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An experimental and theoretical study of the resonant Auger spectrum of the ethene molecule

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Abstract

Resonant Auger spectra of the ethene molecule excited at energies across the $C1s \rightarrow \pi^*$ energy band are reported. Our measurements address the unexpected variation of the intensity of the A state with respect to the other singly ionized valence states. An approach, based on group theory and calculations using Coulomb 4-center integrals, is proposed to explain the behaviour of the intensity of the ground state and excited states of the ion upon resonant excitation. The new method provides a computationally inexpensive route to predict relative intensities of different resonant Auger bands in polyatomic molecules, without the need for an exhaustive knowledge of the potential energy surfaces of the electronic states involved.

Keywords: resonant Auger, ethene, group theory, 4-center integrals



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In the resonant Auger process an inner shell electron is promoted to an excited state (unoccupied orbitals or Rydberg states) upon absorption of a photon. Subsequently, the short-lived neutral intermediate state can rapidly decay by non-radiative emission. While in the case of diatomic molecules experimental results as well as theoretical calculations can describe accurately the resonant Auger process, in the case of larger molecules this is not possible due to the high number of degrees of freedom of the system. As an exception, in the case of the ethene molecule some remarkable theoretical work has been done by the group of Gel'mukhanov [1].

The inner shell resonant processes, in ethene, have been studied mostly in relation to the absorption spectra where the issue of the breaking of the symmetry in the core-excited state leading to the core-hole localization [2–5] has been addressed. Sorensen *et al* [6] concentrated on the study of the Auger decay and Piancastelli *et al* [7] focussed on the induced dissociation processes. From the theoretical point of view, apart from the work of Gel'muhanov, only Fink *et al* [8] have calculated the resonant Auger electron spectrum with an *ab initio* approach by means of a configuration interaction method and the transition rates by using the 'one-center approximation'.

The study of the electron emission when the photon energy is detuned from the resonance maximum (detuning Ω) can provide insights into the system under consideration [7, 9–11]. In the resonant process, indeed, the vibrational distribution of a final electronic state is 'filtered' by the vibrational intensity distribution of the intermediate excited electronic state. In a time-independent formulation, the matrix element which governs the resonant process is formed by two parts: the first linking the ground to the intermediate state and the second linking the intermediate state to the final state. While the absorption process is governed by the dipole matrix element, the decay is controlled by the Coulomb interaction. Therefore, the dipole selection rules hold for the absorption process, while in the decay the selection rules are not expected to be applicable.

Nevertheless, some interest has been drawn by the unexpected changes in the resonant Auger spectra (RAS) reported in the case of the N_2 molecule, where the cation B state shows a weak intensity, when the photon energy crosses the π^* resonance with respect to the other valence states [12–14]. Similar behaviour has also been recorded for the A state of the CO molecule [15]. It is found here, that the ethene molecule also shows a weak decay for the A state, when the photon energy is tuned across the π^* resonance. The accurate description of this phenomenon for N_2 and CO is obtained, thanks to the detailed information about the vibrational distribution of the intermediate and final states, the corresponding potential energy surfaces [12, 14], as well as taking into account the interference between the direct and resonant processes [16]. Similar methodologies cannot be easily implemented when dealing with larger molecules.

A different approach based on group theory, which explains why such a weak decay intensity is associated with the A band upon excitation through the π^* resonance, is proposed here. We aim at calculating the Auger intensities without detailed knowledge of the vibrational distribution of the final (and intermediate) states and neglecting the direct photoemission process. This simplified approach can be helpful for a variety of symmetric molecules showing large variation of resonant Auger intensities.

The measurements were performed at the Gas Phase Photoemission beamline of the ELETTRA storage ring in Trieste, Italy. The line is fed by an undulator, which delivers light in

the range from 14 eV to above 900 eV. A detailed description of the beamline can be found elsewhere [17]. Both the resonant Auger and photoelectron spectra were measured with a photon bandwidth of less than 50 meV. Electron spectra were measured by a VG hemispherical analyser operated at 7 eV pass energy leading to an overall resolution of 140 meV (beamline + analyser). The main axis of the spectrometer was set parallel to the electric field vector of the linearly polarized radiation. X-ray absorption spectroscopy (XAS) spectra have been recorded in total ion yield mode, by means of an ion time flight analyser mounted in front of the electron analyser. The photoelectron spectrum of ethene was also measured at a photon energy of 100 eV. All the spectra have been aligned to the $\nu = 0$ state of the X electronic state whose binding energy is 10.512 eV [1, 18].

In figure 1(a) the absorption bands of ethene corresponding to the $1s \rightarrow \pi^*$ and $1s \rightarrow$ Rydberg transitions are shown. The energy scale has been calibrated assigning the energy of 284.37 eV to the first small feature in the spectrum [4]. The XAS spectrum consists indeed of two main peaks showing a vibrational structure originating from the excitation of several totally and non-totally symmetric vibration modes [1, 3, 5]. The numbers in the XAS spectrum indicate the points at which the electron spectra have been recorded. In figure 1(b), the photoemission spectrum and the RAS spectra are presented. All the electron spectra have been normalized to the background at low binding energy. In figure 1(b) the photoelectron spectrum recorded with a photon energy of 100 eV allows a comparison with the detuned spectra displayed below and is consistent with the literature [18–20], though one-to-one correspondence with the RAS electronic states is not expected [21]. The ground state X $(1b_{3u})^{-1}$ as well as the excited states from A to D show clear vibrational structure.

The first spectrum has been taken at 274.3 eV, negatively detuned ($\Omega = -10$ eV) with respect to the maximum of the π^* resonance (set at 284.37 eV). Although the branching ratio of the A to the X state changes, the first excited state of the ion is clearly visible. The spectrum recorded at 283 eV, i.e. at $\Omega = -1.3$ eV detuned from the top of the resonance, shows the same branching ratio between the A and the X state, still mimicking the lineshape of the photoelectron spectrum. Indeed, as already known from theory, off-resonance spectra reproduce the lineshape of the fast decay in which the potential energy surface of the excited state is not explored [9, 22]. It is noteworthy that the D state exhibits apparently an anomalously strong intensity off resonance: this is due to the relative increase of the atomic C 2s cross-section in comparison to the atomic C 2p cross-section. On resonance, i.e. in the spectra labelled 1–4, the relative intensity of the A state changes drastically. In the spectrum labelled 4 the intensity observed in the region of the A band is mainly due to the Raman dispersion of the vibrational envelope of the X state [1]. The C band displays a different variation of the intensity with respect to the A band going from off- to on-resonance, as well as a change in lineshape. Indeed, while off-resonance the C band is clearly distinguishable, on-resonance this band seems to sit on a rapidly varying background as a function of the photon energy.

The spectrum labelled 5 is taken in between the π^* resonance and the Rydberg part of the absorption spectrum. The corresponding spectrum is off-resonance and positively detuned by $\Omega = +2$ eV. Here, there is a clear indication that the relative intensity of the ionic state A is now increasing with respect to the adjacent X state. The RAS spectra, recorded at the two Rydberg main transition lines, show the presence of all the valence states of the ethene ion, as in the

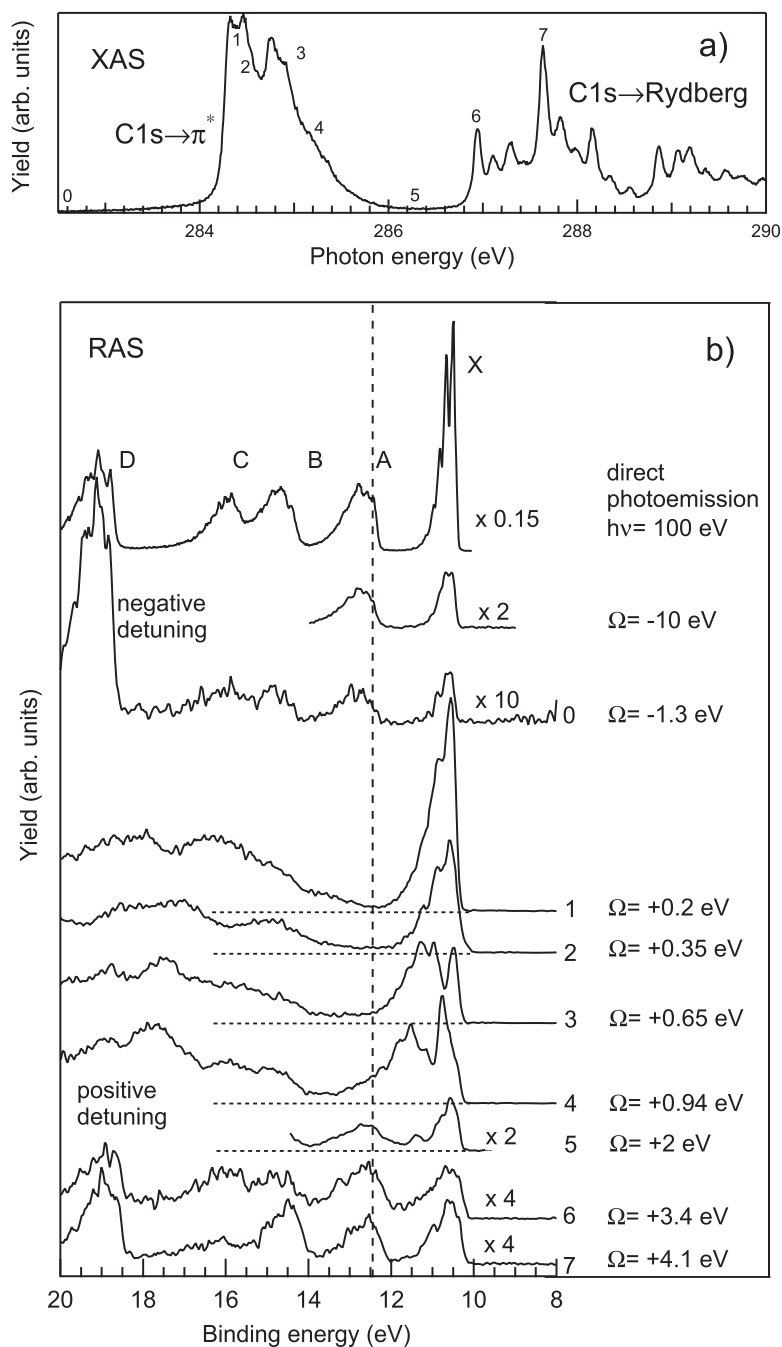


Figure 1. (a) Absorption spectrum of the ethene molecule measured by recording the total ion yield while scanning the photon energy. The numbers correspond to the photon energies at which the numbered spectra in (b) have been recorded. In (b) the comparison between the direct and the resonant process is displayed. The spectra have been taken at photon energy set below, across and above the π^* resonance: the broken lines refer to the vibrational ground state of the A electronic state at 12.446 eV [18].

direct photoemission process, regardless of the differences in the relative intensity of the C state.

In order to guide the eye across the spectra, a broken line has been traced in the figure 1. This line indicates the energy position of the A state as measured by Holland *et al* [18], at 12.446 eV for the vibrational ground state. Some intensity is detected in correspondence to the broken line with the spectrum taken on resonance. Here, it is considered that the contribution of the direct process must be present, but with a very low intensity as suggested by the intensity of the A state in the spectrum negatively detuned by 1.3 eV.

For the A state some intensity at points 3 and 4 is also detected. Besides the contribution of the direct process, this can be ascribed also to the evolution of the vibrational envelope of the X state as a function of the photon energy, as discussed in detail in [1]. One may argue that the angular anisotropy of the Auger decay might affect the present observations. Recent measurements, carried out at the Pleiades beamline (Soleil synchrotron radiation source) at the magic angle, where no angular effects are expected, confirm clearly the variation of the relative intensity of the A state when the photon energy crosses the π^* band [23]. We interpret these observations as a clear manifestation of a strong resonant behaviour of all the valence ionic states of ethene, with the exception of the A state.

The ethene molecule, C_2H_4 , is planar in its ground state and belongs to the D_{2h} symmetry group. With the molecule in the x - y plane and the C-C bond along the x axis, the electronic configuration of the ground state can be written as $(1a_g)^2(1b_{1u})^2(2a_g)^2(2b_{1u})^2(1b_{2u})^2(3a_g)^2(1b_{3g})^2(1b_{3u})^2$, while the π^* LUMO orbital is $1b_{2g}$.

The transitions from core-hole excited $C_{1s}^{-1}\pi^{*+1}$ to the $X-D$ states of $C_2H_4^+$ depend on two-electron integrals:

$$2J - K = 2 \int d\mathbf{r}_1 d\mathbf{r}_2 1s(\mathbf{r}_1) \psi_k(\mathbf{r}_2) G_{12} \psi_u(\mathbf{r}_1) \pi^*(\mathbf{r}_2) - \int d\mathbf{r}_1 d\mathbf{r}_2 1s(\mathbf{r}_1) \psi_k(\mathbf{r}_2) G_{12} \psi_u(\mathbf{r}_2) \pi^*(\mathbf{r}_1), \quad (1)$$

where the J and K are the Coulomb and exchange integrals, respectively, and G_{12} is the Coulomb operator $1/r_{12}$, $1s$ indicates the wavefunction of the molecular orbital (MO) associated with the core hole, ψ_k is the wavefunction of the free Auger electron, ψ_u the wavefunction of the unoccupied MO in the cation final state, and π^* the wavefunction of the HOMO of the core excited intermediate state. The intensity of the Auger transition is $I_{\text{Aug}} = \frac{2\pi}{\hbar} |2J - K|^2$.

These integrals are non-vanishing only if the direct products of the irreducible representations (IR) of all the four wavefunctions are equal to the totally symmetric representation A_g , because the G_{12} Coulomb operator is totally symmetric:

$$\Gamma(\psi_k) \otimes \Gamma(\pi^*) \otimes \Gamma(1s) \otimes \Gamma(\psi_u) = A_g. \quad (2)$$

Let us consider the ethene Auger decay transition occurring from two core hole excited states [3] to five excited cation states:

Table 1. The symmetries of the unoccupied molecular orbital (MO) in $C_2H_4^+$ and the corresponding extracted symmetries for the free electron wavefunction. $\Gamma(\pi^*) = b_{2g}$.

Ionic state	Free Auger electron	
$\Gamma(\psi_u)$	$\Gamma(\psi_k)$	
X	b_{3u}	a_g
A	b_{3g}	a_u
B	a_g	b_{3u}
C	b_{2u}	b_{1g}
D	b_{1u}	b_{2g}

$$C_{1s}^{-1} \pi^{*+1} \left\{ \begin{array}{l} 1a_g^{-1} b_{2g}^{+1} (B_{2g}) \\ 1b_{1u}^{-1} b_{2g}^{+1} (B_{3u}) \end{array} \right\} \rightarrow \left\{ \begin{array}{l} 1b_{3u}^{-1} (X \ ^2B_{3u}) \\ 1b_{3g}^{-1} (A \ ^2B_{3g}) \\ 3a_g^{-1} (B \ ^2A_g) \\ 1b_{2u}^{-1} (C \ ^2B_{2u}) \\ 2b_{1u}^{-1} (D \ ^2B_{1u}) \end{array} \right\}. \quad (3)$$

The $\Gamma(1s)$ can be either $1a_g$ or $1b_{1u}$, and the $\Gamma(\pi^*)$ is b_{2g} . The energies of the two core hole excited states differ only by 0.02 eV [5]. Only the excitations to the u states are dipole allowed (in D_{2h} symmetry), although the g states may come into play if a coupling between the g and u states occurs via vibrational modes of suitable symmetry. Hence we consider the Auger decay starting from the $1s$ core hole of $1b_{1u}$ symmetry. It is worth noting that the interaction energy between these two configurations is small and even a small perturbation of the molecule induces the complete localization of the core-hole [8], making the two C atoms non-equivalent. In this regard, the choice dictated by the symmetry rules is equivalent to considering the core-hole to be completely localized [5, 24].

For every final ionic state (ψ_u) the J and K integrals are non-vanishing only if $\Gamma(\psi_k)$ is equal to the symmetries reported in table 1.

In order to study the effect of the symmetry on the I_{Aug} we have calculated the ground state wavefunction of the ethene molecule in its optimized nuclear geometry and determined the MOs. The calculations were conducted in the framework of the density functional theory using the Becke, 3-parameter, Lee–Yang–Parr functional [25], the wavefunction has been expanded on the aug-cc-pvtz basis set. The GAMESS code [26] has been used to calculate the energy, the MOs and the 4-center Coulomb integrals. The wavefunction ψ_k in equation (1) can be expanded at short range by a linear combination of the MOs of suitable symmetry ϕ_l and at larger range by using plane waves and scattering amplitudes $f_k(\theta, \varphi)$; A is a normalization constant:

$$\psi_k(r) = \sum_l c_l \phi_l + A \left(e^{ikz} + f_k(\theta, \varphi) \frac{e^{ikr}}{r} \right). \quad (4)$$

Table 2. Calculated Auger intensity and vertical binding energies compared with the results of [8]. In the first columns the final ionic states are listed with the corresponding symmetry. The intensities are normalized to 1 (state X) and the 0.0 eV binding energy corresponds to the energy of the ground state vibrational level of the X state, i.e. 10.512 eV [18].

Ionic state	$\Gamma(\psi_k)$	This work		[8]	
		$I_{\text{Aug}}^{\text{av}}$	BE(eV)	I_{Aug}	BE(eV)
X	a_g	1.000	0.00	1.00	0.00
A	a_u	0.031	2.97	0.22	2.94
B	b_{3u}	0.496	4.24	0.38	4.77
C	b_{1g}	0.013	5.41	0.13	6.24
D	b_{2g}	0.349	9.16	0.076	11.52

In contrast to more accurate approaches [16], our wavefunctions of the unbound electron are expanded over the discretized virtual MOs. We have focussed our attention on the short range part of ψ_k because the $1s$, ψ_u , π^* orbitals of equation (1) are mainly localized. The 2J–K can then be expanded in terms of the MOs and plane wavefunctions as follows:

$$2J - K = \sum_l c_l \left[2 \langle 1s(r_1) \phi_l(r_2) G_{12} \psi_u(r_1) \pi^*(r_2) \rangle - \langle 1s(r_1) \phi_l(r_2) G_{12} \psi_u(r_2) \pi^*(r_1) \rangle \right] + PW\text{int}, \quad (5)$$

where $PW\text{int}$ is the integral matrix element involving the long range part of the ψ_k , which will be neglected from now on.

Even if the c_l coefficients of the linear expansion of ψ_k are unknown, we can estimate for every ionic state symmetry (X, A, B, C, D) the I_{Aug} by evaluating the integral matrix elements over the subset of MOs of suitable symmetry (equation 5). In particular, we have considered for every symmetry of the ionic state the average of the integral matrix elements:

$$I_{\text{Aug}}^{\text{av}} \propto \left| \frac{\sum_l^N 1}{N} \left[2 \langle 1s(r_1) \phi_l(r_2) G_{12} \psi_u(r_1) \pi^*(r_2) \rangle - \langle 1s(r_1) \phi_l(r_2) G_{12} \psi_u(r_2) \pi^*(r_1) \rangle \right] \right|^2. \quad (6)$$

In the average of 2J–K integrals only virtual orbitals up to the cutoff energy of 40 eV have been used. This symmetry-based methodology, which makes use of the Coulomb 4-center integral matrix elements, can be applied also to linear molecules with an infinite number of IRs; even if in this case, continuum wavefunctions can be characterized by more than one symmetry, because the result of the direct products requires the coupling among different IRs.

The results of the calculations are reported in table 2: the average of 2J–K integrals as a function of the ionic state symmetry as well as the values reported by Fink *et al* [8] are listed for comparison. Vertical binding energies have been worked out following the Koopmans' theorem by using the eigenvalues of the MOs of the neutral ethene. The calculations have been performed at the B3LYP/aug-cc-pvtz calculation level.

The spectrum taken on resonance ($h\nu = 284.5$ eV) and the photoemission spectrum taken at photon energy of 100 eV are shown in figure 2. In the figure the calculated values (intensity

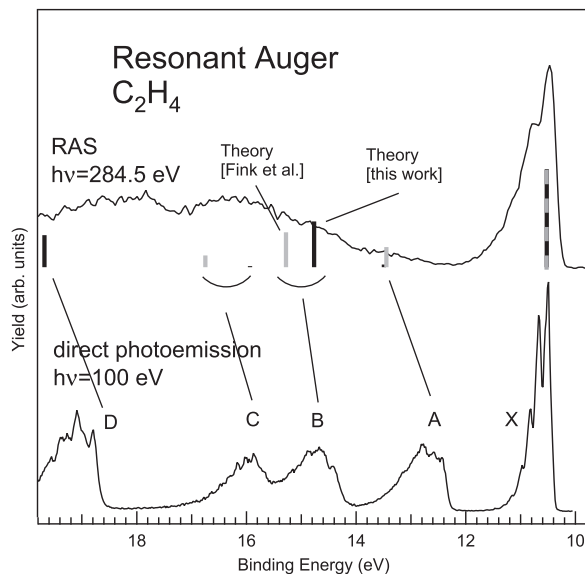


Figure 2. Comparison of the experimental resonant Auger spectrum and calculated final ionized states. The calculated intensities are reported with grey and black bars, which correspond to the data of [8] and the present calculations, respectively. The valence photoemission spectrum recorded at $h\nu = 100$ eV is shown at the bottom of the figure.

versus binding energy) representing the ground state and the first four electronic excited states of the ion have been represented by vertical bars. The grey and black bars are associated with the calculation performed by Fink *et al* [8] and ours, respectively. To allow for the comparison, the intensities of the X states have been normalized to 1. It is noted that while the energy value of the A state reported by Fink *et al* corresponds to the value calculated here, both values are shifted with respect to the value extracted from the high resolution photoemission measurements [18]. On the other hand, the other excited states sit at the binding energies corresponding to the direct photoemission values in contrast with those reported in the literature [6, 8]. In our calculations, the intensity associated with the A state is negligible with respect to that of the X state: it shows 30 times less intensity. This explains why the A band ‘does not resonate’ in the RAS spectra taken across the π^* . However, the same behaviour is predicted for the C state. This can be rationalized considering that the vibrational envelope of the B state may show some intensity at the direct photoelectron energy corresponding to the C final state. Moreover, the population of two holes-one electron states close to the binding energy of the C state, can hinder the actual estimate of its intensity [8].

It is known that new decay channels may open due to changes in the geometry of a molecule in the excited state [27, 28]. Indeed, as for the N_2 molecule, variations in the bond length can lead to the reduction of the intensity of allowed transition channels [12, 14]. Very sophisticated methods have been employed to interpret the RAS process, taking into consideration several effects such as Lifetime Vibrational Interference [29, 30] or the direct-resonant photoionization interference [15, 16], or both at the same time [16, 31]. However, the description of these effects relies on a detailed knowledge of the potential energy surfaces and of the vibrational distribution of the electronic states involved. When dealing with larger molecules these tools become extremely resource demanding and cannot easily be employed.

Vice versa with the formulation proposed in this work, a limited number of parameters can be used to interpret the experimental findings. The use of more sophisticated and updated calculation techniques within the framework of this approach could improve significantly the agreement with the experimental findings, extending this method to more complex polyatomic molecules.

In conclusion, RAS of the ethene molecule are reported. The experimental data show that the intensity of the A band of the molecular ion is not enhanced upon resonant excitation ($C1s \rightarrow \pi^*$). A fast and semi-quantitative approach based on group theory successfully simulates the observed intensity variation of the A band.

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