

Effects of exchange, electron correlation, and relaxation on the L_1 - $L_{23}M_1$ Coster-Kronig spectrum of argon

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A relaxed-orbital multiconfiguration Hartree-Fock calculation of the L_1 - $L_{23}M_1$ Coster-Kronig transitions in Ar has been performed. The effects of exchange between the continuum electron and the bound-state electrons have been examined. With regard to transition energies, excellent agreement with experiment is attained. Calculated transition probabilities are slightly closer to measured rates than in previous theoretical work that does not include complete relaxation, but an important discrepancy still remains that apparently cannot be resolved within the independent-particle framework.

I. INTRODUCTION

The L_1 - $L_{23}M_1$ Coster-Kronig spectrum of Ar has long been a problem area in atomic theory. A theoretical calculation of the energy and transition rates was first reported by Rubenstein.¹ The spectrum was measured a few years later by Mehlhorn,² who found a perplexing discrepancy: The calculated transition rates of Rubenstein exceed experimental rates by a factor of 4. To compute the energy of the continuum electron, Rubenstein used an incorrect 287-eV L_1 -subshell binding energy, whereas from the measured L_1 - MM spectrum, Mehlhorn determined this energy to be (326 ± 0.5) eV. Coster-Kronig transition rates being very sensitive to the energy of the continuum electron, Mehlhorn ascribed the discrepancy of Rubenstein's result to the use of an incorrect L_1 subshell binding energy. McGuire^{3,4} repeated the calculation with three different values of the continuum-electron energy: one obtained from the model potential, the second from ESCA (electron spectroscopy for chemical analysis) measurements,⁵ and the third from experimental Auger-electron energies. The transition rates calculated on the basis of each of these energies, however, still remained about a factor of 4 higher than the measured L_1 - $L_{23}M_1$ probabilities.

Although this discrepancy is large, it is not altogether unexpected. Only over limited range of atomic numbers do calculations of L -shell Coster-Kronig transition probabilities for various elements^{3,6-14} agree reasonably well with measured rates. The most refined calculation in the independent-particle approximation¹⁴ overestimates the L_1 -subshell width by about 10% for heavy elements ($Z > 50$), while for low- Z elements the discrepancy can get as large as a factor of 3. Possible reasons for this difficulty could be (i) many-body interactions in the initial and final atomic systems, (ii) the effects of relaxation of the final ionic state, and (iii) the effect of the exchange interaction between the continuum electron and the final bound-state electrons. These factors were neglected in most earlier calculations.^{1,3,4,6-14} In the present work, we have extensively investigated the effects of final-state relaxation and of exchange between the continuum electron

and bound electrons in the final state, and we have included some of the many-body interactions through initial- and final-state configuration interactions, for the L_1 - $L_{23}M_1$ Coster-Kronig energies and transition rates in argon.

Ohno and Wendin¹⁵ have already demonstrated the strong influence of electron correlation on M -shell Coster-Kronig transitions. Dyllal and Larkins¹⁶ have calculated the L_1 - $L_{23}M_1$ transition rates and energies of argon including the final ionic-state configuration interaction, and reached somewhat improved agreement with experimental results. In the present calculation, we have included both initial and final ionic-state configuration interactions to account for some of the many-body aspects. The effect of exchange between the continuum and bound electrons has been investigated by constructing an antisymmetric $(N+1)$ -electron wave function for the final state that comprises the N -electron double-hole core and the continuum electron. Complete relaxation has been incorporated by determining the initial and final bound-state one-electron orbitals in their respective single- and double-hole configurations and replacing Wentzel's ansatz¹⁷ with a more general transition-rate formula.¹⁸

II. THEORY

A. Transition rate including relaxation

Coster-Kronig transition probabilities including the effect of relaxation are given by¹⁸

$$W = \frac{2\pi}{\hbar} |\langle \psi_f | (H - E) | \psi_i \rangle|^2 \rho(E_f), \quad (1)$$

where ψ_i and ψ_f are the initial and final states of the system, $\rho(E_f)$ is the density of final states, E is the initial total energy, and H is the total Hamiltonian of the system. The initial and final states ψ_i and ψ_f are constructed as linear combinations of Slater determinants U and V from the one-electron orbitals $\{u_i\}$ and $\{v_i\}$, respectively,

$$U = (N!)^{-1/2} \det | u_1, u_2, \dots, u_N |, \quad (2)$$

$$V = (N!)^{-1/2} \det | v_1, v_2, \dots, v_N |.$$

The initial one-electron bound orbitals

$$u_i = |n_i l_i m_{li} m_{si}\rangle, \quad i=1,2,\dots,N$$

and final one-electron bound orbitals

$$v_i = |n'_i l'_i m'_{li} m'_{si}\rangle, \quad i=1,2,\dots,N-1$$

are optimized separately in their respective single- and double-hole configurations. The orbital v_N for the continuum electron is determined in the field of the final

double-hole configuration. Since the basis sets $\{u_i\}$ and $\{v_i\}$ correspond to different Hamiltonians, they are not orthogonal to one another. A general expression for the matrix element $\int U^* A_{op} V dx$, constructed from two nonorthogonal basis sets of spin orbitals $\{u_i\}$ and $\{v_i\}$ [Eq. (2)] with nonorthogonal integrals

$$d_{uv}(kl) = \int u_k^*(x_1) v_l(x_1) dx_1, \quad (3)$$

has been developed by Löwdin,¹⁹

$$\int U^* A_{op} V dx = A_0 D_{UV} + \sum_{k,l} \langle k | A_1 | l \rangle D_{UV}(k | l) + \left(\frac{1}{2}!\right) \sum_{\substack{k_1, k_2, \\ l_1, l_2}} \langle k_1 k_2 | A_{12} | l_1 l_2 \rangle D_{UV}(k_1, k_2 | l_1, l_2) + \dots, \quad (4)$$

where A_0 is a constant, A_1 and A_{12} are one-electron and two-electron operators, respectively,

$$\langle k | A_1 | l \rangle = \int u_k^*(x_1) A_1 v_l(x_1) dx_1,$$

$$\langle k_1 k_2 | A_{12} | l_1 l_2 \rangle = \int u_{k_1}^*(x_1) u_{k_2}^*(x_2) A_{12} v_{l_1}(x_1) v_{l_2}(x_2) dx_1 dx_2.$$

The quantity D_{UV} is a determinant formed from all the nonorthogonality integrals $d_{uv}(kl)$,

$$D_{UV} = \det |d_{uv}(k,l)|, \quad (6)$$

and $D_{UV}(k | l)$, $D_{UV}(k_1, k_2 | l_1, l_2)$, $D_{UV}(k_1, k_2, k_3 | l_1, l_2, l_3)$, \dots , are the cofactors of D_{UV} of orders 1, 2, 3, \dots .

The determinantal wave functions ψ_i and ψ_f for the initial and final states can be constructed by a sequence of angular-momentum couplings and antisymmetrizations. In the case under consideration here, we have for the final $[2p]3s^1 P \epsilon p^2 S$ state.

$$\begin{aligned} \psi_f(^1P) &= |L S M_L M_S\rangle = |0 \frac{1}{2} 0 \frac{1}{2}\rangle \\ &= (6)^{-1/2} (|2p^+_{+1} 3s^-_0 \epsilon p^+_{-1}\rangle - |2p^-_{+1} 3s^+_0 \epsilon p^+_{-1}\rangle - |2p^+_0 3s^-_0 \epsilon p^+_0\rangle + |2p^-_0 3s^+_0 \epsilon p^+_0\rangle \\ &\quad + |2p^+_{-1} 3s^-_0 \epsilon p^+_{+1}\rangle - |2p^-_{-1} 3s^+_0 \epsilon p^+_{+1}\rangle) \end{aligned} \quad (7)$$

and, for the final $[2p]3s^3 P \epsilon p^2 S$ state,

$$\begin{aligned} \psi_f(^3P) &= |L S M_L M_S\rangle = |0 \frac{1}{2} 0 \frac{1}{2}\rangle \\ &= \frac{\sqrt{2}}{3} (|2p^+_{+1} 3s^+_0 \epsilon p^-_{-1}\rangle - |2p^+_0 3s^+_0 \epsilon p^-_0\rangle + |2p^+_{-1} 3s^+_0 \epsilon p^-_{+1}\rangle) \\ &\quad + \frac{1}{3\sqrt{2}} (-|2p^+_{+1} 3s^-_0 \epsilon p^+_{-1}\rangle - |2p^-_{+1} 3s^+_0 \epsilon p^+_{-1}\rangle + |2p^+_0 3s^-_0 \epsilon p^+_0\rangle \\ &\quad + |2p^-_0 3s^+_0 \epsilon p^+_0\rangle - |2p^+_{-1} 3s^+_0 \epsilon p^+_{+1}\rangle - |2p^-_{-1} 3s^+_0 \epsilon p^+_{+1}\rangle). \end{aligned} \quad (8)$$

Here we have used the notation

$$|x^+ y^- z^+\rangle = \frac{1}{\sqrt{3!}} \begin{vmatrix} x(1)\alpha(1) & x(2)\alpha(2) & x(3)\alpha(3) \\ y(1)\beta(1) & y(2)\beta(2) & y(3)\beta(3) \\ z(1)\alpha(1) & z(2)\alpha(2) & z(3)\alpha(3) \end{vmatrix}. \quad (9)$$

The two-electron integrals in Eq. (5) were determined following Slater's procedure.²⁰

B. Electron correlation

Electron correlation was included in the calculation of the $L_1-L_{23}M_1$ Coster-Kronig transition rates by the method of configuration interaction. Atomic state functions were constructed as

$$\psi_i(\Gamma L S) = \sum_j c_{ij} \Phi_j(\gamma_j L S), \quad (10)$$

where the c_{ij} are mixing coefficients, and the Φ_j are configuration state functions built from antisymmetric products of one-electron orbitals

$$\Phi = A \sum_k \theta_k. \quad (11)$$

The coefficients c_{ij} and orbitals θ_k were determined variationally.

The success of the configuration-interaction method hinges on the proper choice of the configuration state functions Φ_j so that they may account for the dominant

correlation effect. For the initial single-hole state, we considered mixing of the following two-configuration state functions:

$$1s^2 2s 2p^6 3s^2 3p^6 {}^2S, \quad (12a)$$

$$1s^2 2s^2 2p^4 ({}^1D) 3s^2 3p^6 {}^2S. \quad (12b)$$

For the final ionic states we considered virtual excitation of the type $3s 3p^6 \rightarrow 3s^2 3p^4 3d$ and performed a multiconfiguration Hartree-Fock (MCHF) calculation with the following configuration state functions for the 1P final ionic state:

$$1s^2 2s^2 2p^5 3s ({}^1P) 3p^6 {}^1P, \quad (13a)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^1S) ({}^2P) 3d {}^1P, \quad (13b)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^3P) ({}^2P) 3d {}^1P, \quad (13c)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^3P) ({}^2D) 3d {}^1P, \quad (13d)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^1D) ({}^2P) 3d {}^1P, \quad (13e)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^1D) ({}^2D) 3d {}^1P, \quad (13f)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^1D) ({}^2F) 3d {}^1P. \quad (13g)$$

For the 3P final ionic state, the following configuration state functions were taken into account:

$$1s^2 2s^2 2p^5 3s ({}^3P) 3p^6 {}^3P, \quad (14a)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^1S) ({}^2P) 3d {}^3P, \quad (14b)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^3P) ({}^4P) 3d {}^3P, \quad (14c)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^3P) ({}^4D) 3d {}^3P, \quad (14d)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^3P) ({}^2P) 3d {}^3P, \quad (14e)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^3P) ({}^2D) 3d {}^3P, \quad (14f)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^1D) ({}^2P) 3d {}^3P, \quad (14g)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^1D) ({}^2D) 3d {}^3P, \quad (14h)$$

$$1s^2 2s^2 2p^5 3s^2 3p^4 ({}^1D) ({}^2F) 3d {}^3P. \quad (14i)$$

The configuration state functions (13d), (13f), and (13g) of the 1P ionic state and (14d), (14e), (14h), and (14i) of the 3P ionic state were considered by Dyall and Larkins.¹⁶

C. Exchange interaction between continuum and bound electrons

As the continuum electron recedes through the electron cloud, it interacts with the remaining doubly ionized atom. Ideally, we should determine the wave function for the continuum electron by solving the Schrödinger equation for a system which consists of a doubly ionized atomic core plus a continuum electron. The problem is greatly simplified, however, if we assume that the wave functions of the bound core electrons are not perturbed by the presence of the continuum electron. In this approximation, one can determine the bound-state one-electron orbitals following a standard technique²¹ and the wave function for the continuum electron can then be calculated in the potential produced by these electrons. To take into account the effect of exchange between the continuum and bound electrons, an antisymmetric $(N+1)$ -electron wave function can be constructed from the product of the continuum and the N -electron core wave functions. Differential equations for the continuum electron obtained in this way are similar to the Hartree-Fock equations for the bound-state electrons.^{22,23} Following Chen *et al.*,²³ the radial equation for the continuum electron is found to be

$$\left[\frac{d^2}{dr_{N+1}^2} - \frac{l_j(l_j+1)}{r_{N+1}^2} + \frac{2Z}{r_{N+1}} + k^2 \right] P_\Gamma(r_{N+1}) - 2V_{\Gamma\Gamma} P_\Gamma(r_{N+1}) - 2W_{\Gamma\Gamma}(r_{N+1}) - \sum_l \delta_{ll_j} \lambda_{ll_j} P_{nl}(r) = 0, \quad (15)$$

where

$$V_{\Gamma\Gamma}(r_{N+1}) = \int \psi^*(\Gamma | X^{-(N+1)} \theta_{N+1} \sigma_{N+1}) \left[\sum_{i=1}^N \frac{1}{r_{N+1,i}} \right] \psi(\gamma | X^{-(N+1)} \theta_{N+1} \sigma_{N+1}) dx^{-(N+1)} d\theta_{N+1} d\sigma_{N+1} \quad (16)$$

and

$$W_{\Gamma\Gamma}(r_{N+1}) = -N r_{N+1} \int \psi^*(\Gamma | X^{-(N+1)} \theta_{N+1} \sigma_{N+1}) (H - E) \psi(\Gamma | X^{-N} \vec{x}_N) dx^{-(N+1)} d\theta_{N+1} d\sigma_{N+1}. \quad (17)$$

The off-diagonal Lagrange multipliers λ_{ll_j} were determined using a technique suggested by Dalgarno.²⁴

III. NUMERICAL CALCULATIONS

The initial and final bound-state one-electron orbitals were obtained using the multiconfiguration Hartree-Fock computer code of Froese Fischer.²⁵ With these known bound-state orbitals, the Hartree-Fock equation for the continuum electron was solved by an iterative technique using solutions without exchange terms as the initial

guess.²³ The asymptotic solutions were obtained by the method of Stewart and Rotenberg.²⁶ Matrix elements of the one-electron operator connecting two bound-state orbitals were calculated with the subroutine *HLL* taken from Froese Fischer's computer code.²⁵ To calculate the matrix element of the one-electron operator connecting a bound-state orbital with a continuum orbital, we first determined the Hartree-Fock equation for the bound-state orbital using the technique of Froese Fischer²¹ and then took a scalar product of this equation with the appropriate continuum orbital.

TABLE I. Mixing coefficients c_{ij} in the eigenvectors $\phi_i = \sum_j c_{ij} \phi_j$.

		Initial 2S state								
$i \backslash j$		1	2							
1		-0.9972	0.0742							
2		0.0742	0.9972							
		Final 1P ionic state								
$i \backslash j$		1	2	3	4	5	6	7		
1		0.8344	0.0097	-0.0379	-0.0752	0.2329	-0.3085	0.3835		
2		0.0197	0.0046	-0.5120	0.3059	0.7149	0.2290	-0.2835		
3		0.1590	-0.2683	0.1994	0.4674	-0.1205	-0.5358	-0.5856		
4		-0.1876	0.6560	-0.0734	-0.3886	0.1914	-0.5338	-0.2377		
5		-0.3289	-0.6760	-0.2127	-0.3780	0.2227	-0.4083	0.1740		
6		0.3610	-0.1912	-0.0588	-0.6142	-0.1194	0.3108	-0.5845		
7		-0.0655	-0.0632	0.8016	-0.1054	0.5654	0.1305	-0.0358		
		Final 3P ionic state								
$i \backslash j$		1	2	3	4	5	6	7	8	9
1		0.8343	-0.0119	-0.0084	-0.0111	-0.0736	-0.0899	0.2323	-0.2934	0.3873
2		0.0615	0.2082	0.1322	-0.4174	0.3302	0.4564	-0.2055	0.4199	0.4747
3		0.0072	-0.0896	0.6022	-0.0884	0.3657	-0.3192	-0.4828	-0.3903	-0.0184
4		-0.1578	-0.5679	0.1413	-0.3551	-0.5996	-0.1365	-0.1178	0.1065	0.3212
5		0.1563	-0.4950	0.2611	0.5146	0.0165	0.6139	-0.0949	0.383	-0.1001
6		-0.3389	0.1523	-0.1536	0.5459	-0.0262	-0.0853	-0.1686	-0.1804	0.6866
7		-0.1086	-0.4415	0.0487	0.0810	0.5357	-0.3438	0.5064	0.3047	0.1729
8		-0.2434	0.3121	0.6318	-0.0158	-0.2141	0.1762	0.5787	-0.1618	0.0770
9		0.2546	0.2559	0.3263	0.3497	-0.2418	-0.3602	-0.1679	0.6488	-0.0608

IV. RESULTS AND DISCUSSION

We have investigated the effect of electron correlation, exchange, and relaxation on the energies and intensities in the $L_1-L_{23}M_1$ Coster-Kronig spectrum of Ar.

A. Effects of electron correlation

The mixing coefficients for the eigenvectors $\psi_i = \sum_j c_{ij} \phi_j$ for the initial and final states are listed in Table I. There is strong mixing among the final ionic-state configuration state functions, which alone reduces the transition rate by $\sim 29\%$. Similar results have been obtained by the conventional configuration-interaction calculation of Dyllal and Larkins.¹⁶ Mixing among the initial configuration state functions is rather modest, reducing the transition rate further by $\sim 2\%$. The effect of initial-state configuration interaction on the energy is, however, quite large: it depresses the initial-state energy level by 2.1 eV. This brings about excellent agreement between the calculated and experimental transition energies. The initial-state configuration mixing also greatly perturbs the $2p$ and $3p$ orbitals. This causes the nondiagonal and diagonal overlap integrals involving these orbitals to differ substantially from zero and unity, respectively. Inclusion of complete relaxation of orbitals in the transition-rate calculation is therefore indicated.

The calculated transition energies and intensities of the

diagram lines for the $L_1-L_{23}M_1$ Coster-Kronig spectrum are listed in Table II. The effects of exchange between the continuum and bound electrons and of relaxation are included. Satellite lines arising from configuration mixing of the final ionic configuration state functions appear on the low-energy side of the diagram line. Inclusion of initial-state configuration interaction results in a few satellites on the higher-energy side of the spectrum. These satellites are very weak and are not included in Table II.

B. Transition rates including relaxation

A relaxed-orbital calculation of transition rates was performed by determining the matrix elements in Eq. (1) to various orders in nondiagonal overlaps $\langle u_i | v_j \rangle$ using Eq. (4). The magnitude of the overlaps $\langle 2s | 3s \rangle$, $\langle 3s | 2s \rangle$, $\langle 2p | 3p \rangle$, $\langle 3p | 2p \rangle$, and $\langle 3p | \epsilon p \rangle$ were substantially larger than others. We therefore considered all terms up to order three involving any two of these overlaps, and up to order two otherwise, excluding, however, terms that are numerically less than 10^{-5} . A multitude of terms survive these criteria, too extensive to be included here; for details, the reader is referred to the first author's thesis.²⁷ Transition rates obtained on the basis of this calculation are reported in Table III. Relaxation causes the (3P) rate to increase by 244%, while the (1P) and total rates are reduced, respectively, by 14% and 12%. The major change in the

TABLE II. Diagram and satellite lines in the $L_1-L_{23}M_1$ spectrum of Ar. The initial and final states refer to the atomic-state functions given in Table I.

Initial state	Final state 1P	Energy (eV)	Rate (10^{-4} a.u.)	Relative intensity
1	1	28.95	255.56	100.0
1	2	20.26	0.17	0.1
1	3	14.91	12.42	4.9
1	4	11.99	13.97	5.5
1	5	10.67	40.39	15.8
1	6	7.35	48.47	19.0
1	7	2.08	1.38	0.5
3P				
1	1	30.29	6.17	100.0
1	2	23.04	0.06	1.0
1	3	20.60	0.01	0.1
1	4	18.51	0.05	0.8
1	5	16.86	0.01	0.1
1	6	11.30	0.27	4.4
1	7	10.54	0.06	1.0
1	8	9.54	0.30	4.8
1	9	7.17	1.26	20.4

(3P) rate is seemingly due to the fact that theory grossly underestimates this transition amplitude. It is interesting to note that if we consider, following Dyall and Larkins,¹⁶ the term containing diagonal overlaps only, we get 50%, 55%, and 50% reductions in the 1P , 3P , and total transition rates, respectively. Though in agreement with experimental total transition rates, these results are substantially different from those obtained from a complete relaxation calculation. Because it is so easy to incorporate such approximate relaxation in transition-rate calculations, it may be worthwhile to know when one must venture into the prodigious labor involved in a complete relaxed-orbital calculation. The terms contributing to the transition amplitude can conveniently be grouped according to the non-

diagonal overlaps that they contain as factors.²⁷ It was found²⁷ that the individual terms contributing to the transition amplitude can be very large, some even larger than the diagram lines. The sum over all terms of each group, however, is rather small. This circumstance can be made more evident by expressing the one-electron integrals in terms of two-electron Slater integrals, which leads to extensive cancellations of terms within each group if one makes the approximation that diagonal overlaps are equal to unity and that $R^k(i,i;f,f) = R^k(i,i;i,f)$. The total contribution of each group will then depend on the magnitude of the remaining two-electron terms, the phase relations among these terms, and the overlaps that they contain as factors. It is difficult, however, to make any *a priori* conjecture as to the magnitude of this contribution without carrying out the actual calculation.

C. Effects of exchange

To investigate the effect of exchange between the continuum and bound-state electrons, the Hartree-Fock equation for the continuum electron was solved with and without the exchange terms. It was seen that the exchange interaction slightly increases the magnitude of the radial Slater integrals for the $L_1-L_{23}M_1$ (1P) transition, there being a corresponding reduction in the magnitude of the $L_1-L_{23}M_1$ (3P) radial integrals. Computing transition rates using these radial Slater integrals, we found that $L_1-L_{23}M_1$ (1P), $L_1-L_{23}M_1$ (3P), and the total transition rate increase, respectively, by about 7%, 38%, and 8%, because of the exchange interaction.

V. CONCLUSION

Present relaxed-orbital multiconfiguration Hartree-Fock calculations including exchange between the continuum and final bound-state electrons lead to good agreement with experimental transition energies and slightly improve the theoretical transition rates in the $L_1-L_{23}M_1$ Coster-Kronig spectrum of Ar. The total calculated transition rates are still about a factor of 2 higher than the ex-

TABLE III. Transition energies (in eV) and rates (in milliatomic units) in the $L_1-L_{23}M_1$ Coster-Kronig spectrum of Ar.

	$L_1-L_{23}M_1$ Energy	(1P) Rate	$L_1-L_{23}M_1$ Energy	(3P) Rate	Total rate
Experiment	28.7	7.6	30.5	5.8	13.4
CI ^a calculation including partial relaxation ^b	32.2	23.75	33.3	0.62	24.37
Present calculation: MCHF	28.9	27.61	30.3	0.13	27.74
MCHF including exchange interaction	28.9	29.66	30.3	0.18	29.84
MCHF including partial relaxation	28.9	13.94	30.3	0.06	14.00
MCHF including exchange and partial relaxation	28.9	14.97	30.3	0.08	15.05
MCHF including exchange and complete relaxation	28.9	25.55	30.3	0.62	26.17

^aCI stands for configuration interaction.

^bApproximate relaxation, including only the terms containing diagonal overlaps (Ref. 16).

perimental values. Relaxation tends to minimize the differences between individual $L_1-L_{23}M_1$ (1P) and $L_1-L_{23}M_1$ (3P) transition rates; inclusion of intermediate coupling and channel-channel interaction¹⁸ should minimize it further by redistributing some intensity from the (1P) line to the (3P) line. The initial and final ionic-configuration interaction reduces the total decay rate by 31%. Inclusion of complete relaxation reduces it further by 12% with respect to calculations that do not include

relaxation.²⁸ The exchange interaction increases the rate by $\sim 8\%$. We conclude that, although these effects are substantial and cannot be omitted from a successful calculation, they do not adequately account for the physical situation. Clearly, the independent-particle model of atomic structure is insufficient to treat the pronounced many-body aspects of radiationless transitions of the type considered here, and more elaborate approaches are required to explain the observed intensities.

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²⁸It is interesting to note that inclusion of only partial relaxation (Ref. 16) leads to a much greater reduction of the discrepancy between experimental and theoretical results, an advance that is wiped out when more complete account of relaxation is taken (cf. Table III).