

Auger Electron Spectra of Molecules: The First Row Hydrides*

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Abstract

A semi-empirical molecular orbital approach primarily developed to predict the Auger energies and transition rates associated with complex polyatomic molecules has been evaluated by reference to the first row hydrides. For this suite of molecules, spanning a range of symmetry classes, high resolution experimental spectra and ab initio energy calculations are available for comparison. The method proposed provides a good first estimate for transition rates. Relative Auger energies are less satisfactory, especially when electron correlation effects are strong. Absolute kinetic energies are too low, principally due to the neglect of electronic relaxation. The usefulness of the approach is mainly for the interpretation of spectra for larger systems where ab initio calculations are not readily accomplished. A need for further experimental measurements obtained using photoelectron-Auger electron coincidence studies is identified to remove uncertainties associated with the extent of satellite contributions present in all the spectral profiles so far recorded. In the present work the satellite contribution to the methane Auger spectrum is estimated to be 16% of the total intensity compared with an earlier estimate in the literature of 49%.

1. Introduction

The Auger electron spectra of polyatomic molecules can be very complex because many possible de-excitation channels may be available depending upon the number of valence electrons and the symmetry of the molecule. For small molecules, such as the first row hydrides and a limited number of other polyatomic molecules, ab initio calculations to obtain the double ionisation state energies have been performed at least at the Δ SCF level; however, for larger systems uniqueness and convergence problems for double hole states present difficulties. Therefore, alternative semi-empirical procedures based upon experience derived from atomic Auger energy calculations have been developed (see Larkins 1990 and references therein). The estimation of ab initio molecular Auger transition rates also presents special difficulties because of the need to model multicentre continuum orbitals. Hence, simpler intra-atomic procedures for estimating molecular Auger rates have been proposed (Siegbahn *et al.* 1975).

In this paper a semi-empirical procedure proposed earlier (Larkins 1987) is appraised with particular reference to the first row hydrides since high

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resolution spectra and good quality *ab initio* energy calculations are available. The aim is to provide a basis for further development of the semi-empirical model, especially for larger polyatomic molecular systems including those containing second-row atoms.

The first row hydrides are all isoelectronic neon-like systems spanning a wide range of symmetries. The number of two-hole final states depends upon the degeneracy of the four valence molecular orbitals. The Auger spectrum of water is the most complex (Siegbahn *et al.* 1975), since all four valence molecular orbitals are non-degenerate, while the methane molecule with T_d symmetry has the simplest spectrum (Spohr *et al.* 1970). The broad spectral profiles for all the hydrides are in contrast to the sharp discrete lines of the normal Auger spectrum of atomic neon (Körber and Mehlhorn 1966; Aksela 1988).

Table 1. Symmetry and number of two-hole final states for the first row hydrides isoelectronic with atomic neon^A

Molecule	Symmetry	$[\nu\nu']^{1,3}\Gamma$	Valence orbitals ν
CH ₄	T_d	7	2a ₁ , 1t ₂
NH ₃	C_{3v}	11	2a ₁ , 1e, 3a ₁
OH ₂	C_{2v}	16	2a ₁ , 1b ₂ , 3a ₁ , 1b ₁
FH	$C_{\infty v}$	11	2σ, 3σ, 1π
(Ne)		(6)	(2s, 2p)

^A Based upon a delocalised molecular orbital RHF model.

2. Theory

2.1 Auger Energies

The major de-excitation pathways for a molecule with a vacancy in an inner-shell core orbital, c , are via a radiative X-ray emission decay or via a radiationless decay with the emission of an Auger electron. For polyatomic molecules containing first row atoms the branching ratio for the decay channels is predominantly in favour of the Auger process. The final ion state has two holes in the valence orbitals ν and ν' which yield a symmetry state $^{2S+1}\Gamma$. Hence, the energy for the Auger transition, $E[c-\nu\nu', ^{2S+1}\Gamma]$, is the difference between the total energies of the initial $N-1$ hole state $E[c]$ and the final $N-2$ double-hole state $E[\nu\nu']^{2S+1}\Gamma$, where square brackets are used to denote double-hole states; that is

$$E[c-\nu\nu', ^{2S+1}\Gamma] = E[c] - E[\nu\nu']^{2S+1}\Gamma. \quad (1)$$

Even for the first row hydrides, the number of two-hole final states $[\nu\nu']^{1,3}\Gamma$ can be substantial, as shown in Table 1, so there have been few fully optimised *ab initio* Auger energy studies even for these molecules. Not all of the double-hole state configurations contribute to the Auger spectrum since some decay pathways are forbidden on symmetry grounds. Electron correlation effects can lead to the splitting of other states, especially those involving inner-valence electrons.

Alternative approaches such as semi-empirical molecular orbital and Green's function methods have been used based upon experience gained from atomic Auger studies. The semi-empirical approach proposed earlier (Larkins 1987) reformulates the energy expression in equation (1) as a difference between core and valence orbital energies, I_c , I_v and $I_{v'}$, with a two-hole correction term $\Delta[vv']^{2S+1}\Gamma$; that is,

$$E(c-vv', {}^{2S+1}\Gamma) = I_c - I_v - I_{v'} - \Delta[vv']^{2S+1}\Gamma. \quad (2)$$

Experimental binding energies chosen from photoelectron data are usually used for the I terms; hence, the semi-empirical problem is reduced to the calculation of the two-hole correction terms $\Delta[vv']^{2S+1}\Gamma$. A convenient way to evaluate these terms is to follow procedures adopted for atomic problems (Shirley 1973; Larkins 1976). The latter has proved to be most satisfactory for predicting Auger energies for transition processes in a wide range of atoms (Larkins 1977).

Table 2. Hole-hole interaction energy expression associated with $1t_2$ double-hole states of the methane molecule

$x = t_{2x}, y = t_{2y}$	
Double-hole state $[1t_2 1t_2]$	Hole-hole interaction energy $\langle 1t_2 1t_2 \rangle$
1A_1	$J_{xx} + 2K_{yx}$
1E	$J_{xx} - K_{yx}$
1T_2	$J_{xy} + K_{yx}$
3T_1	$J_{xy} - K_{yx}$

If for the present any adiabatic relaxation term $R(vv')$ is ignored then $\Delta[vv']^{2S+1}\Gamma = \langle vv' \rangle^{2S+1}\Gamma$, where the interaction energy of a pair of holes in the $N-2$ system is given by

$$\langle vv' \rangle^{2S+1}\Gamma = \langle \Psi[vv']^{2S+1}\Gamma | 1/r_{12} | \Psi[vv']^{2S+1}\Gamma \rangle. \quad (3)$$

Here $\Psi[vv']^{2S+1}\Gamma$ is the two-electron wavefunction of appropriate symmetry formed from coupling the hole orbitals within a molecular orbital framework. This interaction term is sometimes referred to as U_{eff} (Jennison 1980) or U . The two-hole interaction energy term may be expressed in terms of Coulomb and exchange-type integrals of the kind $J_{vv'}$ and $K_{v'v}$ where $J_{vv'} = Q(vv|v'v')$ and $K_{v'v} = Q(vv'|v'v)$ and $Q(ij|kl) = \langle \phi_i(1)\phi_k(2) | 1/r_{12} | \phi_j(1)\phi_l(2) \rangle$. The ϕ represent the one-electron valence molecular orbitals. By way of illustration, the CH_4 molecule has the electronic configuration $1a_1^2 2a_1^2 1t_2^6$ and the energy expressions for the $\langle 1t_2 1t_2 \rangle^{2S+1}\Gamma$ terms are as given in Table 2. The complexity of the computational task increases with the number of double-hole states.

The values for the $\langle vv' \rangle$ terms are usually determined using wavefunctions obtained for the neutral molecule in its ground state, but other approaches are possible which allow for some account of electronic relaxation energy contributions to be included. Ab initio-based wavefunctions may be used to evaluate the $J_{vv'}$ and $K_{v'v}$ integrals, but for larger polyatomic molecules simpler procedures are convenient. A constraint has been that for the intensity

calculations, to be discussed shortly, it is convenient to be able to use expressions based upon a knowledge of the coefficients of the relevant atomic orbitals, 2s and 2p, which form part of the LCAO molecular orbital. Hence, wavefunctions generated from a minimal basis set (MBS) either at the ab initio or all-valence zero differential overlap level have been sought. For the present work most of the calculations have been based upon INDO wavefunctions to gain an insight into the complexity of the problems and the usefulness of a simplified method; however, for methane ab initio wavefunctions are also used.

Table 3. Auger intensity expressions involving non-degenerate and doubly degenerate molecular orbitals^A

State	Intensity expressions $\times\pi$
<i>[a₁ b₁] configurations</i>	
¹ X	$ J_{xy}+K_{yx} ^2$
³ X	$3 J_{xy}-K_{yx} ^2$
<i>[1π 1π] and [1e 1e] configurations</i>	
¹ Σ^+ , ¹ A ₁	$ J_{xx}+J_{yy} ^2$
¹ Δ , ¹ E	$ J_{xx}-J_{yy} ^2+ J_{xy}+K_{yx} ^2$
³ Σ^- , ³ A ₂	$3 J_{xy}-K_{yx} ^2$
<i>[1π 2π] and [1e 2e] configurations</i>	
¹ Σ^+ , ¹ A ₁	$\frac{1}{2} (J_{1x2x}+K_{2x1x})+(J_{1y2y}+K_{2y1y}) ^2$
¹ Δ , ¹ E	$\frac{1}{2} (J_{1x2x}+K_{2x1x})-(J_{1y2y}+K_{2y1y}) ^2+\frac{1}{2} (J_{1x2y}+K_{2y1x})+(J_{1y2x}+K_{2x1y}) ^2$
¹ Σ^- , ¹ A ₂	$\frac{1}{2} (J_{1x2y}+K_{2y1x})-(J_{1y2x}+K_{2x1y}) ^2$
³ Σ^+ , ³ A ₁	$\frac{3}{2} (J_{1x2x}-K_{2x1x})+(J_{1y2y}-K_{2y1y}) ^2$
³ Δ , ³ E	$\frac{3}{2} (J_{1x2x}-K_{2x1x})-(J_{1y2y}-K_{2y1y}) ^2+\frac{3}{2} (J_{1x2y}-K_{2y1x})+(J_{1y2x}-K_{2x1y}) ^2$
³ Σ^- , ³ A ₂	$\frac{3}{2} (J_{1x2y}-K_{2y1x})-(J_{1y2x}-K_{2x1y}) ^2$

^A Based upon equation (4).

2.2 Auger Intensities

The normal Auger transition probability expression based upon the Wentzel (1927) ansatz using a single set of orthogonal one-electron orbitals reduces to an expression involving only the two electrons participating in the transition (Larkins 1990). The expression, in atomic units, is given by

$$I_{vv'}^{cc} = 2\pi |\langle \Psi_f(c\epsilon) | 1/r_{12} | \Psi_i(vv') \rangle|^2, \quad (4)$$

where c and ϵ denote the core hole and continuum orbitals respectively and v and v' denote the generalised multicentre one-electron valence molecular orbital functions. The functions $\Psi_f(c\epsilon)$ and $\Psi_i(vv')$ represent the two-electron wavefunctions of the appropriate symmetry. The more general two-electron matrix elements (equation 4) may be expressed in terms of integrals of the kind $J_{vv'}^{ce}$ and $K_{v'v}^{ce}$, where $J_{vv'}^{ce} = Q(cv|\epsilon v')$ and $K_{v'v}^{ce} = Q(cv'|\epsilon v)$. Transition rate expressions for non-degenerate and degenerate molecular orbitals of various symmetry classes applicable to molecules with different point group symmetry have been derived. The complete set of expressions for non-degenerate and degenerate orbitals is given in Tables 3 and 4. The notation x, y, z has been

Table 4. Auger intensity expressions involving doubly and triply degenerate molecular orbitals^A

State	Intensity expressions $\times\pi$
[1t₂ 1t₂] and [1t₁ 1t₁] configurations	
¹ A ₁	$\frac{2}{3} J_{xx} + J_{yy} + J_{zz} ^2$
¹ E	$\frac{1}{3} (2J_{zz} - J_{xx} - J_{yy}) ^2 + J_{xx} - J_{yy} ^2$
¹ T ₂	$ J_{xy} + K_{yx} ^2 + J_{yz} + K_{zy} ^2 + J_{xz} + K_{zx} ^2$
³ T ₁	$3 J_{xy} - K_{yx} ^2 + 3 J_{yz} - K_{zy} ^2 + 3 J_{xz} - K_{zx} ^2$
[1t₂ 2t₂] and [1t₁ 2t₂] configurations	
¹ A ₁ , ¹ A ₂	$\frac{1}{3} (J_{1x2x} + K_{2x1x}) + (J_{1y2y} + K_{2y1y}) + (J_{1z2z} + K_{2z1z}) ^2$
¹ E	$\frac{1}{6} 2(J_{1z2z} + K_{2z1z}) - (J_{1y2y} + K_{2y1y}) - (J_{1x2x} + K_{2x1x}) ^2 +$ $\frac{1}{2} (J_{1x2x} + K_{2x1x}) - (J_{1y2y} + K_{2y1y}) ^2$
¹ T ₂	$\frac{1}{2} (J_{1x2y} + K_{2y1x}) + (J_{1y2x} + K_{2x1y}) ^2 + \frac{1}{2} (J_{1x2z} + K_{2z1x}) + (J_{1z2x} + K_{2x1z}) ^2 +$ $\frac{1}{2} (J_{1y2z} + K_{2z1y}) + (J_{1z2y} + K_{2y1z}) ^2$
¹ T ₁	$\frac{1}{2} (J_{1x2y} + K_{2y1x}) - (J_{1y2x} + K_{2x1y}) ^2 + \frac{1}{2} (J_{1x2z} + K_{2z1x}) - (J_{1z2x} + K_{2x1z}) ^2 +$ $\frac{1}{2} (J_{1y2z} + K_{2z1y}) - (J_{1z2y} + K_{2y1z}) ^2$
[1t₂ 2t₂] and [1t₁ 2t₂] triplet configurations	
³ A ₁ , ³ A ₂	$ (J_{1x2x} - K_{2x1x}) + (J_{1y2y} - K_{2y1y}) + (J_{1z2z} - K_{2z1z}) ^2$
³ E	$\frac{1}{2} 2(J_{1z2z} - K_{2z1z}) - (J_{1y2y} - K_{2y1y}) - (J_{1x2x} - K_{2x1x}) ^2 +$ $\frac{3}{2} (J_{1x2x} - K_{2x1x}) - (J_{1y2y} - K_{2y1y}) ^2$
³ T ₂	$\frac{3}{2} (J_{1x2y} - K_{2y1x}) + (J_{1y2x} - K_{2x1y}) ^2 + \frac{3}{2} (J_{1x2z} - K_{2z1x}) + (J_{1z2x} - K_{2x1z}) ^2 +$ $\frac{3}{2} (J_{1y2z} - K_{2z1y}) + (J_{1z2y} - K_{2y1z}) ^2$
³ T ₁	$\frac{3}{2} (J_{1x2y} - K_{2y1x}) - (J_{1y2x} - K_{2x1y}) ^2 + \frac{3}{2} (J_{1x2z} - K_{2z1x}) - (J_{1z2x} - K_{2x1z}) ^2 +$ $\frac{3}{2} (J_{1y2z} - K_{2z1y}) - (J_{1z2y} - K_{2y1z}) ^2$
[1t₂ 2e] and [1t₁ 2e] configurations	
¹ T ₂	$\frac{1}{2} (J_{1x2y} + K_{2y1x}) + (J_{1y2x} + K_{2x1y}) ^2 + J_{1z2x} + K_{2x1z} ^2 + J_{1z2y} + K_{2y1z} ^2$
¹ T ₁	$\frac{1}{2} (J_{1x2y} + K_{2y1x}) - (J_{1y2x} + K_{2x1y}) ^2$
³ T ₂	$\frac{3}{2} (J_{1x2y} - K_{2y1x}) + (J_{1y2x} - K_{2x1y}) ^2 + 3 J_{1z2x} - K_{2x1z} ^2 + 3 J_{1z2y} - K_{2y1z} ^2$
³ T ₁	$\frac{3}{2} (J_{1x2y} - K_{2y1x}) - (J_{1y2x} - K_{2x1y}) ^2$

^A Based upon equation (4).

used to denote a degenerate set of molecular orbitals as appropriate. The tables are presented in full because they are not currently available in the literature. They are essential for the calculation of intensities for molecules covering the full range of symmetries.

The ab initio evaluation of these expressions presents considerable difficulties, because of the need to generate a multicentre continuum function. Hence, ab initio molecular transition rate calculations have been few in number.

To simplify the problem, Siegbahn *et al.* (1975) proposed an intra-atomic transition model in which the non-radiative de-excitation process is assumed to be highly localised around one atomic centre (say A) and therefore probes the local electron density. Hence, the core hole wavefunction ϕ_c is described by an atomic wavefunction $\chi_{l_c m_c}^A$ with quantum numbers $l_c m_c$. For the delocalised multicentre molecular orbital ν , expressed in terms of a linear combination of atomic orbitals, only those components on the atom with the core hole are considered such that $\phi_\nu \approx \sum_i c_{vi}^A \chi_i^A$, where i is summed over the atomic basis set on atom A. Furthermore, the multicentre continuum orbital ϕ_e is replaced

by all symmetry allowed atomic uncoupled continuum channels localised on atom A. The implications of this last assumption have not been adequately explored.

Recognising that one must average over all possible initial states with quantum numbers $l_c m_c$ and sum over all possible final states, the expression for $I_{\nu\nu'}^{ce}$ becomes

$$I_{\nu\nu'}^{ce} = \frac{f\pi}{2l_c + 1} \sum_{m_c} \sum_{l_e} \sum_{m_e} I_{\nu\nu'}^{l_c m_c l_e m_e}. \quad (5)$$

For equivalent non-degenerate molecular orbitals ($\nu = \nu'$) $f = \frac{1}{2}$, otherwise $f = 1$ (Larkins and Chelkowska 1990).

For a 1s core hole and an sp basis set to describe the valence molecular orbitals there are nine terms to be evaluated from equation (5). If an spd basis set is used there are 25 terms. The relevant $I_{\nu\nu'}$ terms are obtained from Tables 3 and 4 depending on the symmetries of the valence orbitals. Expressions for the J and K integrals which depend upon l_e and m_e have been presented elsewhere (Larkins and Chelkowska 1990).

The evaluation of these terms required a knowledge of the atomic Auger matrix elements R^k . At the Hartree-Fock level they may be taken from the published work of McGuire (1969), Walters and Bhalla (1971) or Chen *et al.* (1990). For the present work the values by Walters and Bhalla are used. Hence, overall the intensity evaluation can become very complex using this approach.

To illustrate the problem for the case when non-degenerate orbitals are involved, such as the $2a_1$ orbital of the CH_4 molecule, from Table 3 and equation (5) we have

$$I_{2a_1 2a_1}^{1se} = I_{2a_1 2a_1}^{ses} + I_{2a_1 2a_1}^{sep} + I_{2a_1 2a_1}^{sed}, \quad (6)$$

where the Σ_{m_e} is included in the designation. Formally, evaluation of these terms leads to the following contributions to the intensity expression for the carbon Auger intensity associated with the $[2a_1 2a_1] \ ^1A_1$ final state:

$$\begin{aligned} I_{2a_1 2a_1}^{ses} &= 2\pi\{C_{2s}^2 R^0(1ses, 2s2s) + \frac{1}{3}[C_{2p_x}^2 + C_{2p_y}^2 + C_{2p_z}^2]R^1(1ses, 2p2p)\}^2, \\ I_{2a_1 2a_1}^{sep} &= 2\pi C_{2s}^2 [C_{2p_x}^2 + C_{2p_y}^2 + C_{2p_z}^2] [R^0(1sep, 2s2p) + \frac{1}{3}R^1(1sep, 2p2s)]^2, \\ I_{2a_1 2a_1}^{sed} &= \frac{8\pi}{45} [C_{2p_x}^2 + C_{2p_y}^2 + C_{2p_z}^2]^2 [R^1(1sep, 2p2p)]^2. \end{aligned}$$

In practice, for the $2a_1$ orbital the only nonzero coefficient is C_{2s} and, therefore, the intensity expression is reduced to one term.

3. Results and Discussion

3.1 General Spectral Interpretation

The $K-\nu\nu'$ molecular Auger spectra for the first-row hydrides can be broadly divided into three regions involving outer-outer (Region I), outer-inner (Region II) and inner-inner (Region III) valence orbitals aligned to pp, sp and ss atomic-type transitions. A good illustration is the Auger spectrum of methane (Spohr *et al.* 1970) shown in Fig. 1. The challenge is to interpret such a broad profile in

terms of energies and intensities for specific transitions. A complication in any interpretation is the possible presence of satellites due in part to the availability of low-lying unoccupied molecular orbitals. For example, Ramaker (1989) has asserted that for many molecular and solid state carbon $K\text{-}vv'$ spectra about half the total spectral intensity measured results from satellite contributions. The present work for methane is not consistent with this assertion.

In order to further evaluate the semi-empirical approach to Auger energies proposed earlier (Larkins 1987) the results for the first row hydrides using

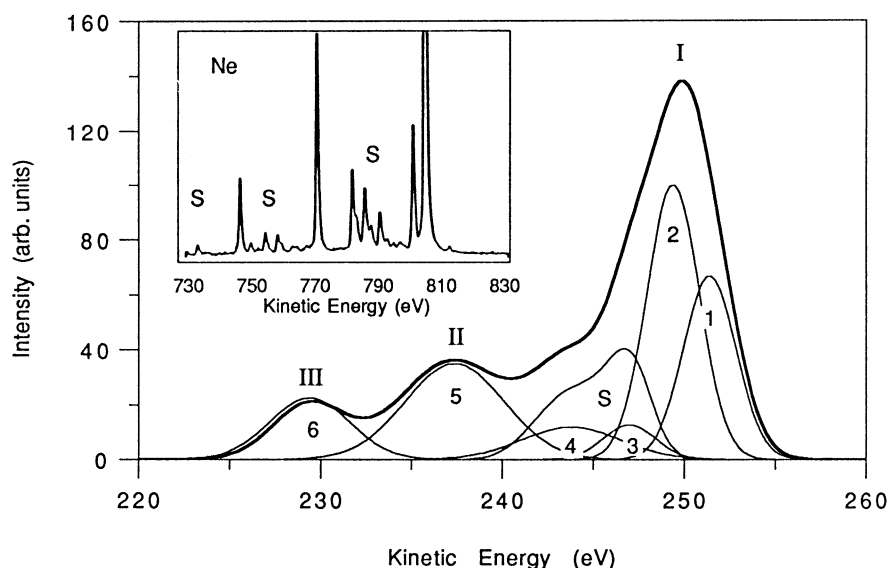


Fig. 1. Experimental methane spectrum by Spohr *et al.* (1970), where the thick curve is fitted with six gaussian peaks to represent the normal Auger contribution (see text). Intensities of peaks are as given by the INDO calculations (Table 6, column 5). The difference spectrum (S) is assigned to satellite contributions. The insert shows the KLL Auger spectra for atomic neon, also with satellites (Aksela 1988).

Table 5. Relative Auger electron energies for methane (eV)

OB: Ortenburger and Bagus (1975). P: Present fit using six gaussian functions to the experimental spectrum of Spohr *et al.* (1970) (see text)

Final state	Ab initio OB	INDO	Semi-empirical		Expt P
			CH ₄	CH ₄ ²⁺	
[1t ₂ 1t ₂] ³ T ₁	-3.0	-2.0	-3.3	-2.6	
¹ E	-2.0	-1.7	-2.5	-1.5	-2.0
¹ T ₂	0.0	0.0	0.0	0.0	0.0
	(251.7)	(249.3)	(248.5)	(248.1)	(249.4)
¹ A ₁	2.4	1.2	2.3	2.3	2.4
[2a ₁ 1t ₂] ³ T ₂	6.7	6.9	5.0	5.4	5.6
¹ T ₂	13.1	9.6	10.9	11.5	12.0
[2a ₁ 2a ₁] ¹ A	21.3	17.4	17.4	18.0	20.0

the INDO method with standard parameters (Pople and Beveridge 1970) and geometries obtained from (Snyder and Basch 1972) are compared with ab initio calculations and experiment.

3.2 The Methane Molecule

3.2.1 Auger transition energies. There have been several ab initio calculations for the energies of the CH_4^{2+} final states from which the Auger energies have been derived (Ortenburger and Bagus 1975; Faegri and Manne 1976; Kvalheim 1982; Hillier and Kendrick 1976). The agreement between the first three calculations is within ± 0.2 eV for the relative energies of the multiplets. A slightly larger variation (± 1.0 eV) is observed between the calculations by Hillier and Kendrick (1976) and other researchers for the $[1t_2 1t_2]$ multiplets. Absolute Auger energy values differ by up to 1.5 eV. Only the ab initio results of Ortenburger and Bagus (1975) are presented in Table 5. The semi-empirical transition energies calculated using equation (2) with ionisation potentials for the $1a_1$, $2a_1$ and $1t_2$ orbitals of 290.8, 23.0 and 14.0 eV respectively (Banna and Shirley 1975) and values for the $\langle vv' \rangle^{2S+1} \Gamma$ terms based upon either INDO or ab initio MBS wavefunctions are presented in Table 5 along with values deduced from fitting six gaussian peaks to the experimental spectrum of Spohr *et al.* (1970) by a procedure described in the next section. The MBS wavefunctions were obtained using the PSI program of Schaefer with a STO-3G basis (Hehre *et al.* 1969).

The INDO calculations are within 3 eV of the ab initio calculations and the experimental values. A common feature of all the INDO work is the underestimation of the multiplet splittings due to the manner in which the J and K energy integrals are estimated within the INDO method. The neglect of the adiabatic relaxation in equation (2) is small in this case, with correction < 1 eV based upon an atomic estimate, such that there is very good agreement between the INDO result and the experimental value for the $[1t_2 1t_2] \ ^1T_2$ transition (Table 5). Results obtained from an equivalent cores model using the NH_4^+ species yielded similar results in both energy and relative intensity values to the CH_4 species.

The calculations based upon J and K values derived from CH_4 ab initio wavefunctions (column 4) show an improved splitting for the multiplets within a double-hole configuration but the separation between configurations and the absolute energies are underestimated. When electronic relaxation is incorporated by using ab initio wavefunctions for CH_4^{2+} based upon the configuration $1a_1^2 2a_1^1 1t_2^2$ the multiplet splittings are further improved overall (column 5) but the separation and absolute energies are still too low by 1–2 eV. Overall, the semi-empirical approach with ab initio J or K integrals is at least as good as the optimised double-hole state calculations when compared with the experimental values shown in column 6.

3.2.2 Auger transition rates. Higashi *et al.* (1982) have calculated the Auger transition rates for methane following the direct determination of the continuum orbitals with a non-spherical potential. The relative rates, normalised to a total $[1t_2 1t_2]$ rate of 100, are shown in Table 6. The bound state orbitals were derived from an SCF calculation for the neutral molecule performed by the one centre expansion method.

Jennison (1980) obtained wavefunctions based upon the HONDO76 program and the intensity method of Siegbahn *et al.* (1975) using R^k values from McGuire (1969). Kvalheim (1982) has adopted a similar approach to the intensity calculations deriving the AO coefficients of the MO from ab initio gaussian calculations along with atomic R^k values from either McGuire (1969) or Walters and Bhalla (1971). The relative intensity values from these previous works along with the present calculations are shown in Table 6. It is encouraging that the relative intensities predicted using the INDO wavefunctions are in good agreement with values based upon SCF wavefunctions determined by Jennison (1980), Kvalheim (1982) and the present MBS values using two sets of wavefunctions. It is evident that the sensitivity of relative intensities to the quality of the wavefunctions is less critical than for relative energy determination.

Table 6. Methane carbon Auger relative intensities calculated by various models

J: Jennison (1980). K: Kvalheim (1982). HHN: Higashi *et al.* (1982). P: Present work (see text for explanation)

Final state	J	K	HHN	INDO	P	MBS
					CH ₄	CH ₄ ²⁺
[1t ₂ 1t ₂] ¹ E	100	37	0	37	37	37
¹ T ₂		56	97	56	56	56
¹ A ₁		7	3	7	7	7
[2a ₁ 1t ₂] ³ T ₂	18	12	12	12	13	14
¹ T ₂	28	35	43	37	39	42
[2a ₁ 2a ₁] ¹ A ₁	21	18	4	19	22	25

The findings of Higashi *et al.* (1982) based upon an explicit determination of the continuum orbital are very different from all other theoretical predictions and the experimental findings. Furthermore, the absolute total CH₄ Auger transition rate of 79.94×10^{-3} a.u. and 3.54×10^{-3} a.u. is too large compared with the present values of 2.20×10^{-3} a.u. calculated using INDO wavefunctions and atomic R^k values from Walters and Bhalla for CH₄ and NH₄⁺ respectively. The Higashi *et al.* values are many times the calculated Ne total Auger rate of 8.83×10^{-3} a.u. (Walters and Bhalla 1971), which should be the upper limit.

3.2.3 Satellite contribution to spectrum. Hutson and Ramaker (1987) have estimated that the methane Auger spectra recorded by Rye *et al.* (1980) contain a satellite contribution of 49% of the total intensity. By analogy with the neon Auger spectrum (Aksela 1988) satellites are undoubtedly present, but the evidence for the magnitude of the satellite contribution is not compelling. Spectra obtained by Spohr *et al.* (1970) using high energy photons, by Rye *et al.* (1980) using electron impact and by Aksela (personal communication) using synchrotron radiation are almost identical.

The experimental methane Auger spectra recorded to date cannot be fitted solely by diagram transitions, because of the presence of satellite contributions, especially in the region 240–50 eV. The contribution of the six diagram transitions shown in Table 6 to the spectrum of Spohr *et al.* (1970) was established by the following procedure. The energy separations between multiplets associated

with the same final double-hole pair were fixed at the *ab initio* values of Ortenburger and Bagus (1975) since there was an excellent consistency between all the calculations so far reported. The relative intensities of the six diagram transitions were also fixed at the INDO values, since there is good agreement between most of the calculations (Table 6). The energy position of the three groups of multiplets and the FWHM of the multiplets were optimised subject to the constraint that multiplets associated with the same final double-hole pair had equal halfwidths. The fitting shown in Fig. 1 was achieved with FWHM values of 3.4, 6.4 and 5.2 eV for the $[1t_2\ 1t_2]$, $[2a_1\ 1t_2]$ and $[2a_1\ 2a_1]$ double-hole pairs respectively. The energy values are given in Table 5. The agreement between the absolute *ab initio* energy calculations and experiment is within 3 eV for all transitions.

The satellite line contribution to the experimental spectrum as determined by difference is also shown in Fig. 1. It represents approximately 16% of the total spectral intensity. By analogy to the Ne KLL spectrum (Aksela 1988) shown as an insert and the previous work by Hutson and Ramaker (1987), the major satellite processes contributing to the spectrum are initial state shake-up and shake-off type processes. The present analysis differs significantly from the previous work in terms of both the magnitude of the total satellite processes and the nature of the contributing processes (Hutson and Ramaker 1987, Fig. 4). Our analysis provides no conclusive evidence for a major resonant Auger contribution or for strong final state shake-off type processes. While the present fitting procedure is at least as valid as that used by previous workers it does require an element of scientific judgement. Experimental photoelectron–Auger electron coincidence studies are required to identify the true diagram line spectrum and so resolve this matter.

3.3 The Ammonia Molecule

3.3.1 Auger transition energies. There have been two *ab initio* calculations for the doubly ionised states of ammonia. Økland *et al.* (1976) reported open-shell SCF calculations of double zeta quality, while Tarantelli *et al.* (1985a) have used *ab initio* Green's functions and configuration interaction methods. These results and the experimental findings of Shaw *et al.* (1977) are given in Table 7. Other experimental results have been reported by White *et al.* (1977) and Camilloni *et al.* (1977). While the experimental transition energies from the three studies are in good agreement, there are a number of differences in the experimental relative intensities (Table 8) which reflect the non-uniqueness of fitting a complex spectral profile and which underline the need for a more definitive spectrum without satellites to be recorded. The semi-empirical transition energies calculated using the experimental binding energies determined by Banna and Shirley (1975) and two-hole interaction energy terms based upon INDO wavefunctions are also presented in Table 7. The calculated absolute Auger energies and the multiplet splittings are underestimated relative to *ab initio* calculations reflecting the neglect of electronic relaxation and the inadequate estimation of the magnitude of the various J and K integrals. Use of an INDO equivalent cores model performing calculations for the OH_3^+ molecule does not improve the position. It should also be noted that there are differences between the *ab initio* and experimental Auger energies of up to 4 eV.

3.3.2 Auger transition rates. The only previous transition rate calculations have been by Jennison (1981) based upon an *ab initio* ground state orbital set and the intra-atomic transition model. They are shown in Table 8 along with the present calculations based upon wavefunctions for both the NH_3 and the OH_3^+ molecules. The calculations are compared with the experimental findings from three independent studies. The variation in the experimental estimates result principally from difficulties in fitting many peaks to such a broad spectral profile, but the mode of excitation is a contributory factor to the satellite strength. Nevertheless, the calculated values are in good agreement with experiment and with the work of Jennison (1981) and provide a useful first estimate of the relative intensities. The total absolute Auger rate was calculated to be 3.88×10^{-3} a.u. (NH_3) or 5.23×10^{-3} a.u. (OH_3^+) using the R^k values of Walters and Bhalla (1971) and INDO wavefunctions.

Table 7. Relative Auger energies for the NH_3 molecule (eV)

OFM: Økland *et al.* (1976). TT: Tarantelli *et al.* (1985a). S: Shaw *et al.* (1977)

Final state	Ab initio OFM	TT	Semi-empirical present work	Expt S
[3a ₁ 3a ₁] ¹ A ₁	0.0 (373.6)	0.0	0.0 (363.5)	0.0 (370.2)
[1e 3a ₁] ³ E	2.16	2.29	-0.3	
¹ E	4.07	3.94	1.0	4.73
[1e 1e] ³ A ₂	8.23	8.10	2.9	
¹ E	10.59	9.91	4.1	10.72
¹ A ₁	12.83	11.77	5.4	13.45
[2a ₁ 3a ₁] ³ A ₁	14.87	14.02	11.2	
¹ A ₁	20.78	19.33	14.2	19.26
[2a ₁ 1e] ³ E	20.88	19.71	14.7	19.26
¹ E	28.55	26.11	18.1	26.54
[2a ₁ 2a ₁] ¹ A ₁	39.72	37.38	28.9	35.56

Table 8. Relative Auger intensities for the NH_3 molecule calculated by various models

J: Jennison (1981). C: Camilloni *et al.* (1977). W: White *et al.* (1977). S: Shaw *et al.* (1977)

Final state	J NH ₃	Present work OH ₃ ⁺	C	W	Expt S	
[3a ₁ 3a ₁] ¹ A ₁	0.53	0.64	0.52	0.52	0.55	0.54
[1e 3a ₁] ³ E	0.01	0.03	0.01			
¹ E	1.00	1.00	1.00	1.00	0.89	1.00
[1e 1e] ³ A ₂	0.00	0.00	0.00			
¹ E	0.63	0.59	0.74	0.73	1.00	0.68
¹ A ₁	0.28	0.18	0.22	0.46	0.14	0.66
[2a ₁ 3a ₁] ³ A ₁	0.12	0.12	0.10	0.07		
¹ A ₁	0.44	0.47	0.38	0.63	0.45	0.52
[2a ₁ 1e] ³ E	0.16	0.14	0.15			
¹ E	0.52	0.42	0.48	0.39	0.29	0.66
[2a ₁ 2a ₁] ¹ A ₁	0.48	0.32	0.34	0.50	0.17	0.36

3.4 The H₂O Molecule

3.4.1 Auger transition energies. The experimental Auger spectrum of water vapour has been measured by Siegbahn *et al.* (1975). The double ionisation energies have been determined by ab initio methods using SCF procedures including limited CI (Hillier and Kendrick 1976; Ågren *et al.* 1975; Ågren and Siegbahn 1980) and Green's function techniques by Tarantelli *et al.* (1985*b*). In view of the many possible double-hole final states in a similar energy range electron correlation effects are very important in determining their energies. The normal Auger line intensity can be split among a number of states, also shake-up and shake-off satellites are considered to be important contributors to the recorded experimental spectrum (Ågren and Siegbahn 1980) making a conclusive interpretation difficult. The semi-empirical model proposed for the MO calculation of Auger transition energies is not suitable for the interpretation of such a complex spectral profile where some states are highly correlated. The energy discrepancies for some states are as large as 10 eV reflecting the breakdown of the independent particle model for this system.

3.4.2 Auger transition rates. The Auger line intensities for the H₂O molecule were first estimated by Siegbahn *et al.* (1975) using the one centre model equation (5) and ab initio wavefunctions. Our calculations performed using INDO wavefunctions are in close agreement with the published work. Recently Carravetta and Ågren (1987) have used the Stieltjes imaging method to calculate the Auger transition rates for the H₂O molecule. The calculated relative rates are very similar in magnitude to those determined by the simpler INDO based approach. The total absolute rate calculated with allowance for configuration hole mixing was 4.79×10^{-3} a.u. compared with a value of 5.66×10^{-3} a.u. calculated in the present work with the intra-atomic model and the R^k values from Walters and Bhalla (1971). The equivalent cores value is larger at 6.8×10^{-3} a.u. It is surprising that the agreement between all the calculations and the fitted experimental spectrum is so encouraging (Siegbahn *et al.* 1975; Carravetta and Ågren 1987), recognising the difficulties involved in a detailed interpretation of the Auger profile due to the many contributing final hole states including satellites. The INDO results do not provide any additional insight for the H₂O system and are therefore not presented in detail here.

3.5 The HF Molecule

3.5.1 Auger transition energies. Kvalheim and Faegri (1979) have undertaken extensive CI calculations to determine the doubly-ionised state energies for the HF molecule. In general, the energy shifts from the RHF values are less than 1 eV, however additional correlation states are identified which result in a sharing of the intensity relative to the single configuration model. When compared with experiment (Shaw and Thomas 1975) there is good agreement, although detailed comparisons cannot readily be made because of difficulties in deconvoluting the experimental spectrum. Other RHF-type calculations for the HF molecule have been reported by Hillier and Kendrick (1976), Faegri (1977) and Faegri and Kelly (1979). Liegener (1982) has used renormalised Green's function theory to estimate the double ionisation energies. While the conventional HF-CI approaches agree for the double ionisation energies to

within 1 eV the discrepancies with the Green's function values are up to 3–4 eV for the deeper ionised states where correlation effects are important. The quality of the semi-empirical energy predictions for the HF molecule have been discussed elsewhere (Larkins 1990). The relative energies are in reasonable agreement, within 2–3 eV, for all the states except the deepest levels where the choice of a single binding energy to represent the highly correlated 2σ orbital is inappropriate due to many electron effects being important. The absolute Auger transition energy values as predicted by the semi-empirical method are up to 9 eV too low (Larkins 1990, Table 6), whereas the ab initio values by other workers are usually within 2 eV. The discrepancy results mainly from an inadequate description of the double-hole relaxation effect, which from comparison with atomic work can be of the order of 4 eV, and an overestimate of the size of the atomic Coulomb integrals derived from an INDO formalism.

Table 9. Relative Auger intensities for the HF molecule calculated by various models

FK: Faegri and Kelly (1979). L: Liegener (1982). ST: Shaw and Thomas (1975)

Final state	FK	L	Present work			Expt ST
			NeH ⁺	HF	Renorm.	
(1) $[1\pi 1\pi] \ ^1\Delta$	1.00	1.00	1.00	1.00	1.0	1.0
(2) $[3\sigma 1\pi] \ ^3\pi$	0.01	0.01	0.00	0.02		
(3) $[1\pi 1\pi] \ ^1\Sigma^+$	0.30	0.30	0.29	0.29		
(4) $[3\sigma 1\pi] \ ^1\pi$	0.85	0.89	0.92	0.73		
(5) $[3\sigma 3\sigma] \ ^1\Sigma^+$	0.28	0.31	0.33	0.20		
(6) $[2\sigma 1\pi] \ ^3\pi$	0.29	0.29	0.17	0.16	0.10	0.05
(7) $[2\sigma 3\sigma] \ ^3\Sigma^+$	0.15	0.16	0.08	0.06		
(8) $[2\sigma 1\pi] \ ^1\pi$	0.65	0.59	0.57	0.52	0.34	0.18
(9) $[2\sigma 3\sigma] \ ^1\Sigma^+$	0.32	0.29	0.27	0.24		
(10) $[2\sigma 2\sigma] \ ^1\Sigma^+$	0.49	0.40	0.35	0.29	0.13	0.05

3.5.2 Auger transition rates. Faegri and Kelly (1979) have calculated ab initio Auger transition rates for HF using spherical waves to model the continuum orbital. The rates are presented in Table 9 relative to the $[1\pi 1\pi] \ ^1\Delta$ rate of 1.99×10^{-3} a.u. set equal to 1.00. The total absolute rate was 8.65×10^{-3} a.u. Liegener (1982) has also estimated the rates by modulating the theoretical values of Faegri and Kelly (1979). The values are also shown in Table 9 column 3 leading to a total absolute rate of 4.83×10^{-3} a.u. The present INDO based calculations (columns 4 and 5) yield a total rate value of 7.40×10^{-3} a.u. (HF) and 8.28×10^{-3} a.u. (NeH⁺). The consistency between the different approaches is most encouraging. The experimental relative intensities for the four major groups of lines 1–5/6, 7/8, 9/10 have been estimated to be 1.00/0.05/0.18/0.05 (Shaw and Thomas 1975) compared with values of 1.00/0.10/0.34/0.13 from the present work and similar findings from the other approaches (Table 9). Hence, there is a discrepancy of about a factor of 2 between the amount of intensity which the various theories predict to be in the three groups of Auger lines relative to the main group. This anomaly warrants further investigation especially since the theoretical predictions are larger, whereas, in the presence of shake-up and shake-off satellites the reverse

prediction is to be expected. The problem would appear to be with the method of background subtraction in the experimental analysis. A new coincidence spectrum is required for the HF molecule.

4. Conclusions

The semi-empirical Auger energy and intensity model based upon using INDO-type wavefunctions has been shown to provide a very good first estimate for both the absolute and relative transition rates for molecular Auger processes associated with the first row hydrides, in close agreement with *ab initio* calculations. The relative energies for the doubly ionised states were predicted to within 5 eV and usually to within 2–3 eV especially when electron correlation effects, leading to the coupling of states and subsequent energy shifts, are not strong. In the latter cases, in particular for the H₂O molecule, the model is unsuitable for energy predictions. However, the total intensity predictions are still useful as a first estimate, since the coupling of states through correlation effects often distributes the intensity across a group of states within the same energy range. The semi-empirical approach was primarily developed to investigate larger polyatomic molecules including those containing second-row atoms such as silicon and sulfur.

Improvements to the theory require better estimates of the *J* and *K* two-electron integral values using *ab initio* wavefunctions and inclusion of an adiabatic relaxation correction similar to that applied earlier for atoms (Larkins 1976). The introduction of such a correction for molecular calculations has been discussed elsewhere (Larkins 1990). An equivalent cones model is to be preferred in this regard. The strength of the semi-empirical theory is that it provides a useful first estimate for the interpretation of complex Auger spectra when the size of the molecule precludes optimised *ab initio* calculations for the double-hole states.

New experimental spectra obtained from photoelectron–Auger electron coincidence studies would also be valuable to remove the satellite contributions to the spectral profile. It has been suggested by Hutson and Ramaker (1987) that for the methane spectra, as presently measured, satellite lines contribute up to 49% of the total intensity; however, on the basis of the present work it is concluded that this is an overestimate and that a value closer to 16% is more reasonable.

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References

- Ågren, H., and Siegbahn, H. (1980). *Chem. Phys. Lett.* **69**, 424.
- Ågren, H., Svensson, S., and Wahlgren, U. I. (1975). *Chem. Phys. Lett.* **35**, 336.
- Aksela, H. (1988). NATO ASI Series B **187**, 15.
- Banna, M. S., and Shirley, D. A. (1975). *J. Chem. Phys.* **63**, 4759.
- Camilloni, R., Stefani, G., and Giardini-Guidoni, A. (1977). *Chem. Phys. Lett.* **50**, 213.
- Carravetta, V., and Ågren, H. (1987). *Phys. Rev. A* **35**, 1022.
- Chen, M., Larkins, F. P., and Crasemann, B. (1990). *At. Nucl. Data Tables* **45**, 1.
- Faegri, K. (1977). *Chem. Phys. Lett.* **46**, 541.

- Faegri, K., and Kelly, H. P. (1979). *Phys. Rev. A* **19**, 1649.
- Faegri, K., and Manne, R. (1976). *Mol. Phys.* **31**, 1037.
- Hehre, W. J., Stewart, R. F., and Pople, J. A. (1969). *J. Chem. Phys.* **51**, 2657.
- Higashi, M., Hiroike, E., and Nakajima, T. (1982). *Chem. Phys.* **68**, 377.
- Hillier, I. H., and Kendrick, J. (1976). *Mol. Phys.* **31**, 849.
- Hutson, F. L., and Ramaker, D. E. (1987). *J. Chem. Phys.* **87**, 6824.
- Jennison, D. R. (1980). *Chem. Phys. Lett.* **69**, 435.
- Jennison, D. R. (1981). *Phys. Rev. A* **23**, 1215.
- Körber, H., and Mehlhorn, W. (1966). *Z. Phys.* **191**, 217.
- Kvalheim, O. M. (1982). *Chem. Phys. Lett.* **86**, 159.
- Kvalheim, O. M., and Faegri, K. (1979). *Chem. Phys. Lett.* **67**, 127.
- Larkins, F. P. (1976). *J. Phys. B* **9**, 47.
- Larkins, F. P. (1977). *At. Nucl. Data Tables* **20**, 313.
- Larkins, F. P. (1987). *J. Chem. Phys.* **86**, 3239.
- Larkins, F. P. (1990). *J. Elect. Spectrosc.* **51**, 115.
- Larkins, F. P., and Chelkowska, E. Z. (1990). Technical Report, Uni. of Tasmania.
- Liegner, C.-M. (1982). *Chem. Phys. Lett.* **90**, 188.
- McGuire, E. J. (1969). *Phys. Rev.* **185**, 1.
- Økland, M. T., Faegri, K., and Manne, R. (1976). *Chem. Phys. Lett.* **40**, 185.
- Ortenburger, I. B., and Bagus, P. S. (1975). *Phys. Rev.* **11**, 1501.
- Pople, J. A., and Beveridge, P. L. (1970). 'Approximate Molecular Orbital Theory' (McGraw-Hill: New York).
- Ramaker, D. E. (1989). *J. Vac. Sci. Technol. A* **7**, 1614.
- Rye, R. R., Jennison, D. R., and Houston, J. E. (1980). *J. Chem. Phys.* **73**, 4867.
- Shaw, R. W., Jr, Jen, J. S., and Thomas, T. D. (1977). *J. Elect. Spectrosc.* **11**, 91.
- Shaw, R. W., and Thomas, T. D. (1975). *Phys. Rev. A* **11**, 1491.
- Shirley, D. A. (1973). *Phys. Rev. A* **7**, 1520.
- Siegbahn, H., Asplund, L., and Kelfve, P. (1975). *Chem. Phys. Lett.* **35**, 330.
- Snyder, L. C., and Basch, H. (1972). 'Molecular Wave Functions and Properties' (Wiley: New York).
- Spohr, R., Bergmark, T., Magnusson, N., Werme, L. O., Nordling, C., and Siegbahn, K. (1970). *Phys. Scripta* **2**, 31.
- Tarantelli, F., Tarantelli, A., Sgamellotti, A., Schirmer, J., and Cederbaum, L. S. (1985a). *Chem. Phys. Lett.* **117**, 577.
- Tarantelli, F., Tarantelli, A., Sgamellotti, A., Schirmer, J., and Cederbaum, L. S. (1985b). *J. Chem. Phys.* **83**, 4683.
- Walters, D. L., and Bhalla, C. P. (1971). *At. Data* **3**, 301.
- Wentzel, G. (1927). *Z. Phys.* **43**, 524.
- White, J. M., Rye, R. R., and Houston, J. E. (1977). *Chem. Phys. Lett.* **46**, 146.

