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Auger emissions from the LiF molecule: Calculation of probabilities and energies

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A new *ab initio* method for computing Auger transition rates in molecules is proposed; it is based on the use of orthogonalized plane waves for the free electron and of Hartree-Fock many-center orbitals for the bound electrons. Transition rates and energies are calculated for the case of the LiF molecule ionized in its deepest shell, and the results are compared with the experimental spectrum. Various levels of approximation are tested for evaluating the partial transition rates of various decay channels, and a consistent improvement in the agreement with experiment is obtained when the plane waves are orthogonalized to the relaxed orbitals of the doubly ionized molecular ion.

I. INTRODUCTION

It is well known that the ionization of an internal shell of an atom or molecule is followed by the emission of ultraviolet or x-ray photons and also of electrons (Auger effect) with energies characteristic of the ionized system. Numerous spectra of the Auger electrons from free molecules have been obtained, the methods of excitation being the impact of electrons or heavy particles[1-9] or the photon absorption.[10-14] The Auger spectra are often of such an accuracy that an effort to obtain a correspondingly accurate prediction of energies, intensities, and line shapes from first-principles calculations seems desirable.

From the standpoint of theory, the Auger effect is an example of a resonant scattering process, the analysis of which has usually been developed within the framework of the following two approximations:[15] (1) neglect of interactions between the primary electron and the Auger electron (or the other collision fragments, if any); (2) complete independence of the phenomena of electron emission and photon emission. Thus the problem has been reduced to the solution of the time-independent many-electron Schrödinger equation subject to appropriate asymptotic conditions for the various decay channels of the system, each channel being identified by specifying the state of the residual doubly charged ion and the angular and spin components of the outgoing electron wave function.

From the standpoint of computation one notes the existence of an ample body of methods (often accompanied by fully developed applications) for the study of the Auger effect in atomic systems,[16-21] whereas for molecules the number is much more limited, because of computational difficulties due to the reduced symmetry, the main difficulty being the incorporation of an adequate description of the electron as it moves outward through the field of the doubly ionized molecule. In particular, while there are a number of calculations of the *energies* of the emitted Auger electrons[1,14,22-25] (which can be carried out accurately by the standard *ab initio* methods of quantum chemistry for bound states), there are very few calculations of emission *probabilities* for molecular systems.[26-30]

Apart from semiquantitative approaches based on atomic decomposition of the Auger transition rates,[22,27,29] past applications of the theory of the Auger effect to molecular systems[26,28,30] have been limited to the evaluation of the Wentzel formula[31] within the framework of the two approximations cited above. The method generally followed is to construct a wave function for the final state which is an antisymmetrized product of a wave function for the residual doubly charged ion (which may or may not involve inclusion of correlation) times a continuum or L^2 orbital for the outgoing electron. In previous calculations the bound orbitals were expanded about one center, while the orbital for the outgoing electron was obtained as an eigenfunction of an operator of Hartree-Fock (HF) type containing a potential expanded also about a single center and constructed in terms of the orbitals of the isolated doubly charged ion (static-exchange approximation). Approaches of this sort are only justified for molecular systems that are quasiatomic as, for example, the hydrides of the second row, but are scarcely appropriate for other types of molecules.

In this paper we present a general method for the calculation of the Auger transition rates in molecules. This method differs from those previously applied in the following respects: (1) use of many-center expansions for both the bound and the continuum orbitals, given in terms of a mixed basis set of L^2 functions and plane waves; and (2) complete evaluation of the transition amplitude from the initial quasibound state Φ to the final states Ψ_f's,

$$A_f = \langle \Phi \mid H - E_\Phi \mid \Psi_{f,E_\Phi} \rangle \ , \tag{1}$$

where Φ and Ψ_f are approximate representations of initial and final states obtained with separate variational calculations, and E_Φ is the energy of the initial quasibound state.

In the present application the continuum electron is simply described by a plane wave of the correct energy (i.e., that determined by the asymptotic conditions), while the effects of the molecular field on it are introduced only by orthogonalizing the plane wave to the bound orbitals of the final state considered, which is described within the Hartree-Fock (HF) approximation. The use of a plane wave for the continuum orbital together with the expansion of the bound orbitals in Gaussian functions makes it possible to evaluate analytically all multicenter integrals arising in the calculation of the transition amplitude (1) (general expressions are given in Ref. 32); furthermore, normalization of the continuum orbital is automatic. For other methods which use an L^2 basis set, normalization requires a numerical fitting to identify the exact asymptotic form of continuum orbital (i.e., the proper hypergeometric function)[33,34] or the use of methods like the Stjelties imaging procedure.[30,35]

Our simple approach is applied in the present work to the calculation of partial transition rates and energies for the Auger electron emitted following ionization of the deepest shell of the LiF molecule, where sufficiently accurate experimental measurements[1] are available. Different levels of approximation are employed for the orbitals of the various decay channel wave functions, which are always given as antisymmetrized products of one Slater determinant (or more than one when required by symmetry) for the doubly charged ion time a plane wave (orthogonalized when indicated) for the outgoing electron.

In Sec. II we describe the method in detail. In Sec. III we present our results for the energies and rates of the Auger decay process in the LiF molecule. In Sec. IV we discuss the quality of the results obtained and the causes of the residual discrepancies between the experimental and calculated data, indicating directions for further improving the results.

II. METHOD

Let us consider an isolated resonance superimposed on several continua. We follow Fano[36] in writing the wave function for the resonant (almost bound) state in the neighborhood of the resonance energy E_r by means of an expansion of the type

$$\Xi_{\alpha,E}=a_\alpha(E)\Phi+\sum_{\beta=1}^{N_c}\int_0^\infty \chi_\beta^-(\tau)c_{\beta\alpha}(\tau,E)d\tau , \tag{2}$$

where Φ is a quadratic-integrable normalized wave function and the $\chi_\beta^-(\tau)$'s are N_c noninteracting continuum functions which fulfill the appropriate ingoing wave boundary conditions. Disregarding interference effects between the discrete and the continuum part of $\Xi_{\alpha,E}$, one can define the partial transition rate into channel β as follows:[15]

$$\Gamma_\beta=\frac{2\pi}{\hbar}\,|\langle\Phi|H-E\,|\chi_\beta^-(\mathcal{E})\rangle|^2,\quad \mathcal{E}=E-E_\beta , \tag{3}$$

where E_β represents the energy of the doubly charged ion defined by the asymptotic conditions into channel β.

At the simplest level of approximation one can use in (3), instead of the noninteracting continuum function $\chi_\beta^-(\mathcal{E})$, a simple representation $\Psi_{\beta,\mathcal{E}}$ of the decay channel β, identified asymptotically by the energies E_β and $\mathcal{E}$ of the two fragments and by the values of the proper angular and spin components. (Note that, in general, these channel representations will be mutually interacting.) Furthermore, since the experimental Auger spectrum we want to interpret identifies a channel only in terms of the kinetic energy of the outgoing electron, to predict the measured transition rates one has to sum over all the partial rates Γ_β relative to the channels characterized asymptotically by the same kinetic energy of the outgoing electron.

In the present work we describe each decay channel β as the following antisymmetrized product having the correct spin symmetry:

$$\Psi_{\beta,\mathbf{k}}(1,\ldots,N-1)=\hat{A}[\Theta_\beta(2,\ldots,N-1)\eta_{\beta,\mathbf{k}}(1)] , \tag{4}$$

where $\hat{A}$ is the partial antisymmetrizer for particle 1 with respect to the others, Θ_β is the HF wave function for the doubly charged ion, and $\eta_{\beta,\mathbf{k}}$ is the continuum orthogonalized spin orbital for the outgoing electron

$$\eta_{\beta,\mathbf{k}}(1)=(1-P_\beta)e^{i\mathbf{k}\cdot\mathbf{r}_1}\sigma_\beta . \tag{5}$$

In (5) σ_β represents the spin function and $P_\beta=\sum_{j=1}^{N_\beta}|\varphi_{\beta,j}\rangle\langle\varphi_{\beta,j}|$ the projector constructed from the N_β occupied spin orbitals of the wave function Θ_β, while the normalization is chosen to be

$$\langle\Psi_{\gamma,\mathbf{k}}|\Psi_{\gamma',\mathbf{k}'}\rangle=(2\pi)^3\delta(\mathbf{k}-\mathbf{k}')\delta_{\gamma,\gamma'} . \tag{6}$$

The quantity we compare with the measured Auger rate for channel β is the following:

$$W_\beta=\int\frac{2\pi}{\hbar}\,|\langle\Phi|H-E_r\,|\Psi_{\gamma,\mathbf{k}}\rangle|^2 \times\delta\left[E_r-E_\beta-\frac{\hbar^2k^2}{2m}\right]\frac{d\mathbf{k}}{(2\pi)^3} , \tag{7}$$

where E_β and $\hbar^2k^2/2m$ are the energy of the residual ion and of the outgoing electron, respectively, at infinite separation. This expression can be further simplified by approximating the resonance energy with $E_r\simeq E_\Phi=\langle\Phi\,|H\,|\Phi\rangle$, i.e., by neglecting the energy shift Δ due to the coupling between bound and continuum states.[15] Thus the partial decay rate for each channel β is approximated as follows:

$$W_\beta=\frac{mk}{(2\pi)^2\hbar^3}\int|\langle\Phi\,|H-E_\Phi\,|\Psi_{\beta,k,\hat{k}}\rangle|^2d\hat{k} , \tag{8}$$

where $k=1/\hbar\sqrt{2m(E_\Phi-E_\beta)}$. We observe that because of the integration over $\hat{k}$ in (8) the continuum electron is really described by a series, in general infinite, of spherical Bessel functions of increasing order,[37] each one multiplied by the appropriate spherical harmonic.

Summarizing, in the present approach the main approximations introduced are the following: (1) no channel interaction, i.e., no electron correlation is taken into account apart from that due to the antisymmetrization of the wave functions; and (2) no variational optimization of the orbital for the outgoing electron is performed.

We note also that the wave function (5) used for describing the outgoing electron does not exhibit the correct asymptotic behavior, but this fact is probably not relevant as far as the integral in (8) is concerned, as it is dominated by the molecular region, where, instead, the orthogonalization of the plane wave to the occupied orbitals plays a crucial role.

As for the determination of the HF wave functions, we note that the bound orbitals are derived as linear combinations of modified Gaussian functions[38] with coefficients obtained by solving separately for each state, the proper HF equations. This requires in general the use of variational techniques for open shells, and in several cases involves additional complications stemming from the fact that the wave function sought is not the lowest in energy of its symmetry, as will be better described in connection with the applications to the LiF molecule.

III. CALCULATION OF AUGER ENERGIES AND TRANSITION RATES FOR THE LiF MOLECULE

We have applied our method to the calculation of the Auger energies and transition rates of the LiF molecule ionized in its deepest shell, with a view to comparing our results with the recent measurements of the Auger spectrum of gaseous LiF in the energy range from 600 to 680 eV.[1] A quantitative description of the location in energy of the peaks of this spectrum had previously been made[1] by means of *ab initio* calculations [at the multiconfiguration self-consistent-field (MCSCF) level] of the Auger emission energies and by comparison with other similar spectra (those of the Ne atom and of the HF molecule), but there were previously no *ab initio* estimates of the Auger transition rates relative to this spectrum.

The ionization of the LiF molecule with electrons of ~3000 eV produces mainly one almost bound state that in an independent-particle description corresponds to the configuration $^2\Sigma^+$ $(1\sigma^1 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4)$. For that state, as well as for several states of the doubly charged ion produced by the Auger process, we have calculated HF wave functions using the basis set of 62 modified Gaussian functions given in Table I. The exponents of the s and p basis functions were taken from Ref. 39; the calculations were carried out in the Born-Oppenheimer approximation at an internuclear distance ($R=2.955$ a.u.), which corresponds to the experimental equilibrium distance for the neutral molecule.[40]

The Auger energies resulting from these calculations are given in Table II; they are in excellent agreement with the experimental data, the maximum relative error being $\leq 0.3\%$ and the maximum absolute error $\simeq 2$ eV.

The HF wave function for the doublet initial state, corresponding to a single ionization of the core, is obtained simply by requiring at every step of the self-consistent-field (SCF) process the correct filling of the orbitals, as proposed in Refs. 41 and 42.

With regard to the bound states of the doubly charged ion produced by the Auger decay we observe that in each of the symmetries $^1\Pi$ and $^3\Pi$ there are two states of interest and four in symmetry $^1\Sigma^+$; this poses problems for the variational determination of the HF wave functions

TABLE I. Modified Gaussian basis set used in LiF calculations. Note that the d_{z^2}'s functions are defined as in Ref. 38.

Symmetry	Fluorine Exponents	Coefficients	Symmetry	Lithium Exponents	Coefficients
s	23 342.0000	1.0	s	1782.900 00	1.0
s	3431.0000	1.0	s	267.100 00	1.0
s	757.7000	1.0	s	60.070 00	1.0
s	209.2000	1.0	s	16.780 00	1.0
s	66.7300	1.0	s	5.403 00	1.0
s	23.3700	1.0	s	1.906 00	1.0
s	8.6240	1.0	s	0.717 90	1.0
s	2.6920	1.0	s	0.263 40	1.0
s	1.0090	1.0	s	0.077 16	1.0
s	0.3312	1.0	s	0.028 54	1.0
p	65.6600	1.0	p	2.565 00	1.0
p	15.2200	1.0	p	0.485 90	1.0
p	4.7880	1.0	p	0.145 40	1.0
p	1.7320	1.0	p	0.052 92	1.0
p	0.6206	1.0	p	0.020 26	1.0
p	0.2070	1.0			
p	0.0660	1.0			
d_{z^2}	1.7320	1.0	d_{z^2}	0.145 40	1.0
d_{z^2}	0.6206	1.0	d_{z^2}	0.020 26	1.0
d_{z^2}	0.2070	1.0			
d_{z^2}	0.0660	1.0			

TABLE II. HF energies for the LiF ions calculated with the basis set given in Table I at internuclear distance $R=2.955$ a.u. and by means of independent SCF processes for each state; ΔE_{HF}, ΔE_H, ΔE_{expt} indicate the differences in energy with respect to the initial state $^2\Sigma^+$ calculated by us, by Hotokka *et al.* (Ref. 1), and measured (Ref. 1).

Transition	Hole configuration state	E_{HF} (a.u.)	ΔE_{HF} (eV)	ΔE_H (eV)	ΔE_{expt} (eV)
1	1σ: $^2\Sigma^+$	−81.741 500			
2	$\pi_+\pi_-$: $^3\Sigma^-$	−105.734 588	652.7	652.0	652.2
3	$4\sigma\pi_+$: $^3\Pi$	−105.714 699	652.2	651.6	650.3
4	$\pi_+\pi_+$: $^1\Delta$	−105.629 468	649.9	649.2	648.5
5	$4\sigma\pi_+$: $^1\Pi$	−105.609 632	649.3	648.7	647.7
6	$\pi_+\pi_-$: $^1\Sigma^+$	−105.526 636	647.1	648.6	646.6
7	$4\sigma4\sigma$: $^1\Sigma^+$	−105.539 617	647.4	646.4	644.8
8	$3\sigma\pi_+$: $^3\Pi$	−104.923 948	630.7	630.4	630.5
9	$3\sigma4\sigma$: $^3\Sigma^+$	−104.908 740	630.3	629.9	629.6
10	$3\sigma\pi_+$: $^1\Pi$	−104.548 457	620.5	618.8	621.8
11	$3\sigma4\sigma$: $^1\Sigma^+$	−104.540 838	620.3		620.3
12	$3\sigma3\sigma$: $^1\Sigma^+$	−103.810 355	600.4	600.3	602.6

corresponding to the states higher in energy in each of these symmetries. Concerning the second state in the symmetries $^1\Pi$ and $^3\Pi$, it is sufficient to require at every step of the SCF process the correct orbital filling to obtain an HF wave function, the energy of which is an upper bound of the exact electronic energy, even if the wave function is not orthogonal to the one lower in energy.[43] For the symmetry $^1\Sigma^+$, the situation is the following: The second state, that having two vacancies in $(1\pi_+1\pi_-)$, is automatically orthogonal to the lower state $(4\sigma4\sigma)$ because of the type of the configuration, while for the third and fourth states having vacancies in $(3\sigma4\sigma)$ and in $(3\sigma3\sigma)$, respectively, it is necessary to use appropriate techniques to avoid variational collapse. We have determined the wave functions for these states with variational approaches which explicitly force maintenance of the orthogonality of the state of interest to the states lying lower in energy, by means of techniques proposed by one of us.[44,45]

Auger transition rates

To test our method for the calculation of Auger transition rates we have used the following four different approaches of increasing degree of accuracy with respect to the quality of the wave functions used.

(1) In the most simplified approach we represent both the initial and the final states by means of wave functions whose bound orbitals have been obtained from an HF calculation for the ground state of the neutral molecule. The transition amplitude (1) for a given channel f is approximated as follows:

$$A_f=c_f\left[\left\langle 1\sigma(1)n\lambda(2)\left|\frac{1}{r_{12}}\right|e^{i\mathbf{k}\cdot\mathbf{r}_1}n'\lambda'(2)\right\rangle \pm\left\langle 1\sigma(1)n\lambda(2)\left|\frac{1}{r_{12}}\right|e^{i\mathbf{k}\cdot\mathbf{r}_2}n'\lambda'(1)\right\rangle\right], \tag{9}$$

where $n\lambda$ and $n'\lambda'$ represent the two bound orbitals of the initial state involved in the decay process,

$$|k|=1/\hbar\sqrt{2m[(\varepsilon_{n'\lambda'}+\varepsilon_{n\lambda})-\varepsilon_{1\sigma}]}\,,$$

with ε_j the eigenvalues of the Fock matrix for the ground-state bound orbitals connected with the initial and final energies as well as with the energy of the neutral molecule $E_{\mathrm{HF}}(\mathrm{LiF})$ in the following way:

$$\begin{aligned} E_i&=E_\Phi\simeq E_{\mathrm{HF}}(\mathrm{LiF})-\varepsilon_{1\sigma}\,,\\ E_f&\simeq E_{\mathrm{HF}}(\mathrm{LiF})-\varepsilon_{n\lambda}-\varepsilon_{n'\lambda'}\,. \end{aligned} \tag{10}$$

c_f is a coefficient which depends on the nature of the final state of the doubly charged ion: singlet $(+)$ or triplet $(-)$. Note that the approximation (9), used also by other authors[16] disregards the requirement that the continuum orbital be orthogonal to the bound orbitals.

(2) As a second approach we use a procedure analogous to the preceding one with bound orbitals derived from an HF calculation for LiF$^+$ in the state

$$^2\Sigma^+(1\sigma^1 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4)\,,$$

in place of those for the ground state of the neutral molecule and with $|k|=1/\hbar(2m\Delta E_f^{\mathrm{expt}})^{1/2}$, where $\Delta E_f^{\mathrm{expt}}$ stands for the experimentally determined energy of the Auger electron in the decay channel f.

(3) As a third approach we improve the previous approximation by imposing the orthogonality of the continuum orbital $\eta_{f,\mathbf{k}}$ with respect to the bound orbitals of Θ_f,

$$\begin{aligned} \eta_{f,\mathbf{k}}(\mathbf{r})&=(1-P_f)e^{i\mathbf{k}\cdot\mathbf{r}}\sigma_f\,,\\ P_f&=\sum_{j=1}^{N_f}|\varphi_{f,j}\rangle\langle\varphi_{f,j}|\,, \end{aligned} \tag{11}$$

where P_f is a projector constructed with the occupied orbitals of the final state Θ_f of the doubly charged ion and $|k|=1/\hbar(2m\Delta E_f^{\mathrm{expt}})^{1/2}$ as in (2). Note that under this approximation the expression of the Auger transition rate reduces exactly to the Wentzel formula.

(4) Finally we carry out a complete calculation of the transition amplitudes (1), using for the initial state Φ and for the final states of the residual-ion HF wave functions obtained from separate variational calculations, which produce a different orbital relaxation for each state; for the outgoing electron we choose an orthogonalized plane

TABLE III. W_i: Values of the relative transition rates for the various decay channels of the LiF ion, calculated with the four different approaches explained in Sec. III and compared with the experimental values.

Transition	Hole configuration state	W_1	W_2	W_3	W_4	W_{expt}
1	$\pi_+\pi_-$: $^3\Sigma^-$	0.00	0.00	0.00	0.00	0.01
2	$4\sigma\pi^+$: $^3\Pi$	0.01	0.01	0.004	0.003	0.02
3	$\pi_+\pi_+$: $^1\Delta$	1.00	1.00	1.00	1.00	1.00
4	$4\sigma\pi_+$: $^1\Pi$	1.01	0.98	0.98	0.98	0.91
5	$\pi_+\pi_-$: $^1\Sigma^+$	0.21	0.25	0.17	0.17	0.27
6	$4\sigma4\sigma$: $^1\Sigma^+$	0.36	0.37	0.32	0.33	0.32
7	$3\sigma\pi_+$: $^3\Pi$	1.51	1.66	0.92	0.64	0.20
8	$3\sigma4\sigma$: $^3\Sigma^+$	0.77	0.82	0.47	0.34	0.07
9	$3\sigma\pi_+$: $^1\Pi$	0.10	0.09	0.13	0.06	0.42
10	$3\sigma4\sigma$: $^1\Sigma^+$	0.06	0.05	0.07	0.22	0.17
11	$3\sigma3\sigma$: $^1\Sigma^+$	0.43	0.32	0.12	0.15	0.21
	W_{tot} (eV)	0.132	0.320	0.243	0.242	?

wave with a wave vector having a modulus

$$|\mathbf{k}| = 1/\hbar[2m(E_i^{\mathrm{HF}} - E_f^{\mathrm{HF}})]^{1/2} .$$

We observe that in the evaluation of the transition amplitude, one must take account of the fact that the orbitals of the initial and the final states are mutually nonorthogonal, and that in this scheme the explicit orthogonalization of the plane wave to the bound orbitals of the final state is not necessary, because it is automatically included in the antisymmetrization process.

The values of the partial Auger rates relative to that for the most prominent transition in the spectrum and calculated by means of the four methods described above are displayed in Table III, together with the corresponding experimental values. We have also calculated a total Auger decay probability of 0.242 eV which is consistent with those measured or calculated for analogous systems such as HF ($\simeq$0.23 eV),[26] Ne ($\simeq$0.24 eV),[18] and F ($\simeq$0.1–0.2 eV).[46] The experimental linewidths given in Ref. 1 and ranging between 1.5 and 1.9 eV probably show large effects due to the nuclear motion, as suggested also by the authors.

Finally, in Fig. 1 we compare the experimental spectra[1] with those obtained by superposition of Lorentzians, one for each channel considered in Table III, with widths equal to those given in Ref. 1 and heights equal to (a) the measured relative transition rates given in Ref. 1, (b) the relative transition rates calculated by us.

IV. DISCUSSION OF RESULTS AND METHOD

First of all we observe that in the analysis of the Auger spectrum of the LiF molecule we have not taken into account possible contributions due to *KLL* shake-up and *KL-KLL* shake-off processes that probably contribute to the structure of the spectrum in the energy range between 633–640 eV and 608–610 eV.[1] This is also the reason for the differences between the experimental spectrum and that reproduced by means of Lorentzians with heights equal to the measured ones, shown in Fig. 1.

Concerning the calculated value of the Auger energies, as already remarked in Sec. III, they are in excellent agreement with the experimental results—a demonstration of the fact that the errors arising from the neglect of electronic correlation and relativistic effects in the initial state cancel those arising from the same neglect in the final state.

Concerning the relative Auger transition rates, we notice that there is a tendency towards improvement in passing from approach (1) to (4), even if it seems that the introduction of the orthogonalization of the plane wave [approach (3)] is more important—as far as affecting the quality of the results goes—than the effects associated with relaxation of the bond orbitals [approach (4)].

As for the use of orbitals of the ion LiF$^+$ in the initial Auger state instead of the orbitals of the ground state of the neutral molecule, comparing the effect on the Auger transition rates calculated as per Wentzel [approaches (1) and (2)], one sees the only noticeable difference in the total decay rate, which increases by a factor 2.5 because of the more localized character of the orbitals of the ion.

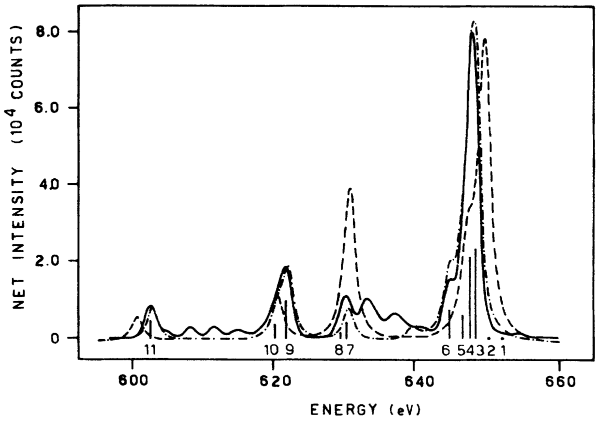

FIG. 1. Experimental Auger spectrum (——) of gaseous LiF (Ref. 1), compared with those obtained by means of superposition of Lorentzians, one for each channel considered in Table III, with parameters given in Ref. 1 (—·—·—·) and with parameters calculated by us (— — —), using the fourth approach described in Sec. III.

Concerning the values of the relative Auger transition rates, we note that those calculated by us differ from the experimental ones by at most 35%, except for the transitions 2, 7, 8, and 9 of Table III. Notice that transition 2 corresponds to a transition prohibited at the atomic level (state $^3P^-$ of Ne) and hence its value in the molecule is very small; since it is determined as the difference of comparable terms, its calculation requires particularly great accuracy. As for transitions,$^{7-9}$ we observe that they involve always the 3σ orbital which nearly coincides with the $2s$ orbital of F, aside from minor $2p$-type contributions. Analyzing the amplitudes of such transitions given as per Wentzel and approximating each molecular orbital by means of the atomic orbital corresponding to its dominant part, one sees that these amplitudes are given as the sum of contributions of the type

$$[(2p_{\mathrm{F}}k \mid 2s_{\mathrm{F}}1s_{\mathrm{F}})\pm(2s_{\mathrm{F}}k \mid 2p_{\mathrm{F}}1s_{\mathrm{F}})] .$$

The first term is the matrix element of a Coulomb operator $J_{1s,2s}$ which decreases rapidly with the distance from the F atom, since the $1s$ orbital is concentrated near F, and since all the multipole moments of the charge distribution ($1s2s$) are zero. The second integral is the matrix element of the Coulomb operator $J_{1s,2p}$ which generates a potential of dipole type which decreases more slowly than the preceding one, while the distribution of charge ($2sk$) is concentrated in the zone of the maximum of the $2s$ orbital, i.e., in a zone which is again relatively near the nucleus. All of this suggests that in transitions$^{7-9}$ there is a problem of critical balancing between the contributions of the two integrals given above, each one of which would require a better description of the continuum orbital near the F nucleus. It appears that the better description needed can best be obtained by means of variational-type approaches for the construction of the continuum orbital, such as, for example, the Lippmann-Schwinger method (see Nesbet[47]).

Finally, we note that obtaining better agreement between the theoretical and experimental results will require taking into account the effects of the channel interaction (i.e., electron correlation)—that can be relevant especially in the case of the first two $^1\Sigma^+$ states of the doubly charged ion, which are quite close in energy as well as also the effects due to the nuclear motion.

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