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# Relative extent of double and single Auger decay in molecules containing C, N and O atoms

A. Hult Roos,<sup>1</sup> J.H.D. Eland,<sup>2,1</sup> J. Andersson,<sup>1</sup> S. Zagorodskikh,<sup>3,1</sup> R. Singh,<sup>1</sup> R.J. Squibb,<sup>1</sup> and R. Feifel<sup>1,\*</sup>

<sup>1</sup>*Department of Physics, University of Gothenburg, Origovägen 6B, 412 96 Gothenburg, Sweden*

<sup>2</sup>*Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom*

<sup>3</sup>*Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden*

We show that the proportion of double Auger decay following creation of single 1s core holes in molecules containing C, N and O atoms is greater than usually assumed, amounting to about 10% of single Auger decay in many cases. It varies from molecule to molecule, where the size of the molecule have a positive correlation to the amount of double Auger decay. In neon, examined as a related benchmark, the proportion of double Auger decay is similar to that in methane, and is in the order of 5%.

## INTRODUCTION

When photon absorption or high energy particle impact creates a vacancy in the 1s shell of a light atom the dominant and immediate consequence is Auger decay. The major process is single Auger decay, in which one electron from an outer shell refills the inner hole while a second electron is ejected; the final products are a doubly charged ion and two electrons. Double Auger decay is always less abundant; it differs in that after the hole is filled two electrons are ejected from the outer shell and a triply charged ion is created. While the existence of double Auger decay is well known, knowledge of its relative extent is minimal, known only to a limited extent in the case of atoms where the relative yields of doubly and triply charged species can be measured by mass spectrometry. Such measurements are not normally possible for molecules, whose triply charged ions invariably and doubly charged ions usually dissociate into fragments.

In recent times, it has become popular to perform experiments in which two positive ions from dissociation of doubly-charged parent species are detected in coincidence. Early experiments of this sort induced double ionization of molecules using extreme ultraviolet radiation, whose energy was insufficient to cause triple ionisation in any way. Extensive later work, Refs. [1–5], has used synchrotron radiation from storage rings to produce double ionization by the Auger effect, but has generally ignored the occurrence of triple ionization by double Auger decay, assuming it to be of negligible abundance. Our own work in this area has suggested that at least in some specific cases (see Refs. [6–8]) the fraction of double Auger decay is considerable, of the order of 10%. We therefore decided to investigate this question systematically, first in a number of carbon, nitrogen and oxygen compounds. The ideal means to do this is to hand in the combination of storage ring synchrotron radiation together with a magnetic bottle time-of-flight electron spectrometer capable of multi-electron detection[9].

In examining the relative extent of double Auger (DA)

versus single Auger (SA) decay, it is natural to ask how this quantity varies between different atoms and for the same atom in different molecular environments. In this first series of experiments we have chosen molecular targets to address these questions.

## EXPERIMENTAL

Experiments were carried out at beam line U49/2 PGM-2 of the electron storage ring BESSY-II at the Helmholtz Zentrum Berlin operated in single bunch mode. The magnetic bottle time-of-flight electron spectrometer has been described before (see Ref. [9]), so here we recount only its basic operational form and the special arrangements for this particular project. The magnetic bottle collects essentially all electrons emitted in an ionization process, and guides them through a 2 m long flight tube towards a microchannel plate detector (MCP). The flight times of the electrons are measured in reference to the synchrotron light pulses. The flight times are then converted to kinetic energies for the electrons by a simple conversion formula [9] fitted to known Kr and Ne Auger and photolines [10, 11]. The energy resolution of the spectrometer ranges from 50 meV at low kinetic energy up to about 10 eV for electrons of 600 eV. Our objective in this project is to determine the ratio of DA to SA, equivalently the ratio of triple ionization to double ionization following creation of a single core hole. The directly measured quantity is the ratio of valid three-electron coincidence counts to valid two-electron coincidences and this must be divided by the effective collection and detection efficiency for electrons (hereafter  $f_e$ ) to give the true DA/SA ratio. So to maintain constant  $f_e$  throughout the runtime for the measurements, physical parameters of the apparatus including the positions of all components and the strengths of the magnetic and electric fields were kept strictly constant once optimized. The absolute value of  $f_e$  also depends on the gain of the MCP detector, determined by the applied voltages, and

on the settings of the gain and discriminator levels in the detection electronics. In order to eliminate interference by accidental coincidences, all the runs were done at total electron count rates far lower than the light pulse rate. The light pulse rate was 1.25 MHz but a more relevant rate is the inverse of the total electron flight time range (5  $\mu$ s), 200 kHz, in comparison to the total count rate that was limited to less than 600 Hz.

#### Determination of the electron collection efficiency as a function of electron energy

The collection efficiency was determined over the full energy range of the experiment from the single Auger decay in the rare gases Kr and Ne. The absolute collection efficiency was determined from the expressions of the total coincidence rate,  $C_{SA}$ , as

$$C_{SA} = N_{SA} f_e^2 ,$$

and the detection rate of Auger electrons as

$$A_{SA} = N_{SA} f_e .$$

The collection efficiency may then be determined from the ratio  $f_e = C_{SA}/A_{SA}$ , where  $N_{SA}$  is the true number of single Auger events in the source region and where it is assumed that the collection efficiency is the same for Auger and photoelectrons. Relative collection efficiencies, determined as described below, show that this condition is fulfilled for measurements over a useful range of energies, allowing absolute collection efficiencies to be determined. For instance, when Kr is ionized at 110 eV photon energy the photoelectron energy is 16 eV and the Auger energies range from 24 to 56 eV and in this range the relative efficiencies are the same within the experimental error. Although triple ionisation of Kr also occurs at this photon energy both directly and by DA, by selecting resolved Auger electrons and subtracting background contributions we eliminate such interference.

To determine the relative collection efficiency over a wider energy range we used the single Auger decay of Ne at photon energies from the  $1s^{-1}$  threshold (870 eV) up to 1420 eV. The same method used above can not be used, first because the efficiency for the photoelectron and Auger electron are likely to differ due to a large energy difference, and because of overlap effects in the spectra. With our experimental resolution the Auger electrons at an energy of 740-810 eV cannot be fully distinguished from valence shell electrons on the high energy side and from DA electrons and direct multiple ionization on the low energy side of the spectra. They are also inextricably overlapped by Auger electrons from satellite states, so the measured intensity of the Auger signal is higher than from pure SA signal. But the proportion of these contributions to the intensity of the Auger electron

signal is thought to be constant over our energy range, because the cross-section for valence and direct multiple ionization are much lower than for Auger ionization. The contribution from DA is necessarily constant as it arises from the creation of the same core hole as for SA. The satellite contribution is relatively small and we assume that it is constant at high photon energy. With this assumption the coincidence rate can be written as

$$C_{SA} = N_{SA} f_e^A f_e^P ,$$

where  $f_e^A$  and  $f_e^P$  are the collection efficiencies for the Auger and photoelectron respectively. Likewise, the Auger electron detection rate can be written as  $A_{SA} = k N_{SA} f_e^A$ , where  $k$  is a constant greater than unity. The apparent collection efficiency for the photoelectron,  $f_e' = C_{SA}/A_{SA}$ , is reduced by the factor  $k$  relative to the absolute efficiency. The value of  $k$  is estimated by comparing  $f_e$  obtained from the Kr data and  $f_e'$  from the Ne data in the low energy range, and then normalize the value of  $k$  accordingly. The results are shown in Fig. 1. The efficiency is close to 54% at very low energy and goes up close to 58% at 250 eV, before dropping slowly down to 35% at an electron energy of 800 eV.

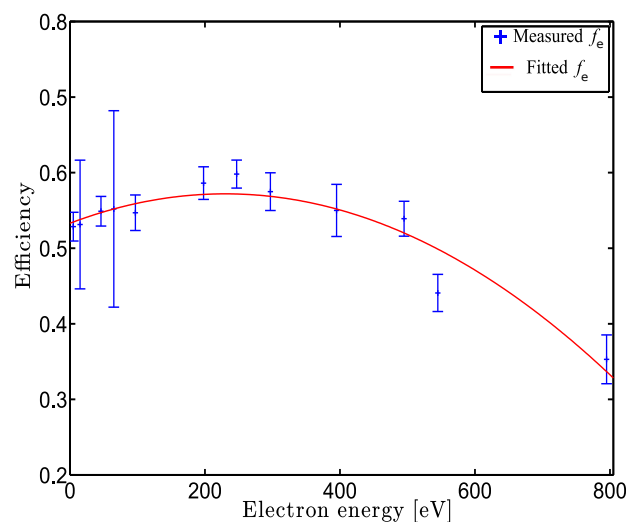


FIG. 1. Collection plus detection efficiency of the magnetic bottle spectrometer. Error bars display the standard error in each data point.

#### Treatment of false coincidences

Although there are essentially no purely accidental coincidences at the low count rate used in this work, there are plenty of false and unwanted but real coincidences. These must be avoided during measurements or subtracted afterwards. The major source is collision of

primary electrons with metal surfaces, mainly the conical magnet and the gas delivery needle, releasing secondary electrons. The main source of primary electrons are single Auger electrons, which when hitting a surface generate one or two secondaries while the corresponding photoelectron goes to the detector in a normal way. This will generate a false double or triple coincidence, with a valid photoelectron. The secondaries are likely to be of quite low energy, contributing to the false signal at high apparent double or triple ionization energies. Their effect can be greatly reduced by selecting events with total electron energy of pairs or triples corresponding to energies in the correct range for double and triple ionization. In contrast if a photoelectron of a SA event hits a surface and releases secondaries while the Auger electron is detected normally, the summed electron energy is quite likely to be in an acceptable range. To handle such false signals we generate a background for subtraction by accepting electrons with flight time close to the time of the photoline, since the spectrum of background electrons is smooth on the time scale. By such stratagems we attempt to ensure subtraction of the majority of false coincidences. The fraction of the raw total SA and DA signals subtracted as background are 2-3% and 4-8% respectively, while the statistical uncertainties are typically 0.5% and 6%. For a typical ratio of 10:1 between SA and DA, the uncertainty in the final proportion of SA and DA would be of the order of 2%, even if the background subtractions are out by as much as 50% of their magnitude.

Besides generating secondaries, primary electrons may also lose energy in inelastic collisions with gas or surfaces but still be detected; this produces weak low energy tails on real signals and adds to the tails on the high energy sides of the ionization spectra. The existence of such tails is clear, but the magnitude of the effect is difficult to judge as the tails spread over a wide energy range. The total intensity, where it can be measured is of the order of 2% of the primary peak area.

## RESULTS AND DISCUSSION

### Characteristics of the spectra and distributions

From the recorded spectra of the samples containing C, N and O atoms, several common characteristics are apparent:

1. The SA (double ionization) and DA (triple ionization) spectra overlap; there are apparently some doubly charged states above the minimum triple ionization energy.
2. As seen from Fig. 4, the Auger electron pair distributions in DA have the highest intensity for very unequal energy sharing; they look like the distribu-

tions for high excess energies in double ionization of He (Refs. [12, 13]).

3. Spectra of triple ionization from pairs excluding the most unequal energy sharing have higher onset and are less intense at low energy than those including unequal sharing.

Similar observations to these have been made before in connection with individual triple ionization spectra (see refs. [14, 15]), and their origins are closely related to the occurrence of indirect double ionization. Besides resolution limitations there is another trivial reason for overlap of the raw spectra, in the imperfect detection efficiency of the apparatus. Some real DA events are detected not as triples but as doubles, and because of the dominant unequal energy sharing many of these appear in the energy range of real triple ionization. When the detection efficiencies are known these false electron pairs can be subtracted, and this has already been done in the spectra of CH<sub>4</sub> and CO<sub>2</sub> shown in Figs. 2 and 3. These spectra have already been recorded and further analysed in Refs. [14] and [15], respectively. Real overlap between SA and DA spectra arises because there are many ways of taking three electrons out of the orbitals of a molecule, so there are many triply charged states above the ground state, typically covering a range of 10 to 15 eV. Each of these has a series of Rydberg-like doubly-charged states leading up to it, which, once formed can dissociate to doubly charged fragments instead of ionizing to triply charged products. Many of them do dissociate very rapidly to doubly charged fragments, because all triply-charged ion cores are made highly unstable by loss of bonding and

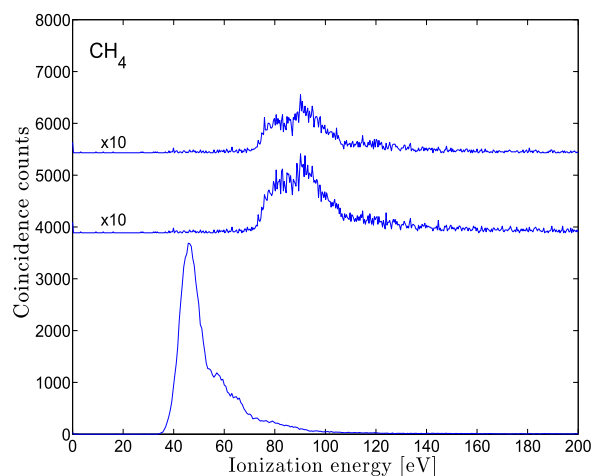


FIG. 2. Final state spectra from single and double Auger decay of a C 1s vacancy in methane at the photon energy of 356 eV. Bottom: Single Auger (double ionization). Middle: Double Auger (triple ionization) taking all electrons. Top: Double Auger taking only electrons with more than 10 eV.

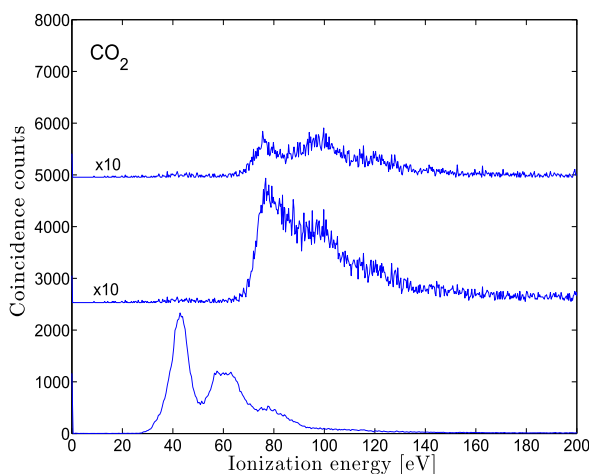


FIG. 3. Final state spectra from single and double Auger decay of a C 1s vacancy in carbon dioxide at the photon energy of 312 eV. Bottom: Single Auger (double ionization). Middle: Double Auger (triple ionization) taking all electrons. Top: Double Auger taking only electrons with more than 10 eV.

Coulomb repulsion. Those that ionize to triply charged products may do so after partial dissociation, producing low energy electrons. Thus we interpret the spectra of triple ionization from more equal energy sharing as spectra of molecular processes, preceding major fragmentation and occurring by direct double Auger decay, and the spectra dominated by unequal sharing as representing mainly dissociative processes from indirect decay.

It is worth mentioning here that characterisation of stepwise double Auger from molecules after 1s ionisation is effectively impossible, because of the broadness of bands characteristic of both the final triply ionised states and of any intermediate doubly ionised states which could provide stepwise indirect pathways. All the triply ionised states and many possible doubly charged intermediate states will be dissociative, so vertical transitions involving them will give broad bands, overlapping each other and the direct double Auger processes at low electron energy. It is highly probable, however, that indirect double Auger decay happens in molecules just as it does in atoms. While it is not the purpose of this paper to examine this question in detail, we note that the occurrence of such processes is supported by the changes in intensity and in spectrum shape observed when most of the possible indirect processes are excluded. For the ratios of DA to SA we use the total triple ionization after core hole production, including both direct and indirect processes, as this is the proportion that must be taken into account when interpreting, for instance, ion pair data from Auger decay. We also derive “direct” DA spectra by applying an arbitrary minimum energy of 10 eV for the Auger electrons. This choice is found to retain about

TABLE I. Percentage of overall single and double Auger decay following single photoionization of C 1s, N 1s, and O 1s core holes.

Molecule	SA [%]	DA [%]	Error <sup>a</sup>
Ne	94.7	5.3	±0.9
Carbon 1s			
CH <sub>4</sub>	93.7	6.3	±0.6
C <sub>2</sub> H <sub>2</sub>	91.8	8.2	±0.8
C <sub>2</sub> H <sub>4</sub>	91.5	8.5	±0.8
C <sub>2</sub> H <sub>6</sub>	91.2	8.8	±0.8
CO	90.8	9.2	±0.8
CO <sub>2</sub>	85.7	14.3	±1.3
Nitrogen 1s			
N <sub>2</sub>	90.6	9.4	±0.9
NH <sub>3</sub>	91.8	8.2	±0.8
Oxygen 1s			
O <sub>2</sub>	92.9	7.1	±0.7
CO	90.8	9.2	±0.9
CO <sub>2</sub>	90.3	9.7	±0.9
H <sub>2</sub> O	93.4	6.6	±0.7

<sup>a</sup> Standard error.

half the total DA signal as “direct”, which can be seen in Figs. 2 and 3. The minimum triple ionization energies seen in the “direct” spectra provide useful estimates of triple ionization energies at the molecular geometry. The energies required to produce charge-separated fragments are considerably lower because of the reduced Coulomb repulsion.

### Proportions of double and single Auger decay and their interpretation

The results of the data treatment outlined in this study are the double and triple ionization spectra of each sample in coincidence with selected photolines. In the conversion of the relative number of SA and DA counts to real proportions of single and double Auger decay, the relative numbers of single and double Auger counts have to be divided by the relevant collection efficiencies. The collection efficiency, which can be seen in Fig. 1, is the major source of uncertainty in the derivation of the real single and double Auger decay proportions. The efficiency for the photoelectrons is always common to both the single and double Auger events, so the relative SA count is divided by the efficiency for the Auger electrons while an effective collection efficiency is necessary for each one of the Auger electron pairs in DA. This effective efficiency for the DA count is estimated from the Auger electron energy distributions, which are revealed in coincidence maps of the electron pairs. The pair distributions for some samples are shown in Fig. 4.



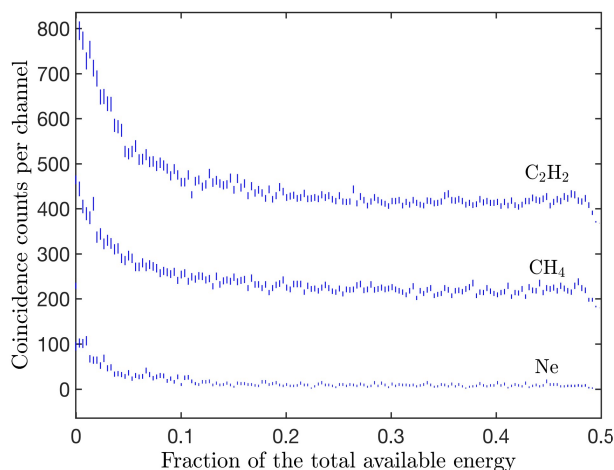


FIG. 4. Auger electron pair distribution after 1s hole creation in Ne, CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>.

The necessary correcting factor for the real ratio of DA to SA is given by the expression  $f_e^{\text{SA}} / (f_e^{\text{DA,fast}} \cdot f_e^{\text{DA,slow}})$ , where  $f_e^{\text{SA}}$  is the efficiency for the SA and  $f_e^{\text{DA,fast/slow}}$  are the efficiencies for the fast and slow DA electrons respectively. Since a large part of the DA intensity is concentrated at the low and high ends of the energy distribution of the Auger pairs (see Fig. 4), the correction factor can be approximated as  $f_e^{\text{SA}} / (f_e^{\text{DA}})^2$ , where the efficiency for the DA electrons are approximated as the geometric mean of those at high and low energy in the pair distribution. From this estimation, the values used for the correction factor were: for C 1s, 1.86; for N 1s 1.79; and for O 1s 1.72, with an estimated uncertainty of 9% on all the values. For Ne the correction factor estimated as 1.25 has a bigger uncertainty because of a larger energy spread in the DA energy distribution.

The final percentage of overall single and double Auger decay after selective C 1s, N 1s, and O 1s photoionization of the sample molecules are listed in Table I. The table also includes percentage values for SA and DA decay after 1s photoionization of Ne. The Ne values were determined as a benchmark in the same way as the molecular ones; the error limits have been estimated conservatively in all cases. The error in the DA count is compounded of the statistical part including the subtracted background count, and the considerably larger uncertainty in the correction factor obtained from the effective collection efficiency. The major contribution to the error in DA comes from the fit of a second order function to the measured values of the collection efficiency.

From Table I we see that the proportion of DA approaches or surpasses 10% for each set of selective 1s photoionization, which is more than has typically been assumed in the past. In the case of Ne the intensity for

the proportion of DA can be compared with previous determinations from doubly and triply charged ion yields as function of the photon energy. In Ref. [16], Carlson, Hunt and Krause found 22% Ne<sup>3+</sup> from K<sup>-1</sup> ionization. Krause et al. (Ref. [17]) got a similar value. Saito and Suzuki [18] found 23% Ne<sup>3+</sup> at photon energies above 1000 eV, but their figures suggest that much of this is from decay involving satellite states above the simple K hole. In Ref. [19], Kanngiesser et al. found close to 6% Ne<sup>3+</sup> from K<sup>-1</sup> photoionization, more in line with our determination.

Among the molecules in each set of 1s ionizations the clearest trend is that the larger molecules have higher proportions of DA. This trend may perhaps be attributed to the increase in the number of valence electrons/orbitals available for the double Auger decay process in the larger molecules. Because the data have been analysed in exactly the same way with fixed correction factors for each set of 1s ionization, the relative uncertainties between the values of the DA fraction in each set of molecules are much smaller than the overall error limits given. Thus the apparent difference in the proportion of DA between acetylene (C<sub>2</sub>H<sub>2</sub>) and ethane (C<sub>2</sub>H<sub>4</sub>), for instance is probably real.

A full quantum treatment of the proportions of single and double Auger is not yet available, and presents a significant challenge for current theoretical methods; a major problem stems from the need to represent two and

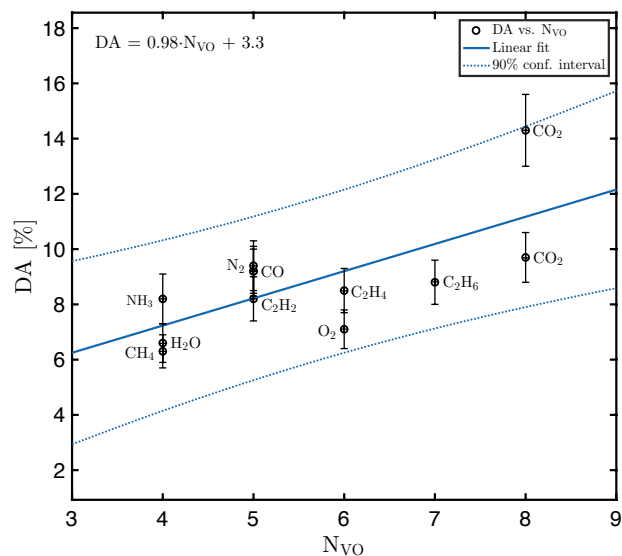


FIG. 5. The proportion of double Auger from Table 4, as a function of the number of available valence orbitals for the Auger decay pathways. The linear fit (solid line) show the trend among the molecules in Table 4, with a 90 % confidence interval (dashed lines) for the fit.

three electrons in the continuum. However, higher proportion of DA in larger molecules may be qualitatively understood from a first approximation using a model based on Fermi's golden rule. Considering only first-row atoms, the initial vacancy in an 1s orbital is filled in a first independent step by a valence electron from the  $n = 2$  shell. The second step, where competitive Auger processes eject one or two further electrons, may be treated as similar to single or double photoionization induced by a single virtual photon, mathematically expressed as recombination matrix element multiplied by the ionization matrix element. For 1s Auger decay, this treatment may be justified by the fact that the single-virtual-photon recombination is strongly localized. Following from the golden rule, the two Auger pathways will have partial rates proportional to the density of states available for each pathway. As a zeroth-order model these densities are taken as proportional to the total number of available two-hole or three-hole final states of the doubly or triply charged final products. Although the number of two- and three-hole final states may be outnumbered in reality by states of mixed and distant configuration, they probably carry the majority of the oscillatory strength, and can crudely be estimated from the numbers of valence orbitals in each molecule. On the basis that the binding energies, which are of the order of 300 to 540 eV for C to O, is considerably greater than the binding energies of the final states, which are of the order of 30 to 150 eV, the expected effect from the excess energy available in each process, i.e. energy of the hole-state minus the final state, on the phase-space density is neglected. While such a simplistic analysis helps understanding the general trend, it most likely will not entirely reproduce every detail. In this respect, it should primarily be regarded as motivation for further theoretical investigation.

The treatment of the ratio of DA to SA introduced above can be seen in Figure 5, where the percentage of DA for the molecules in Table I is plotted versus the number of available valence orbitals ( $N_{VO}$ ) in each molecule. In this figure, a linear fit has been used to show the trend in increased percentage of DA as the number of available valence orbitals for the Auger decay is increased. The trend of an increasing proportion of double Auger with an increase in the number of available valence orbitals is perceived from Fig. 5. Although the trend is clear, the treatment does not explain the apparent difference in proportion of DA in  $CO_2$  when the initial vacancy is created in either the C 1s or the O 1s orbital.

## CONCLUSIONS

The relative extent of double and single Auger decay in molecules containing C, N, and O atoms was determined using a versatile multi-electron coincidence technique. The single and double Auger decays in coincidence

with 1s photoelectrons were recorded using a time-of-flight magnetic bottle spectrometer. Careful correction to the double and triple ionization spectra, according to the experimental electron collection efficiency, allowed us to obtain the proportion of single to double Auger decay in each molecule. After photoionization from the C 1s, N 1s, or O 1s orbital, the clearest trend observed is that larger molecules have higher proportion of double Auger decay. The true parameter governing this trend may be the number of available valence electrons in each molecule. For each set of C 1s, N 1s, or O 1s photoionization the proportion of double Auger decay approaches or surpasses 10 % for the heavier molecules, which is more than has typically been assumed in the past. In even larger molecules the proportion may be yet higher. Further investigations of the fraction of double Auger in large molecules would be interesting and probably highly relevant to studies of dissociative ionization after site specific core ionization.

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\* raimund.feifel@physics.gu.se

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