_{ij}) \left[N_{LL}^i j_L - \sum_{L''} J_{L'L''}^o \cot g \delta_{l''}^j j_{L''}^j \right] \quad (2.4)$$

In the above formulae f_l^{III}, g_l^{III} are the solutions of the Schrodinger equation in the outer sphere region III, with Coulombic plus short range potential, behaving asymptotically, for $r \mapsto \infty$, as

$$\begin{aligned} f_l^{III}(kr) &\mapsto (\pi k)^{-1/2} \frac{1}{r} \sin(kr - \frac{1}{2}l\pi + \omega_c) \\ g_l^{III}(kr) &\mapsto (\pi k)^{-1/2} \frac{1}{r} \cos(kr - \frac{1}{2}l\pi + \omega_c) \end{aligned} \quad (2.5)$$

$$\omega_c = \frac{Z}{k} \ln(2kr) + \arg \Gamma[l + 1 - i\frac{Z}{k}] \quad (Z = 1)$$

$k = E^{1/2} = [h\nu - I]^{1/2}$ is the photoelectron wave-number, I being the ionization threshold and $h\nu$ the incident photon energy, $f_l^j(r_j)$ is the solution of the Sch. eq. inside the j -th atomic sphere, $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neuman functions respectively, ($x \equiv \kappa r$ where $\kappa = [E - \bar{V}]^{1/2}$, \bar{V} being the muffin-tin constant), $[f, g]_{Ij}$ and $[f, g]_{III}$ denote the Wronskian $f \frac{dg}{dr} - g \frac{df}{dr}$ evaluated at the boundary of the j -th muffin-tin sphere or the outer sphere respectively, $J_{LL'}^i$ and $N_{LL'}^i$ are the structure factors given by

$$\begin{bmatrix} J_{LL'}^i \\ N_{LL'}^i \end{bmatrix} = \sum_{\bar{L}} i^{\bar{l}+l'-l} (-1)^m [4\pi(2\bar{l}+1)(2l'+1)(2l+1)]^{1/2} \begin{pmatrix} \bar{l} & l' & l \\ o & o & o \end{pmatrix} \begin{pmatrix} \bar{l} & l' & l \\ \bar{m} & m' & -m \end{pmatrix} \begin{bmatrix} j_l(\kappa R_{ij}) \\ n_{\bar{l}}(\kappa R_{ij}) \end{bmatrix} Y_{\bar{L}}(\hat{R}_{ij}) \quad (2.6)$$

$\cot g\delta_l^i$ and $\cot g\delta_l^o$ are respectively the cotangent of the phase shifts for the potential inside the j -th muffin-tin spheres and outside the outer sphere, given by

$$\cot g\delta_l^i = \frac{[n_l, f_l^i]_{I_j}}{[j_l, f_l^i]_{I_j}} \quad \cot g\delta_l^o = \frac{[n_l, g_l^{III}]_{III}}{[j_l, g_l^{III}]_{III}} \quad (2.7)$$

Finally, j^o is the site of the photoionized atom, whereas o as a site denotes the center of the outer sphere, L_f is the l, m of the final state selected by the dipole selection rule according to the symmetry properties of the initial state $\psi_{in} = \Phi_l(r)Y_{lm}(\hat{r})$.

The above form of the cross section given by (2.1), (2.2), (2.3) and (2.4) has been obtained through a formal solution of the multiple scattering equations as given in ref.(8) eq.(16) and (17), by solving first for $A_{L'}^{II'o}$, the component amplitude of the wave function in the interstitial region referring to the outer sphere, in the set of equ.s (17) and substituting in the set of equ.s (16). A detailed derivation and a thorough discussion of these equations will be given elsewhere. For our purposes we only notice⁴ that a sufficient condition for the occurrence of a continuum resonance is that an eigenphase of the K -matrix goes rapidly through $\pi/2$, quite similarly to the case of scattering from a spherically symmetric potential. This means that at a resonance, $DetK \mapsto \infty$ and consequently, since from equ. (2.3) $K \simeq M^{-1}$,

$$DetM = 0 \quad (2.8)$$

This condition defines an implicit relation of the type

$$\mathcal{F}[\kappa_r R_{ij}, \hat{R}_{ij}, \cot g\delta_l^i(E_r)] = 0 \quad (2.9)$$

between the reduced wave vector of the resonance $\kappa_r = [E_r - \bar{V}]^{1/2}$ and the relative position $\hat{R}_{ij} = \hat{R}_i - \hat{R}_j$ of the various atomic scatterers in the molecule, with phase shifts $\delta_l^i(E)$.

A very simple application of equ. (2.9) occurs either in (effectively) diatomic molecules (e.g. C_2H_n group) or in atomic clusters where the main m.s. resonance is due to the first coordination shell, at distance R from the photoabsorbing atom.

In such a case, equ. (2.9) reduces to

$$\mathcal{F}[\kappa_r R, \cot \delta_j^i(E_r)] = 0 \quad (2.10)$$

A further simplification is achieved if we suppose that the atomic phase shifts $\delta_j^i(E)$ are smooth functions of E , so that $\frac{1}{R} \frac{d\delta}{dE} \ll 1$ (this is in practice always true if one is away from the energy region where atomic resonances are located, which is the bound valence region for the cases under consideration).

Moreover if we are to compare geometrically different atomic clusters with the same atomic constituents we must further assume that the phase shifts are "transferable", in the sense that they are functions only of the atomic species and rather insensitive to the environment. This is the most delicate assumption in that in the near edge region the phase shifts can be sensitive to the valence charge distribution which itself depends on the chemical environment. We shall defer discussion on this point to the next section.

Under the above assumption, equ. (2.10) reduces to

$$\mathcal{F}(\kappa_r R) = 0 \quad \text{or} \quad \kappa_r R = \text{const} \quad (2.11)$$

This in fact the relation empirically observed in the cases mentioned in the introduction, provided transferability of the phase shifts and smoothness in their energy dependence are reasonably well satisfied assumptions. The extent to which equ. (2.11) is obeyed depends critically on these latter, as well as in general on the applicability of the multiple scattering theory to the description of the photoelectron final state wave function.

A relation of this kind was to be expected in the framework of the multiple scattering model under the above assumptions, in the sense that the resonance condition in such a case reduces to a boundary condition effect. In fact the wave function is required to be either zero or to have cusps at the singularities of the various atomic potentials, so that one can loosely speak of a "cage effect" giving rise to the resonant behaviour.

How sharp the resonance is determined on how steeply $\text{Det}M(E)$ crosses zero at the resonance energy E_r .

Equ. (2.11), when valid, implies that, if for two different systems we know bond length and resonance energies measured from the ionization threshold, one must have

$$(E_{r_1} - \bar{V}_1)R_1^2 = (E_{r_2} - \bar{V}_2)R_2^2 \quad (2.12)$$

which can be used for bond length determination provided we know \bar{V}_1 and \bar{V}_2 , the respective muffin-tin constants. A way to determine these constants from experimental data is described in ref.(11), although an 'a priori' estimate can be obtained by imposing that the WKB phase be approximately equal to

$$\int_{\vec{r}}^{\vec{r}'} [E - V(\vec{r})]^{\frac{1}{2}} dr \simeq [E - \bar{V}]^{1/2} |\vec{r} - \vec{r}'| \quad (2.13)$$

for all straight paths in the interstitial region along the direction of propagation of the photoelectronic wave.

Obviously, in the most general case, it is the condition (2.9) that must be used to correlate resonance position, geometry and type of phase shifts. However it turns out so exceedingly complicated that the problem of correlating absorption cross section with structure is better tackled by actually computing the cross section under some reasonable structural assumption and then compare with the experimental observations.

What we want to point out here, is that some simple correlations, as those illustrated in the introduction, between structure and absorption spectrum have a sound theoretical justification that can be used, with " caveat ", to extract useful informations.

Finally, before finishing this section, we want to illustrate the dependence of the resonance condition on the polarization of the incident radiation.

From the type of arguments given above, it would seem that once the condition (2.8) is satisfied, one should observe a resonating behaviour irrespective of the polarization of the incident light. This is not so, as deeper insight into the expression for the absorption cross section will reveal. Again, by choosing the simple case of a diatomic molecule, one can bring out the relevant features of the problem, free from inessential complications.

The key to the understanding is the use of symmetrized basis functions transforming according to irreducible representations of the molecular point group (in our case the $C_{\infty v}$ group, since in the final state the two atoms are not equivalent even if they were in the initial ground state). In such basis the K -matrix is block diagonal, in the sense that off diagonal elements between basis functions belonging to different irreducible representations are zero. So is M , the scattering matrix. In the case of the $C_{\infty v}$ group, Y_{l_0} belongs to the unidimensional representation A_1 , whereas Y_{lm} ($m \neq 0$) belongs to the bidimensional E_m representation with partner function Y_{l-m} . Similarly the z -component of the dipole operator belongs to the A_1 repr. whereas the x - y components are

partner functions in the $E_1 \equiv \Pi$ representation.

In such a way the polarization of the incident light selects, through the Wigner-Eckart theorem, which diagonal sub-block of the entire K -matrix or M -matrix is effectively used in the expression for the absorption cross section, the rest being factored out. So it may well happen that the condition $DetM = 0$ is realized only for one or more of the sub-blocks but not for all. This means that those polarization which select these particular sub-blocks present a resonance structure in the spectrum, which may be completely absent for other polarizations. This is exactly what happens for the photoabsorption spectra of polarized light from oriented molecules with cylindrical symmetry (e.g diatomic molecules, O_2 , N_2 , CO) : for incident polarization along the bond (z -polarization) the absorption spectrum presents a strong resonance feature (the well known $l = 3$ resonance), whereas for polarization orthogonal to the bond the spectrum is featureless¹⁴. We shall illustrate these results in a little more detail in the next section, where we shall discuss also the case of non cylindrical symmetry, like C_2H_4 .

It is clear however that for any cluster and any point group we can apply the same arguments as above. Use of the properly symmetrized basis functions transforming according to the symmetry group of the cluster in the final state, beside allowing for a dimensional reduction of the secular matrix M , selects a particular sub-block of the K -matrix which is pertinent to the particular incident polarization chosen for the experiment. A complete account of the symmetrized version of the continuum multiple scattering equations that we use is given in ref. (2) to which the interested reader is referred for details.

Next section will be devoted to presenting the experimental data and to the discussion of the computed spectra in the light of the considerations developed above.

3. COMPUTED VERSUS EXPERIMENTAL SPECTRA FOR DIATOMIC MOLECULES (N_2) AND FOR THE SERIES C_2H_n ($n = 2, 4, 6$).

Core electron excitation spectra of gas-phase molecules have been studied for many years by means of various experimental techniques ranging from electron loss to bremsstrahlung and synchrotron radiation spectroscopy. In most cases resonance structures, of varying energy position, width and intensity are observed below the K 1s ionization threshold. The most pronounced of

them fall within a Ryd or so below this latter and are due to transitions to partially filled molecular orbitals or to unfilled orbitals which are pulled below the vacuum level by the Coulomb interaction with the created core hole. Above threshold other much broader resonances are typically observed. These are continuum resonances better known as 'shape resonances' in that molecules with the same geometrical arrangement of the constituent atoms show similar spectral features in the near edge region². This is also the general outlook presented by the absorption spectra of molecules of the C_2H_n type with $n = 2, 4, 6$ shown in fig.1.

The XANES of C_2H_2 and C_2H_4 were obtained by Bianconi et al.¹² by transmission measurement as a function of gas pressure using monochromatized Synchrotron radiation emitted by the storage ring SPEAR. For this purpose the 2-m grazing incidence monochromator ("grasshopper") on the 4^o line at the Stanford Synchrotron Radiation Laboratory was used. For more details regarding the experimental method the reader is referred to ref.(13) where similar measurements were taken for N_2 and N_2O in the gas phase, from where we reproduce the N_2 absorption spectrum (fig.2). Also shown in fig.3 are the K-XANES of N_2 oriented molecule on Ni ¹⁴. The XANES of C_2H_6 in fig.1 are taken from ref.(12b).

As is generally the case for diatomic molecules⁹ there is only one broad continuum resonance above the ionization threshold (figs.1,2). Within 1 Ryd of this latter and from the high energy side weaker structures are observable, superimposed to the broad continuum feature in the case of C_2H_2 , C_2H_4 . As noticed in other similar cases² these structures correspond to double electron transitions (shake up transitions), in which, concomitant to the ionization process, another electron is promoted from an occupied valence orbital to an empty molecular orbital of the same symmetry type. We shall not further pursue this aspect of the absorption spectra since we are mainly interested in the broad continuum feature.

This type of resonance, or "shape resonance" was first explained by Dehmer and Dill⁹ for diatomic molecules as a relative increase, around a particular energy, in the amplitude of the final state continuum wave function of σ symmetry near the photoionized atom in the molecule. The increase was ascribed to the caging effect of the centrifugal barrier in the outer sphere for an $l = 3$ partial incoming wave referred to the center of the molecule, taken midway between the two atomic sites, coupled through the molecular field to the $l = 1$ wave of the photoelectron (for K-shell absorption) around the site of the photoionized atom. Before fully analyzing the validity of this interpretation, we present the results of our calculations for oriented N_2 and C_2H_n ($n = 2, 4, 6$) molecules in fig.s 4,5,6,7. For each molecule, we have taken the z axis along the main bond ($N - N$

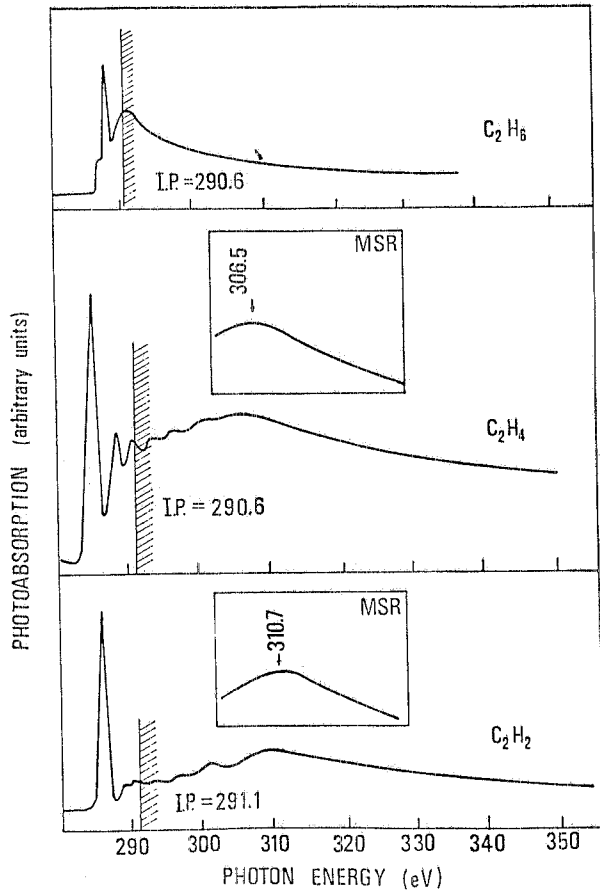


Fig. 1 - Experimental absorption spectra for C_2H_2 , C_2H_4 (Ref.12a) and C_2H_6 (Ref.12b). This latter spectrum is obtained by electron energy loss spectroscopy.

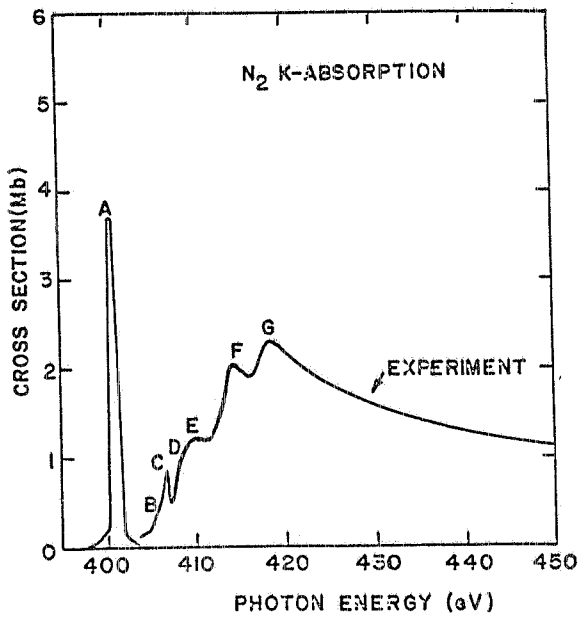


Fig. 2 - Experimental absorption spectrum for N_2 in the gas phase (from Ref.13).

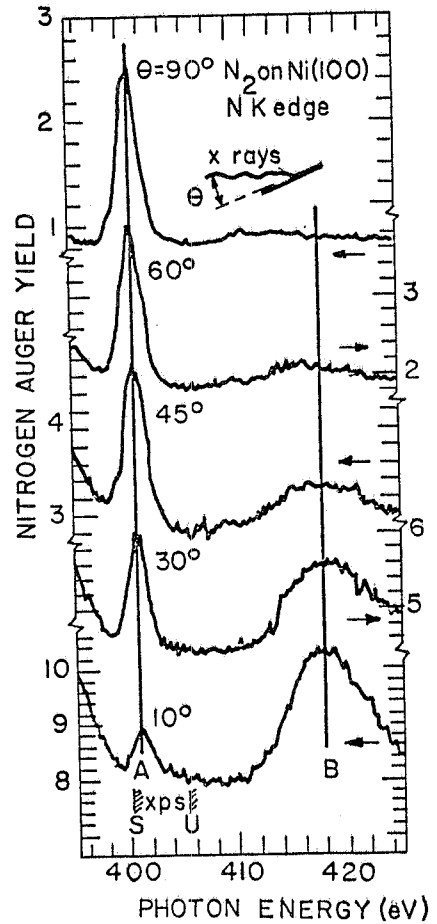


Fig. 3 - Experimental absorption spectrum for N_2 chemisorbed on Ni (from Ref. 14).

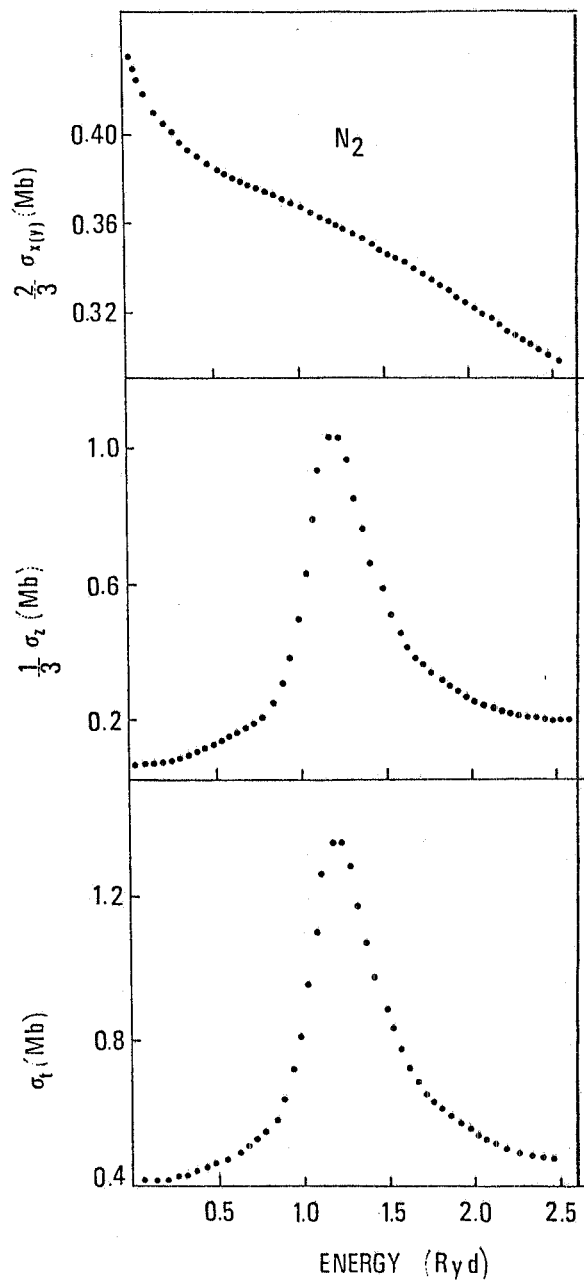


Fig. 4 - Calculated photoabsorption spectra for oriented N_2 molecule for longitudinal polarization $\sigma_z(E)$, transverse polarization $\sigma_x(E) = \sigma_y(E)$ and for random orientation $\sigma_{tot} = \frac{1}{3}(\sigma_z + \sigma_z + \sigma_y)$.

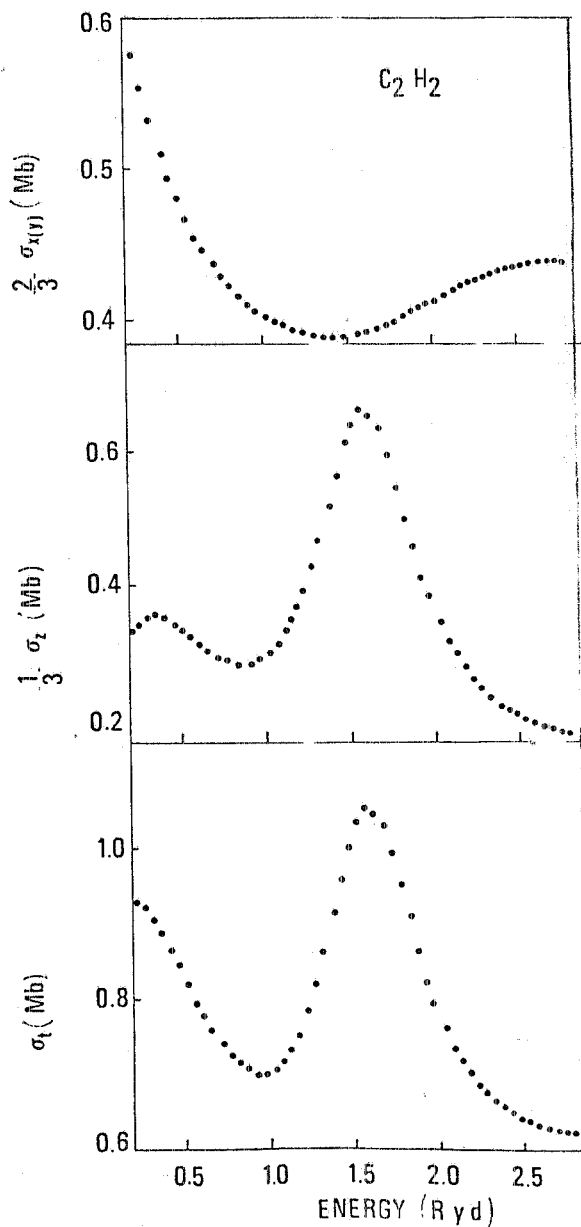


Fig. 5 - Same as Fig. 4 for C_2H_2 molecule.

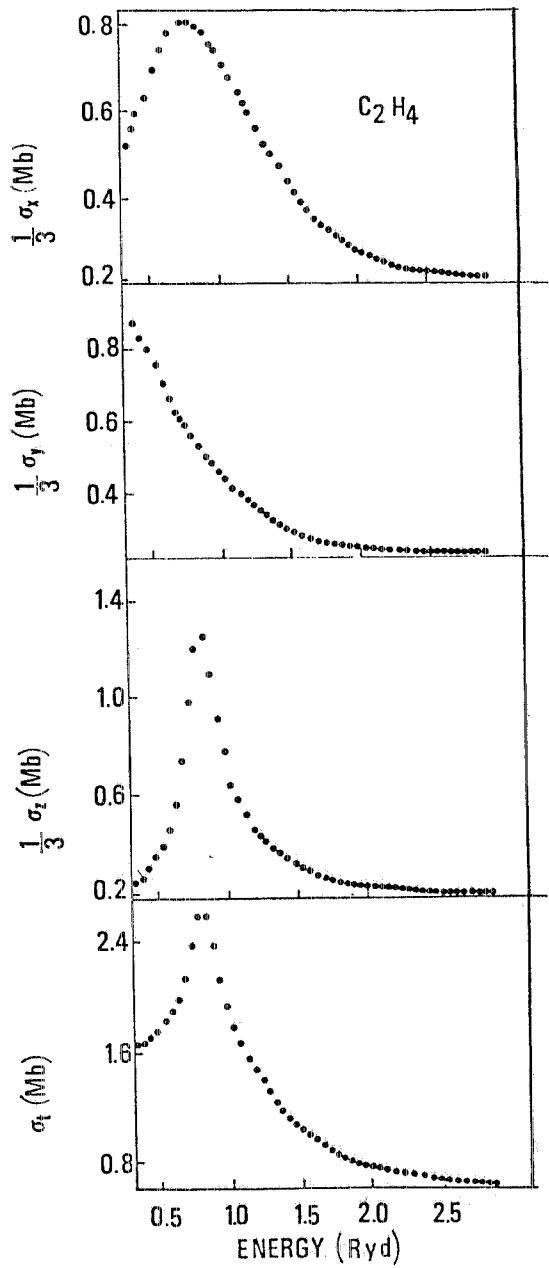


Fig. 6 - Same as Fig. 4 for C_2H_4 planar molecule. In this case $\sigma_z \neq \sigma_y$.

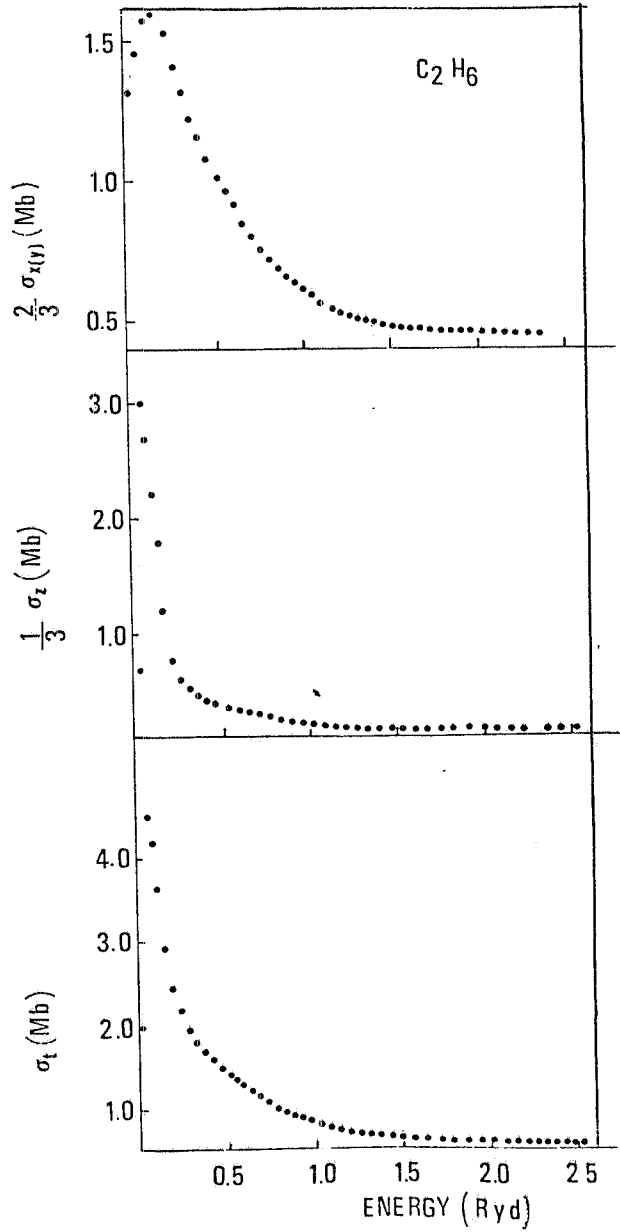


Fig. 7 - Same as Fig. 4 for C_2H_6 molecule.

or $C - C$) and in the case of the planar C_2H_4 the x axis was assumed to lie in the plane of the molecule. In each case we have chosen to plot the continuum cross sections

$$\sigma_{\alpha}(E) = 4\pi^2\alpha h\nu \sum_{\underline{L}} |D_{\underline{L}}^{-}(E; \hat{\epsilon} \parallel \hat{\alpha})|^2 \quad (3.1)$$

for $\hat{\alpha} = \hat{x}, \hat{y}, \hat{z}$ as well as the sum

$$\sigma_{tot}^{unp}(E) = \frac{1}{3} \sum_{\alpha}^{\underline{x,y,z}} \sigma_{\alpha}(E) \quad (3.2)$$

corresponding to the total cross section for either unpolarized light and fixed molecular orientation or polarized incident light and random molecular orientation.

The cross section for incident light polarized along a direction with polar angles θ, ϕ with respect to the molecular frame of reference is given by

$$\sigma(E; \theta, \phi) = 4\pi^2\alpha h\nu \sum_{\underline{L}} |D_{\underline{L}}^{-}(\hat{\epsilon} \parallel \hat{x})\sin\theta\cos\phi + D_{\underline{L}}^{-}(\hat{\epsilon} \parallel \hat{y})\sin\theta\sin\phi + D_{\underline{L}}^{-}(\hat{\epsilon} \parallel \hat{z})\cos\theta|^2 \quad (3.3)$$

so that the knowledge of the σ_{α} 's sufficient for the determination of the cross section in the most general case. As it should be

$$\frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} d\phi \sin\theta d\theta \sigma(E; \theta, \phi) = \frac{1}{3} \sum_{\alpha}^{\underline{x,y,z}} \sigma_{\alpha}(E) = \sigma_{tot}^{unp}(E) \quad (3.4)$$

Few comments are in order regarding these spectra. First of all the ionization threshold $E_t = h\nu - I = 0$ is determined with reference to a final state potential which is not self-consistently determined. Hence the energy separation of the various continuum resonances from ionization threshold cannot to be expected to agree with experiments. To our experience (see also ref.1) the effect of self consistency in multiple scattering molecular calculations is a more or less rigid shift of the whole spectrum toward lower energies, consequent to a redefinition of the muffin-tin constant with respect to the zero of the potential at infinity.

Despite this the computed spectra clearly show all the essential features of their experimental counterpart. All molecules show the by now well known $l = 3$ resonance due to transition of a K shell electron to a continuum state of σ -symmetry (A_1 rep.) when the polarization of the incident radiation is parallel to the axis of the molecule (z polarization).

Transitions to states of π symmetry (E_1 rep.) when incident light is polarized perpendicular to the bond (x, y polarization), show no resonant behaviour in the C_2H_2 molecule ($C_{\infty v}$ final state group) as anticipated in section 7. However in both C_2H_4 (C_{2v} f.s. group) and C_2H_6 (C_{3v} f.s. group) spectra in trasverse polarization (x pol. in C_2H_4 , B_1 rep.; x, y pol.s in C_2H_6 , E rep.) it is possible to observe a resonance of $l = 2$ character at around the same energy as for z polarization. The reason for this is that the presence of the hydrogen atoms, despite their weak scattering power, cannot be entirely neglected. This fact is born out by observation of the z polarization spectrum in C_2H_2 . Indeed in this polarization, for the purely diatomic molecule N_2 there is only one definite $l = 3$ resonance, due to caging of the wave between the two N atoms, whereas an additional resonance is present at lower energy in C_2H_2 , due to a shallow trapping of the wave along the $C - H$ bond. K -matrix partial wave decomposition of this resonance (in practice examination of the relative weight of the $|D_{\underline{L}}^-|^2$ components building up the cross section in (3.1) at the resonant energy) shows that it is due for a 40% to an $l = 0$ component, another 40% to an $l = 2$ component, the rest being due to an $l = 1$ component. This is to be compared with the $l = 3$ resonance due mainly for a 70% to the $l = 3$ component, the rest being more or less equally divided between the $l = 0, 1, 5$ components. For the N_2 molecule, instead, the resonance is made up for 90% by the $l = 3$ component, the remaining 10% being equally shared between the $l = 0, 1, 2$ components. In the case of C_2H_4 , a similar breakdown shows a 75% contribution of the $l = 3$ component, supplemented by a 10% contribution of the $l = 0$ and $l = 2$ components (plus rest) for the z resonance, whereas the x resonance is made up substantially of a 60% $l = 2$ and a 40% $l = 1$ contribution. For C_2H_6 , in xy polarization the $l = 1$ component contributes 30%, the $l = 2$, 50%, the $l = 3$, 20%; in z polarization the $l = 3$ component contributes 78% supplemented by an equally shared 22% contribution from the $l = 0, 1, 2$ components.

Notice that in all cases the presence of the extra resonances having orbital character other than $l = 3$ disappear as a spectral feature when the total cross section (3.2) for random molecular oriented is computed. This is so in the case of C_2H_4 and C_2H_6 because the resonance for transverse (x, y) polarization is superimposed to the $l = 3$ resonance for longitudinal (z) polarization, whereas in the case of C_2H_2 the non resonating contribution of the transverse polarization to the total cross section swamps the $l = 2$ resonance present in the longitudinal polarization. We believe, however, that the effect of the side atoms (in this case H) on the spectrum of a substantially diatomic molecule ($C - C$) is a real one and can be verified experimentally.

A hint in this direction can be found in K-shell absorption spectra from oriented diatomic

molecules (N_2 , NO , CO) chemisorbed on Ni , by polarized incident radiation¹⁴. The authors observe in the continuum part of the spectrum a second broad much less intense resonance (called Y) either lower (CO) or superimposed (N_2 , NO) onto the σ $l = 3$ strong resonance (called B), whose polarization dependence is very weak. They have no precise explanation for this extra intensity and attribute its presence to "other final state channels involving multielectron excitations". While this is not an unreasonable assumption, in our opinion this intensity might be due to the presence of the surface atoms of the substrate (Ni) on which the molecules are chemisorbed. This is also in keeping with the finding that no such intensity is observed in the O K-shell spectra of CO and NO , chemisorbed in Ni , implicitly suggesting that the two molecules stick on the substrate with the oxygen further away from the surface.

This interpretation needs further study and investigation, but, if confirmed, would yield a simple way to discriminate which atom lies near to the surface.

(In this connection it is useful to note that in fig.s 4,5,6,7 the cross section σ_α ($\alpha = x, y, z$) for oriented molecules and polarized incident light have been reduced by a factor 1/3. Hence resonant behaviour is much more dramatic for oriented molecules than for gas phase, as it is apparent from ref. 14. This fact makes it possible to detect resonant intensity in the oriented case more easily than it would be otherwise possible in the gas phase).

Table I gives a summary of the various parameters used in the calculation of the photoabsorption cross sections for the molecules in question, whereas Table II gives the position E_r of the $l = 3$ resonance for z polarization relative to the ionization level (vacuum level) and to the muffin-tin level respectively, the value of the centrifugal potential $\frac{l(l+1)}{R_{C-C}^2}$ for incoming $l = 3$ wave [$l(l+1) = 12$] at the radius R_{C-C} , the average height of the centrifugal barrier at the same R position, $\frac{l(l+1)}{R_{C-C}^2} + \bar{V}$, and the products $(E_r - \bar{V})R_{C-C}^2$.

Throughout energies are measured in Rydberg and lengths in atomic units.

Moreover fig.8 contains information about the actual muffin-tin potential used in the calculations for N_2 , C_2H_2 , C_2H_4 , (C_2H_6 is similar). It gives the value of the potential at the boundaries of the atomic spheres, in the interstitial region, at the boundary of the outer sphere and at some point further away.

Reference to this figure is sufficient to convince oneself that the quantity $\frac{l(l+1)}{R_{C-C}^2} + \bar{V}$ represents only an average height of the centrifugal barrier in such molecules. In practice such a barrier is asymmetric, being higher along the direction perpendicular to the bond, and lower along the bond. Nevertheless it seems sufficient to trap the final photoelectron in a σ -type state. The energy at

Table I. Summary of the various X- α parameters for the multiple scattering calculation in N_2 and C_2H_n ($n = 2, 4, 6$) molecules. The symbol R_{C-C} (C-C bond length) stands for R_{N-N} when referred to the N_2 molecule. θ_{C-H} is the angle between the C-C bond and the C-H bond.

Molecule	f.s. Symmetry group	R_{C-C} (a.u.)	R_{C-H} (a.u.)	θ_{C-H}	o.s.R. a.u.	\bar{V}_{int} (Ryd)	α
N_2	$C_{\infty v}$	2.068	---	---	2.17	-1.61	0.75
C_2H_2	$C_{\infty v}$	2.276	2.004	180°	4.18	-0.78	0.75
C_2H_4	C_{2v}	2.522	2.021	120°	4.18	-0.87	0.75
C_2H_6	C_{3v}	2.911	2.093	109° .4	4.18	-0.97	0.75

Table II. Table summarizing for the four molecules in question the position of the $l = 3$ resonance E_r for z polarization referred to the vacuum level and to the muffin-tin level, the centrifugal potential $\frac{l(l+1)}{R_{C-C}^2}$ for an incoming $l = 3$ wave at the radius R_{C-C} (or R_{N-N}), the average height of the centrifugal barrier $\frac{l(l+1)}{R_{C-C}^2} + \bar{V}$ at the same point location and the product $(E_r - \bar{V})R_{C-C}^2$. Again R_{C-C} stands for R_{N-N} when referred to the N_2 molecules.

Molecule	E_r (Ryd) (Ryd)	$E_r - \bar{V}$ (Ryd)	$\frac{l(l+1)}{R_{C-C}^2}$ (Ryd)	$\frac{l(l+1)}{R_{C-C}^2} + \bar{V}$ (Ryd)	$(E_r - \bar{V}) \cdot R_{C-C}^2$ Ryd · (a.u.) ²
N_2	1.21	2.82	2.806	1.196	12.00
C_2H_2	1.56	2.34	2.316	1.536	12.16
C_2H_4	0.81	1.68	1.886	1.010	10.68
C_2H_6	0.10	1.07	1.416	0.446	8.43

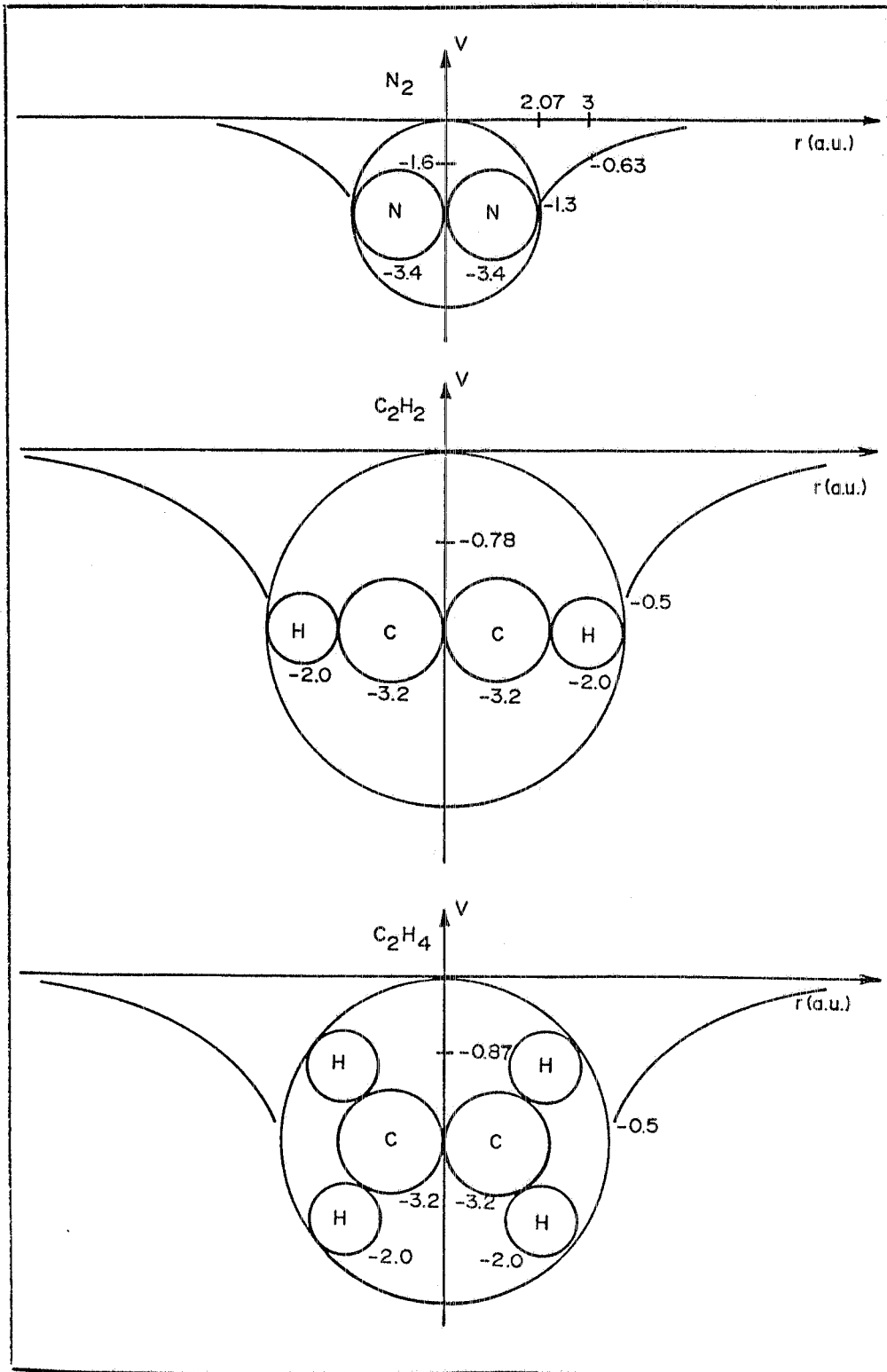


Fig. 8 - Values of the muffin-tin potentials used in the calculation for N₂, C₂H₂, C₂H₄ at the boundaries of the atomic spheres, in the interstitial region, at the boundary of the outer sphere and at some point further away.

which such a confinement occurs represents a compromise between the requirements that such energy be low enough to enable the photoelectron to overcome the barrier to escape to infinity (or to penetrate it if one thinks equivalently in terms of scattering states), though at the same time being high enough for the trapping to be effective.

In the light of these considerations it seems plausible to invoke a mechanism of confinement based on a centrifugal barrier effect, which turns out to have a physical basis in the cases under study. However such mechanism does not lend itself to more than a qualitative interpretation of the resonance phenomenon. No quantitative relation can be established between resonance energy and barrier height. Moreover, the mechanism seems unable to discriminate between a σ and a π resonance and so does not lead to a definite prediction of the character of the resonant state unless other considerations are invoked. Further, how to predict, a priori, the l -character of the resonance? And what is the meaning of centrifugal barrier in the case of extended media (graphite, for example, to speak of the C-C bond) where the some sort of resonances are observed?

Clearly a more general concept is needed, which encompasses the case of centrifugal barrier, when applicable, and at the same time is of more general and quantitative character. We think, as emphasized in ref.4, that the language of potential scattering, generalized to non spherically symmetric cases, is the right context in which to frame all these resonance phenomena.

Condition (2.10) is exactly of this character, derived, as it is, in the framework of the scattering theory. It makes a definite quantitative prediction, which reduces to equ. (2.12) if the atomic phase shifts are smooth functions of the energy and are transferable among the different systems under comparison.

Unfortunately, as seen from the last column of Table II, this prediction does not seem to be satisfactorily verified for the C-C bond in the C_2H_n ($n = 2, 4, 6$) series.

The source of this failure is to be traced back to the breakdown of one or both the assumptions underlying the validity of equ. (2.12). A look at Table III and fig.s 9,10, where the variation of $\cot\delta_l^C(E)$ ($l = 0, 1, 2$) as a function of energy is given for the carbon atom in C_2H_2 and C_2H_4 , seems to indicate that the trouble is to be ascribed more to an appreciable variation of $\cot\delta_0^C(E)$ with energy in the interval of interest than to a poor transferability of the C phase shifts among the various molecules. Indeed in the cases under study the position of the resonance ranges from 1.56 to 0.10 Ryd, an interval wide enough for $\cot\delta_0^C(E)$ to vary by nearly a factor of three. Notice that the values for $\cot\delta_2^C(E)$ have been reduced by a factor 10^{-2} , so that the $l = 2$ partial waves are not effectively scattered by the C atoms in the above energy range. Hence only the variation

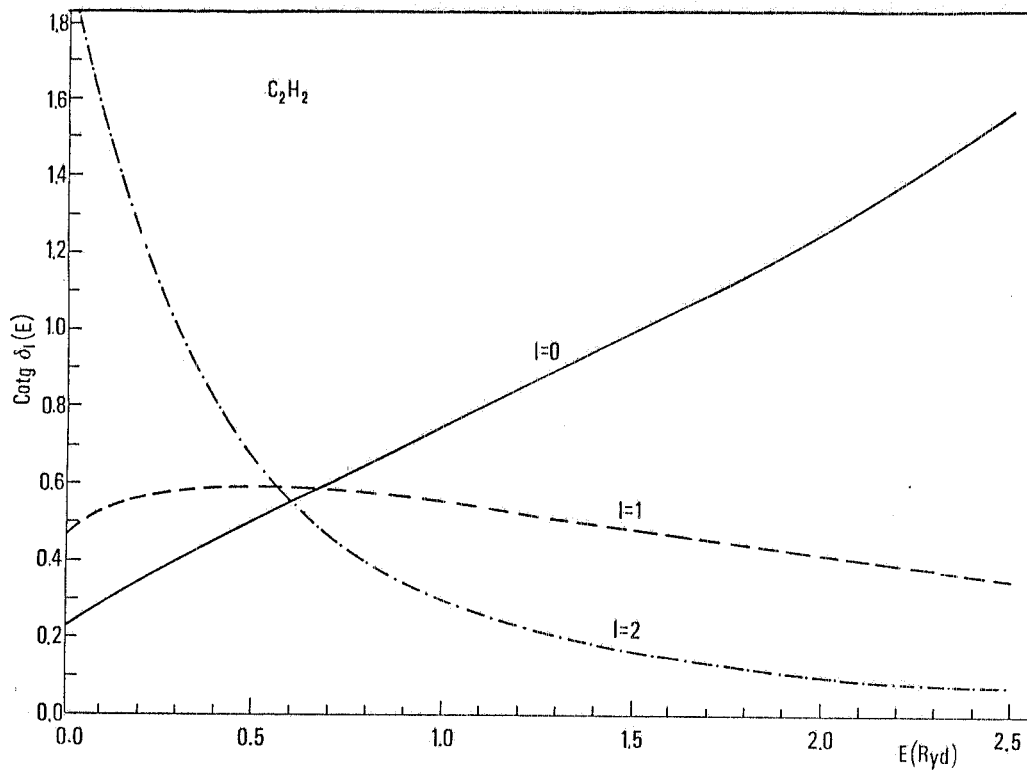


Fig. 9 - Variation of $\cotg \delta_1^C(E)$ as a function of energy for Carbon atomic phase shifts in the C_2H_2 molecule for $l=0$ (continuous curve), $l=1$ (dashed curve) and $l=2$ (dot-dashed curve). Notice that the value for $\cotg \delta_2^C$ has been reduced by a factor 10^{-2} .

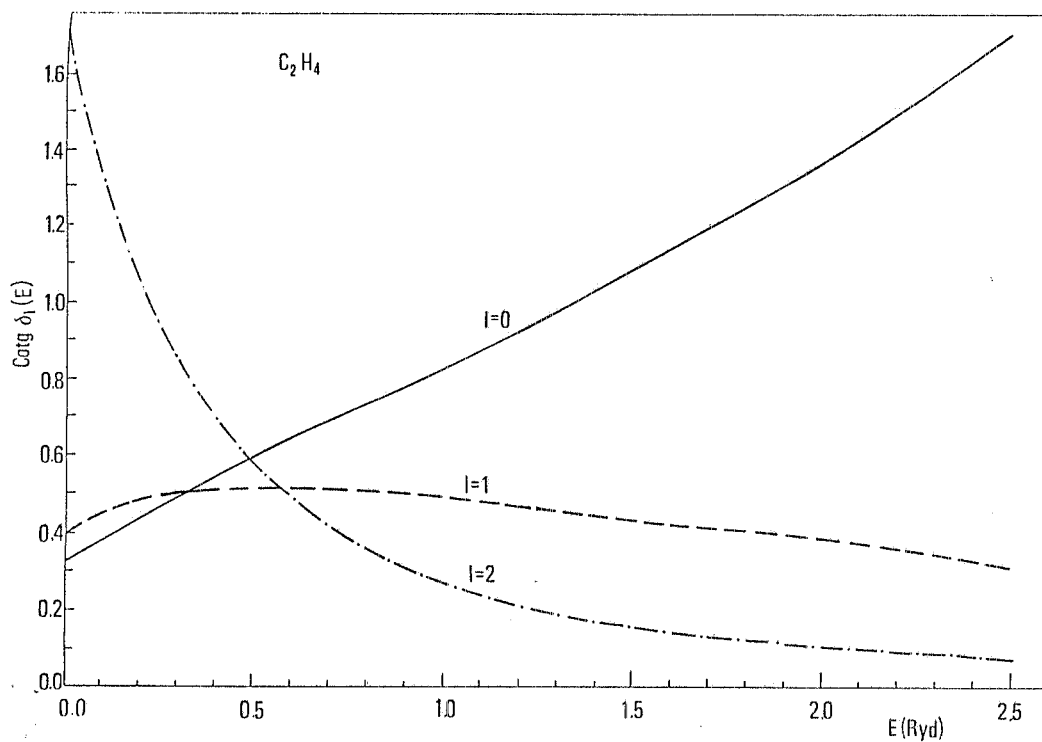


Fig. 10 - Same as Fig.9 in the C_2H_4 molecule.

Table III. Variation of $\cot g \delta_l^C(E)$ ($l = 0, 1, 2$) as a function of energy, $\delta_l^C(E)$ being the carbon atomic phase shift in C_2H_2 and C_2H_4 . Values taken from fig.s 9 and 10.

E (Ryd)	C_2H_4			C_2H_2		
	$\cot g \delta_0$	$\cot g \delta_1$	$\cot g \delta_2 \cdot 10^{-2}$	$\cot g \delta_0$	$\cot g \delta_1$	$\cot g \delta_2 \cdot 10^{-2}$
0.0	0.33	-0.40	1.74	0.24	-0.47	2.19
0.5	0.59	-0.52	0.58	0.58	-0.59	0.66
1.0	0.84	-0.50	0.28	0.75	-0.55	0.30
1.5	1.09	-0.44	0.16	0.99	-0.48	0.16
2.0	1.37	-0.38	0.10	1.26	-0.42	0.10
2.5	1.70	-0.33	0.07	1.57	-0.36	0.07

Table IV. Test for the variation of the product $(E_r - V)R_{C-C}^2$ as a function at the $C - C$ bond length in C_2H_2 . R_0 is the natural bond length equal to 2.28 a.u.

$\Delta R / R_0$	R(a.u.)	$E_r - \bar{V}$ (Ryd)	$(E_r - \bar{V}) R^2$
0	2.28	2.35	12.17
+10%	2.51	2.02	12.72
+20%	2.74	1.75	13.13
-10%	2.05	2.82	11.33
-20%	1.82	3.39	11.23

of $\cot g \delta_o^C(E)$ is important for our argument.

As a check on this hypothesis we have performed a test calculation of several C K-shell absorption cross sections for the C_2H_2 molecule in z polarization, for varying C-C bond lengths up to $\pm 20\%$ of the actual experimental length, in order to eliminate one of the possible sources of breakdown of equ. (2.12), namely non transferability of the atomic phase shifts. The results for the product $(E_r - \bar{V})R^2$ are given in Table IV.

It can be noticed, then, that in such case a variation of 10% of the bond length, as the one between C_2H_2 and C_2H_4 , entails only a variation of 0.55 in the product $(E_r - \bar{V}) \cdot R^2$, as due to the variability of $\cot g \delta_i(E)$, face to a variation of 1.5 in the same quantity between C_2H_2 and C_2H_4 , as seen from Table II. The conclusion to be drawn from this result is that the variability of $\cot g \delta_i(E)$ alone, cannot be held responsible for the bigger than expected variation in the position of the resonance $E_r - \bar{V}$ in the case of C_2H_4 . Since the C phase shifts do not vary appreciably in going from C_2H_2 to C_2H_4 , the only conclusion left is that the different atomic environment of the carbon atom in the two cases caused by the different number and different geometrical arrangement of the Hydrogen atoms is responsible for the unexpected discrepancy. In other words the scattering power of the hydrogen atoms cannot be completely neglected. This obviously applies to C_2H_6 too. In this last case, however, the large range of variation in the position of the resonance energy is the main cause of the failure of the relation $\kappa_r \cdot R = const.$

That the presence of the H atoms cannot be neglected, can also be inferred by the presence of the extra resonance at low energy in C_2H_2 for z polarization, already mentioned. This latter is clearly due to the presence of the hydrogen atoms (since it is absent in N_2) and represents a trapping of the photoelectron in between the $C-H$ bond in a $l = 2$ asymptotic state. Similarly this presence is responsible for the resonances observed in C_2H_4 and C_2H_6 in transverse polarization, not observed neither in N_2 nor in C_2H_2 , because at their linearity.

The term resonance is properly used here, in that a plot of the sum of the eigenphases of the K -matrix shows a rather rapid rise in a fairly narrow range of energy in correspondence of the maximum in the absorption cross section, just like what happens for the main $l = 3$ σ -resonance. (See fig.11).

Having so recognized the cause of the failure of the relation $\kappa_r \cdot R = const.$, we pass on to compare the calculated spectra of fig.s 4-7 for N_2 and the series C_2H_n with the experimental results. It is clear that the general qualitative one electron continuum features of the experimental data are satisfactorily reproduced by the calculation. Both polarized and unpolarized spectra agree

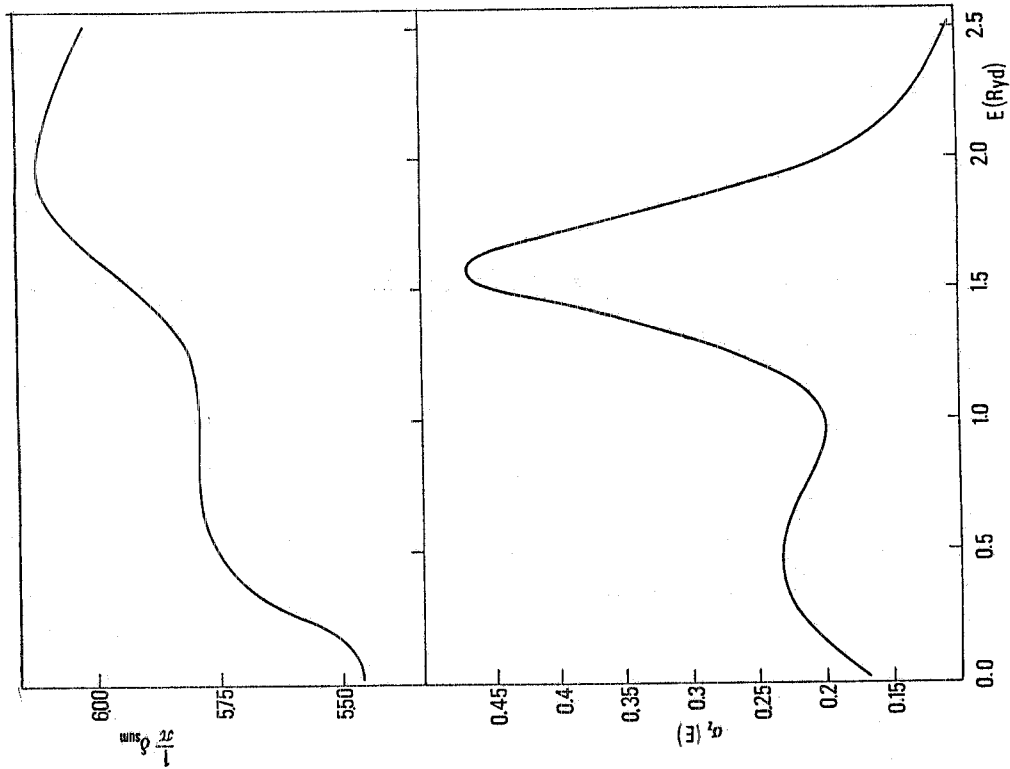


Fig. 11 - (a) Plot of K-matrix eigenphase sum (defined as $\pi \bar{\delta} \text{ sum} = \sum_i \arctg(U^\dagger K U)_{ii}$) where U is the unitary matrix that diagonalizes K) for z-polarization in C_2H_2 ; (b) corresponding absorption spectrum.

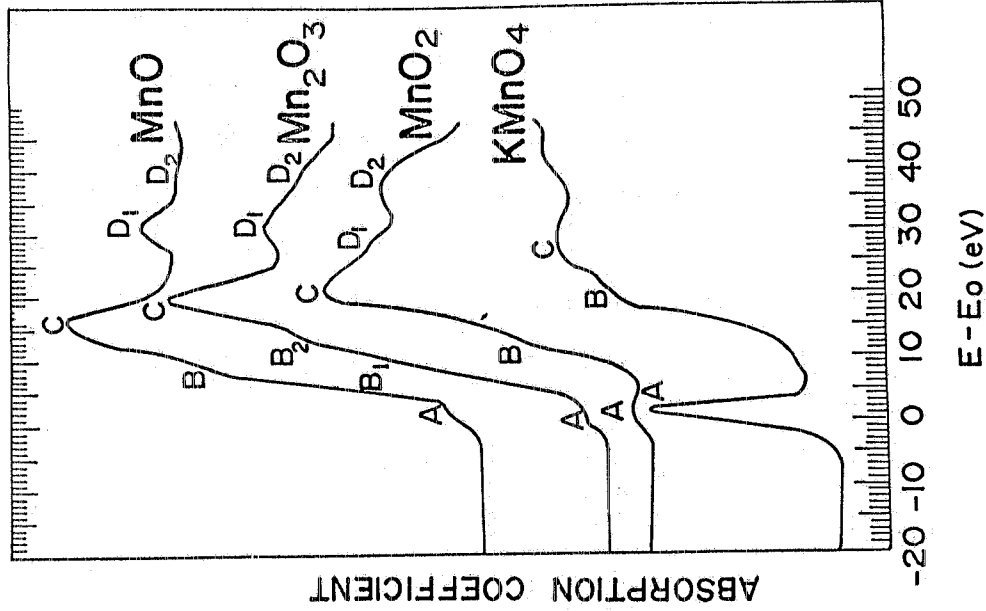


Fig. 12 - X-ray photoabsorption spectra for a series of Mn oxides taken from Ref. 6.

qualitatively with their measured counterpart, when available. However, as anticipated in section 2, quantitative agreement cannot be expected due mainly to the muffin-tin approximation for the final state potential and to a lack of self-consistency for this latter. While self-consistency is expected to affect mainly the absolute position of the ionization threshold and not the resonance position relative to the muffin-tin zero, inclusion of non muffin-tin terms in the potential can affect this relative position, since the multiple scattering matrix is modified¹⁵. Indeed the deviation of the true potential from the muffin-tin model is particularly strong in the case of diatomic molecules, both because of the highly asymmetric distribution of charge and because of the very short bond length which leaves most of the charge outside the muffin-tin spheres. Hence a muffin-tin model in this case turns out to be quite simplified.

Despite this, it is sensible to investigate whether the relation $(E_r - \bar{V}) \cdot R^2 = const$, which is a consequence of the muffin-tin model, is still verified at the experimental level, i.e. in terms of experimental quantities only. As it is, of course, this relation contains the quantity \bar{V} which is not derivable from experiments. There is however a way to eliminate this unwanted parameter by establishing a similar relation referring to bound states. These latter appears as poles on the negative energy axis of the T -matrix. Due the relation $T = K(I - iK)^{-1}$ between the T -matrix and K -matrix, the condition for a pole, in the multiple scattering model, takes the form⁷

$$Det(I - iK) = 0 \quad (3.5)$$

For bound states above the muffin-tin level \bar{V} ($E_b - \bar{V} > 0$) this condition, in the case of a diatomic molecule, takes again the form

$$\mathcal{F}'\left([E_b - \bar{V}]^{\frac{1}{2}} R, \cot g \delta_l(E_b)\right) = 0 \quad (3.6)$$

Under the assumption that the energy E_b of the bound state is sufficiently away from an atomic bound state, condition (3.6) gives

$$(E_b - \bar{V}) \cdot R^2 = c' \quad (3.7)$$

where in general the constant c' is substantially less than the constant appearing in the analogous relation for resonant states in the continuum

$$(E_r - \bar{V}) \cdot R^2 = c \quad (3.8)$$

Taking the difference of the two equations gives

$$\Delta_{\pi\sigma}R^2 \equiv (E_r - E_b)R^2 = c - c' = c'' \quad (3.9)$$

where $\Delta_{\pi\sigma} \equiv (E_r - E_b)$ is the energy difference between the continuum resonant state of σ symmetry and the bound state of π symmetry.

Equ.(3.9) is the sought relation involving only measurable quantities. Table V gives the product $\Delta_{\pi\sigma}R^2$ in Ryd.(a.u.)² for the four molecules of interest.

Notice that for the case of C_2H_4 two values are given for $\Delta_{\pi\sigma}$. The value 1.60 Ryd. is derived from photoabsorption spectra (see fig.1) whereas the value 1.3 Ryd. is what one derives from electron energy loss spectra of ref. (12b).

Also notice that $\Delta_{\pi\sigma}$ is not definable in the case of C_2H_6 , since there is no empty π^* orbital to be occupied as a final state. The value $\Delta_{\pi\sigma} = 0.4$ Ryd indicated in Table V refers to the energy separation of the σ -resonance from the hypothetical location of a π -resonance assumed to lie at the same energy as for C_2H_2 and C_2H_4 .

A look at the Table shows that the value for N_2 is quite different from the values for the series C_2H_n . This was to be expected on the basis of the non transferability of the phase shifts and in this sense the agreement of the calculated values in Table II for $(E_r - \bar{V}) \cdot R^2$ between N_2 and C_2H_2 is to be considered fortuitous.

Next we observe that the relation (3.9) is reasonably verified for C_2H_2 and C_2H_4 , whereas we get a particularly small value for C_2H_6 . This is in keeping with the interpretation put forward when discussing the variation of the product $(E_r - \bar{V}) \cdot R^2$ within the series C_2H_n . Indeed as long as the spread in resonance energy for two different systems is not too large, one can safely assume constancy of the atomic phase shifts, assumed to be transferable. As a consequence the relation (3.9) is likely to be verified. Moreover the fact that the value $\Delta_{\pi\sigma}R^2$ for N_2 is different from the values for series C_2H_n , indicates that application of the relation (3.8) or its equivalent (3.9) is safe only for chemical bonds between the same atomic species, provided of course the different valence state does not drastically alter the atomic phase shifts.

Finally we notice that the relation (3.9) is particularly useful in that it allows to measure energies relative to an experimental feature, namely any pre-edge feature that has either an excitonic character (as in extended media) or is the manifestation of a vacant final bound state, as in molecular systems. Alternatively one can use equ.s (3.7) and (3.8) to determine \bar{V} , the average effective muffin-tin constant, knowing the continuum resonance energy and the bond length,

Table V. Experimental values for R_{C-C} (R_{N-N}), $\Delta_{\pi\sigma}$ and their product $\Delta_{\pi\sigma}R^2$, taken from figs 1 and 2. $\Delta_{\pi\sigma}$ is the energy difference between the continuum resonance state of σ symmetry and the bound state of π symmetry in the molecular spectra. For C_2H_6 , where no empty π^* valence level is present, in order to define $\Delta_{\pi\sigma}$ we refer the σ -resonance to an hypothetical location of the π^* resonance assumed to lie at the same energy as for C_2H_2 or C_2H_4 . The second value of $\Delta_{\pi\sigma}$ for C_2H_4 is derived from electron energy loss spectroscopy (ref. 12b).

molecule	$\Delta_{\pi\sigma}$ (Ryd)	R_{C-C} (a.u.)	$\Delta_{\pi\sigma}R^2$
N_2	1.32	2.07	5.65
C_2H_2	1.85	2.28	9.62
C_2H_4	a) 1.60	2.52	a) 10.16
	b) 1.3		b) 8.21
C_2H_6	0.42	2.91	3.6

a) photoabsorption

b) energy loss spectroscopy

Table VI. Experimental values for R_{Mn-O} , Δ_{CA} and their product $\Delta_{CA}R^2$ in a series of Mn oxides, taken from fig.12. Δ_{CA} is the energy difference between the two spectral features labelled C and A in fig.12.

oxide	R_{Mn-O} (a.u.)	Δ_{CA} (Ryd)	$\Delta_{CA}R^2$
MnO	4.20	1.18	20.81
Mn_2O_3	3.80	1.47	21.22
MnO_2	3.55-3.64	1.62	20.42-21.46
$KMnO_4$	3.02	2.06	18.79

provided a pre-edge feature is present.

We may recall at this point that our considerations on the relation between peak position and bond length in the series of *Mn* oxides, in the introduction of this papers, were based on the relation (3.9), in that energies were meant to be measured from the pre-edge feature representing transition to an excitonic state of *Mn* 3d character. (See also Table VI).

3. CONCLUSIONS

We have shown in the previous sections that the condition (2.8) for the occurrence of a continuum shape resonance of a Breit-Wigner type in photoabsorption spectra can be used to establish a relation between resonance energy and bond length in diatomic molecules or at least in clusters where the first neighbours to the photoionized atom, responsible for the resonance, are at nearly the same distance, provided one considers only breathing modes. We have also discussed the conditions under which a relation of the type (3.8) might be valid. First of all a muffin-tin model for the potential must be applicable and an average potential in the interstitial region \bar{V} be definable along the lines of equ.(2.13). Atomic phase shifts must be transferable among systems under comparison (at least modulo π , since the phase shift dependence is through a cotg function) and their dependence on energy be negligible in the range of variation of the resonance energy. Finally the coordination geometry must be the same in all systems. The presence of the unwanted parameter \bar{V} can be eliminated from equ. (3.8) by reference to any pre-edge feature representing a transition of the photoelectron to an empty valence bound state or to an excitonic state in extended media. These feature are more insensitive to variation of the bond length than are continuum resonance features. The resulting relation (3.9) can then be cast in terms of experimentally measurable quantities only and the validity of the underlying assumptions checked against the experimental data. We have already discussed the implications of the variation of the quantity $\Delta_{\pi\sigma}R^2$ in the case of N_2 and C_2H_n in Table V. The case of the series of *Mn* oxides of ref.(6) is still more illuminating. For this series Table VI shows the product $\Delta_{CA}R^2$, where Δ_{CA} is the energy separation between the first strong absorption maximum labelled *C* in ref.(6) (a shape resonance due to the *Mn* — *O* coordination) and the pre-edge feature *A* (a transition to a *Mn* 3d final state), and *R* is *Mn* — *O* bond length. The oxygen coordination is in all cases

octahedral around the Mn atom (with some degree of distortion) except for the permanganate salt $KMnO_4$ where it is tetrahedral. We see that the product Δ_{CAR}^2 is constant, within 2% , for the Oxides having the same octahedral coordination, whereas it varies as much as 10% in going to tetrahedral coordination. This simple fact shows the influence, to be expected, of the coordination geometry on the location of the shape resonance. Indeed condition (2.8) for the resonance contains a dependence on the geometry of the atomic cluster through the structure factors.

It is interesting however to remark that a determination of the bond length R obtained through use of any one of the products Δ_{CAR}^2 disregarding coordination geometry is in error by at most 5%, reduced to about 1% if comparison is made within the same coordination. As a consequence sometimes one can obtain a reasonably accurate estimate of a bond length through use of equ.(3.9) disregarding differences in coordination geometry. As a side remark, we notice that the inflection point in the rising edge also follows the first main absorption maximum, so displaying a strong final state effect on its energy position. Care must therefore be exercised in attributing any shift of the edge to an initial state effect.

An interesting field of application of (3.8) or (3.9) is the bond length determination of molecules chemisorbed on metal surfaces. Indeed, since the interaction of the chemisorbed molecule with the metal substrate broadens its sharp electronic levels into resonances, it can be speculated that a muffin-tin model for such molecule will be more appropriate than it would be in the gas phase. Moreover the dependence of the atomic phase shifts on the valence charge distribution will be considerably weakened. Hence the underlying assumptions for the validity of equ. (3.8) seem to be better met in this case, provided, as shown by Stöhr et al.¹⁶, that calibration of equ.(3.8) for bond length determination is obtained through reference to chemisorbed molecules on the same metal surface, as reference systems. This is because the perturbation induced by the metal surface on the chemisorbed molecular system can be quite strong. In this connection it is not surprising that Stöhr et al find that \bar{V} , the average muffin-tin molecular interstitial potential, as determined by the use of equ.(3.8) for chemisorbed reference molecules, is "constant ($\simeq 9eV$) for different low- Z molecules with bonds between C , N , and O atoms on various d-band metals". Indeed the quantity \bar{V} for chemisorbed molecules coincides with the muffin-tin level of the metal substrate, as one can infer from the fact that overall Fermi level of the whole system, molecule plus metal substrate, is fixed by this latter. Hence it comes to no surprise that the \bar{V} value so obtained coincides with the same value as found in LEED experiments using the same metals. This procedure has the potentiality to become a promising technique for bond length determination of chemisorbed molecules.

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