

Interatomic radiative transition rates for the sodium fluoride crystal

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Interatomic electric-dipole radiative transition rates for the NaF crystal are calculated for initial $1s$, $2s$, and $2p$ holes in the Na^+ ion. The crystal is simulated by a $(\text{NaF}_6)^{5-}$ cluster embedded in a large number of point ions, and the one-electron molecular orbitals are obtained from open-shell restricted-Hartree-Fock calculations of the initial state and final states. This allows the transition matrix element to be calculated in the self-consistent-field (ΔSCF) formalism where both initial- and final-state determinantal wave functions are used, and the nonorthogonality of the two sets of molecular orbitals is taken into account. One interatomic radiative transition, the $K\beta_1$ satellite line, has been observed as a high-energy satellite of the Na $K\alpha_1\alpha_2$ line. The measured intensity ratio $\beta_1/\alpha_1\alpha_2$ is 1.2×10^{-2} ; our theoretical ratio is 1.13×10^{-2} . This level of agreement between theory and experiment is similar to, but somewhat better than, that recently obtained by us for interatomic Auger transitions in NaF, using molecular orbitals from the same calculations. The other interatomic radiative transitions in NaF have considerably smaller transition energies and unobservably small transition rates. The sensitivity of the rates to the choice of Hartree-Fock Gaussian basis set is explored. Rates based on a single determinantal wave function are compared with the ΔSCF rates. The one-center approximation for the $K\beta_1$ rate was found to account for 82% of the rate.

I. INTRODUCTION

Interatomic radiative transitions have been associated with satellite peaks in x-ray emission spectroscopy by Aberg *et al.*¹ and by Urch.^{2,3} Reference 1 is concerned with alkali halides, including the NaF crystal for which we have recently completed a series of interatomic Auger rate calculations.^{4,5} In Ref. 1 the $K\beta_1$ high-energy satellite line to the Na $K\alpha_1\alpha_2$ x-ray line is identified as a "cross transition" which fills the Na $1s$ hole from the valence band. This terminology is appropriate since the molecular orbitals of the valence band are localized primarily on the fluorine ions. Reference 2 is concerned with low-energy satellites of diagram lines in a fairly large collection of oxides, carbides, nitrides, and fluorides having varying degrees of ionicity. The low-energy satellite arises when a core hole is filled from a part of the valence band localized primarily on the $2s$ orbitals of the ligand neighbors of the atom with the initial core hole. The x-ray diagram line arises from a part of the valence band localized on both the hole-containing atom and $2p$ orbitals of its ligand neighbors. In both investigations an LCAO-MO analysis of the valence molecular orbital (MO) associated with the satellite transition is undertaken. This leads to the important conclusion that the interatomic satellite transition is mediated entirely by the covalent bonding between the atomic orbitals on the neighbors and orbitals of the hole-containing atom. In the LCAO-MO representation, the part of the transition dipole matrix element involving the product of the core atomic orbital (AO) and a neighbor AO is negligible. This localized, one-center approach to core-valence x-ray emission theory in solids has been developed and applied to molecular x-ray emission processes by others,⁶⁻⁸ with considerable success in comparison with experiment and

with full *ab initio* calculations.⁷⁻¹⁰

There are several reasons for new theoretical work on the radiative decay of core holes in the NaF crystal. First, the radiative decays compete with the Auger decays and have been proposed as a mechanism for interatomic charge transfer in NaF.¹¹ Second, direct measurements allow a test of the theory for the ratio of the intensity of the $K\beta_1$ satellite to the main $K\alpha_1\alpha_2$ line of the sodium ion. The comparison between theory and experiment provides additional information on the validity of the $(\text{NaF}_6)^{5-}$ molecular cluster simulation of the NaF crystal and the Hartree-Fock calculations of the cluster MO's. Since the radiative and Auger matrix elements emphasize different regions of space, the additional test is significant. Finally, it will be possible to address three questions of technical interest in the *ab initio* theory of molecular radiative transitions.⁷⁻¹⁰ The first concerns the sensitivity of the radiative rates to the Gaussian basis set used in the Hartree-Fock calculations; the second is the comparison of ΔSCF radiative rates with those based on a single-determinantal wave function. The last question, probably the most interesting one, concerns the validity of the local, one-center approximation mentioned above. Further study of this question is of particular interest because a recent paper shows that within the framework of CNDO/2 theory the use of the one-center approximation leads to substantial errors in the carbon K -hole total transition rates in CO, HCN, and CO_2 .¹²

The rest of the paper is organized as follows. The theory of the radiative transition rate calculations is presented in Sec. II, building as much as possible on Refs. 4 and 5. The intraatomic and interatomic radiative rates for filling Na $1s$, $2s$, and $2p$ holes in the NaF crystal are presented in Sec. III. Our conclusions are summarized in Sec. IV.

II. THEORY

Atomic units (a.u.) will be used except where otherwise indicated. A rate of one a.u. is equivalent to $4.134 \times 10^{16} \text{ sec}^{-1}$ and to a linewidth contribution of 27.212 eV. For comparison, the Na atom $K\alpha_1\alpha_2$ transition rate is 2.464×10^{-4} a.u. and the Na(*KLL*) Auger rate is 107.6×10^{-4} a.u.¹³ The $(\text{NaF}_6)^{5-}$ cluster used to simulate the NaF crystal was embedded in a large cubic array of point ions which provided an appropriate external Madelung potential. Restricted Hartree-Fock calculations were done for the singlet ground state, and open-shell restricted Hartree-Fock calculations were done for the doublet Na 1s, 2s, and 2p hole states. Two basis sets (*A* and *B*) were used. These calculations are reported in Ref. 4; the influence of the basis sets on the Auger calculations is reported in Ref. 5. The orbitals from the ground-state wave function were used as final-state orbitals for transitions which resulted in a valence-band hole.

It is helpful to adopt a notation similar to that used in Ref. 12. The rate for the transition in a molecular system from an initial state *i* with a hole in spin orbital *W*, represented by the wave function $\Psi^i[W]$, to a final state *f* with a hole in spin orbital *X*, represented by the wave function $\Psi^f[X]$, with the associated emission of an x-ray photon of energy E_{if} , is given by the expression

$$\Gamma_{X \rightarrow W} = \frac{4}{3} (E_{if})^3 \alpha^3 |\mathbf{M}_{fi}|^2, \quad (1)$$

where α is the fine-structure constant, $\frac{1}{137.036}$. Within the dipole approximation for orthonormal wave functions the transition moment \mathbf{M}_{fi} is given by

$$\mathbf{M}_{fi} = \left\langle \Psi^f[X] \left| \sum_j \mathbf{d}_j \right| \Psi^i[W] \right\rangle, \quad (2)$$

where \mathbf{d}_j is the one-electron dipole operator, and the sum extends over all the electrons in the system. Since the dipole operator is diagonal in the electron spin operator, *X* and *W* must correspond to the same spin projection. We shall take this to be the spin-up projection. Thus in our $(2N - 1)$ -electron system, each doublet wave function will contain N ($=35$) spin-down electrons and $N - 1$ spin-up electrons. With this convention, the symbols *X* and *W* can be the indexing numbers of the spatial molecular orbitals (MO's) in a predetermined standard ordering system with $1 \leq X, W \leq N$, and $W \neq X$. To fix the signs of the determinantal wave functions, we place all the spin-up orbitals first and all the spin-down orbitals next, and fill the MO's in the standard order. If a single set of orthonormal MO's ψ_j is chosen to represent both the initial- and final-hole states, then the transition moment \mathbf{M}_{fi} of Eq. (2) reduces to the one-electron dipole element

$$\mathbf{M}_{fi} = \langle \psi_W | \mathbf{d} | \psi_X \rangle, \quad (3)$$

multiplied by $(-1)^{(W-X-1)}$. In our application of Eq. (3) the ψ_j will be the orbitals from the initial-state Hartree-Fock functions. If $\psi^i[W]$ and $\Psi^f[X]$ are determinantal functions from distinct Hartree-Fock calculations, the method of Lowdin¹⁴ can be used to compute \mathbf{M}_{fi} . Let

the final-state MO's be called χ_i and the initial-state MO's be called ψ_j . Then the inner product $\langle \Psi^f[X] | \Psi^i[W] \rangle$ is given by¹⁴

$$\langle \Psi^f[X] | \Psi^i[W] \rangle = \Delta \Delta_{XW}, \quad (4)$$

with

$$\Delta = \det\{S_{ij}\}, \quad (5)$$

and

$$S_{ij} = \langle \chi_i | \psi_j \rangle. \quad (6)$$

In Eq. (4) the symbol Δ_{XW} stands for the determinant obtained by crossing out the *X* row and *W* column in Δ . In Eq. (4), the determinant Δ arises from the spin-down electrons and Δ_{XW} arises from the spin-up electrons. For dipole allowed transitions, χ_W and ψ_X have opposite parities so Δ_{XW} vanishes. Following Ref. 14, the dipole matrix element is given by

$$\mathbf{M}_{fi} = \Delta \sum_j \sum_k \langle \chi_j | \mathbf{d} | \psi_k \rangle \Delta_{XW}(j; k), \quad (7)$$

where $\Delta_{XW}(j; k)$ is a cofactor in Δ_{XW} and the sums go over $N - 1$ terms. $\Delta_{XW}(j; k)$ is the determinant obtained from Δ_{XW} by crossing out its *j*th row and *k*th column and multiplying the resulting determinant by $(-1)^{j+k}$. Equation (7) was evaluated using standard linear algebra subroutines, starting with the $N \times N$ matrices S_{ij} and $\langle \chi_i | \mathbf{d} | \psi_j \rangle$.

As described in Ref. 5, the MO's are represented by expansions in the spherical harmonics Y_{lm} centered on the Na^+ ion, with $l \leq 35$. Using the spherical harmonic expansions for the products xY_{lm} , yY_{lm} , and zY_{lm} of the Cartesian coordinates x, y, z with the Y_{lm} , it is straightforward to obtain the one-electron dipole matrix elements as sums over radial integrals. These are done by Simpson's rule using the same radial mesh used for the Auger matrix elements. This is not the best way to compute dipole matrix elements for a Gaussian basis set expansion. However, it fits into the framework already developed for the Auger rate calculations and provides an additional check on our computational methods. The overlap matrix Δ was obtained from the overlap matrix of basis functions and the LCAO-MO coefficients of the two wave functions.

III. RESULTS AND DISCUSSION

The Hartree-Fock wave functions available for these calculations consisted of ground-state and Na 1s, 2s, and 2p hole determinantal wave functions for the $(\text{NaF}_6)^{5-}$ cluster.⁴ The ground-state MO's were used to describe final F 2p hole states, which occur in the valence band of the solid. The transition energies were deduced from the x-ray photoemission spectra of Citrin, Rowe, and Christman.¹⁵ Two different Gaussian basis sets (*A* and *B*) were used for the Hartree-Fock calculations.⁴ Both are of good quality, and basis set *B* allows a somewhat greater degree of freedom for the transfer of charge between the Na and

TABLE I. Radiative transition rates for the NaF crystal summed over all MO's corresponding to the final-state hole. Δ SCF rates using the cluster ground-state MO's for F 2*p* final states, except for line 2 which is based on initial-state MO's. Basis set *A* was used.

Initial-state hole	Final-state hole	Energy (eV) ^a	Theory rate (a.u.) ^b
Na 1 <i>s</i>	Na 2 <i>p</i>	1040.9	2.74[−4] ^c
Na 1 <i>s</i>	F 2 <i>s</i>	1042.7	1.28[−7]
Na 1 <i>s</i>	F 2 <i>p</i>	1063.2	3.10[−6]
Na 2 <i>s</i>	Na 2 <i>p</i>	32.7	5.10[−7]
Na 2 <i>s</i>	F 2 <i>p</i>	55.0	1.49[−8]
Na 2 <i>p</i>	F 2 <i>p</i>	22.3	4.08[−8]

^aCalculated from Tables I and III of Ref. 15.

^bOne atomic unit (a.u.) corresponds to $4.134 \times 10^{16} \text{ sec}^{-1}$.

^cThe number in square brackets is the power of 10 by which the number preceding it is to be multiplied.

F ions. Two types of transition matrix element were studied. The simplest was based on the single set of MO's from the initial-state wave function, using Eq. (3). The other utilized the MO's from both initial and final states in Eq. (7). The rates were averaged over initial-state sublevels and summed over final-state sublevels. The rates for transitions to F 2*p* hole states were summed over all the F 2*p* MO's, that is, over the valence band.

Table I summarizes the results. Line 1 concerns the Na $K\alpha_1\alpha_2$ transition observed in the work described in Ref. 1 and by Keski-Rahkonen, Reinikainen, and Mikkola.¹⁶ A comparison of our rate with other theoretical data is given in the next paragraph. Line 2 concerns an unobserved interatomic transition of nearly the same energy. Line 3 describes the interatomic $K\beta_1$ x-ray satellite line.^{1,16} The authors of Ref. 16 found the intensity ratio of $K\beta_1$ to $K\alpha_1\alpha_2$ to be equal to 1.2×10^{-2} . The ratio obtained from Table I is 1.13×10^{-2} . The agreement is excellent. The ratio measured in Ref. 1 was 1.6×10^{-2} . This value, which is included in the tabulation of Ref. 16, does not agree with our result as well as the more recent higher resolution value. We will return to the theoretical ratio in the next paragraph. The remaining lines in Table I concern lower energy transitions which have not been observed. This is not surprising since the theoretical Auger rates for filling the Na 2*s* and 2*p* holes are 2.36×10^{-2} a.u. and 5.57×10^{-3} a.u., respectively.⁵

Table II summarizes the results of several different theoretical evaluations of the $K\alpha_1\alpha_2$ and $K\beta_1$ transition rates. The 10–24% variation of the rates is similar to that found in Ref. 7. The interatomic $K\beta_1$ rate is seen to be not more sensitive to the different calculational procedures than the $K\alpha_1\alpha_2$ rate. As Table II shows, the $K\alpha_1\alpha_2$ rates for the Na atom^{13,17} are close to the ones obtained by us. In principle, the same Hartree-Fock-Slater calculations were carried out in Refs. 13 and 17. The transition rate and oscillator strength given in Ref. 17 lead to a transition energy of 1110 eV. We believe that this large value accounts for the difference in the two rates. The value used for the $K\alpha_1\alpha_2$ rate influences the ratio of the $K\beta_1$ intensity to that of the $K\alpha_1\alpha_2$ line. However the discrepancy between the atomic value ob-

tained by Walters and Bhalla and our Δ SCF values is about 10%. The use of the atomic rate from Ref. 17 leads to an intensity ratio of 1.26×10^{-2} .

We now consider the validity of the local one-center theory for the interatomic $K\beta_1$ transition in NaF. Following Refs. 1–3, we first report the rate obtained from distant interactions alone. This was done by setting equal to zero all the LCAO-MO coefficients for the F 2*p* T_{1uz} MO's which refer to Gaussian basis functions on Na. When this is done the norms of these two MO's decrease by 5 and 1%. The $K\beta_1$ rate from an initial-state calculation with basis set *B* becomes 0.532×10^{-6} a.u. or about 18% of the entire rate from Table II. In Refs. 1–3 the distant contributions were found to be completely negligible. Next we consider the one-center theory from a slightly different point of view. In terms of a minimal basis set,^{1–3} the F 2*p* T_{1u} MO's contain a fraction of the Na 2*p* AO. The need to treat the core-hole wave functions realistically precludes the use of a minimal basis set in the present instance. However, if the Na basis function contribution to the F 2*p* MO's is expressible as a fraction *f* of the Na 2*p* AO, the ratios of the corresponding LCAO-MO coefficients should be nearly constant and equal to *f*. (The Na 2*p* MO is predominantly localized on the Na ion in the Na 1*s* core-hole wave function.) Table III lists the Na p_z Gaussian basis functions, the LCAO-

TABLE II. Comparison of theoretical radiative transition rates for the $K\alpha_1\alpha_2$ and $K\beta_1$ transitions in NaF.

Transition	Calculation	Basis set	Rate (a.u.)
$K\alpha_1\alpha_2$	Δ SCF	<i>A</i>	2.74[−4]
		<i>B</i>	2.51[−4]
	Initial state	<i>A</i>	3.12[−4]
		<i>B</i>	3.12[−4]
		McGuire ^a	2.92[−4]
$K\beta_1$	Δ SCF	<i>A</i>	2.46[−4]
		<i>B</i>	2.46[−4]
	Initial state	<i>A</i>	3.10[−6]
		<i>A</i>	3.09[−6]
		<i>B</i>	2.95[−6]

^aReference 17, Na atom.

^bReference 13, Na atom.

TABLE III. Ratios of LCAO-MO coefficients $C(k, \text{MO})$ for F $2p$ and Na $2p$ MO's.

AO ^a	$\zeta(k)^b$	$C(k, \text{Na } 2p)^c$	$\frac{C(k, \text{F } 2p')^d}{C(k, \text{Na } 2p)}$	$\frac{C(k, \text{F } 2p'')^e}{C(k, \text{Na } 2p)}$
20	239.91	0.0024	0.0555	0.0295
23	74.03	0.0131	0.0488	0.0324
26	24.06	0.0720	0.0557	0.0300
29	8.34	0.2293	0.0499	0.0332
32	3.16	0.3945	0.0622	0.0291
35	1.25	0.3750	0.0306	0.0423
38	0.53	0.1379	0.0228	-0.0162
41	0.21	0.0089	-10.5821	-2.8442

^aNa p_z -type basis function number in basis A .

^bExponent of primitive Gaussian basis function.

^cNa $2p$ designates the Na $2p T_{1uz}$ MO from an initial-state calculation.

^dF $2p'$ designates the lower T_{1uz} MO generated primarily by F $2p$ basis functions.

^eF $2p''$ designates the upper T_{1uz} MO generated primarily by F $2p$ basis functions.

MO coefficients for the Na $2p T_{1uz}$ MO, and the coefficient ratios for the two F $2p T_{1uz}$ MO's. The ratios are fairly constant up to AO number 32 and then start to vary considerably. The sum of the squares of these constants times the $K\alpha_1\alpha_2$ rate is about equal to 1.2×10^{-6} a.u., compared to the value 3.09×10^{-6} from Table II. Thus hybridization with the Na $2p$ AO does not account for the interatomic rate.

Both our tests of the local one-center approximation show that the situation is more complex than that envisaged in terms of minimal basis-set theory. Indeed, if a less diffuse basis were used on the fluorine atoms, the distant contributions to the matrix elements could be reduced. As is the case with atomic spectra, the key task in the prediction of radiative transition rates is the genera-

tion of good wave functions. Once these are available, it is straightforward to compute the transition matrix elements without further approximation.^{7-10,12} The one-center theory remains nonetheless a useful tool for the qualitative understanding of interatomic x-ray spectra in solids¹⁻³ and molecules.⁶⁻⁸

IV. SUMMARY

We have shown that the same $(\text{NaF}_6)^{5-}$ molecular cluster simulation of the NaF crystal which provided a quantitative account of the interatomic Auger spectrum^{4,5} can also provide a quantitative account of the NaF x-ray spectrum resulting from initial Na core holes, including the interatomic $K\beta_1$ satellite line. The same methods can be applied to other solids and to their surfaces provided that an adequate simulation of the solid by a molecular cluster can be found. We also tested the local one-center picture of interatomic radiative transitions on the $K\beta_1$ transition and found the theory not to apply in a quantitative sense. This result is in agreement with the findings in Ref. 12 and with analogous tests which we carried out on the local theory of interatomic Auger transitions.⁵

In conclusion, we want to point out that the general rule for light elements—that Auger deexcitations are generally much faster than radiative deexcitations—is verified for the interatomic transitions studied in our work. On the basis, the decay of the Na $2p^2$ two-hole state in NaF, discussed in Ref. 11, should occur by Auger and not by radiative transitions.

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