reactions, but our phenomenological form may not be sufficiently sophisticated to show its increased importance at the lower energies relevant to μ capture. Although our crude phenomenology works surprisingly well, we are still without a microscopic theory of its origin. Therefore our results, especially for absolute magnitudes, should be taken with caution. Better data, particularly for high-energy nucleons in π- and μ-capture and coincidence experiments, will allow us to correlate these processes without extrapolation of the nuclear recoil function from the strong reaction which may be the weakest link in our analysis.

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[a] Permanent address: Department of Physics, Technion–Israel Institute of Technology, Haifa, Israel.

[b] Permanent address: Department of Physics, University of Pennsylvania, Philadelphia, Pa. 19104.

[1] P. Singer, in Springer Tracts in Modern Physics, edited by G. Höhler (Springer, Berlin, 1974), Vol. 71, p. 39; N. C. Mukhopadhyay, Phys. Rep. 30C, 1 (1977), and references therein.

[2] H. Baer et al., in Advances in Nuclear Physics, edited by M. Baranger and E. Vogt (Plenum, New York, 1977), Vol. 9, p. 177.

[3] S. Frankel et al., Phys. Rev. Lett. 36, 642 (1976); H. Brody et al., Phys. Lett. 71B, 79 (1977).

[4] S. Frankel, Phys. Rev. C 17, 694 (1978); R. D. Amado and R. M. Woloshyn, Phys. Rev. Lett. 36, 1435 (1976), and Phys. Rev. C 16, 1255 (1977).

[5] See M. Perl, High Energy Hadron Physics (Wiley, New York, 1974).

[6] The interaction of the incident and the unmeasured proton with other hadrons is ignored in the $(p, 2p)$ case.

[7] H. Primakoff, Rev. Mod. Phys. 31, 802 (1959).

[8] C. Werntz, Phys. Rev. Lett. 41, 1030 (1978).

[9] Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, edited by K. H. Hellwege (Springer-Verlag, Berlin, 1973), New Series, Group. 1, Vol. 7.

[10] M. H. Krieger, thesis, Columbia University Report No. NEVIS-172, 1969 (unpublished); R. M. Sundelin and R. M. Edelstein, Phys. Rev. C 7, 1037 (1973); W. O. Schröder et al., Z. Phys. 268, 57 (1974).

[11] W. C. Lam et al., Phys. Rev. C 10, 72 (1974).

[12] The 1s pion absorption widths are 0.195±0.012 keV for Li and 3.12±0.012 keV for C (see Ref. 2).

[13] D. Renker et al., Phys. Rev. Lett. 41, 1279 (1978).

Post-Collision Interaction in the Selenium $L_2M_{4,5}M_{4,5}$ Auger Spectrum Following Photoionization

M. K. Bahl,[a] R. L. Watson, and K. J. Irgollic

Cyclotron Institute and Department of Chemistry, Texas A & M University, College Station, Texas 77843

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The $L_{2,3}M_{4,5}M_{4,5}$ Auger spectrum of selenium in a variety of compounds has been measured following near-threshold photoionization of the $2p_{1/2}$ level by monochromatic Al $K\alpha_{1,2}$ radiation. The energy difference between the $L_2M_{4,5}M_{4,5}$ and the $L_3M_{4,5}M_{4,5}$ Auger peaks was observed to increase by as much as 1.1 ± 0.1 eV as the $2p_{1/2}$ binding energy approached to within 1.1 eV of the ionization threshold. The energy shifts are compared with the predictions of a semiclassical analysis by Niehaus which takes into consideration the influence of the Coulomb field of the slow photoelectron on the Auger process.

Auger decay following inner-shell photoionization is not usually affected by the energy of the incident photon. However, when the photon energy is very close to the ionization threshold of the electron being ejected, the subsequent emission of an Auger electron may occur while the slowly receding photoelectron is still in the near vicinity. In such a situation, the Auger spectrum is expected to be influenced by what is termed post-collision interaction (PCI).[1,2] The only previous evidence of an observable PCI effect in inner-shell photoionization has recently been reported by Schmidt et al.,[3] who examined the $N_5O_{2,3}O_{2,3}$ $^1S_0$ Auger peak of xenon using synchrotron radiation. Despite a fairly large background caused by the presence of second-order reflected photons in the incident beam, these investigators observed a small upward energy shift (135 meV) and a broadening of the $^1S_0$ Auger peak at a photon energy 0.8 eV above the N_5-electron ionization thresh-

TABLE I. Core-level shifts and $L_{2,3}M_{4,5}M_{4,5}$ Auger data for a variety of selenium compounds.

Compound	Average core-level energy shift (eV)	$L_2M_{4,5}M_{4,5} - L_3M_{4,5}M_{4,5}$ energy difference (eV)	$L_2M_{4,5}M_{4,5}/L_3M_{4,5}M_{4,5}$ intensity ratio
$MoSe_2$	− 0.9	41.05 ± 0.05	0.42 ± 0.02
$FeSe_2$	− 0.6	41.00 ± 0.05	0.37 ± 0.01
Se metal	0	41.26 ± 0.06	0.31 ± 0.01
SeO_2	3.4	41.48 ± 0.05	0.17 ± 0.01
H_2SeO_3	3.5	41.5 ± 0.1	0.19 ± 0.01
H_2SeO_4	5.4	42.1 ± 0.1	0.10 ± 0.01

old. In the work presented here, we have utilized the L_2 binding-energy shifts in selenium, resulting from different states of chemical combination, to study the effect of near-threshold photoionization on the $L_2M_{4,5}M_{4,5}$ Auger spectrum with a conventional monochromatized x-ray source. This technique has made possible the first investigation of PCI in the photoionization of a deeply bound state, where the effects are greatly enhanced due to the shorter Auger decay lifetimes.

The choice of selenium was dictated by the energy of the monochromatic Al $K\alpha_{1,2}$ radiation (1486.6 eV) employed in the Hewlett-Packard 5950A spectrometer used for these studies. The binding energy of a $2p_{1/2}$ electron in selenium metal (with respect to the vacuum level), $B_{2p_{1/2}}{}^v$, is 1480.1 eV.[4] By taking advantage of the chemical shift exhibited by different compounds of selenium, we can bring the $2p_{1/2}$ binding energy quite close to the Al $K\alpha_{1,2}$ energy. This is shown in Table I where the average chemical shifts of the core levels of selenium in a variety of different compounds (measured relative to selenium metal) are listed. It is apparent from this table that (neglecting the small variation of the work function from one compound to another) the $2p_{1/2}$ binding energy varies from 1485.5 eV in H_2SeO_4 to 1479.2 eV in $MoSe_2$, thus making it feasible to examine the effect of PCI from 1.1 to 7.4 eV above the ionization threshold.

The experimental details were similar to those described previously.[5] An electron flood gun was used to bombard the samples during the measurements in order to obtain the sharpest possible electron spectra by minimizing charging effects. All samples except selenium metal were powdered and dispersed on gold-coated aluminum plates having striated surfaces. Selenium metal was prepared by vacuum evaporation, and charging shifts were monitored by observing the gold $4f_{7/2}$

photopeak (whose energy was taken to be 84.0 eV) originating from a small gold spot evaporated onto the surface of the sample. Charging effects in the powdered samples were monitored by observing the carbon $1s$ photopeak originating from hydrocarbon contamination. This photopeak was found to have an energy of 285.0 ± 0.1 eV as measured relative to the gold $4f_{7/2}$ photopeak in the selenium metal sample. Although care was taken to minimize and correct for charging shifts, the experimental quantity of primary interest (i.e., the energy difference between the $L_2M_{4,5}M_{4,5}$ and $L_3M_{4,5}M_{4,5}$ Auger peaks) is not altered by charging since the two Auger peaks shift by exactly the same amount.

A comparison of the selenium $L_{2,3}M_{4,5}M_{4,5}$ Auger spectra of $FeSe_2$ and H_2SeO_4 is shown in Fig. 1. The two spectra have been aligned so that the $L_3M_{4,5}M_{4,5}$ Auger peaks coincide. It may be seen that the energy difference between the $L_2M_{4,5}M_{4,5}$ and $L_3M_{4,5}M_{4,5}$ Auger peaks is larger in H_2SeO_4, where the energy above threshold, ΔE ($\equiv h\nu - B_{2p_{1/2}}{}^v$), is only 1.1 eV, than it is in $FeSe_2$ where $\Delta E = 7.1$ eV. The Auger spectra for the various selenium compounds were carefully analyzed using a least-squares peak-fitting procedure in which each component of the Auger structure was represented by a fitting function consisting of a Gaussian plus an exponential tail. The results of this analysis are given in columns 3 and 4 of Table I where the energy differences and intensity ratios are listed. The effect of PCI is clearly demonstrated by the steady increase in the Auger peak separation as the $2p_{1/2}$ binding energy approaches the Al $K\alpha_{1,2}$ energy. Close examination of the H_2SeO_4 spectrum also revealed the presence of a high-energy tail on the main $L_2M_{4,5}M_{4,5}$ peak; however, overlap with the higher energy multiplet component (see Fig. 1) prevented a detailed analysis of the peak shape.
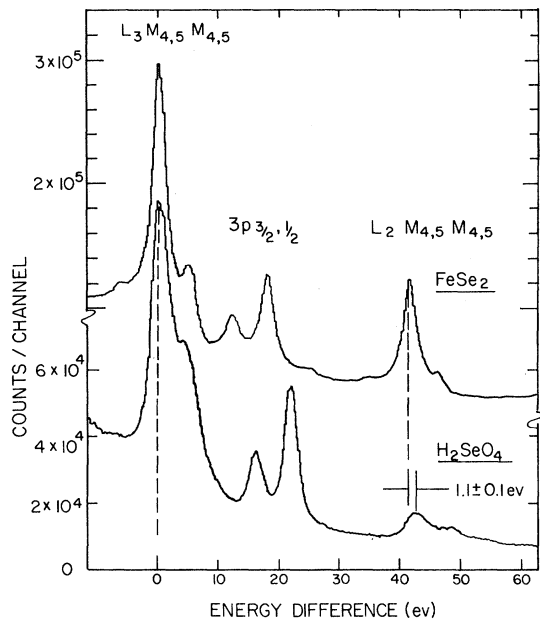
FIG. 1. A comparison of the selenium $L_{2,3}M_{4,5}M_{4,5}$ Auger spectra of $FeSe_2$ and H_2SeO_4 showing the effect of PCI. The two spectra have been aligned so that the $L_3M_{4,5}M_{4,5}$ Auger peaks coincide.

Another interesting feature is the rapid decrease which occurs in the $L_2M_{4,5}M_{4,5}/L_3M_{4,5}M_{4,5}$ intensity ratio in going from $MoSe_2$ to H_2SeO_4. This behavior reflects the variation of the $2p_{1/2}$ photoionization cross section near threshold.

A theoretical analysis of PCI in Auger processes following near-threshold inner-shell photoionization has recently been carried out by Niehaus.[2] In this work, semiclassical formulas are derived which describe the influence of the slowly receding photoelectron on the Auger decay of an inner-shell ionized atom. The results predict an asymmetric Auger peak having a high-energy tail and an energy shift which satisfies the relationship[6]

$$[2(\xi + \delta)]^{1/2} - \xi(5\xi + 4\delta) = 0, \quad (1)$$

where the reduced energies δ and ξ are related to ΔE (the energy above threshold) and ϵ (the Auger peak energy shift) by $\tau = 1/\Gamma$ (the mean lifetime) according to the equations

$$\xi = \epsilon\tau^{2/3},$$
$$\delta = \Delta E\tau^{2/3}, \quad (2)$$

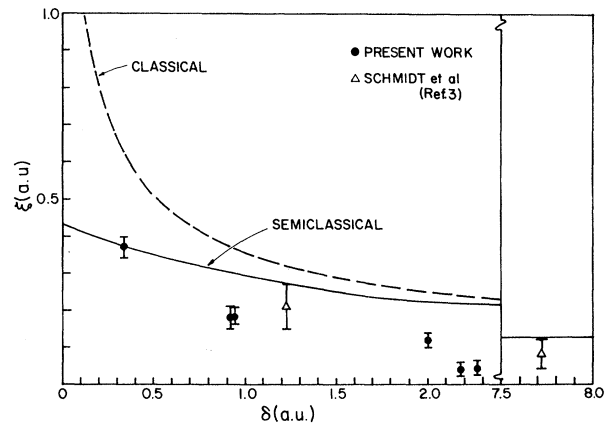with all quantities in atomic units. When $\epsilon \ll \Delta E$, Eq. (1) reduces to the classical result obtained

FIG. 2. The reduced Auger-peak shift ξ as a function of the reduced energy above threshold δ. The semiclassical result of Niehaus (Ref. 2) is shown by the solid curve, whereas the classical result of Barker and Berry (Ref. 7) is shown by the dashed curve.

earlier by Barker and Berry[7], namely,

$$\xi = 1/2\sqrt{2\delta}. \quad (3)$$

In order to compare our results directly with the predictions of Eq. (1) it is necessary to know the unperturbed Auger-peak energy separation for photoionization far from threshold. Since this energy separation is just the $2p_{1/2}-2p_{3/2}$ spin-orbit interaction energy, it may be obtained directly from x-ray measurements as the energy difference between $K\alpha_1$ and $K\alpha_2$. Unfortunately, we were unable to find sufficiently accurate selenium K-x-ray energies in the literature. We therefore took advantage of the high-precision K-x-ray energies for elements 29 through 33 listed by Bearden[8] and the fact that $\ln(E_{K\alpha_1} - E_{K\alpha_2})$ varies linearly with $\ln Z$ in this region to extrapolate the energy difference for selenium using a least-squares fit. The unperturbed $2p_{1/2}-2p_{3/2}$ energy separation for selenium was found to be 40.87 eV with an error of ± 0.05 eV, as estimated from the goodness of the least-squares fit.

The Auger-peak energy shifts obtained in the present experiment are compared with the theoretical results of Niehaus in Fig. 2. The solid line in this figure shows the semiclassical dependence of ϵ on δ as required by Eq. (1), while the dashed curve shows the classical result given by Eq. (3). The experimental values of ϵ and ΔE were converted to ξ and δ, respectively, using $\Gamma = 1.13$ eV, as measured recently by Krause and Oliver.[9] Also plotted in Fig. 2 are the two energy shifts measured by Schmidt et al., reduced

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using the experimental value of $\Gamma = 100$ meV.[3]
Both sets of experimental data fall below the
semiclassical curve at high values of δ, and it is
apparent that the energy shifts measured for se-
lenium decrease faster with increasing δ than do
the semiclassical predictions.

An interesting question arises concerning the
effect of extra-atomic relaxation on PCI in solids.
Normally, extra-atomic relaxation, associated
with the adjustment of neighboring atoms to the
new potential produced by the doubly ionized atom
resulting from photoionization followed by Auger
decay, contributes to the energy of the emitted
Auger electron.[10] However, when the photoelec-
tron remains in the near vicinity during the emis-
sion of the Auger electron, the extra-atomic re-
laxation contribution to the Auger electron energy
may be expected to decrease. The difference be-
tween the extra-atomic relaxation energies for a
singly ionized and a doubly ionized selenium atom
is estimated to be of the order of 3 eV.[4] Thus,
it is likely that extra-atomic relaxation will have
a nonnegligible effect on the observed Auger-
peak shifts in the near-threshold photoionization
of these solid compounds.

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(a)Present address: Materials Research Center,
Northwestern University, Evanston, Ill. 60201.
[1]See R. Morgenstern, A. Niehaus, and U. Thielmann,
J. Phys. B 10, 1039 (1977), and references therein.
[2]A. Niehaus, J. Phys. B 10, 1845 (1977).
[3]V. Schmidt, N. Sandner, W. Mehlhorn, M. Y. Adam,
and F. Wuilleumier, Phys. Rev. Lett. 38, 63 (1977).
[4]M. K. Bahl, R. L. Watson, and K. J. Irgollic, to be
published.
[5]M. K. Bahl, R. L. Watson, and K. J. Irgollic, J.
Chem. Phys. 66, 5526 (1977).
[6]As a result of a typographical error, a factor of 4
was omitted before the δ in the second term of Eq. (16)
in Ref. 2.
[7]R. B. Barker and H. W. Berry, Phys. Rev. 151, 14
(1966).
[8]J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).
[9]M. O. Krause and J. H. Oliver, to be published.
[10]D. A. Shirley, Phys. Rev. A 7, 1520 (1973).

Reduced Equations of Motion for Molecular Multiphoton Processes

Shaul Mukamel
Department of Chemistry, William Marsh Rice University, Houston, Texas 77001
(Received 2 October 1978)

I derive reduced equations of motion for molecular multiphoton processes by constructing
a set of relevant operators and adopting the Mori projection-operator technique. The intra-
molecular dephasing processes which play a dominant role in the quasicontinuum are proper-
ly incorporated by utilizing the representation of exact molecular states. The resulting equa-
tions include dephasing operators expressed in terms of intramolecular dipole correlation
functions, and interpolate between the coherent and incoherent driving limits.

Studies of molecular multiphoton processes
(MMP) induced by the interaction of infrared la-
sers with polyatomic molecules under collision-
less conditions are providing a revolutionary
new method for studying the dynamics of highly
excited molecules and chemical reactions and
achieving laser-controlled chemistry.[1-9] It is
clear[4-9] that after the absorption of a few in-
frared quanta, the molecule is pumped into the
quasicontinuum where the high density of molec-
ular states changes the nature of the molecular
driving from coherent to totally incoherent. De-
spite numerous experimental and theoretical ef-

forts, the appropriate description of the absorp-
tion process and the nature of the quasicontinuum
dynamics are not yet understood.

I present here a microscopic derivation of re-
duced equations of motion (REM) for MMP, start-
ing with the complete Liouville equation. The
approach is "hydrodynamiclike" and is based on
the choice of a few relevant molecular operators
corresponding to level populations and coherences
and then making use of Mori's projection-opera-
tor technique[10] utilizing a new partial-time-or-
dering version.[10,11]

Consider a polyatomic molecule irradiated with