

APPLICATION OF A GREEN'S FUNCTION METHOD TO THE CALCULATION OF PHOTOELECTRON SPECTRA

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ABSTRACT

An introduction is given to the many - body effects, which reveal themselves in photoelectron spectra, and to their origin. The consequences of these effects are discussed. The Green's function method is outlined as a tool for the accurate calculation of ionisation energies and the associated pole strengths. Applications are discussed. These include the question of the accuracy which is achieved. Formaldehyde, benzene, CS, CS₂, N₂, p-quinodimethane and the vibronic coupling in butatriene are given as examples.

INTRODUCTION

Photoelectron (PE) spectroscopy has proved since longtime to be a versatile tool to investigate the electronic structure of atoms, molecules, solids, and surfaces.¹⁻⁵ More recently the classic techniques, namely, X-ray induced PE spectrometry (XPS) and ultraviolet PE spectroscopy (UPS), have been complemented by dipole (e, 2e) spectroscopy⁶ and PE spectroscopy using synchrotron radiation from storage rings,^{7,8} which allow continuous tuning of the photon energy over a wide range. These instrumental developments have produced a wealth of data on the magnitude and energy dependence of photoionization cross sections as well as on the angular distribution of photoelectrons. An alternative technique, which has contributed considerably to our understanding of the electronic structure of atoms and molecules, is the so-called binary (e, 2e) spectroscopy.^{9,10}

An extremely useful concept to rationalize the huge amount of data provided by PE and (e, 2e) spectroscopies is the single-particle picture or shell model. In the simplest case of closed-shell atoms, for example, each line in the PE spectrum can be associated with an electronic orbital to a first approximation. Jahn-Teller splittings, and so on lead to additional complications, but still the resulting somewhat broader "bands" in the PE spectrum can be associated with individual molecular orbitals (MOs). In this sense, PE spectroscopy is considered a "spectroscopy of orbitals" and helps us to understand the electronic structure and compounds of chemical interest.¹⁻⁵ The fine structure of the bands in molecular PE spectra gives, moreover, direct information on the bonding properties of the MOs.³⁻⁵

Corrections to this simple picture arise because of electron correlation, which is not considered in the self-consistent field (SCF) model of independent electrons. As has been known since the early days of PE spectroscopy, these residual correlation and relaxation effects lead to the appearance of additional weak bands in the PE spectrum. These so-called shake-up or satellite bands correspond to excitation processes accompanying the ionization.¹¹ Associated with the appearance of satellite bands is a shift and a reduction of the intensity (compared to the independent-particle model) of the main band representing the MO. This simple picture of main lines and accompanying shake-up lines has been confirmed by numerous studies of valence and core ionizations in atoms and molecules (e.g., see refs. 1-6,9,10).

The first indications that the concept of main ionizations and accompanying shake-up transitions may lose its validity for ionization out of deeper valence orbitals of molecules came from theoretical studies on H₂O,¹² CO,^{13,14} and N₂.¹⁴ These calculations, which were based on the Green's function method^{12,14} or the configuration-interaction (CI) technique,¹³ predicted satellite lines on both sides of the main line representing the inner-valence orbital, in contradiction to the familiar shake-up picture, which can explain only satellite lines at the higher binding-energy side of the main line.¹¹ The origin of the phenomenon is the quasi-degeneracy of the inner-valence single-hole configuration with certain configurations representing two holes in the outer-valence shell and one particle in a virtual orbital. The interaction of these quasi-degenerate configurations via the residual electron-electron interaction leads to a redistribution of the intensity associated with the inner-valence orbital. If the interaction is sufficiently strong, the intensity may be distributed over numerous lines and it is no longer possible to discern between main lines and satellite lines. This effect has been termed the breakdown of the molecular orbital picture of ionization.^{14,15}

The calculations on N₂, CO, CO₂, CS₂, and other small molecules¹⁴⁻¹⁷

explained a posteriori the observation (by XPS) of very broad bands with a half-width of several electron volts for the more tightly bound electrons.^{23,18} The limited experimental resolution and the existence of additional broadening mechanisms in molecules, such as vibrational excitation and dissociation, usually prevent the direct observation of the theoretically predicted line splittings. Recent high-resolution studies employing synchrotron radiation have revealed, however, substructures of the broad inner-valence bands in N_2 and CO which are in qualitative agreement with the theoretical predictions.^{19,20} The generality of the breakdown phenomenon in the inner-valence region has also been convincingly established by numerous (e, 2e) spectroscopic studies (e.g., see refs. 16,21-27).

In the last few years Green's function calculations based on the two-particle-hole Tamm-Dancoff approximation (2ph-TDA)^{28,29} have been performed to study the complete valence-shell ionization spectra of numerous small- and medium-size molecules (see refs. 30-32 and references therein). Although the calculations are not of really quantitative accuracy owing to limitations of the method and the finite basis sets employed,^{30,31} the breakdown of the MO picture of ionization as a general phenomenon in the inner-valence region is now well established. Depending on the size, symmetry, and chemical properties of the molecule, the outer-valence orbitals may also be affected, that is, the intensity of several main lines may be strongly reduced compared to the SCF model and low-lying and intense satellite lines may appear.

The breakdown of the MO picture as a qualitative phenomenon has also been confirmed by a number of subsequent theoretical studies using different computational techniques. Calculations based on Green's function or propagator methods have been performed, for example, by Herman et al.³³ (N_2), Misha and Öhrn³⁴ (N_2 , H_2O) Cacelli et al.³⁵ (HF , H_2O , NH_3), and Baker³⁶ (C_2H_4). Calculations based on CI techniques generally yield very similar results, as is shown, for example, by Honjou et al.³⁷ (N_2 , CO , O_2 , NO), Langhoff et al.³⁸ (N_2 , CO), Müller and co-workers³⁹⁻⁴¹ (CS , C_2H_2 , H_2O), and Nakatsuji and Yonezawa⁴² (H_2O , CO_2 , N_2O , CS_2 , COS). Calculations using semiempirical model Hamiltonians were also quite successful.⁴³⁻⁴⁷ It is generally found that strong correlation effects in the inner-valence region are accompanied by low-lying and intense satellite structure in the outer-valence region.⁴⁷⁻⁵¹

A closely related phenomenon is the apparent missing of certain inner-shell ionization lines in the PE spectra of heavy atoms such as Xe.^{2,52} Lundqvist and Wendin⁵³ and Wendin and Ohno⁵⁴ have shown that this effect is caused by an unusually strong coupling of the single-hole configuration with an underlying two-hole-one-particle continuum. This phenomenon has subsequently been discovered in a whole series of elements but seems to be confined to deep core levels of relatively heavy

atoms. For a comprehensive review, the reader is referred to the recent article by Wendin.⁵⁵

The breakdown of the MO picture in molecules is a fundamental effect and is of relevance far beyond the field of photoionization experiments. High-resolution X-ray emission, for example, is an alternative technique used to investigate valence hole states in molecules,⁵⁶ and the breakdown of the MO picture has been identified in the X-ray emission spectra of a variety of molecules.^{57,58} Autoionization of core-excited states may also populate these levels.⁵⁹ Related correlation phenomena are expected to occur in more complicated excitation processes such as the Auger effect. The severe limitations of the single-particle picture in interpreting molecular Auger spectra have recently been pointed out by Agren and Siegbahn,^{60,61} Kvalheim,⁶² Jennison and co-workers,⁶³ Aksela and co-workers,⁶⁴ and Liegener.⁶⁵ The breakdown of the MO picture also has important consequences for the understanding of nuclear dynamics in ionization processes, in particular, photodissociation⁶⁶ and photon-stimulated ion desorption.^{67,68}

The breakdown of the MO picture may be classified as a final-state correlation effect, that is, as configuration interaction taking place in the cation. There are additional correlation phenomena that have to be taken into account in a quantitative description of photoionization experiments, for example, initial-state correlation and correlation in the continuum. These effects are separable only in an approximate sense. The many-body Green's function or CI methods which are used in the actual calculations are only briefly sketched, since comprehensive reviews can be found elsewhere.^{28,32,69-71} In addition to the accuracy achievable with the Green's function method the qualitative and quantitative aspects of the breakdown of the MO picture are discussed for a few selected examples.

Koopmans' Approximation

The simplest method to calculate ionization energies is based on Koopman's theorem and is called Koopmans' approximation.⁷² The method is simple to apply and reasonably successful in that it permits to assign experimental ionization spectra. In the Hartree-Fock (HF) approximation the wave function consists of a Slater determinant built from molecular spin orbitals $|\phi_i\rangle$

$$\Psi_0 = \det |\phi_1\bar{\phi}_1 \dots \phi_i\bar{\phi}_i \dots \phi_n\bar{\phi}_n|. \quad (1)$$

($|\phi_i\rangle$ without the bar denotes that the orbital is associated with a spin function with $m_s = +1/2$, and with the bar that the orbital is associated

with a spin function with $m_s = -1/2$) which are solutions of the HF equations

$$F|\phi_i\rangle = \varepsilon_i|\phi_i\rangle \quad (2)$$

with ε_i the orbital and F the HF operator

$$F = h + \sum_i 2 J_i - K_i, \quad (3)$$

where h is the one-electron operator, $J_i = \langle \phi_i(2) | 1/r_{12} | \phi_i(2) \rangle$ the Coulomb and $K_i = \langle \phi_i(2) | 1/r_{12} | \phi_i(1) \rangle$ the exchange operator. The HF operator contains only an average interaction between the electrons resulting from the integration over the coordinates of the other electrons. Because of this approximate interaction one has neglected an energy contribution, the so-called correlation energy. If one approximates the ionic wave function by

$$\psi_i = \det |\phi_1\bar{\phi}_1 \dots \phi_i \dots \phi_n\bar{\phi}_n|, \quad (4)$$

where the electron has been taken out of the spin orbital $|\bar{\phi}_i\rangle$ leaving all other orbitals unchanged one obtains for the energy difference

$$E_i(\psi_i) - E_o(\psi_o) = I_i = -\varepsilon_i. \quad (5)$$

The i -th ionization energy is thus approximately given by the negative of the i -th orbital energy. This is Koopmans' approximation which has proved to be very useful. With the Ansatz Eq. (4) for the ionic wave function, in which the molecular orbitals of the neutral groundstate are used for the ionic state one has neglected the so-called relaxation energy of the electrons. Ejection of an electron will always lead to a charge rearrangement and the ionic wave function should be constructed from orbitals appropriate for the ion. Thus Koopmans' approximation involves the neglect of the correlation energy both in the ion and the neutral state and the neglect of the reorganization energy in the ion. In the outer valence region of many molecules this approximation is quite acceptable as these two neglected effects tend to cancel to a certain degree, but there can be no guarantee that the approximation is reliable. There are quite a number of molecules and there are whole classes of molecules where Koopmans' approximation fails badly in supplying the correct ordering of ionic states. Ionic states can be quite close together in energy and thus one needs accurate means of calculating the ionization energies which take into account the effects of electron correlation and reorganization. The

relaxation energy can be obtained by separate SCF calculations and the correlation energy by performing separate configuration interaction (CI) calculations for the ionic states and the ground state. These methods appear as a logically consistent improvement in the calculation of ionization energies. There is, however, also a direct way to calculate ionization energies, the method of Green's functions^{28,73} (For general text on Green's functions see, e.g., Ref. 74).

Before discussing the method of Green's functions let us point out another consequence of Koopmans' theorem, which we would like to call Koopmans' hypothesis. This will clarify the physical model underlying Koopmans' approximation. In a closed shell molecule and in the SCF approximation each electron pair occupies one of the orbitals $|\phi_i\rangle$ once with $m_s = 1/2$, once with $m_s = -1/2$. The total energy, the electron density, many properties are reasonably well described by this model. In this respect it can be said that the model—the molecular orbital (MO) model—acquires a certain degree of reality. One can now take an electron out of each orbital. A photoelectron spectrum should thus consist of as many lines as there are orbitals. The reason for this is that the photon interacts only with one electron at a time, the transition operator is a one-particle operator. It is not implied that the orbital energies are (aside from the sign) accurate approximations to the ionization energies—reorganization and correlation effects will necessarily modify the values—but it is implied in using Koopmans' approximation that to each orbital corresponds one line in the PES. This has well been borne out in many PES in the outer valence region and in ESCA spectra for the core region. The physical model thus appears to be sound. The MO scheme and the resulting schematic PES are sketched in Fig. 1. It is, however, long known in photoelectron spectrometry that in addition to the one-electron transitions mentioned above two-electron transitions can also be observed which are ionization combined with simultaneous excitations. This process is also sketched in Fig. 1. These processes lead to the so-called satellite lines. They usually have small intensities and borrow this intensity from the main transitions via many-body effects. If their intensities are small the physical model underlying Koopmans' approximation is a valid one, but if their intensities become large this model becomes shaky and must be abandoned. Koopmans' approximation then burns down to pure mathematics. One still calculates an orbital energy but it has little relation to an ionization energy. A relation may still be thought of to exist if the intensities of the two-electron transitions are borrowed from the simple one-electron transitions. This shows that a discussion of ionization spectra and Koopmans' approximation cannot be based on the energetics alone, but should take the intensities into consideration.

It has been found in the studies of atoms (in particular the interpreta-

tion of the Xe ESCA spectrum by Wendin and Ohno⁵⁴ and in calculations on a large number of molecules (see, e.g., Refs. 15,16,32,75-77; Ref. 32 contains a fairly complete list) that the satellite lines acquire a considerable intensity in the inner valence region. A main line frequently ceases to exist and the intensity is distributed over a large number of lines. Things may become even worse. It may occur that the intensity of a satellite line is not borrowed from a single simple transition but from several ones. In this case neither the energetics nor the intensity borrowing can be understood in a MO model. (In addition, interference effects can be observed).

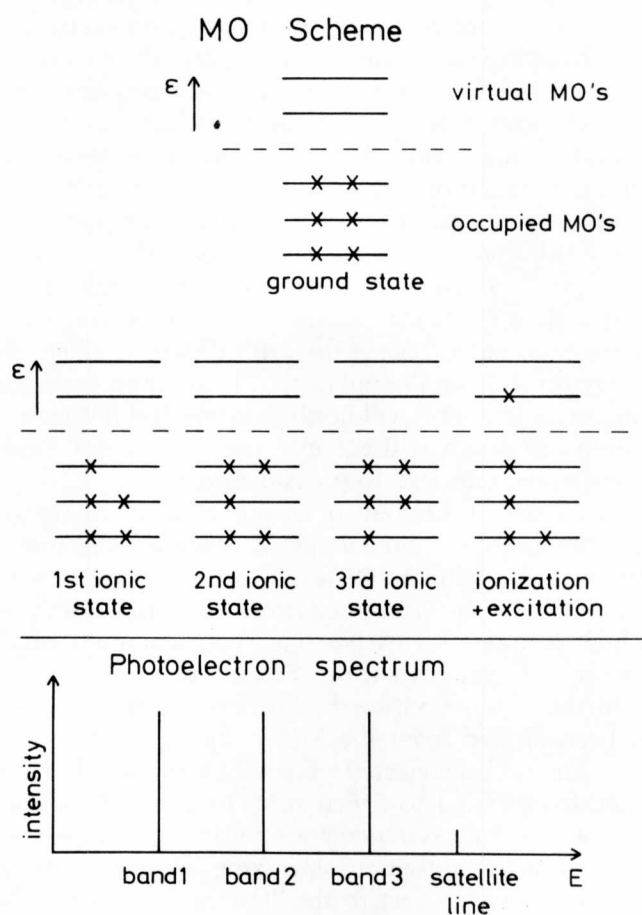


Fig. 1 MO scheme for the ground state, for the ionic states obtained by simple one-electron ejection processes and for ionization plus excitation processes together with the corresponding schematic photoelectron spectrum.

Extremely strong effects of this type have recently been found in several molecules and even for the first ionization processes.⁴⁹ A one-to-one correspondence between lines in the PES and the MO's seems to exist but a MO interpretation of the PES is totally impossible. There are also other effects such as vibronic coupling which can lead to complications in a PES. Koopmans' hypothesis may thus frequently fail to meet reality or even if it seems to be in agreement with reality it may be so for the wrong reason.

Let us discuss some of the effects which may be possible to observe in PES. This will not be a complete list to avoid too many complications. In particular, we will be mainly concerned with energetic phenomena and less with intensity phenomena. When we increase the energy of the radiation incident on the atom or molecule we will first excite electrons to valence and to Rydberg states, the latter forming the so-called Rydberg series which converge to the various ionization thresholds. When ionization occurs the electron is no longer bound but is excited into the continuum. Ionization is not a resonance phenomenon as absorption so any energy beyond the ionization energy will be absorbed and will appear as kinetic energy of the ejected electron. The first ionization process is expected to be a simple one-electron transition. As satellite lines may appear at very low energies it is still an open question whether this holds always. Bound neutral excited states may lie in the ionization continuum. These superexcited states do not in general disturb a PES from an energetic point of view but may do so from the intensities. If the superexcited state does not decay into an ionic state it will not be observed; if it does decay — this is called autoionization — it will enhance the intensity of the ionization band. This may sometimes lead to gross distortions.

If two ionic states of different or of the same symmetry are separated by an energy about equal to the energy of vibrational quanta the Born-Oppenheimer approximation may break down. Vibrations of the appropriate symmetry couple the electronic states. This may lead to great complications which manifest themselves in a very complicated vibrational structure or even in the appearance of new bands.

For the further discussion we shall denote a configuration where an electron has been ejected from the MO p by p^{-1} and a configuration where one electron has been ejected from MO k and another one simultaneously excited from MO l to a virtual MO j by $k^{-1}l^{-1}j$. If two configurations p^{-1} of the same symmetry are fairly close together in energy one would not expect a configuration mixing because of the content of Brillouin's theorem. And in fact to the authors' knowledge this has not been found until recently. In propynol and in propiolic acid this configuration mixing does occur.⁴⁹ The number of bands is unchanged but instead of being described by configuration p^{-1} and q^{-1} , the ionic states

have to be described in the simplest approximation by $ap^{-1} + bq^{-1}$ and $bp^{-1} - aq^{-1}$, where $a \sim b$. It is clear that this configuration mixing is mediated via two-hole-one particle configurations, because the Hamiltonian matrix element between p^{-1} and q^{-1} is zero. With increasing ionization energy other processes become possible. In addition to ionizing one electron, another one may be simultaneously excited. If the energy of configuration p^{-1} , $E(p^{-1})$ is close to $E(k^{-1}1^{-1}j)$ for some configuration $k^{-1}1^{-1}j$ then there will be configuration mixing and a redistribution of intensity. Thus several lines of roughly equal intensities may appear in the PES for ionization out of the orbital p . For molecules consisting of first row atoms $E(k^{-1}1^{-1}j)$ is larger than the energy of the neutral ground state by 15 to 25 eV. Thus effects will be found at higher energies affecting mainly 2s lines of the first row atoms. An important factor which enters $E(k^{-1}1^{-1}j)$ is the excitation energy of the molecule. If a molecule has very low lying excitations these many-body effects will appear at lower energy. The spectrum will depend on two other quantities; the first one is the interaction matrix element between the configuration p^{-1} and $k^{-1}1^{-1}j$. This is approximately given by V_{pjkl} , where

$$V_{pjkl} = \iint \phi_p^*(1)\phi_j^*(2) \frac{1}{r_{12}} \phi_k(1) \phi_l(2) d\tau_1 d\tau_2.$$

Such a matrix element is expected to be large only if the virtual orbital j is localized in space as the occupied orbitals are. Therefore sufficiently large interaction between the relevant configurations can be expected especially for those molecules that possess low lying valence type excited states. If V_{pjkl} is nearly zero for some reason, no many-body effects will be observable in spite of the quasidegeneracy of p^{-1} and $k^{-1}1^{-1}j$. The second factor which enters is the density of the $k^{-1}1^{-1}j$ configurations in energy space. If the density is low in the energy region of the single hole configuration, p^{-1} , the breakdown phenomenon will only occur if there is an accidental quasidegeneracy. The intensity is then distributed only over a few lines. If the density is high on the other hand the intensity becomes distributed over numerous lines each having only a few percent of the total intensity. Since larger molecules have a high density of configurations the breakdown phenomenon will dominate their ionization spectra in the inner valence shell. In the neighborhood of the double ionization threshold the density of the configurations is very high and the configurations $k^{-1}1^{-1}j$ may constitute a continuum.

To explain in more detail what is happening in the mixing of single hole configurations with two-hole-one-particle configurations, we have plotted in Fig. 2 an artificial schematic ionization spectrum. In the upper spectrum the simple hole states (Koopmans' states) are separated from the

states resulting from ionization plus excited. The transitions to the former states are allowed in a one-particle model, and the lines have unit relative intensities, whereas the transitions to the latter ones are forbidden, and the states have thus only been marked by the energies. The density of these states is low in the low energy region and high in the high energy region. When we permit configuration mixing the schematic spectrum drawn in the lower part of Fig. 2 results. The lines first split into few lines (due to occurring near degeneracies) in the lower energy part and at higher energies are completely smashed to pieces.

From this overview we conclude that ionization spectra of molecules are not as simple as may be thought on the basis of Koopmans' hypothesis. A great number of complications arise. These are a source of information on the electronic and vibronic structure of molecules and present a challenge to the spectroscopist and to the theoretician.

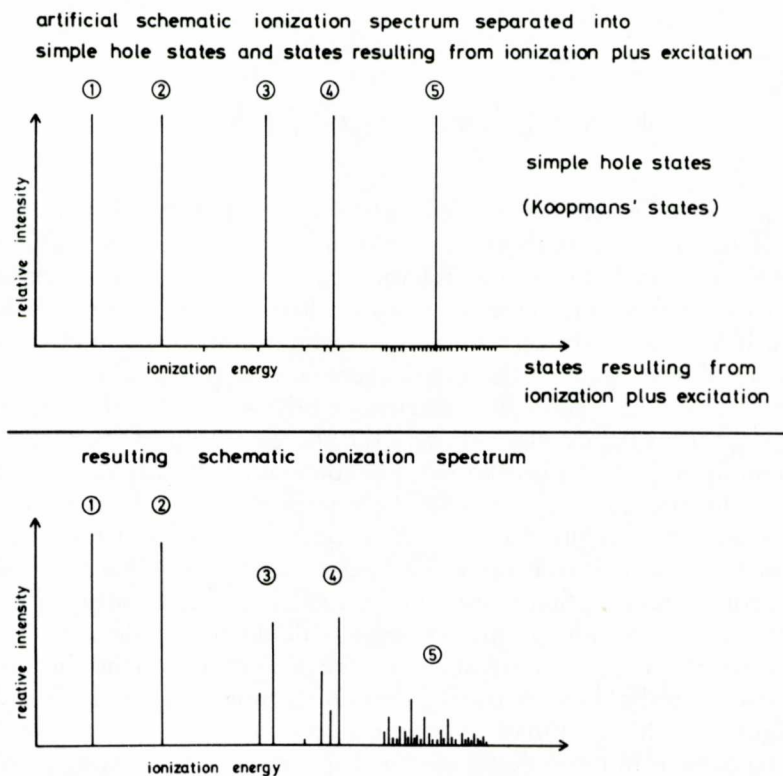


Fig. 2 Artificial schematic ionization spectrum separated into simple hole states and states resulting from ionization plus excitation (upper part) and the schematic ionization spectrum obtained by including configuration mixing (lower part).

The Green's Function Method

The necessity to assign PES and to analyze the physical background of the complications which have been discussed and thus to understand them demands theoretical developments. This can be done using CI techniques, perturbation techniques or the method of Green's functions. We will describe some aspects of the method of Green's functions as they are relevant for the calculation of ionization energies in the outer and inner valence region.

The one-particle Green's function is defined in time, state space as the expectation value with respect to the exact ground state wave function of a time-ordered product of annihilation and creation operators for electrons in one-particle states

$$G_{kl}(t, t') = -i \langle \psi_0^N | T \{ a_k(t) a_l^\dagger(t') \} | \psi_0^N \rangle. \quad (6)$$

$a_k(t)$, $a_k^\dagger(t')$ are operators in the Heisenberg representation with H the full Hamiltonian of the system.

$$a_k^\dagger(t) = e^{iHt} a_k^\dagger e^{-iHt}. \quad (7)$$

They annihilate (create) electrons in one-particles states $|k\rangle$. The operators fulfill the anticommutation relations $[a_k, a_l^\dagger]_+ = \delta_{kl}$ with all other anticommutators vanishing. T is Wick's time ordering operator which orders the operators so that time increases from right to left. A permutation of the operators from the original ordering by the action of T is accompanied by a change of sign. With the help of the Fourier transformation one can go over from time, state space to energy, state space

$$G_{kl}(\omega) = \int_{-\infty}^{\infty} G_{kl}(t, t') e^{i\omega(t-t')} d(t-t'). \quad (8)$$

By inserting the decomposition of unity and performing the integration one arrives at the spectral representation of the Green's function

$$G_{kl}(\omega) = \lim_{\eta \rightarrow +0} \left\{ \sum_n \frac{\langle \psi_0^N | a_k | \psi_n^{N+1} \rangle \langle \psi_n^{N+1} | a_l^\dagger | \psi_0^N \rangle}{\omega + A_n + i\eta} \right. \quad (9)$$

$$\left. + \sum_m \frac{\langle \psi_0^N | a_l^\dagger | \psi_m^{N-1} \rangle \langle \psi_m^{N-1} | a_k | \psi_0^N \rangle}{\omega + I_m - i\eta} \right\} \quad (9)$$

with $A_n = E_o^N - E_n^{N+1}$ the vertical electron affinity and $I_m = E_m^{N-1} - E_o^N$ the vertical ionization energy. By calculating the poles of the Green's function one thus obtains directly the ionization energies and the electron affinities. The ionization energies and electron affinities are best calculated from the Dyson equation which is formally equivalent to the spectral representation but more amenable to numerical calculations

$$G(\omega) = G^o(\omega) + G^o(\omega)\Sigma(\omega)G(\omega). \quad (10)$$

The Dyson equation connects the Green's function with the HF Green's function $G_{kl}^o = \delta_{kl}/(\omega - \epsilon)$ and the quantity $\Sigma(\omega)$ which is called the self-energy potential. $\Sigma(\omega)$ is the exact potential seen by an electron due to the interaction with its surroundings. The Green's function have inverses

$$G^{-1} = (G^o)^{-1} - \Sigma(\omega). \quad (11)$$

Thus instead of calculating the poles of G we calculate the zeros of G^{-1} .

The details of the Green's function method as used here are given in detail elsewhere^{28,29,73,78} and will not be discussed. The computational aspects are presented in ref. 32. A number of review articles exist^{28,31,76}. It should only be mentioned that two different and distinct approximations to the one-particle Green's function, are used. The self-energy $\Sigma(\omega)$ itself has poles. A perturbation expansion of $\Sigma(\omega)$ is only justified far away from the poles. This region is the outer valence region, where ionization gives rise only to negligible satellite line structure. The computational method is called the outer valence Green's function method (OVGF). It is exact to third order in the electron-electron interaction with higher order terms approximated by a renormalization procedure.⁷³ In the energy range where poles of the self-energy appear one needs to conserve the correct analytical structure of the poles. This can be done by selective infinite summations. An algebraic diagrammatic construction scheme (ADC) has been developed as a systematic means of obtaining approximations to $\Sigma(\omega)$ which meet the requirement that the pole structure of $\Sigma(\omega)$ has the correct analytical form and which are accurate to a given order either the third order (ADC(3) or extended two-particle-hole Tamm-Dancoff approximation (extended 2ph-TDA) or the fourth order (ADC(4)).⁷⁸ This is an extension of previous work.²⁹ The ADC(3) method includes as excitation spaces all simple hole and particle and all 2hlp and 2plh configurations. The extended 2ph-TDA method is as accurate as the OVGF method in the outer valence region because both are accurate to third order. In the inner valence region where satellite lines domin-

ate the states are described correctly only to first order.⁷⁸ The agreement to be expected is thus semiquantitative or only qualitative. The reason is the following. In the inner valence region one finds an infinite number of ionic states which converge to the double ionization threshold and a continuum of states beyond this. A finite and in general only small basis is used to describe such states. This is why one calculates only pseudostates which at best give a rough idea of the spectral distribution. For a proper description one would need a close to infinite basis and the inclusion of higher excitations.

Applications

For the calculations the MUNICH integral, SCF, and transformation package written by G. Diercksen and W.P. Kraemer⁷⁹ has been used. The Green's function and 2ph-TDA calculations have been performed with programs written by the author.

*The Accuracy of the GF Calculations*⁸⁰

The main interval, i.e., the interval between the first affinity pole and the first ionization pole of the self-energy contains the outer valence ionization energies. A PES in general consists in the low energy range of many closely spaced bands. One thus needs high accuracy in the computed ionization energies in order to reliably assign a PES. This is a requirement to both the computational method and to the basis set. But besides accuracy one needs stability of the results - stability with respect to basis set variations. One could call this stability if large basis sets are used and one would better call it basis set insensitivity if one is dealing with smaller basis sets. A double zeta basis will be called a small basis set to avoid misunderstanding. The accuracy which can be achieved and the stability with respect to basis set extension and variation has been examined with the Green's function method and the results are published in ref.⁸⁰ and compared with literature values. We would like to discuss the results for N₂, H₂O, and HCl.

The N₂ molecule represents a good test case since Koopmans' approximation predicts an incorrect ordering for the ²Π_u and ²Σ_g states and only by including the electronic correlation energy can the correct ordering of states be obtained. Calculations have been performed with the (11s7p)/[5s4p] basis set³⁷ supplemented with 1,2 and 3 d-type functions and with 2 d-type and 1 f-type functions. The experimental values and the results of the OVGf calculations are given in Table 1. The results obtained with a double zeta basis set are given as well.

Table 1: Ionization Energies of N₂ Calculated with the OVGf Method and with Different Basis Sets (all values in eV).

	9s5p	11s7p1d	11s7p3d	11s7p2d	11s7p2d1f	exp ⁴
3σ _g	14.85	15.41	15.45	15.53	15.52	15.60
1π _u	16.34	16.74	16.76	16.75	16.83	16.98
2σ _u	18.37	18.89	18.91	18.96	18.98	18.78

For the large basis sets the maximum error is approximately 0.2 eV, for the double zeta basis set the errors are exceptionally large, but N₂ represents a very critical case.

Similar results are obtained for the H₂O molecule. Five calculations have been performed with the (11s7p/6s1p)/[5s4p/3s1p] basis set supplemented with 1,2,3 and 4 d-type functions and with 3 d-type and 1 f-type functions. All basis sets have been completely exhausted. Table 2 lists the calculated ionization energies and the experimental values (centroids).⁴

Table 2: Ionization Energies of H₂O Calculated with the OVGf Method and with Different Basis Sets (all values in eV).

	9s5p	11s7p1d	11s7p2d	11s7p3d	11s7p4d	11s7p3d1f	exp ⁴
1b ₁ (π)	12.37	12.78	12.87	12.83	12.81	12.90	12.78
3a ₁	14.32	14.78	14.85	14.85	14.84	14.85	14.83
1b ₂	18.95	18.94	18.98	18.94	18.92	18.91	18.72

The maximum error is again about 0.2 eV. The results of a calculation with a double zeta basis is enclosed as well; again this basis is insufficient for obtaining accurate results. We thus conclude that the OVGf method gives accurate and stable results. The data obtained with the double zeta basis set are, however, somewhat disappointing. But it should be mentioned that in particular N₂ is among the worst representatives.

It has been occasionally observed that the ionization energies calculated theoretically are lower than experimental ones although large basis sets including polarization functions have been used (e.g., H₂S⁸, C₂H₄^{84,85}). In such a case the neutral ground state is less well described than the ionic state and ground state correlation energy is lacking. It has been found that a large number of polarization functions including very diffuse ones are required to alleviate this situation (for a detailed discussion, see Ref. 41). This is also the case for HCl⁴⁴ (see Table 3).

Table 3: Ionization Energies of HCl Calculated with the OVG Method and with Different Basis Sets (all values in eV).

	(12s9p/4s)	(12s9p1d/4s1p)	(12s9p2d/4s1p)	(12s9p5d1f/4s1p)	exp ^a
1 π	12.19	12.29	12.52	12.66	12.79
2 σ	16.27	16.44	16.50	16.67	16.72

a) Centroids estimated from the spectra in Ref. 4 and Ref. 87

Using a basis set of double-zeta quality one obtains a rather large error both for the 1 π and the 2 σ ionization energy. Both energies are calculated too small. Addition of a polarization function on each center only slightly improves the situation. Adding another d-type function on the Cl atom (with a rather small exponential parameter) gives a more substantial improvement. The calculation with 5 d- and 1f-type function proves to be in very good agreement with experiment.

Application to formaldehyde^{88,89}

The formaldehyde molecule is well studied by photoelectron spectroscopy. The HeI spectrum exhibits four bands. There have been many discussions in the literature about the assignment of the third and the fourth band. According to the original proposal of Baker et al.^{90,4} the third IP corresponds to the 1b₂ MO and the fourth IP to the 3a₁ MO. Their argument was based on the analysis of the vibrational structure of both bands. Brundle et al.⁹¹ on the other hand favoured the reverse assignment on the basis of an ab initio calculation. Recently a X α -scattered wave calculation employing overlapping spheres has been performed⁹² and the ordering proposed by Baker et al. was obtained. Previous Green's function calculations⁹³ as well as Rayleigh-Schrödinger perturbation calculations⁹⁴ predicted the ordering given by Koopmans' theorem to be the correct one. To settle this problem definitely the IP's have been recalculated with the Green's function method employing an extensive basis set^{88,89}.

The interpretation of the vibrational structure in the PES of H₂CO has proved to be difficult as well owing to the accidental degeneracy of vibrational frequencies in some of the ionic states. Especially for the second band (1b₁ (π)) of H₂CO and D₂CO no assignment of the vibrations involved could be given, although the vibrational structure is well resolved and apparently simple. For these reasons the vibrational structure of the bands was calculated as well.

The basis set used in the calculation is (11s7p1d/6s1p)/[5s3p1d/3s1p]⁸². The final results for the IP's are given in table 4.

Table 4: IP's of formaldehyde (in eV)

Symmetry	IP	IP(exp) ^a
2b ₂	10.84	10.9
1b ₁	14.29	14.5
3a ₁	16.36	16.2
1b ₂	17.13	~17.0

a) estimated centroid of the band in the PES of H₂CO⁺

The computed values are within 0.2 eV of the experimental ones. Because of this agreement it can be concluded that the third band has to be assigned as 3a₁ and the fourth one as 1b₂. Koopmans' theorem thus supplies for this molecule the correct ordering of states. The ordering deduced from the overlapping spheres X_α-scattered wave calculation is incorrect.

In calculating the vibrational structure according to the method in ref. 95 only the three totally symmetric normal vibrations ν₁, ν₂ and ν₃ are taken into account.

We show the calculated vibrational structure together with the corresponding band in the experimental spectrum in figs. 3 to 6.

H₂CO and D₂CO represent complicated examples since the structure of several bands is the result of a superposition of two nearly degenerate normal modes. It is therefore essential to employ correct ionic state vibrational frequencies in drawing the spectra. Having calculated only linear vibrational coupling constants we are not in a position to predict the frequency change due to ionization. Therefore the experimental ionic frequencies are used to draw the calculated vibrational structure. Although the ionic frequencies are not unambiguously known for most of the ionic states of H₂CO and D₂CO it is found that they can easily be determined from the structure observed in the spectrum with the help of the calculated Franck-Condon factors. An exception is only the fourth band because of its low intensity, the very complex vibrational structure and the severe overlap with the third band. However, the vibrational structure calculated for this band is very complex and does not critically depend on the frequencies chosen in drawing the spectra.

The first band (fig. 3) corresponds to a nonbonding electron. The calculated vibrational structure is in satisfactory agreement with experiment showing that all three normal modes are weakly excited.

The second band corresponds to ionization of the 1b₁ CO π-bonding electron and exhibits the expected strong excitation of the C-O stretching mode ν₁ (fig. 4). The higher resolution spectra, however, reveal that the lines are doublets for both molecules. Thus at least one other mode must

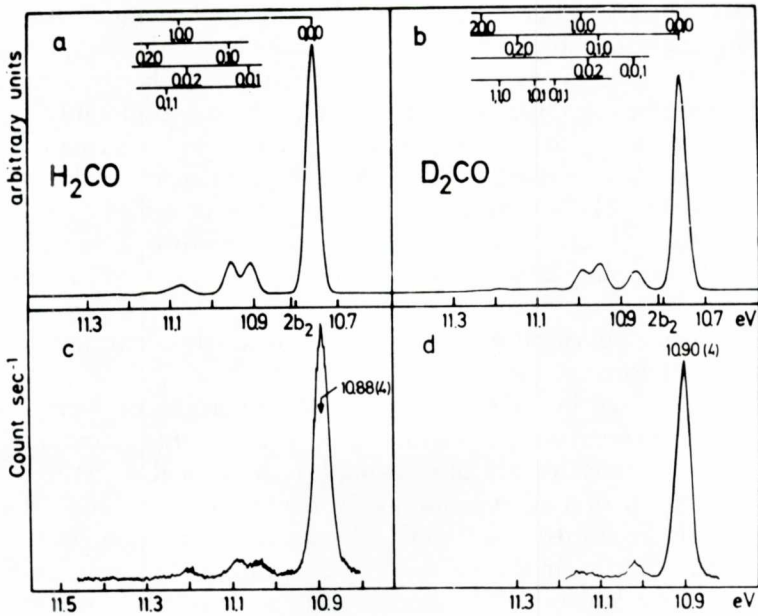


Fig. 3 The calculated (a), (b) and observed (c), (d) first band in the photoelectron spectrum of H_2CO and D_2CO .

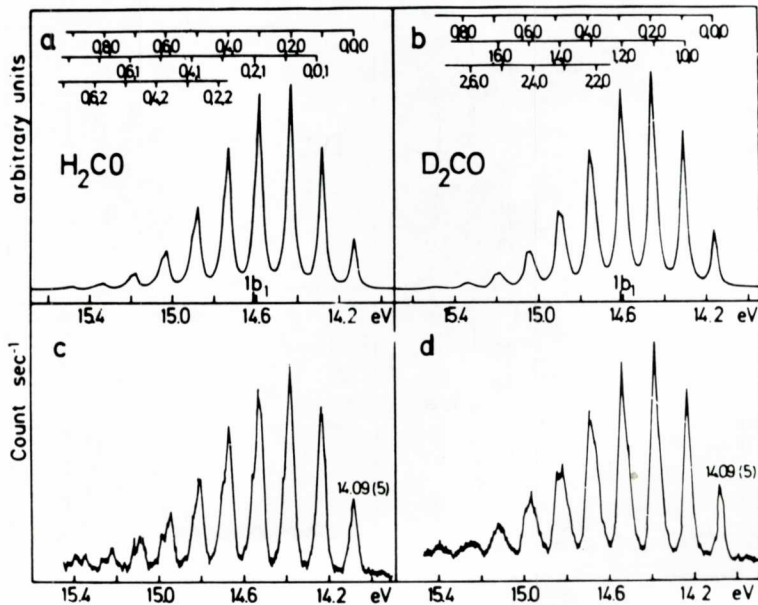


Fig. 4 The calculated (a), (b) and observed (c), (d) second band in the photoelectron spectrum of H_2CO and D_2CO .

be excited. The assignment of this mode has caused difficulties. According to Turner et al.⁴ the structure is due to ν_2 , together with one quantum of the C-H stretching mode ν_1 . It is then difficult to explain, however, the lack of isotope effects. One would expect ν_1 to be considerably reduced for D_2CO and thus the accidental near degeneracy of both frequencies in H_2CO should be removed for D_2CO . The problem is resolved by the calculations. For H_2CO the vibrational structure is due to excitation of ν_2 and ν_3 , for D_2CO , on the other hand, the structure is due to ν_1 and ν_2 . Thus the coupling is completely different for these two isotopic species.

The calculated vibrational structure is in nearly quantitative agreement with experiment.

The third band in the spectrum of H_2CO consists of a single series of narrow lines (fig. 5). From a comparison with the third band of D_2CO which shows a considerably more complex vibrational structure due to strong excitation of both ν_2 and ν_3 Turner et al.⁴ concluded that the simplicity of the third band of H_2CO was due to a degeneracy of the frequencies ν_2 and ν_3 in the ionic state. This interpretation is confirmed by the present calculations. We find strong excitation of ν_2 accompanied by weak excitation of ν_3 in the case of H_2CO . For D_2CO , on the other

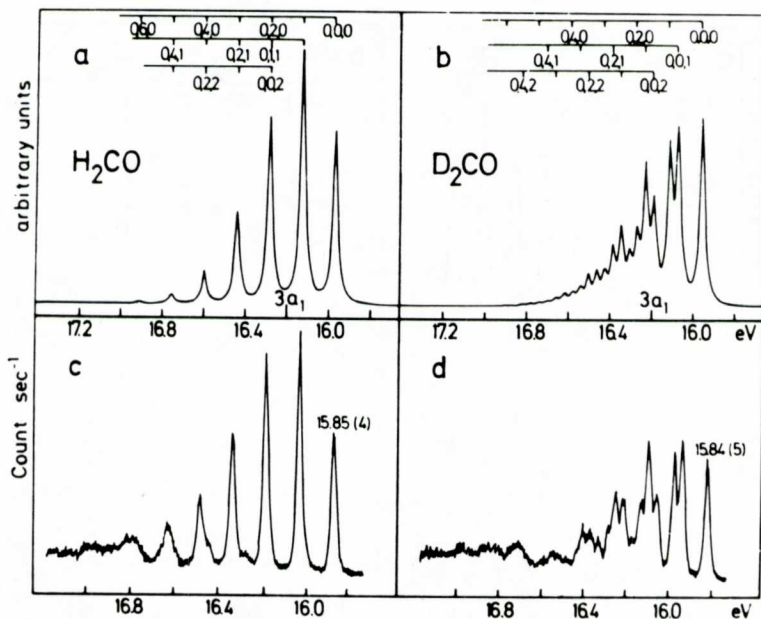


Fig. 5 The calculated (a), (b) and observed (c), (d) third band in the photoelectron spectrum of H_2CO and D_2CO .

hand, both ν_2 and ν_3 are calculated to couple strongly, the coupling of ν_3 being even stronger than that of ν_2 .

The fourth band appears as a complex and diffuse structure in the spectra of both H_2CO and D_2CO (fig. 6). From the calculated coupling parameters we see that all three normal vibrations are strongly excited in the case of D_2CO , whereas for H_2CO only ν_1 and ν_3 couple strongly. In both cases a very complex vibrational structure results in agreement with the experimental situation. It is seen that excitation of three normal modes leads to a vibrational structure of such a complexity that it cannot be resolved with present-day spectrometers. From the computed vibrational structure it is now obvious that the third band of H_2CO has to be assigned as $3a_1$ and the fourth one as $1b_2$. The vibrational mode ν_1 is not excited in the third band of D_2CO but should appear in the fourth band. In the experimental spectrum there is clearly no indication of the ν_1 mode in the third band.

*Application to Benzene*⁹⁶

Owing to the fundamental importance of the benzene molecule in chemistry it has been extensively investigated. Many investigations by

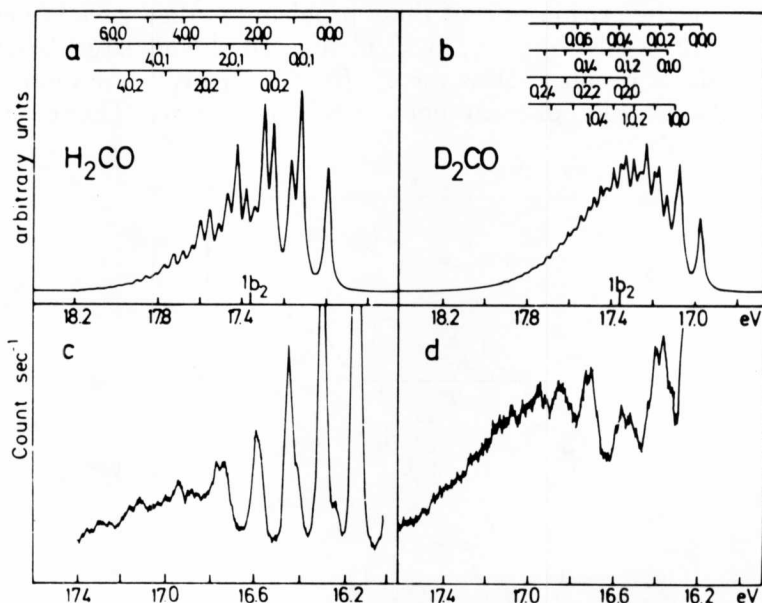


Fig. 6 The calculated (a), (b) and observed (c), (d) fourth band in the photoelectron spectrum of H_2CO and D_2CO . Note that the intense lines at lower energies in parts (c) and (d) belong to the third band. The fourth band is the diffuse structure centered at about 17.0 eV. Note also that the experimental spectrum of H_2CO (c) has been recorded with less amplification than that for D_2CO (d).

photoelectron spectrometry do exist (see ref. 96 for a list of references). But in spite of all this work a few points in the assignment of the spectrum remained controversial for a long time. The overlapping of bands and the possibility of Jahn-Teller splitting in the ionic states rendered the assignment of the bands difficult. It was agreed that 8 IP's should lie in the energy range up to 21.21 eV and that the first IP of benzene is due to ionization from the degenerate e_{1g} (π) orbital. The next two IP's are attributed to the degenerate e_{2g} (σ) and the nondegenerate a_{2u} (π) orbitals, but the relative order could not be unambiguously established. The convergence of Rydberg series, the perfluoro effect, deuterium substitution, the vibrational structure and many other data were used to assign the spectrum, but agreement could not be reached; the assignment remained a matter of interpretation. Another controversy concerned the relative ordering of the $2a_{1g}$ and $1b_{1u}$ IP's at 15.45 eV and 16.85 eV (the MO's are again numbered starting with the first valence orbital). This problem was settled by Gelius using intensity arguments to interpret the ESCA spectrum.⁹⁷ As the $1b_{1u}$ MO has strong C 2s character in contrast to the $2a_{1g}$ MO it should appear with higher intensity in the ESCA spectrum. This is the case for the band at 15.45 eV.

Theoretical calculations on the SCF level of approximation were of little help in the clarification of these problems as they gave rather divergent results. Only the ab initio calculations employing larger basis sets gave acceptable results. But as the e_{2g} (σ) a_{2u} (π) MO's are quite close together the inclusion of many-body effects is necessary. The results are given in Fig. 7.

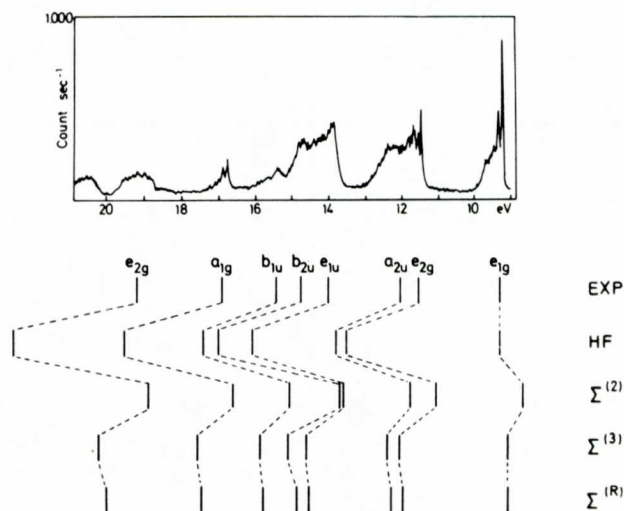


Fig. 7 He I PES of benzene from ref. 4 and calculated vertical ionization energies.

In this case there is no change of ordering in going from the Koopman' approximation result to the final results. The e_{2g} IP is smaller than the $a_{2u}(\pi)$ IP and the $1b_{1u}$ IP smaller than the $2a_{1g}$ IP to mention only the two most controversial points.

But due to these basis set deficiencies it might still be argued that the ordering of the second and third IP's is open to some debate as they are separated by only 0.3 eV. In this case the calculation of the vibrational structure of the two bands could bring the decision. Due to the high symmetry of benzene and as only totally symmetric vibrations couple in first order to the electronic motion the vibrational structure in the PES can be computed. This has been done for the e_{2g} and a_{2u} bands neglecting, however, the Jahn-Teller effect in the e_{2g} band. The results are given in Fig. 8. Comparing with the experimental spectrum in Fig. 7 it becomes obvious that the onset of the second band system cannot be due to the a_{2u} band which shows strong vibrational structure. As the a_{2u} band cannot show a Jahn-Teller effect we can make a definite assignment.

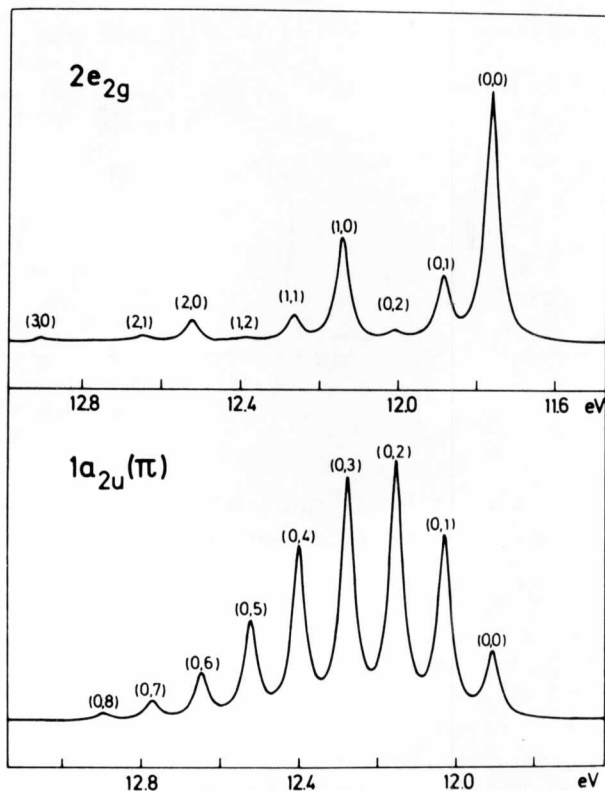


Fig. 8 The calculated vibrational structure of the $2e_{2g}(\sigma)$ and $1a_{2u}(\pi)$ bands of benzene.

Actually every chemist should have argued for the present assignment. The a_{2u} (π) MO is the lowest occupied π -orbital and must be strongly C-C bonding and thus should show strong vibrational excitation. This is not the case for the onset of the second hand system. Instead, it was argued that the onset of the second hand system shows weak vibrational excitation and thus the a_{2u} (π) MO is nonbonding!

Application to the CS Molecule

The PES of CS (Fig. 9) contains four bands⁹⁸ below 20 eV instead of three bands (due to ionization from 7σ , 2π , and 6σ ; ionization of 5σ electrons occurs above 20 eV), i.e., there is one band too many. This phenomenon can be explained by the TDA calculations (see Fig. 10). The solution for the 7σ ionization energy occurs in the main interval of the self-energy and leads to a large pole strength; the same is the case for 2π ionization.

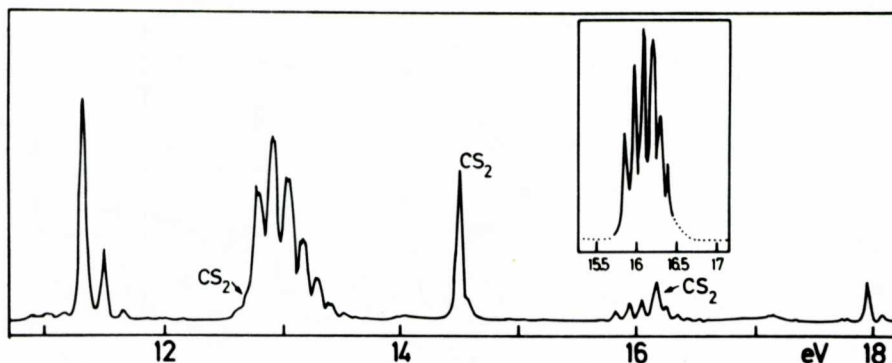


Fig. 9 The PES of CS from ref. 98.

In the case of the 6σ orbital one solution is still found in the main interval but close to the first pole and another solution of approximately equal pole strength in the first interval. These two solutions explain the experimental finding. The 6σ line is split into two lines at about 16 and 18 eV by final state correlation effects. None of these lines corresponds to simple ionization from the 6σ orbital.

The 5σ orbital energy lies in the midst of many poles of the self-energy. Here we find many solutions of about equal intensity. The orbital picture of ionization thus breaks down for ionization out of the 6σ and 5σ orbitals. The line spectra for 7σ , 6σ , and 5σ ionization are given in Fig. 10.

Application to CS₂¹⁷

As the next example we consider CS₂; the PES of this molecule contains two intense satellite lines at very low energy (about 14.1 and 17.0 eV).^{4,17} Both arise from $2\pi_u$ ionization, but their intensity (about 4% and 16%) is still small compared to the main line. We will not discuss this point in detail) but turn to the energy region above 20 eV. The ESCA spectrum⁹⁹ is reproduced in Fig. 11. It shows a broad band extending over about 20 eV which contains little structure.

In the orbital model two bands ($4\sigma_u$ and $5\sigma_g$) should be found in this energy range. But this clearly cannot explain the observed structure. Vibrational broadening cannot account for it either. The explanation is given by the calculated spectrum (Fig. 12). The $4\sigma_u$ and $5\sigma_g$ lines are smashed to pieces by many-body effects and numerous lines appear instead of the expected two lines. The two calculated spectra differ in some details which is to be expected, because of the complicated nature of these resonance states, but both explain the observed spectrum in a very satisfactory way.

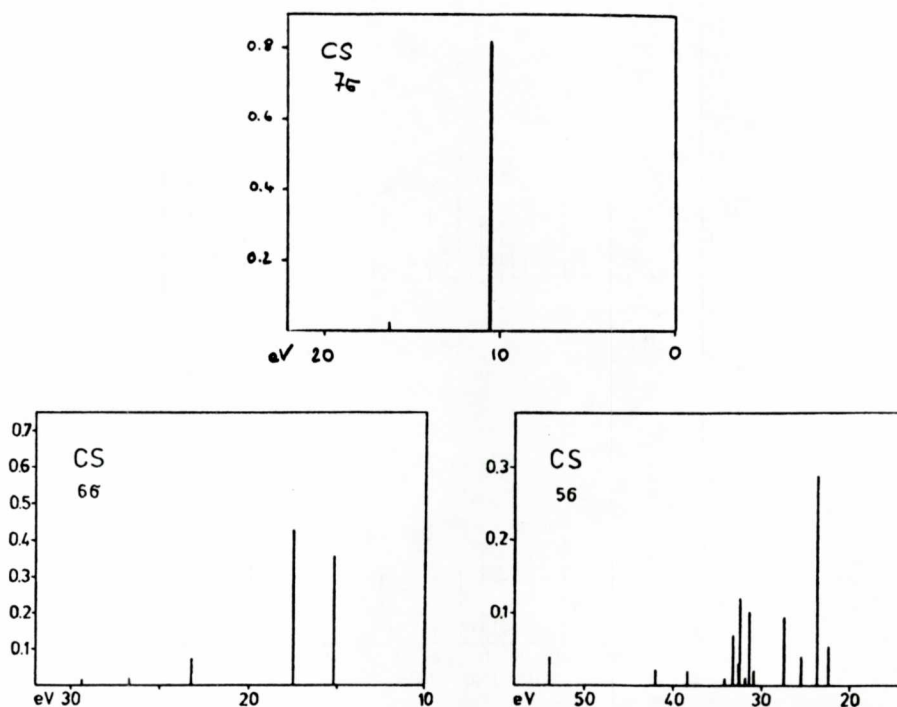


Fig. 10 The calculated ionization spectra of CS (7σ , 6σ and 5σ orbitals). Note the different ordinate scale for the 5σ spectrum.

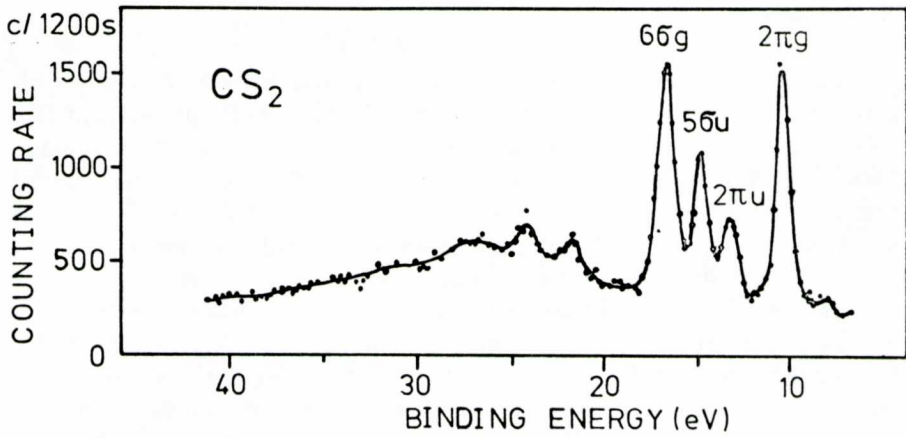


Fig. 11 MgK_{α} PES of CS_2 as recorded by Allan et al.⁹⁹

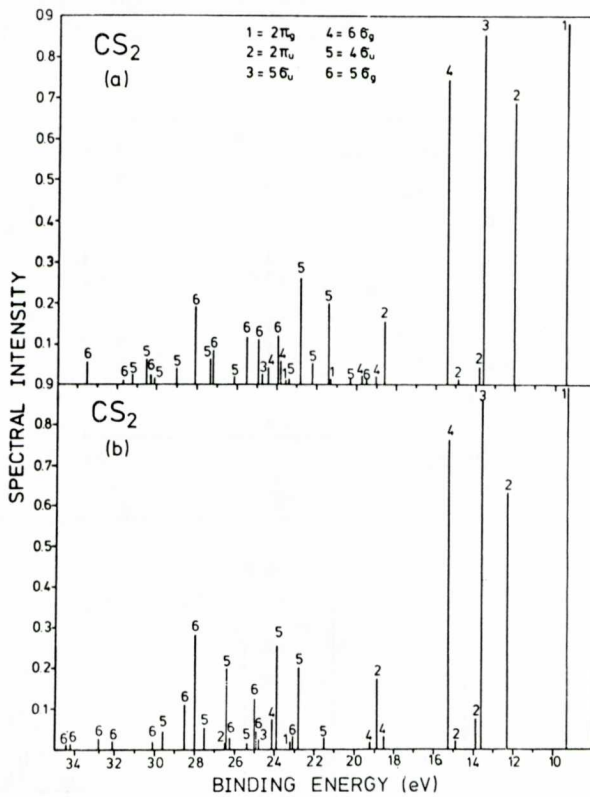


Fig. 12 Calculated positions and relative intensities for the ionic states arising from valence ionization of CS_2

a) basis set (12s9p/9s5p); b) basis set (12s9p2d/9s5p1d)

Application to N_2^{14}

The ESCA spectrum of N_2 in the range from 20 to 45 eV¹⁰⁰ is plotted in fig. 13. It contains some structure between 20 and 35 eV and a broad band between about 35 and 40 eV.

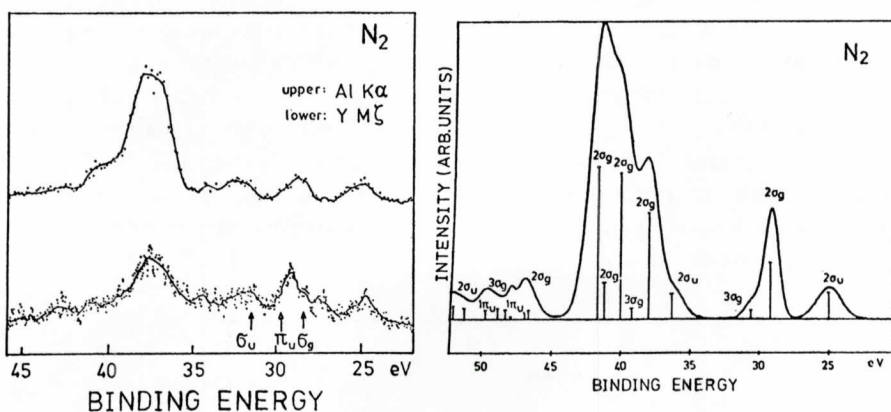


Fig. 13 Calculated and observed inner valence spectrum of N_2 (from ref. 100).

The theoretical spectrum drawn underneath is obtained from the TDA calculation which uses only a double zeta basis set.¹⁴ The calculation demonstrates that the unusual width and strange shape of the band between about 35 and 40 eV is due to the fact that excitation to several ionic states occurs instead of only to the simple $2\sigma_g$ hole state. None of the three major lines in this energy range corresponds to an excitation to a simple $2\sigma_g$ hole state but they do obtain their intensity from this transition.

An improved calculation by the extended 2ph-TDA method and employing a large basis set (11s7p1d) gives improved values of the ionization energies in particular in the outer valence region where the same accuracy is achieved as with the OVGf method but the results in the inner valence region do not change qualitatively.¹⁰¹

The ionization of the $2\sigma_g$ inner valence orbital of N_2 provides an interesting, though complicated, example for the interaction of several close-lying electronic states through vibrational modes. The experimental ionization spectrum of the inner valence orbital in N_2 exhibits a few bands and we concentrate here on the most intense band ranging from approximately 36 to 40 eV binding energy. Fig. 14 shows this band as measured by Krummacher et al.¹⁹ using monochromatic synchrotron radiation of

44.1 eV. Several calculations on the ionic states included in this band are available.^{14,33,38,101} They all clearly indicate that several electronic states of the ion fall into the 36-40 eV energy range and may thus participate in the vibronic coupling problem leading to the observed structure of the band. To investigate this structure a simple model has been introduced¹⁰² which takes into account 20 interacting ionic states. Using vibronic coupling constants estimated by the 2ph-TDA, the calculation makes clear that the experiment cannot be understood without consulting theory. The multistate vibronic coupling mechanism leads to strong nonadiabatic effects. These tend to smooth out the envelope of the band and make it look like a vibrational progression of a single electronic transition as seen in Fig. 14. It should be noted however, that the "vibrational spacings" in this spectrum are not equidistant nor monotonic. High resolution spectra and more elaborate calculation are necessary to resolve the nature of the underlying nonadiabatic effects.

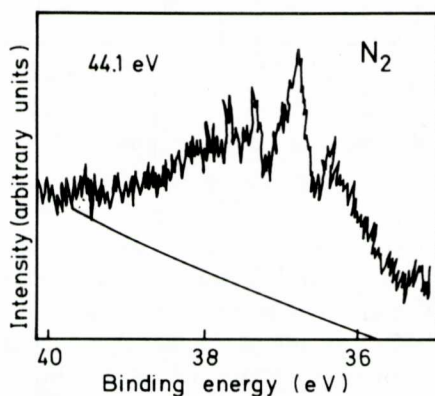


Fig. 14 Inner valence region of the PES of N_2 measured by Krummacher et al.¹⁹ using monochromatic synchrotron radiation of 44.1 eV.

*Application to p-quinodimethane (PQDM)*¹⁰³

We have seen above that satellite lines are very abundant in photoelectron spectra. Surprisingly it came as a surprise that such lines appear in larger organic molecules at very low energies. In 1975 Koenig et al. assigned a weak feature in the PES of PQDM to a satellite line.^{50,104} His interpretation was not universally accepted.¹⁰⁵ But a considerable amount of research both by spectroscopy and by theoretical calculations established that Koenig's original interpretation is most likely the correct one.^{47,50,105-108} Since this time the search for low energy satellite lines is a very active field of research.

We have applied the extended 2ph-TDA method to this molecule. The calculation employed a double-zeta basis set. The ionization spectrum calculated with this method in the entire valence region is plotted in fig. 15 which also contains the PES from ref. 104. From the figure we conclude that the one-particle model of ionization applies only to ionization from the orbitals $2b_{3u}(\pi)$, $1b_{1g}(\pi)$, $3b_{3g}$, $5a_g$, $4b_{2u}$, $4b_{1u}$, $2b_{3g}$, $3b_{2u}$ and $2b_{2u}$ but not to ionization from some of the lowest binding energy orbitals $18 = 1b_{2g}(\pi)$ and $16 = 1b_{3u}(\pi)$ although appreciable satellite line structure is also found for the other cases. According to the extended 2ph-TDA calculation the $1b_{2g}$ line is split into two strong and one weaker component. The first component is calculated to lie a bit at lower energy than the $1b_{1g}$ line and the second component slightly before the $3b_{3g}$ line. All semiempirical and ab initio calculations agree that the two components contribute to the second and third band systems in the PES.

The configurations which contribute dominantly to the line are $1b_{2g}^{-1}$, $2b_{3u}^{-2} 2b_{2g}$ and somewhat less $1b_{1g}^{-1} 2b_{2u}^{-1} 1a_u$. The first two configurations contribute to both components of the line with about equal weight and no line can be called the main line and the other one the satellite line.

The second low energy line which splits is the $1b_{3u}(\pi)$ line. Here we obtain again two strong and one somewhat weaker component (fig. 15).

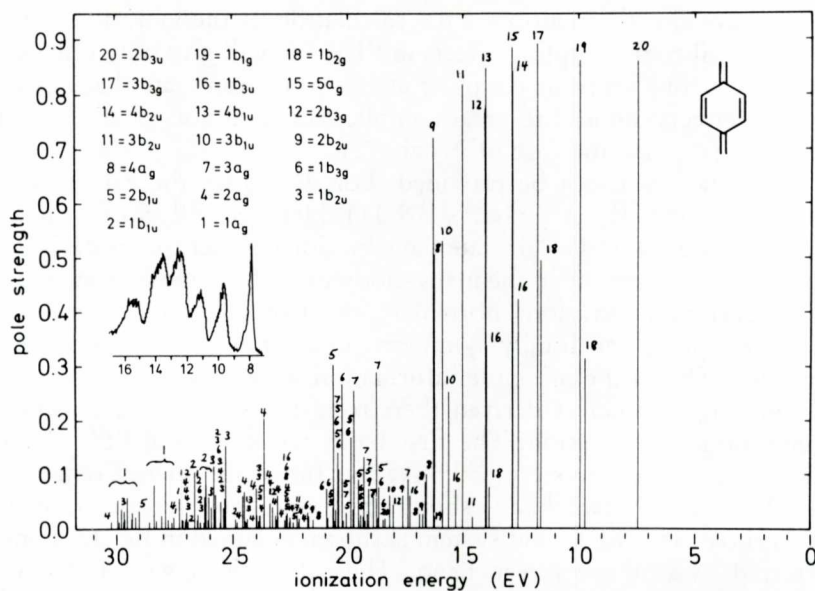


Fig. 15 Valence ionization spectrum of p-quinodimethane as calculated with the extended 2ph-TDA method; only lines with a pole strength greater than 0.01 are plotted. The experimental spectrum is from ref. 104.

The first component contributes to the fourth band system ($5a_g$ and $4b_{2u}$ ionization) and the second one to the fifth band system ($4b_{1u}$ and $2b_{3g}$ ionization). The dominant configurations are in this case $1b_{3u}^{-1}$ and $2b_{3u}^{-2}$ $3b_{3u}$ and with somewhat smaller weight $1b_{2g}^{-1}$ $2b_{3u}^{-1}$ $2b_{2g}$ and $1b_{2g}^{-1}$ $1b_{1g}^{-1}$ $1a_u$. Thus the dominant excitation process is in this case not the HOMO-LUMO excitation but the excitation from the HOMO into a higher lying virtual orbital.

Above about 16 eV a very dense structure of lines is found typical for the complete breakdown of the molecular orbital model of ionization. As mentioned before this structure can only be considered as qualitatively correct.

There is a unifying aspect which permits to predict whether strong correlation effects are to be expected for a molecule without performing detailed calculations.⁴⁸ If a molecule possesses low lying non-diffuse virtual orbitals, i.e., virtual orbitals localized in the same region of space as the occupied ones this is an indication that strong many-body effects are to be expected. This is in congruence with the fact that the HOMO-LUMO excitation is frequently the dominant process for explaining the satellite lines.

*Vibronic coupling effects in butatriene*¹⁰⁹

We have shortly mentioned the calculation of the vibrational structure and of vibronic coupling effects in PES. We will give only one example of very strong vibronic coupling effects to demonstrate that not only electronic effects can lead to great complications but also vibronic coupling effects. (see also the case of N_2 above).

The details will not be provided. For details on the calculation of vibronic coupling effects see ref. 's 109-111. Here we will shortly mention the case of butatriene. To calculate the vibrational structure the derivatives of the orbital energies or in the many-body case of the ionization energies with respect to the various normal modes (totally symmetric and for vibronic coupling non-totally symmetric ones of appropriate symmetry) are needed. This is the principle information which has to be computed. The coupling parameters derived therefrom determine the intensities in the vibrational progression. The first band system in the PES of butatriene¹¹² presented a mystery,^{112,112} see fig. 16. In the energy range from about 9 to 10.5 eV two bands should be found, but the spectrum does contain three. This first band system is shown enlarged in fig. 17. Band 1' is referred to as the mystery band. The calculations with the OVGf method and different basis sets are shown in fig. 17 as well. It is seen that only two ionization processes ($1b_{3g}$ (π) and $2b_{3u}$) can be assigned to this band system. The clue to the mystery band lies in the fact that the ${}^2B_{3g}$

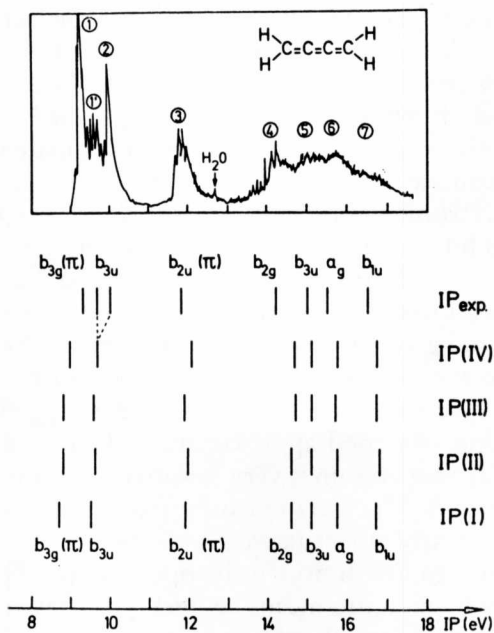


Fig. 16 PES of butatriene from ref. 112 and ionization energies calculated by the OVGf method with different basis sets.

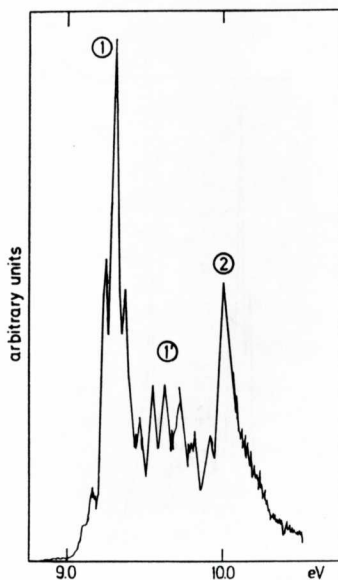


Fig. 17 The first band system in the PES of butatriene (ref. 112). The band 1' is referred to as the mystery band.

(π) and ${}^2B_{3u}$ states are quite close in energy so that the Born-Oppenheimer approximation breaks down. The two states are coupled by a vibration of a_u symmetry which is the torsional vibration. In this way the vibrational structure can, however, not be explained at all. The coupling to the totally symmetric modes is very important. Fortunately it is only one totally symmetric mode (one of the CC stretching modes) which couples strongly to the electronic motion in this particular case. One mode modulates the potential for the other one; thus the two modes cannot be separated. This effect is of fundamental importance (see also C_2H_4 ¹¹⁰ and HCN¹¹¹). The ab initio data give a qualitative explanation for the mystery band but they do not give a good fit to the experimental spectrum. Adjusting, however, the energies and the coupling constants an excellent fit to the experimental spectrum is obtained. The underlying vibronic coupling Hamiltonian¹⁰⁹ thus is a good approximation. This theoretical spectrum is given in fig. 18. The spectrum is very sensitive to minor variations in the coupling constants. A 5% variation only from the calculated coupling constants gives a nearly quantitative fit to the experimental spectrum. With the experience gained at present it appears hopeless to determine all parameters purely by ab initio means and get quantitative agreement with experiment. The parameters should be calculated in an ab initio manner to understand the physics underlying the observed phenomenon i.e. which vibrations are involved and how strong; but to obtain quantitative agreement requires a fitting.

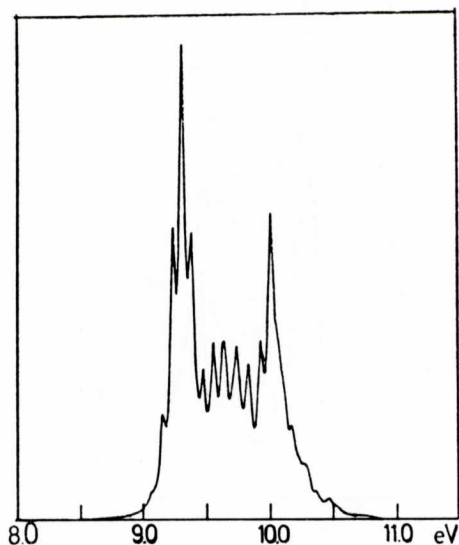


Fig. 18 Calculated first band system of the PES of butatriene (ab initio data plus fit).

The case of the first band in butatriene is the case of very strong vibronic coupling. The Born-Oppenheimer and the Franck-Condon approximations break down completely. Individual lines can in general no longer be associated with the individual electronic states or with the individual vibrational modes. The lines are of combined electronic and vibrational origin and are mixed of totally and nontotally symmetric modes.

Concluding Remarks

We hope to have demonstrated the usefulness of Green's functions in the calculation and interpretation of PES. The complexity of electronic and vibrational processes which find their expression in PES require powerful computational tools and both theoretical and numerical developments. It is also apparent that many physical effects can only be discovered by extensive applications to a large number of molecules.

Acknowledgement

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