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$L_{2,3}MM$ Auger electron spectrum of the HCl molecule

H. Aksela and S. Aksela
Department of Physics, University of Oulu, SF-90570 Oulu 57, Finland

M. Hotokka
Department of Physical Chemistry 2, Chemical Center, S-22007 Lund 7, Sweden

M. Jäntti
Department of General Sciences, Helsinki University of Technology, SF-02150 Espoo 15, Finland

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The high-resolution Auger electron spectrum of HCl has been measured in the gas phase with the use of electron-beam excitation. The fine structure of the spectrum has been interpreted and compared with the calculated line energies. The energies of the initial states in HCl^+ and the final states in HCl^{2+} have been calculated in the molecular-orbital linear combination of atomic orbitals self-consistent-field approach, with the correlation effects being taken into account in the frame of the configuration-interaction technique. The relative line intensities have been discussed in the light of the analogy to the Auger spectrum of the next-neighbor and isoelectronic element argon.

I. INTRODUCTION

Auger spectra of free atoms have been studied extensively during the past few years and they are mostly quite well understood. This is also true for molecules in which the electrons participating in the Auger transition are core electrons. On the other hand, the Auger transitions in molecules involving the ejection of valence electrons have not been studied equally extensively, and only very few of them are well understood. In fact, the list of molecules for which high-resolution Auger spectra have been obtained and interpreted is far from being exhaustive.[1–4] Detailed calculations have been made for the Auger process in some simple molecules which have well-separated Auger lines to allow a detailed comparison of the intensities and energies of molecular transitions with observed experimental peaks.[5–9] Until now, these studies have almost exclusively concentrated on the *KLL* transition.

A great deal of further work is necessary before the knowledge of the Auger electron spectra of molecules reaches the stage already attained for the Auger electron spectra of free atoms. In order to arrive at a better understanding of the spectra of the simplest diatomic molecules, we will report in this paper a detailed analysis of the $L_{2,3}MM$ Auger spectrum of the HCl molecule. HCl is isoelectronic with the rare-gas element Ar, whose atomic Auger spectrum has been studied extensively. The HCl molecule is of such size that *ab initio* calculations of the energies of the Auger transitions can quite easily be done with the present-day computers. Experimentally, the measurement of the Auger spectrum of HCl is fairly easy, because it appears in the gas phase at room temperature and the cross section for the ionization in the $L_{2,3}$ levels by an electron beam is high, giving an intensive Auger spectrum.

II. RESULTS AND DISCUSSION

A. Experiment

The $L_{2,3}MM$ Auger electron spectrum has been measured with the cylindrical mirror-type electron spectrometer at the University of Oulu. The relative energy resolution $\Delta E/E$ of the analyzer is typically 0.05%. The pressure of the HCl molecular vapor in the target region has been about 10^{-1} Pa during the measurements. The primary ionizations in the molecules have been caused by a 2-keV and 0.5-mA electron beam. A microcomputer system has been used to control the measurement and to collect the data. Further details of the spectrometer have been described elsewhere.[10]

The measured intensity at each point in the spectrum has been divided by a factor proportional to the electron kinetic energy to correct the variation in spectrometer dispersion with energy. The experimental $L_{2,3}MM$ spectrum of HCl after dispersion correction is shown in Fig. 1.

The Ar $L_{2,3}MM$ spectrum falls in a slightly higher energy region than the HCl spectrum, which is why the spectrum of Ar can be used conveniently for energy calibration. The HCl spectrum has been calibrated using the main lines of the Ar spectrum

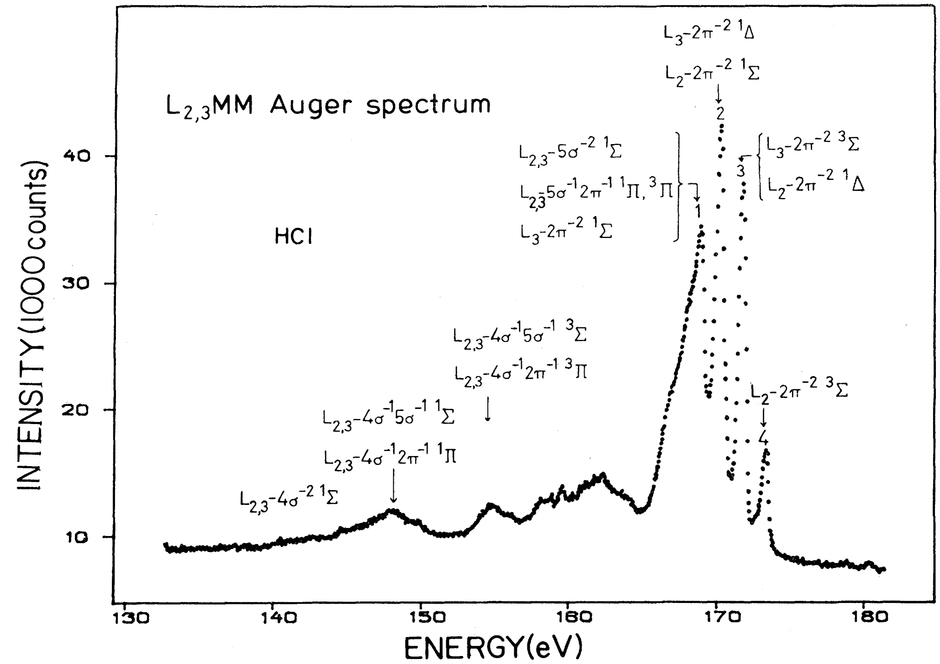

FIG. 1. $L_{2,3}MM$ Auger electron spectrum of HCl excited with 2-keV electrons.

as reference lines with the energies given in Ref. 11. For the energies of the strongest peaks (numbers 2 and 3 in Fig. 1) of the HCl spectrum, the values 170.2 and 171.7 eV are obtained as the average of two individual calibration runs, the first with the Ar $L_{2,3}MM$ spectrum (Fig. 2) and the second with the Ar $L_{2,3}M_1M_1$ spectrum (lying 10 eV higher in energy), as the reference spectra.

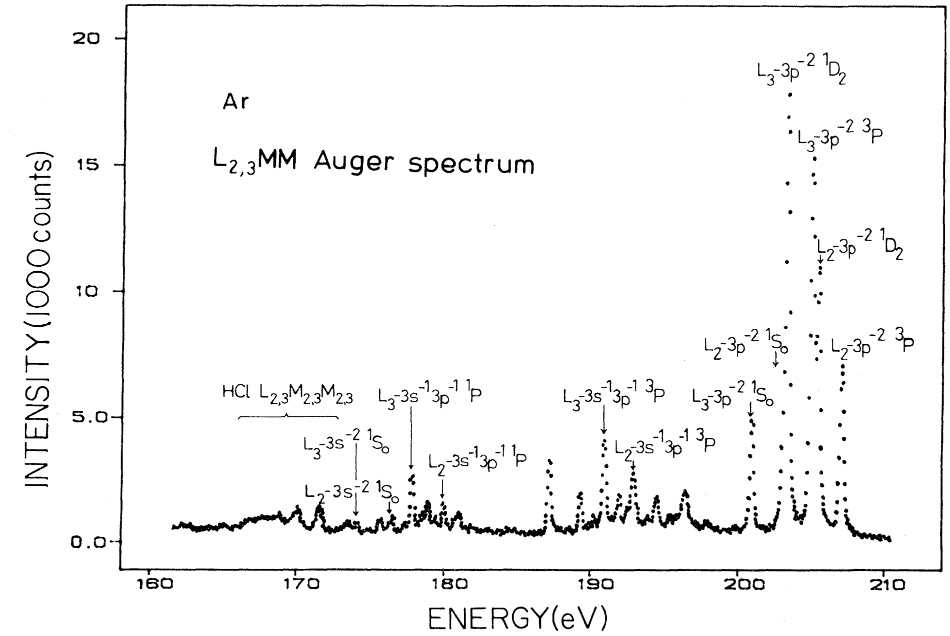

FIG. 2. $L_{2,3}MM$ Auger spectrum of Ar used as reference spectrum in the calibration and interpretation of the HCl spectrum. Assignments of the Ar peaks are from Refs. 11 and 12.

In order to determine whether the inelastic scattering of Auger electrons in the sample gas has an influence on the spectrum, the energy-loss spectrum for 500 eV electrons in HCl has been measured (Fig. 3).

B. Assignments of peaks

The HCl molecule is isoelectronic with the rare-gas atom argon. Therefore a tentative interpretation of the main features of the $L_{2,3}MM$ spectrum of HCl can be made on the basis of the similarity between the HCl molecule and the argon atom. The spectrum of HCl can, in the first approximation, be understood in terms of the energy-level structure of Ar perturbed by a displacement of one proton from the Ar core to the equilibrium distance found in HCl. This perturbation causes the splitting of the atomic p orbitals of Ar to the σ and π molecular orbitals in HCl. The electronic ground-state configuration of HCl is thus $(1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 2\pi^4)\,{}^1\Sigma^+$ as compared with the parent configuration $(1s^2 2s^2 2p^6 3s^2 3p^6)\,{}^1S$ of Ar.

In the Auger transition the chlorine atom is singly ionized in the initial state, which in the $L_{2,3}MM$ spectrum under consideration means a parent $2p$ vacancy. If the $2p_{1/2,3/2}$ initial vacancy state has an appreciable molecular character, its degeneracy will be split. It can be assumed, however, that this state is essentially atomic in character, the molecular splitting being notably smaller than the inherent width of the Auger lines. The theoretical results discussed in Sec. II C agree well with this assumption. Owing to the pronounced relativistic nature of the initial $2p_{1/2,3/2}$ core-hole state, the spectrum consists of two partly overlapping groups of lines separated by the $2p_{1/2}$-$2p_{3/2}$ spin-orbit splitting.

In the final state of the $L_{2,3}MM$ transitions of HCl, two electrons are missing from the 4σ, 5σ, and 2π molecular orbitals. The fine structure of both L_2 and L_3 groups, which in the Ar spectrum is due to the states $(2s^{-2})\,{}^1S$; $(2s^{-1}2p^{-1})\,{}^1P$, ${}^3P$; and $(2p^{-2})\,{}^1S$, ${}^1D$, ${}^3P$, is in the HCl spectrum due to the valence states $(4\sigma^{-2})\,{}^1\Sigma$; $(4\sigma^{-1}5\sigma^{-1})\,{}^1\Sigma$, ${}^3\Sigma$; $(4\sigma^{-1}2\pi^{-1})\,{}^1\Pi$, ${}^3\Pi$; $(5\sigma^{-2})\,{}^1\Sigma$; $(2\pi^{-2})\,{}^1\Sigma$, ${}^3\Sigma$, ${}^1\Delta$; and $(5\sigma^{-1}2\pi^{-1})\,{}^1\Pi$, ${}^3\Pi$.

The binding energy of the $2p_{3/2}$ core electrons in HCl and the $2p$ spin-orbit splitting have been determined experimentally to be 207.4 and 1.6 eV, respectively, using x-ray photoelectron spectroscopy.[13,14] Experimental binding-energy values obtained by electron energy-loss spectroscopy applying the binary $(e,2e)$ method[15] are 12.8 eV for the 2π, 16.5 eV for the 5σ, and ~30 eV for the 4σ valence orbitals of HCl. On the basis of these experimental binding-energy values, the Auger energies can be estimated to be in the region from 165 to 175 eV for the $L_{2,3}M_{2,3}M_{2,3}$ group, from 150 to 155 eV for the $L_{2,3}M_1M_{2,3}$ group, and around 137 eV for the $L_{2,3}M_1M_1$ group, if we assume the correction arising from the relaxation and hole-hole interaction effects to be of the order of 10 eV analogously with argon. By comparing the measured Auger spectrum with the estimated group positions and with the corresponding spectrum of Ar (Fig. 2), the assignments of the groups given in Fig. 1 have been achieved.

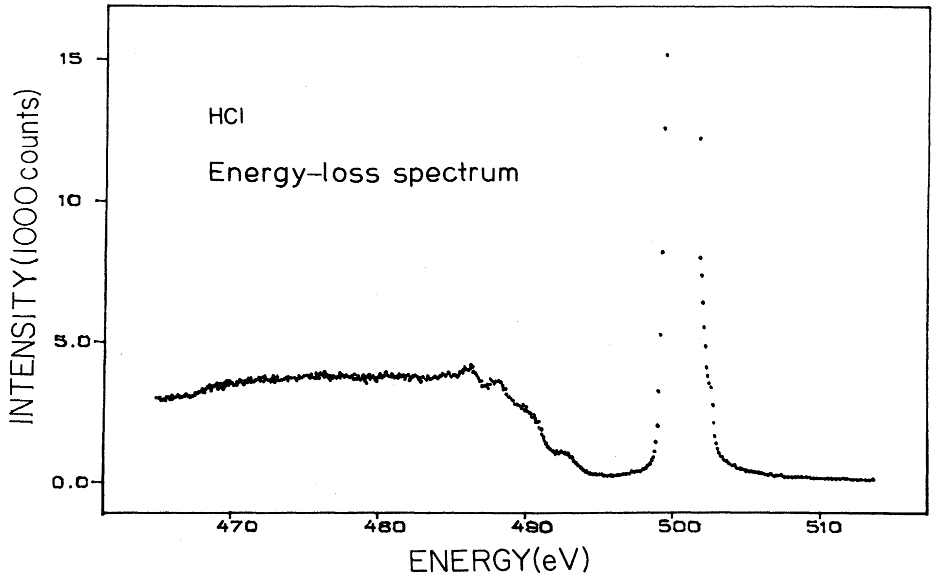

FIG. 3. Energy-loss spectrum of the primary electrons scattered from the HCl gas.

The transitions with the final states $4\sigma^{-2}$ can hardly be identified from the spectrum, but they are assumed to form the broad maximum with a very low intensity around 140 eV. This broad, weak structure does not show any clear fine structure so that the transitions with $2p_{1/2}$ and $2p_{3/2}$ initial vacancy states cannot be identified separately.

Corresponding to the Ar $(3s^{-1}3p^{-1})\,^1P$ final states, the structure below 150 eV can be identified to originate from the transitions with the $(4\sigma^{-1}5\sigma^{-1})\,^1\Sigma$ and $(4\sigma^{-1}2\pi^{-1})\,^1\Pi$ final states. The structure at 10—15 eV higher kinetic energies may be attributed to the triplet states $^3\Sigma$ and $^3\Pi$ of the same configurations, corresponding to the $(3s^{-1}3p^{-1})\,^3P$ state in the Ar^{2+} parent. The fine structure is not resolved, nor are the L_3 and L_2 groups separated due to the very broad linewidths. The structure around 160 up to 165 eV is most probably due to the satellite transitions with two holes in the $L_{2,3}$ and $M_{2,3}$ shells in the initial state and three holes in the $M_{2,3}$ shell in the final state. The peaks due to the inelastic scattering of Auger electrons in the HCl gas (Fig. 3) are also associated with this satellite structure.

On the contrary, the $L_{2,3}M_{2,3}M_{2,3}$ group in the energy region from 165 to 175 eV shows a distinct fine structure, the four maxima lying approximately at the distance of the spin-orbit splitting from each other. The number of peaks is, however, much smaller than the number of expected lines which are due to the final valence states $(5\sigma^{-2})\,^1\Sigma$, $(2\pi^{-2})\,^1\Sigma$, $^3\Sigma$, $^1\Delta$, and $(5\sigma^{-1}2\pi^{-1})\,^1\Pi$, $^3\Pi$ in both the L_2 and the L_3 groups, indicating that several of the lines overlap. The identification of the four maxima can be based on the similarity between the HCl molecule and the argon atom: The molecular perturbation will split the parent final state $(2p^{-2})\,^1D$ of Ar into three levels $(2\pi^{-2})\,^1\Delta$, $(2\pi^{-2})\,^1\Sigma$, and $(5\sigma^{-1}2\pi^{-1})\,^1\Pi$ in HCl. The $(2p^{-2})\,^1S$ parent in Ar becomes $(5\sigma^{-2})\,^1\Sigma$ in HCl. The $(2p^{-2})\,^3P$ parent in Ar will split into two levels $(2\pi^{-2})\,^3\Sigma$ and $(5\sigma^{-1}2\pi^{-1})\,^3\Pi$ in HCl.

Assuming that the intensities of the "daughter" peaks roughly follow their statistical distribution, the intensities of the "parent" lines can be divided between the daughters. On the basis of this rough assumption, a major part of the intensity of the main ^1D line of Ar is transferred to the $(2\pi^{-2})\,^1\Delta$ line in HCl, and we will assign the two main peaks (numbers 2 and 3 in Fig. 1) in the HCl spectrum to correspond to the transitions with this final state and with the initial $2p_{3/2}$ and $2p_{1/2}$ vacancy states, respectively. On the basis of Hund's rules the $(2\pi^{-2})\,^1\Sigma$ and $(2\pi^{-2})\,^3\Sigma$ lines should lie at both sides of the $(2\pi^{-2})\,^1\Delta$ line, the former on the left and the latter on the right, and we will therefore assign the $L_3\rightarrow(2\pi^{-2})\,^1\Sigma$ line to belong to peak 1, the $L_3\rightarrow(2\pi^{-2})\,^3\Sigma$ line to peak 3, the $L_2\rightarrow(2\pi^{-2})\,^1\Sigma$ line to peak 2, and the $L_2\rightarrow(2\pi^{-2})\,^3\Sigma$ line to peak 4. The intensity of the ^1S parent line is in the first approximation transferred to the $(5\sigma^{-1})\,^1\Sigma$ line, and according to the energy examination, the $L_3\rightarrow(5\sigma^{-2}2\Pi^{-1})\,^1\Sigma$ lines should lie on the lowest energy in the group, i.e., on the low-energy shoulder of peak 1; and the $L_2\rightarrow(5\sigma^{-2})\,^1\Sigma$ line lies at the distance of the spin-orbit splitting from it towards higher energy, yet belonging to the region of peak 1. The main part of the intensity of the ^3P parent line can be assumed to be transferred to the $(5\sigma^{-1}2\pi^{-2})\,^3\Pi$ line; and we therefore conclude that peak 1 most probably also contains the $L_{2,3}\rightarrow(5\sigma^{-1}2\pi^{-1})\,^3\Pi$ lines with the $L_{2,3}\rightarrow(5\sigma^{-1}2\pi^{-1})\,^1\Pi$ line on their left side.

C. Calculation of the energies of the $L_{2,3}M_{2,3}M_{2,3}$ transitions

In order to arrive at a more-detailed understanding of the observed structure of the $L_{2,3}M_{2,3}M_{2,3}$ groups, the energies of these transitions were calculated theoretically at the next step of the analysis. The HCl molecule is singly ionized in the initial state and doubly ionized in the final state of the Auger process. The Auger transition energies can hence be obtained as differences between the energies of the initial and final states involved in the transitions.

A series of pilot computations on the initial and final states of interest were performed using a restricted Hartree-Fock package UIBMOL-MOLECULE[16] and a Cartesian-Gaussian basis set[17] contracted to the double-zeta level and augmented with two d functions. The final state electron configurations $5\sigma^{-2}$, $5\sigma^{-1}2\pi^{-1}$, and $2\pi^{-2}$ giving rise to six valence states were considered. The splitting obtained from these calculations was notably larger than that observed in the experimental spectrum, however. It was therefore found desirable to employ more advanced quantum chemical methods, which take the electron correlation properly into account. Correlation effects seem to be of particular importance in this molecule.

The CI calculations reported here were performed on the CRAY-1S computer at the Daresbury Laboratories of the Science and Engineering Research Council, United Kingdom, using programs belonging to the ATMOL package.[18] The following three basis sets of atom-centered Cartesian-Gaussian functions, ranging from double to extended, were tested.

(a) Double-ζ basis. For chlorine, a set of 10 s-type and 6 p-type functions[17] were contracted to the double-ζ level. The hydrogen basis set was taken from Dunning[19] with the orbital exponents scaled by a factor of 1.2.

(b) Double-ζ + polarization basis. The previous basis set was augmented with two d-type functions on chlorine (the orbital exponents being 1.0 and 0.8) and two p-type functions on hydrogen (with orbital exponents of 1.0 and 0.8).

(c) Extended basis. The $14s,10p$ basis set of Huzinaga and Arnau[20] was contracted to the $10s,8p$ level and augmented with the d functions of basis b. For hydrogen, a basis set of 6 s-type primitives[21] and the previous two p functions were used. The size of this basis set was chosen so that the calculations would be repeatable on a local computer.

Equipped with these basis sets and the direct CI program,[18,22] total energies of the lowest valence state of HCl^{2+} in each symmetry, $^3\Sigma$, $^1\Delta$, $^1\Sigma$, $^3\Pi$, and $^1\Pi$, were computed. The results are shown in Table I. Also shown in Table I are the CI energies for the initial core-hole states.

It can be seen that the $2p_\sigma$ and $2p_\pi$ (or $2p_{1/2}$ and $2p_{3/2}$) core-hole states have very nearly the same energy in a nonrelativistic calculation, indicating that these orbitals have retained their atomic character, as expected. The energy difference of these initial core-hole states is due to spin-orbit splitting which was calculated to be 1.60 eV in the Cl^- ion. These computations were carried out with the computer code of Grant *et al.*[23] Therefore two sets of Auger transitions lying about 1.6 eV apart are expected. A third series originating from the $(2\sigma^{-1})\,^2\Sigma$ initial state should be found at an energy higher by about 60 eV than the two overleaved sets originating from the $(3\sigma^{-1})\,^2\Sigma$ and $(1\pi^{-1})\,^2\Pi$ initial states.

D. Discussion

Atomic Dirac-Fock calculations have given the energy difference of 1.6 eV for the $2p_{1/2}$ and $2p_{3/2}$ initial hole states in good agreement with experimental photoelectron measurements.[12,13] Furthermore, the molecular splitting in the initial state was found to be 0.1 eV. By also taking the calculated energy splitting of the final state (Table I) into account, it is obvious even from the theoretical point of view that the spectrum consists of two overlapping line groups shifted by the initial state spin-orbit splitting from each other.

The spread of the theoretical spectrum is, however, larger than that of the experimental one. In spite of this, a comparison of the experimental and theoretical energies in Table II shows that an unambiguous assignment of the lines is possible. Single-configuration assignments have been kept unchanged in Table II, although the theoretical energies refer to the CI calculations. The theoretical

TABLE I. Theoretical total and relative energies of the core-hole and the lowest valence states of HCl based on CI calculations.

Basis set	State	CI energy (a.u.)	Relative energy (eV)
		HCl^{2+} valence states	
Double ζ	$^3\Sigma$	−458.743 281	0
	$^1\Delta$	−458.674 237	1.88
	$^1\Sigma$	−458.638 670	2.85
	$^3\Pi$	−458.603 693	3.80
	$^1\Pi$	−458.542 789	5.46
Double ζ + polarization	$^3\Sigma$	−458.864 961	0
	$^1\Delta$	−458.802 278	1.71
	$^1\Sigma$	−458.757 061	2.94
	$^3\Pi$	−458.717 788	4.00
	$^1\Pi$	−458.662 571	5.51
Extended	$^3\Sigma$	−458.986 222	0
	$^1\Delta$	−458.922 220	1.74
	$^1\Sigma$	−458.876 436	2.99
	$^3\Pi$	−458.839 119	4.00
	$^1\Pi$	−458.739 787	6.71
		HCl^+ core-hole states	
Double ζ	$(2s^{-1})\,^2\Sigma$	−450.135 315	69.71
	$(2p_\sigma^{-1})\,^2\Sigma$	−452.697 014	0
	$(2p_\pi^{-1})\,^2\Pi$	−452.700 895	−0.11

TABLE II. Experimental and theoretical energies (in eV) and experimental relative intensities (in percent) of the $L_{2,3}M_{2,3}M_{2,3}$ Auger lines of HCl.

Line number in Fig. 4	Energy Expt.	Theor.	Intensity	Transition
1	166.7		7.0	$L_3 \rightarrow (5\sigma^{-2})\,^1\Sigma$
2	167.10	166.08	5.2	$L_3 \rightarrow (5\sigma^{-1}2\pi^{-1})\,^1\Pi$
3	167.73		10.9	$L_2 \rightarrow (5\sigma^{-2})\,^1\Sigma$
4	168.22	167.59	7.2	$L_3 \rightarrow (5\sigma^{-1}2\pi^{-1})\,^3\Pi$
5	168.67	167.79	10.4	$L_2 \rightarrow (5\sigma^{-1}2\pi^{-1})\,^1\Pi$
6	169.00	168.65	7.8	$L_3 \rightarrow (2\pi^{-2})\,^1\Sigma$
7	169.82	169.30	9.1	$L_2 \rightarrow (5\sigma^{-1}2\pi^{-1})\,^3\Pi$
8	170.24	169.88	16.0	$L_3 \rightarrow (2\pi^{-2})\,^1\Delta$
9	170.63	170.36	2.0	$L_2 \rightarrow (2\pi^{-2})\,^1\Sigma$
10	171.53	171.59	6.3	$L_3 \rightarrow (2\pi^{-2})\,^3\Sigma$
11	171.79	171.59	13.0	$L_2 \rightarrow (2\pi^{-2})\,^1\Delta$
12	171.30	(173.30)	5.0	$L_2 \rightarrow (2\pi^{-2})\,^3\Sigma$

transitions are obtained by shifting the energetically highest ($L_2 \rightarrow$valence^{-2},$^3\Sigma$) transition to its experimental position (an adjustment of 2.2 eV) and using the energies computed with the double-ζ + polarization basis. The other set corresponding to transitions from the L_3 shell is obtained by using the nonrelativistic energy difference of the two initial core-hole states and the relativistic splitting of the $2p_{1/2}$ and $2p_{3/2}$ atomic-hole states. A correction for the spread would give an excellent agreement between theory and experiment.

Owing to the fact that the calculated final-state splitting is somewhat larger than the experimental, the fit to the experimental spectrum using the calculated splitting did not yield any meaningful results for the intensities of the individual lines. In order to find some estimate for the fine structure of the experimental spectrum, a set of Voigt functions was fitted to the $L_{2,3}M_{2,3}M_{2,3}$ line group: Six lines were used in the region of peak 1, one line between peaks 1 and 2, two lines for peaks 2 and 3, and one line for peak 4. In the first fit only one linewidth of 0.6 eV was used, but the result was not satisfactory. A considerably better fit was obtained by using broader lines for the low-energy part than for the high-energy part of the spectrum. The fitted curve is

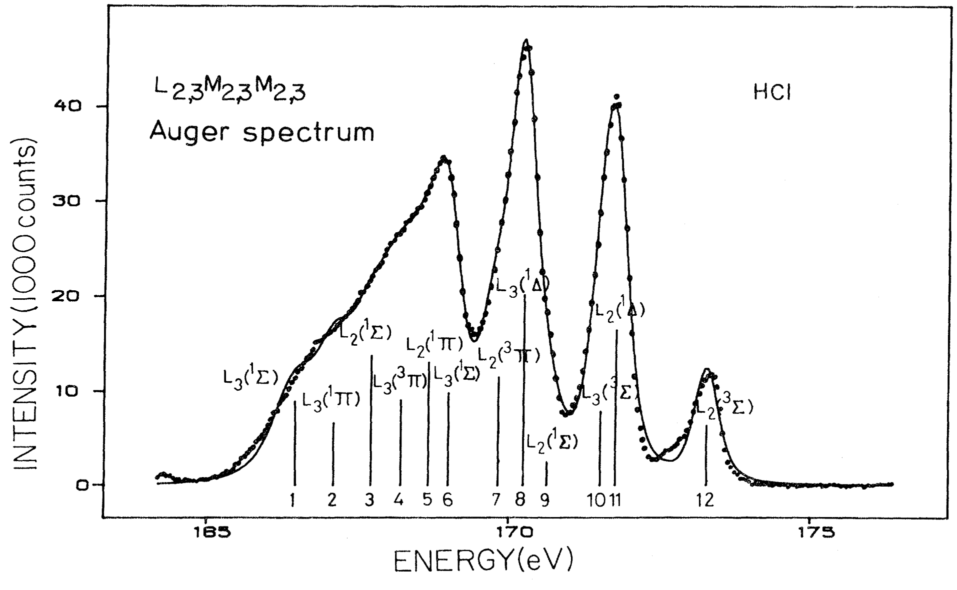

FIG. 4. $L_{2,3}M_{2,3}M_{2,3}$ Auger spectrum of HCl after background subtraction and dispersion correction. The solid curve and vertical lines represent a least-squares fit of standard functions (with Voigt profile) to the data.

shown in Fig. 4, and the energies and intensities of the resulting peaks are given in Table II. Presently, the widths of 0.9, 0.7, and 0.5 eV were used for the lines 1 and 3, for the lines 2, 4, 5, and 7, and for the lines 6, 8, 9, 10, 11, and 12, respectively. The obtained increase in linewidth may be caused by the increase in the vibrational broadening, which obviously depends on the amount of the σ nature in the vacancy configuration.

From the calculated final-state energies we find the order of the lines in both groups to be $^1\Sigma$, $^1\Pi$, $^3\Pi$, $^1\Sigma$, $^1\Delta$, and $^3\Sigma$ from lower to higher energies. By comparing the calculated and experimental energy splittings, the identification of the lines given in Table II was performed. Consideration of the line intensities of Table II shows a lack of harmony in some cases when compared with the argon spectrum. Intensity considerations, for example, favor an interpretation of the lines 4 and 5 opposite to the one given in Table II. We should, however, keep in mind that the experimental results are not very accurate in cases where the lines lie in close proximity to each other. Therefore the relative splittings and intensities of the lines in the region of peaks 1, 2, and 3 should not be taken too literally. The results of Table II also show the L_3:L_2 intensity ratio to be 1:1, which strongly deviates from the statistical ratio. At least to some extent, this result may be caused by the inaccuracies in the decomposition procedure rather than by any physical effect.

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