Theoretical lifetimes of the Al ^2S, ^2P, ^2D, and ^2F states

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The natural lifetimes of the aluminum $3s^2nl$, $n = 3-12$, $l = 0-3$, have been calculated using wave functions that were obtained by direct numerical integration of the Schrödinger equation with a central potential to describe the ionic core and experimental term energies as input. The strong perturbation of the $3s^2nd$ ^2D series by the yet to be experimentally identified $3s3p^2$ ^2D perturber has been explicitly treated semiempirically by using experimental mixing coefficients. Inclusion of at least this perturbation is essential for good agreement with experiment. The effects of blackbody radiation are also explicitly included and have a dramatic effect on the lifetimes of the np states. Core-polarization effects are also included in the transition matrix elements.

The excited states of Al, and especially the members of the ^2D series, have attracted particular attention in the literature because of the strong mixing of the $3s3p^2$ ^2D with the $3s^2nd$ states. Actually the former state, which has not yet been identified experimentally, is believed to be spread along the whole nd ^2D series, and theoretically there is disagreement as to whether it lies above or below the ionization limit. Various approaches have been used to calculate the percentage of mixing of the nd states with the perturber, starting with the well-known work of Weiss [1].

Experimentally, the various series of singly excited states have not been extensively or completely studied. For instance, the np states have not been observed between $n = 8$ and 26. Recent measurements [2–4] using a two-laser excitation technique have provided detailed information of the upper parts of the Rydberg series with n larger than about 30.

The lifetimes of these states have only recently been measured [5–7] using direct and stepwise laser excitation of the relevant states and detection of the fluorescence. Although the ns and nf states are "well behaved," the np states show, what turns out from the present calculation to be, strong black-body radiation effects, and the nd states show strongly perturbed behavior due to the $3s3p^2$ state.

This paper presents calculations using a method developed to treat alkali-metal-like and alkaline-earth-metal-like systems when the Rydberg series are not strongly perturbed [8–11]. In the present case the method has been augmented to take into account the series mixing in a simple way when that is possible and meaningful. In the following, the bare essentials of the method are outlined and the approach is described which consists of including the effect of channel mixing in simple cases.

The wave functions of the aluminum nl states were obtained by the Coulomb approximation with a central potential core (CACP) method [8], i.e., by direct inward integration of the Schrödinger equation

$$\left[\frac{d^2}{dr^2} - V(r) - \frac{l(l+1)}{r^2} + E_{nl} \right] P_{nl}(r) = 0 , \quad (1)$$

where the central potential $V(r)$ is obtained from a Hartree-Slater-type self-consistent-field calculation where the exchange-term coefficient may be varied to fit experimental energies. The energy levels E_{nl} are obtained from the available experimental term values [12,13] of Al and, where necessary, from extrapolation or interpolation to levels not observed experimentally.

The case of Al is substantially different from that of the alkali metals and their isoelectronic sequences, because the valence electron in the ground state $3p$ and the first excited one $3d$ is not residing in an otherwise empty shell. The $3s^2$ subshell has strong correlations and affect, at least, the lower excited states, the outer orbitals of which penetrate substantially the core. To treat satisfactorily such a system, one must perform a full multiconfiguration, close-coupling, or a configuration-interaction (CI) calculation such as the ones by Weiss [1], Trefftz [14], and Taylor, Bauschlicher and Langhoff [15]. One can, however, attempt to perform an approximate calculation using the polarizability of the core (essentially that of $3s^2$) to represent the correlation and virtual core-excitation effects. To that end, a model potential can be used which, by adjusting its parameters, reproduces the one-electron experimental binding energies. Because from previous experience we found that such a potential sometimes has secondary (presumably spurious) minima, an alternative method was used, whereby a model potential $V(r)$ was obtained from a self-consistent Hartree-Slater-type calculation by varying the coefficient x of the exchange term

$$V_x(r) = x \left[\frac{81}{32\pi^2} \rho(r) \right]^{1/3} \frac{1}{r} \quad (2)$$

TABLE I. Lifetimes (in ns) of the $3s^2ns$ states of aluminum for different temperatures.

State	Present calculation			Expt.
	0 K	300 K	600 K	
$4s$	9.54	9.54	9.54	6.78(6)[a]
$5s$	25.8	25.8	25.8	24(4)[b]
$6s$	55.5	55.5	55.0	52(6)[b]
$7s$	103	102	99.6	99(8)[b]
$8s$	172	169	162	169(17)[b]
$9s$	267	259	245	321(40)[b]
$10s$	392	375	350	462(45)[b]
$11s$	552	521	480	
$12s$	750	700	641	
$13s$	990	949	895	

[a]Reference [24].
[b]Reference [5].

in the Hartree-Slater equation [16,17] so that the $3p$, $3d$, $4s$, and $4f$ orbitals had an eigenvalue equal to the experimental binding energy. The quantity $\rho(r)$ above is the spherically averaged total electronic charge density. The method is, therefore, a variant of the $X\alpha$ approach [17]. The values of the coefficients x were slightly larger than one, x being equal to 1 and $\frac{2}{3}$ for the Hartree-Slater and Hartree-Kohn-Sham approximations, respectively. As noted by Cowan [17], when $x = 1$, Koopmans's theorem holds and the eigenvalue has the physical significance of a binding energy. This is not, however, true for $x \neq 1$. Therefore the above approach is clearly only a practical tool, like a model potential, to provide a physically correct and monotonic potential to describe the core. The higher members of the series for each symmetry, when calculated in the respective potentials, had eigenvalues very close to the experimental binding energies with the largest deviations of about 1% found for the nd states. The above adjustments to the coefficient x resulted in different values for the core radii r_{cl} for each symmetry l. The necessary radial matrix elements were calculated using the expression.

$$\left\langle nl \left| r \left[1 - \frac{\alpha_d}{r^3} [1 - \tfrac{1}{2}(e^{-(r/r_{cl})^3} + e^{(-r/r_{cl'})^3})] \right] \right| n'l' \right\rangle \quad (3)$$

similar to the one used by Norcross [18]. The static polarizability α_d was calculated from the formula

$$\alpha_d = \sum_n \frac{f_{n0}}{(E_n - E_0)^2} = \frac{4}{3} \sum_n \frac{S_{n0}}{[(E_n - E_0)/\mathcal{R}]^2}, \quad (4)$$

where $\mathcal{R}$ is the Rydberg constant and where the sum normally includes the continuum states and gives a lower bound of the actual value when use is made of accurate oscillator strengths f_{n0} and line strengths S_{n0} [19]. As was pointed out by Beck and Nicolaides [19], for alkaline-earth-metal-type atoms and ions the sum converges rapidly. The best values for the line strengths available in the literature [20,21] for the transitions $3s^2 - 3s3p$, $3s4p$, i.e., $S(3s - 3p) = 10.1a_0^2$ and $S(3s - 4p) = 0.0196a_0^2$ from Refs. [20] and [21], respectively, were used to obtain the value $\alpha_d = 24.74a_0^3$. The core radii (matrix-element cutoffs) used were $r_{c0} = 4.197a_0$, $r_{c1} = 3.634a_0$, $r_{c2} = 4.758a_0$ and $r_{c3} = 5.143a_0$. The transition probabilities, oscillator strengths, and lifetimes are obtained using standard formulas [8].

When treating high-lying Rydberg states, their spacing being small, the experimental results are affected by the stimulated emission and absorption of black-body-radiation (BBR) photons from the excited state under study. This effect, which normally depletes the population of the state and shortens the lifetime of a state, was also explicitly included using the standard method [8].

The new element in the present application is the inclusion of channel-mixing effects. To that end, the full wave function of an nd state is written (for the simple case of two interacting configurations) as

$$|3s^2nd\rangle' = \alpha|3s^2nd\rangle + \beta|3s3p^2\rangle, \quad (5)$$

where the mixing coefficients α and β are obtained either from an *ab initio* calculation [1,14,15,22] or from a semiempirical fit of the experimental data, e.g., a fit of the ex-

TABLE II. Lifetimes of the $3s^2np$ states of aluminum (in ns).

State	Present calculation				Expt.
	One-channel CACP	Two-channel CACP			
	0 K	0 K	300 K	600 K	(Ref. [6])
$4p$	66.0	66.0	66.0	66.0	
$5p$	235	242	242	238	
$6p$	508	544	538	486	540(30)
$7p$	868	938	888	739	920(70)
$8p$	1339	1445	1288	1020	1250(70)
$9p$	1934	2080	1749	1343	1520(90)
$10p$	2730	2929	2322	1736	1950(100)
$11p$	3632	3886	2941	2163	2410(170)
$12p$	4769	5093	3696	2682	2880(260)

TABLE III. Lifetimes of the $3s^2nd$ states of aluminum (in ns).

| State | One-channel CACP 0 K | Two-channel CACP | | | W | T | B | Expt. | |
		0 K	300 K	600 K	0 K			Ref. [5]	Ref. [7]
$3d$	6.18	6.22	6.22	6.22	13.6	14.9	14.4	16(3)	14.0(2)
								13.7(4)[a]	12.3(5)[b]
$4d$	48.7	13.2	13.2	13.2	26.6	26.8	17.3	29(4)	29.5(7)
$5d$	151	13.5	13.5	13.5	11.4	12.2	9.19	15(3)	13.2(3)
$6d$	116	18.1	18.1	18.1	13.0	13.7	11.6	17(3)	14.0(2)
$7d$	135	26.9	26.9	26.7	18.3	18.9	21.9	24(4)	21.3(4)
$8d$	177	39.4	39.3	39.1	27.0	27.6	28.3	30(4)	29.3(4)
$9d$	238	53.9	53.7	53.7	35.2	39.9		46(5)	45.7(16)
$10d$	318	66.7	66.4	65.9		53.5		59(6)	60.9(20)
$11d$	419	83.1	82.8	82.3		71.3		75(6)	72.5(20)
$12d$	554	112	112	112		94.5			118(4)

[a]Reference [25].
[b]Reference [26].

perimental energy term values using multichannel-quantum-defect theory and standard fitting techniques [23]. Such a simplified two-channel approach should be dependable for high n, but is not expected to be accurate for lower states were *multi*configuration interactions may be present, as is the case in the Al nd states.

In the present case there are several calculations of the ^2D series and of the percentage in the mixing of the $3s3p^2$ with the $3s^2nd$ states [1,14,15,22]. The work of O'Mahony [22] especially shows the energy dependence of the mixing through the eigenvalue quantum defects that are seen to be strongly energy dependent at the beginning of the Rydberg series. A recent calculation [4], which determines the mixing coefficient by analyzing the measured fine structure of the $3s^2nd$ states in comparison with the fine structure of the perturber $3s3p^2$, disagrees with the recent and extensive close-coupling [14] and CI [15] calculations on the percent mixing over the series. The combined experimental-theoretical values of Ref. [4] for α and β were used for the present calculations. To obtain the appropriate effective quantum numbers n^* for and calculate the $3s3p^2$ component of the wave functions

in Eq. (5), the $3s^2nd$ levels were assumed to be members of the $3s3p(^3P)np$ series with the series limit $3s3p(^3P_0)$ (at 85 671.40 cm^{-1}). As was also discussed by Weiss [1], the $3s3p^2$ component dominates the "character" of the $3s^2nd$ wave functions, even though it does not dramatically affect the energies.

Tables I–IV give lists of the calculated lifetimes along with all the available experimental values and the limited number of previous theoretical estimates, and Figs. 1–3 show graphically the behavior of the lifetimes as functions of the effective quantum numbers and temperature and the comparison with experiments. We discuss the ns, np, nd, and nf series separately because different effects are dominant in each.

$3s^2ns$ series

The members of this series are not perturbed, nor are the members of the np series to which they decay. There-

TABLE IV. Lifetimes of the $3s^2nf$ states of aluminum (in ns).

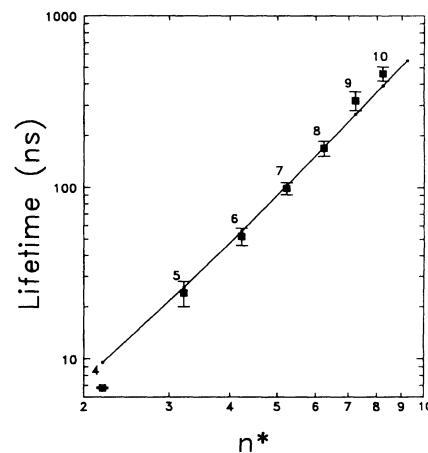| State | One-channel CACP 0 K | Two-channel CACP | | |
		0 K	300 K	600 K
$4f$	56.5	62.0	62.0	61.9
$5f$	103	113	113	112
$6f$	170	186	186	181
$7f$	263	287	284	273
$8f$	386	419	412	391
$9f$	542	588	573	541
$10f$	736	799	774	730
$11f$	972	1054	1028	980

FIG. 1. Lifetimes of states in the ^2S series in aluminum. The experimental points are from Jönsson and Lundberg (Ref. [5]), except for the $4s$ point from Klose (Ref. [24]).
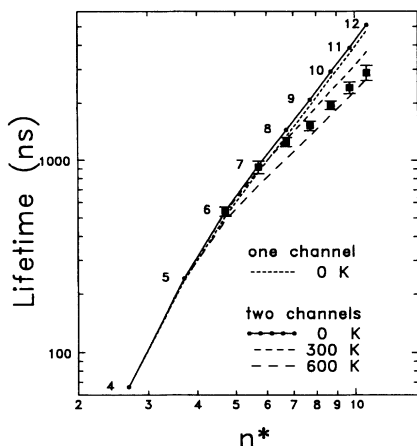
FIG. 2. Lifetimes of states in the ^2P series of aluminum. The experimental points are from Jönsson et al. (Ref. [6]).

fore, one expects a typical n^{*3} behavior for the lifetimes, especially since they are not significantly affected by the ambient black-body radiation. The agreement with the available experimental data of Jönsson et al. [6] is generally satisfactory except for the 9s and 10s states. The experimental lifetimes of these two levels appear to deviate from the general trend and there exists no obvious reason for it. Remeasurement of lifetimes in the higher n values would be desirable. The present calculation disagrees with the older measurement for the 4s state by Klose [24]. Remeasurement of this state would also seem desirable.
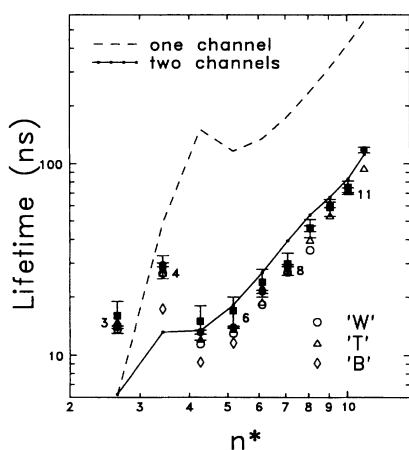
FIG. 3. Lifetimes of states in the ^2D series in aluminum. The experimental points are ■ from Ref. [5] and ● from Ref. [7]. The dashed line represents a "straight" CACP calculation (see text) neglecting the $3s3p^2$ perturbation on the series. The solid line represents the results obtained including the mixing in the simple fashion of Eq. (5). W, T, and B represent calculations performed in the same way except that the transition probabilities for the nd-3p branch were taken from Wiese, Smith, and Miles (Ref. [29]), Trefftz (Ref. [14]), and Taylor, Bauschlicher, Jr., and Langhoff (Ref. [15]), respectively.

$3s^2np$ series

This series is also unperturbed; the lifetimes of its members are affected, however, from the branching to the perturbed $3s^2nd$ series. The $np \rightarrow nd$ transitions are considerably weaker than the $np \rightarrow ns$ ones and the effect may not be noticeable. The slightly nonuniform behavior of the lifetimes at low principal quantum numbers n should be attributed to the perturbation of the nd series. The effect that is very noticeable in the present series is the one due to the ambient black-body radiation, i.e., reduction of lifetimes due to stimulated emission and absorption of black-body-radiation photons. We see that the lifetimes of the upper members of the series are strongly affected by the BBR effect even at room temperature and the lifetime τ versus n^{*3} behavior is clearly not followed. The experimental work of Jönsson et al. [6] does not make clear at which temperature the lifetimes of Al were measured. Therefore, we give in Table II, the lifetimes of this series at 0, 300, and 600 K. The agreement of the experimental values with the calculated ones at room temperature (300 K) is satisfactory, although there is better agreement of the higher levels with the calculation at 600 K. Thus, inclusion of the BBR effect explains the lifetime behavior of this series that departs from the n^{*3} form. This finding, also found for the p states of other systems [8,9], should encourage future reports of experimental lifetimes of p states to quote always the temperature of the atoms during the measurements.

$3s^2nd$ series

As mentioned above, this is the celebrated series that has attracted considerable attention, both experimental and theoretical, because of the "missing" $3s3p^2\,^2D$ level in the observed spectra. The early work of Weiss [1] established that this state strongly interacts with and is spread over the whole $3s^2nd\,^2D$ series. This result was verified by a later analysis by Lin [27] and the more recent ab initio calculations of Trefftz [14] and Taylor, Bauschlicher, and Langhoff [15], although the latter two works disagree on the "position" of the perturber $3s3p^2$. In our calculation the nd states were described as mixtures of pure nd states with the perturber, cf. Eq. (5), and the mixing coefficients were taken from the recent work of Buurman et al. [4]. Table III gives the results both without and with the accounting for the series perturbation. The improvement due to including the series perturbation, even in this simplified way, is striking. The poor results for $3d$ and $4d$ are due mainly to the fact that the effective quantum number alone is not enough to produce accurate wave functions for these two orbitals that are strongly perturbed and, in addition, do penetrate substantially into the ion core. It seems that a full calculation is necessary in this case for an accurate prediction of the two lifetimes. Similar dramatic improvements, using two-channel mixing coefficients from semiempirical or ab initio calculations, were also obtained for the Sr $4snp\,^1P_1$ lifetimes [28].

Faced with the inability of the above method to account in a satisfactory way for the lifetimes of the $3d$ and $4d$ states, and recognizing that the major complication

arises from the "$3s^2nd$"-$3s^23p$ transitions, I used for these transitions the more accurate oscillator strengths available in the literature [14,15,28] and for the rest of the branches I used the transition probabilities obtained by the CACP method outlined above. The results are shown in Fig. 3 and Table III, labeled as W, T, and B when using the "$3d$"-$3p$ oscillator strengths of Wiese, Smith, and Miles [29], Trefftz [14], and Taylor, Bauschlicher, Jr., and Langhoff [15], respectively. With the exception of some of the values obtained using the data of Ref. [15], the agreement with experiment is excellent.

$3s^2nf$ series

Like the np series, this one is only affected through the transitions to the perturbed nd series and this effect is no-

ticeable in the lower members of the series. Since the nf-nd is the dominant branch of decay, the values in Table IV should be considered as tentative. There are no measurements or other calculations available for comparison.

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