Double-electron excitation channels at the L edges of atomic Hg

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X-ray-absorption measurements at the L_3 , L_2 , and L_1 edges of Hg vapor have been performed using synchrotron radiation. The onset of multielectron excitation channels involving 2p (or 2s) and 4felectrons has been revealed. The experimental onset energies are compared with self-consistent-field Dirac-Fock (SCF-DF) calculations and Z+1 estimates, which, in this specific case, were inaccurate. The importance of these features in x-ray-absorption fine-structure structural data analysis for sixth-period elements is addressed, and the SCF-DF onset energies, covering the elements Hf-Rn, are presented.

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There is a wide recent interest towards accurate measurements of x-ray-absorption cross sections of elements or simple molecules related to the presence of observable multielectron effects [1-5]. The failure of the simple one-electron picture in describing the photon absorption phenomenon is often seen directly as the appearance of additional resonance peaks or shake-up and shake-off channel onsets in the spectra which cannot be associated with the excitation of a single electron. This topic is of fundamental interest in the fields of atomic, chemical, and condensed-matter physics. A general introduction can be found in a recent paper by Schaphorst et al. [1], devoted to the theoretical interpretation of the K-edge spectrum of Kr. A particularly important applied aspect of this research field consists in the identification of reliable "atomic background" models, in order to correctly isolate the structural oscillation occurring in condensed phases or molecular aggregates, usually referred to as xray-absorption fine structure (XAFS). These effects have been discussed, for instance, in some details at the Br Kedge of HBr and Br_2 [2].

Besides noble gases, very few elements can be studied as isolated atoms, thus providing absorption cross sections freed from the XAFS. In this respect the case of Hg, the subject of the present research, is particularly interesting: it is a heavy element (Z = 80) where relativistic effects become dominant, its ground-state electronic configuration is closed shell $|{\rm Xe}|\bar{4}f^{14}5d^{10}6s^2,$ there is a completely filled shell of f electrons, and clearly it represents a prototype for several sixth-period metals often studied by x-ray-absorption spectroscopy. Previous measurements of vapor Hg were performed by Keski-Rahkonen etal. [6], but only related to a limited energy range around the edge. From the experimental point of view Hg can be easily vaporized with a reasonable x-ray-absorption thickness, which allows for detection in absorption mode with good signal-to-noise ratios. Hg vapor is composed of isolated atoms providing thereby absorption spectra lacking any XAFS signal. This is a very important requirement if low-contrast features have to be unambiguously assigned. The purpose of this communication is to present atomic x-ray-absorption spectra of Hg, to identify multielectron excitation effects, and to provide a reliable atomic background model for structural studies at the Hg L edges and, by analogy, also at the corresponding edges of neighboring elements.

X-ray-absorption spectra at the Hg L_3 , L_2 , and L_1 atomic absorption edges have been measured at the LURE laboratories (Orsay-Paris), during dedicated beam time on the D42-EXAFS 1 beam line equipped with a Si(331) channel-cut monochromator. The Hg vapors container was a 80 cm long cylindrical glass cell ending with Teflon windows sealed with vyton O-rings. The cell was evacuated and heated to 200 °C. Hg vapors from the vapor pressure of a liquid Hg droplet were injected through a side pipe until the Hg density in the cell was about $4.4(4) \times 10^{-5}$ g/cm³, yielding a reasonable absorptance. The side pipe was disconnected and the temperature raised to 240 °C to avoid possible condensation on the windows. Checks were performed to ensure the stability of the sample which successively has been measured for a total of four hours at the various edges.

The absorption spectra have been corrected for the absorption of the Teflon windows which is a smooth function of the energy and are reported in absolute scale in Fig. 1 for the L_3 edge and Fig. 2 for the L_2 and L_1 , respectively, as a function of the energy above threshold (E_t) . The ordinate scale is the cross section in cm²/g, which may be in absolute error up to about 10%. The shape of the spectra is however extremely reliable with signal-to-noise ratios of about 2000, 900, and 400 for the three edges, respectively.

An accurate explanation of the atomic absorption cross-section profile in the edge region, in terms of oneelectron transitions to discrete and continuum states, has been already given [6]. In the threshold region we simulated the L_3 and L_2 edges with an arctangent function convoluted with a Gaussian function representing the ex-

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FIG. 1. L_3 edge of atomic Hg as a function of the energy above threshold E_t . The lower curve represents the same spectrum magnified in ordinate by a factor of 6 on the same energy scale. The slope change due to the opening of double-electron excitation channels is evident (arrow).

perimental resolution ($\sigma = 1.6$ eV reasonable for the 1.5 mm vertical slit used). At the L_1 edge the transition to the 6p discrete level generates an observable resonance peak that can be simulated with an additional Lorentzian peak (convoluted with the Gaussian function). The core-hole width Γ (half width at half maximum) which optimized the agreement between model and experiment resulted, $\Gamma(L_3) = 2.8(3)$ eV, $\Gamma(L_2) = 3.1(3)$ eV, $\Gamma(L_1) = 5.4(5)$ eV, which compare nicely with semiem-pirical evaluations [7] and previous experimental values [6]. The energy position of the inflection point of the arctangent function fitting the edges has been taken as



FIG. 2. L_2 edge (upper panel) and L_1 edge (lower panel) of atomic Hg. E_t is the energy above threshold.

origin for the energy scales E_t .

Besides these atomic features, the cross section is expected to decay smoothly as a function of the energy after each edge. On the contrary in our spectra some evident slope changes can be noticed (arrows in Figs. 1 and 2). In order to highlight these anomalies, we subtracted from the raw absorption data the average linear decay interpolated in the range $E_t \in [20, 420]$ eV. The resulting deviations $\Delta \alpha$ are plotted in Fig. 3 on a similar scale as a function of E_t , for the L_3 , L_2 , and L_1 edges. The ordinate scales are normalized to the absorptance discontinuity at each edge. This presentation makes the data directly comparable and guarantees a coherent extraction of the linear background among the three edges. The experimental spectra of the L_3 and L_2 edges reported in Fig. 3 show unambiguously the presence of an abrupt slope change around 135(5) eV, which amounts to 2.0(2) $\times 10^{-4}$ eV⁻¹, with basically identical characteristics for the two spectra, while a hump is evident at exactly the same energy in the L_1 spectrum. It is not surprising that the L_3 and L_2 edges are very alike while the L_1 is different due to different symmetries of the channels.

It is natural to try to assign such features to doubleelectron excitation channels. The expected intensity of the channels can hardly be estimated in advance; nevertheless, some reasonable guesses can be guided looking at the number of electrons and difference in the principal quantum numbers (n) involved in the shake-up transition. In this way the shake-up of one of the 14 4f electrons to the 5f level is expected to provide the most intense effect, while in comparison the shake-up and shake-



FIG. 3. Deviations from the average linear decay interpolated in the range $E_t \in [20-420]$ eV for the L_3 , L_2 , and L_1 edges. Data have been normalized to the corresponding values of the absorptance discontinuity at the main edge. Dashed vertical lines A, B, and C, are drawn in correspondence with $\Delta_{\rm DF}$ energies for multiple excitation edges.

off channels of one of the 10 4d, 10 5d, 6 5p or, ultimately, the 2 5s electron to the respective available 6d, 6d, 6p, and 7s levels should be weaker. In order to unambiguously assign the experimental features to the onsets of double-electron excitation channels, we performed selfconsistent-field Dirac-Fock (SCF-DF) relativistic calculations for several atomic configurations of the Hg atom by using the Desclaux code [8]. The configurations examined are reported in Table I and indicated with the holes or extra electrons with respect to the ground-state Hg configuration. The onset energy for shake-up channels with respect to the corresponding continuum threshold is calculated using differences of total energies of singly ionized atomic configurations (Δ_{DF}) ; for instance the $4f \rightarrow 5f$ shake-up energy at the L_3 edge is calculated as $\Delta_{\rm DF} = E([2p_{3/2}4f]5f) - E([2p_{3/2}])$. The results are found identical (within 0.2 eV) for the various L edges; as a consequence we used in Table I the symbol [2*] to indicate either of the $2p_{3/2}$, $2p_{1/2}$, or $2s_{1/2}$ holes. Some of these energies are reported in Fig. 3 as vertical dashed lines at the corresponding abscissa. The less accurate estimations by using the Z+1 approximation [3,5] are reported in the third column.

Looking at Fig. 3 it is clear that the slope change at the L_3 and L_2 edges and the hump at the L_1 edge coincide in energy with the onset of the shake-up channel associated with 4f electrons (dashed line B). The stringent energy agreement, the evident similarity of the L_3 and L_2 experimental abrupt slope changes at that energy, and, especially for the L_3 case, the high quality of the spectra, allow undoubtedly the assignment of the above feature to the double excitation edge involving one 2p (or 2s) and one 4f electron. We claim that this is the first identification of a double excitation channel in the Hg atomic absorption cross section. The present investigation confirms earlier results [4] where an unusual analysis of the Pb L_3 edge of PbO₂ has shown similar features at-

TABLE I. Values of the onset energies for the Hg $L_{3,2,1}$ double excitation edges, according to $\Delta_{\rm DF}$ calculations (second column) and the Z+1 model (third column).

			Figure 3
Configuration	$\Delta_{ m DF}~({ m eV})$	$Z{+1}~({ m eV})$	label
[2*]	0.0	0.0	
$[2*5d_{5/2}]6d_{5/2}$	23.4	12.5	
$[2 * 5d_{3/2}]6d_{3/2}$	25.6	14.7	
$[2*5p_{3/2}]6p_{3/2}$	72.4	73.5	A
$[2*5p_{1/2}]6p_{1/2}$	90.7	94.6	
[2 * 5s]7s	137.4	136	
$[2*4f_{7/2}]5f_{7/2}$	132.3	117	B
$[2 * 4f_{5/2}]5f_{5/2}$	137.2	122.2	
$[2*4d_{5/2}]6d_{5/2}$	382.4	385.0	
$[2*4d_{3/2}]6d_{3/2}$	403.1	405.7	
$[2*4f_{7/2}^2](5f_{7/2})^{2a}$	286.3	$255^{ m b}$	C
$[2*4f_{5/2}^2](5f_{5/2})^{2\mathbf{a}}$	296.6	$283^{ m b}$	
$[2s4f_{7/2}]5f_{7/2}6p_{3/2}{}^{ m c}$	122.2		
$[2s4f_{5/2}]5f_{5/2}6p_{3/2}{}^{ m c}$	126.9		

^aThree-electron excitation edge.

^bValues obtained adding up the corresponding (Z+1) and (Z+2) onset energies.

^cDouble-electron discrete resonance in the L_1 case.

tributed to the simultaneous excitation of one 2p and one 4f electron, assigned on the basis of the Z + 1 approximation. We remark that in our study the absence of any structural signal associated with bonding atoms makes any observation extremely reliable.

The experimental shape of the [2p4f] double-electron excitation channel is essentially a slope change starting from the expected lowest shake-up channel energy, suggesting that the shake-off channels contribution becomes eventually dominant. In fact, while the intensity of a single shake-up channel saturates, that of shake-off increases approximately linearly with the energy. This was clearly shown by calculations on atomic Kr [1], but qualitatively similar trends are expected here as well. We point out that the contribution to the atomic cross section of the above features, herein experimentally exhibited in vapor Hg, has been already taken into account in a previous work to model with accuracy and reliability the atomic background of the L_3 liquid-Hg spectrum [9]. In that study particularly interesting structural information, involving triplets of Hg neighboring atoms, were obtained.

Two other weak features have been tentatively assigned to different multielectron excitation channels according to labels A and C in Fig. 3 and Table I. In particular weak but reproducible anomalies in the slope of the three spectra (line C in Fig. 3) can be identified about 300 eV above threshold, in excellent agreement with the expected onset of a three-electron excitation channel where two 4f electrons perform a shake-up to the 5f level (see Table I). The rise (C) of the absorptance above threshold should be mainly due to shake-off processes whose transition probability is enhanced by the wider phase space



FIG. 4. Difference of total energy SCF-DF calculations for the configurations $E([2p_{3/2}4f_{7/2}]5f_{7/2}) - E([2p_{3/2}])$ lower points and $E([2p_{3/2}4f_{5/2}]5f_{5/2}) - E([2p_{3/2}])$ upper points as a function of the atomic number Z. The energies provide an estimate of the energy position of the slope change in the absorptance of L edges of sixth-period elements.

available. It should be noted that while the [2*4f] channels have been unambiguously assigned and identified, the certain identification of the other weaker features will require further investigations.

Clearly, the [2p4f] channel onset is not expected to be unique of the Hg atom, but should be present with similar characteristics at L edges of other sixth-period atoms. This list includes many important elements such as Re, Os, Ir, Pt, Au, Pb, and Bi, which have been the subject of several structural studies. The extraction of the XAFS signal should account correctly for the slope change in the atomic background which occurs at different energies above the main edges for different elements. A theoretical estimate of the $4f \rightarrow 5f$ shake-up channel onset energy can be helpful in this analysis and for this reason we report in Fig. 4 a list of values calculated in the $\Delta_{\rm DF}$ approximation for the free atom as a function of the atomic number for elements in the range Z = 72-86.

The results obtained in the present investigation are of general importance in the fields of atomic and condensedmatter physics. An x-ray-absorption experiment has been performed on an isolated sixth-row atom, where relativistic effects are important, to identify possible multielectron excitation effects. The study has undoubtedly shown the onset of the simultaneous excitation of a 2p(or 2s) and a 4f electron about 135 eV above each of the Hg L edges. The shape of the experimental spectrum suggests that both shake-up and shake-off channels, which eventually dominate, contribute to the absorptance. Other small features, including a possible triple-electron excitation channel, have been tentatively assigned, stimulating further experimental and theoretical investigations. These identifications are among the few performed with certainty on elements different from noble gases. This was achieved because the isolated atom could be studied in the vapor phase. The present investigation also stimulates theoretical work attempting to reproduce the cross-section shapes and intensities, in addition to channel-onset energies. A second reason for keen applied interest lies in the fact that double-electron edges appear to significantly alter the atomic background in heavy elements as well, and in particular the shake channels involving 4f electrons are expected to produce relevant features in many sixth-period atoms.

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