Brief Reports

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Three lowest bound states of Mg^-

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We calculate, including many-body effects, that the three lowest bound states of Mg^-, $2p^6 3s 3p^2\,{}^4P$, $2p^6 3p^3\,{}^4S^0$, and $2p^5 3s 3p^3\,{}^6P$, have electron affinities 0.360, 0.514, and 1.321 eV, respectively. The transition $3s3p^2\,{}^4P \rightarrow 3p^3\,{}^4S^0$ is found to have an electric dipole oscillator strength of 0.295. The lifetimes of the $J=\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$, ${}^4P$ levels are estimated to be 7.8, 9.8, and 1.6 ns, respectively.

I. INTRODUCTION

Mg^-, like Be^-, is known to have no[1,2] bound ground state; in both cases core $ns^2np(n=2,3)$ is a shape resonance. Again, like[3,4] Be^-, the lowest bound excited state $nsnp^2\,{}^4P$ has been theoretically predicted[5] to have a positive electron affinity (EA of 0.32 eV). The two other[3,4] bound states in $Be^-[1s^2 2p^3\,{}^4S^0, 1s2s2p^3\,{}^6S^0]$ have been recently conjectured[6] to have counterparts in Mg^- as well.

Yet, on the other hand, recent experimental work has reported no success[7] in observing Mg^-, while Be^- has been[8] seen.

It is the purpose of this article to provide quantitative results for the EA's of the two additional proposed[6] bound states of Mg^- and for the electric dipole oscillator strength connecting two of them (${}^4P \rightarrow {}^4S^0$) as this may provide a means of optically detecting the species, much as was done[9] for Li^-. We also comment on the possibility as to whether other bound states higher in energy and spin ($S \geq \frac{7}{2}$) might exist. Finally, estimates of the lifetimes of the ${}^4P$ levels are provided.

We also note that several recent review articles discussing bound negative ion states exist.[6,10–12]

II. METHOD

We begin with the restricted Hartree-Fock approximation (RHF) implemented with the Froese-Fischer program[13] using the nonrelativistic Hamiltonian. It is well known by now that electron correlation effects can make critical contributions to EA's; Table I will later illustrate that this is also true for Mg^-.

As is explained in considerable detail elsewhere[14–16] the

TABLE I. Energetics for Mg^- and its thresholds.

State	RHF[a]	M-shell correlation[b]	$\epsilon(2p3p)$[c]	EA[d]
$3s3p^3\,{}^4P^0$	−199.546 713	−0.006 411 7	−0.002 416 9	
$3s3p^2\,{}^4P$	−199.550 806	−0.015 506 9	−0.002 474 7	0.360 0.32[e] 0.390[f]
$3p^2\,{}^2P$	−199.384 181	−0.008 603 5	−0.006 541 4	
$3p^3\,{}^4S^0$	−199.390 374	−0.022 508 1	−0.005 438 3	0.514[g]
$2p^5 3s3p^2\,{}^5D^0$	−197.677 429	−0.017 209 8	−0.002 368	
$2p^5 3s3p^3\,{}^6P$	−197.713 304	−0.030 373 4	−0.001 903	1.321

[a]Restricted Hartree-Fock result in a.u.
[b]Correlation energy associated with excitation from the M-shell only in a.u. Includes triple excitations for Mg^-.
[c]Double excitations of the form $2p3p \rightarrow$ in a.u.; calculated in the presence of the M-shell effects.
[d]Electron affinity in eV.
[e]Reference 5.
[f]Reference 6.
[g]Includes the effects of relativity, which lower the EA 0.0034 eV, as computed with the program of J. P. Desclaux [Comput. Phys. Commun. **9**, 31 (1975)].

method used to treat correlation is a perturbation directed configuration interaction theory whose most elemental parts are one-electron functions, i.e., spin orbitals. The adjustable parameters of the method, chosen by the energy variational principle, are the configurational coefficients and the "virtual" radial functions, which are the non-RHF radials needed to complete the radial space. As before, the virtual radial functions are represented, prior to orthogonalization, as single Slater-type orbitals (STO's).

First-order perturbation theory predicts that only those configurations differing from those in the RHF function by single and double excitation are present in the correlation function. For negative ions, however, it has been found[3,4] that at least the most important triple and quadruple excitations must be included as well.

Although this formalism substantially limits the complexity of the correlation function, for a species with more than a few electrons rather extensive computations would be required if excitations were permitted from all the occupied spin orbitals. Based on earlier experience,[4-6,17] it seems that for at least the larger EA (≥ 0.3 eV, say), the error in neglecting differential correlation effects associated with the core electrons ($1s$, $2s$, $2p$ subshells here) is $\leq 15\%$ of the total value of the EA. In Be^-, for example,[4] the core contributed ~ 0.050 eV out of ~ 0.300 eV.

In this work, we shall assume that differential core correlation effects are small. However, as a partial check on this assumption, these effects have been calculated for the $2p3p$ excitations, as these are among those expected to show the largest percentage change in going from atom to ion.

III. ENERGETIC AND OSCILLATOR STRENGTH RESULTS

The M-shell radial basis set used to correlate all six states was a $2s$, $2p$, $2d$, $2f$, $1g$ fully optimized set (i.e., two STO's were used to span the virtual d radial space, etc.). For the negative ions, an extra $1p\,1d$ set was added. No s radials were required in the M shell for the $^4S^0$ and ^3P states. Direct comparison with the results of Weiss[5] shows that for both the $^3P^0$ and ^4P our M-shell total energies are slightly lower (it should be noted our work contains triple excitations, while the former[5] does not).

For the two lowest states of Mg^- and their thresholds, $2p3p$ correlation was computed by enriching the above set (except for $^5D^0$ and ^6P) with $1s$, $1p$, $1d$ STO's localized, finally, somewhere between the L and M shells, and allowing all excitations of the type

$$2p3p \rightarrow s^2 + ss' + v_p^2 + v_p v_p' + v_d^2 + v_d v_d' + s v_d \ ,$$

where s stands for both a virtual s, v_s, and when allowed, the $3s$. These effects are found to contribute $\leq 5\%$ to the total EA (see Table I). It is also of interest to note that if transferability arguments (threshold versus ion) were valid,[14] $2p3p$ correlation would be twice as large in the ^4P as in the $^3P^0$ and $\frac{3}{2}$ as large in the $^4S^0$ as in the ^3P state. As can be seen from the table, the effects are much more nearly comparable, owing to the considerable change occurring in the $3p$ radial function. At some point in the future it may be worthwhile to examine the role of pure L shell correlation ($2l2l' \rightarrow$), on these EA; although percentage changes are expected to be small, the amount of energy is large (> 7 eV).

The electric dipole oscillator strength for the transition $3s3p^2\,^4P \rightarrow 3p^3\,^4S^0$ has been computed using the M-shell wave functions and energies, using our standard methods,[18] which include the effects of nonorthonormality. We obtain 0.299 for the length and 0.291 for the velocity forms of the transition operator.

It is of interest to note that unlike[4] Be^-, the threshold line ($^3P^0 \rightarrow {}^3P$) is not nearly coincidental in wavelength with the $^4S^0 \rightarrow {}^4P$ line. This may ease optical detection.

IV. ON OTHER POSSIBLE BOUND STATES OF Mg^-

It appears generally[6,10,19] that the most favorable term candidates for bound states are those of highest spin (to avoid lower thresholds), and within a fixed S, the highest L, and configurations in which the outermost subshell is multiply occupied. In a few cases, a bound state also can be formed[6] by adding an np electron to a core ns parent of the neutral atom. For a given species (fixed Z,N) subshells of the lowest n (less orthogonality) and l (lower centrifugal barrier) are favored.

We have found that the RHF results are a very useful way to further screen the candidates, in two respects: (1) if after careful extrapolation (decreasing Z by as little as 0.05) the RHF solution cannot be obtained due to difficulties in the solution process,[13] or (2) if the candidate is unbound at the RHF level (i.e., a solution has been found, but it lies above its RHF threshold) by say, ≥ 0.5 eV or more, than it is highly unlikely that the candidate represents a bound (nonrelativistically) state.

As examples, $Mg^- 3s^2 3p\,^2P^0$ did not yield a RHF solution and $Mg^- 3s3p^2\,^2P$ was 1.75 eV above the RHF threshold (the ^2S and ^2D terms of this configuration have Mg $3s^2\,^1S$ as their threshold, and so are obviously unbound). The only other member of the doublet or quartet terms that requires a comment is the $^2S^0$. If bound, this would be associated with the $3p^2 4p$ configuration, with $3p^2\,^3P$ as a threshold; but, no RHF solution could be found.

In the sextets, it appears that only the ^6P is bound ($2p^5 3s3p^2$ as threshold is capable of generating ^6SPDFGH . . . even or odd with addition of a continuum ϵl electron). For the octets, either $1s^2 2s^2 2p^4 3s3p^3 3d\,^8F^0$ or $1s^2 2s^2 2p^4 3s3p^3 4s\,^8P^0$ would appear most favorable; however, no RHF solution for either could be obtained.

For $S = \frac{9}{2}$, $1s^2 2s^2 2p^3 3s3p^3 3d^2\,^{10}F$ appears most favorable, but again a RHF solution could not be obtained. We chose not to investigate $S = \frac{11}{2}$ or $\frac{13}{2}$ as their formation in the laboratory would appear unlikely at present.

V. LIFETIME OF THE ^4P LEVELS

Detection of this species by nonoptical means may well depend critically upon the lifetime of the lowest bound state. We crudely estimate that the lifetime of the $J = \frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ levels are 7.8, 9.8, and 1.6 ns, respectively.

To produce this estimate, which is based on the autoionization golden rule, the initial states were treated within the RHF approximation and the final states at the frozen core[20] level. In addition to neglecting correlation, the effects of nonorthogonality are also absent.

Nonrelativistically, the ^4P levels do not decay. Relativistic decay is introduced by either incorporating relativistic effects

into the wave function or into the Hamiltonian. The $3s^2\epsilon s$ and $3s^2\epsilon d$ channels are then open. Since the latter involves two-electron relativistic effects[21] or correlation plus one-electron relativistic effects, we examine only the former possibility. Here, first-order perturbation theory (FOPT) in conjunction with the one- and two-body spin-orbit, two-body spin-other-orbit, two-body spin-spin operators ($=H_{FS}$) of the low-Z Pauli approximation[22] is used to mix $3s3p^{2\,2}D_{3/2,5/2}$ and $3s3p^{2\,2}S_{1/2}$ into the $3s3p^{2\,4}P$.

Under these conditions, the various lifetime (in sec) τ are found by evaluating the formula

$$\tau=\frac{2.42\times10^{-7}}{2\pi\beta_J^2\langle \text{core}\,3s3p^{2\,2}l_J|H_{nr}|\,\text{core}\,3s^2\epsilon l^{\,2}l_J\rangle^2}\ ,$$

where within FOPT, and the low-Z Pauli approximation, the mixing coefficient is given by

$$\beta_J=\frac{\langle \text{core}\,3s3p^{2\,4}P_J|H_{FS}|\,\text{core}\,3s3p^{2\,2}l_J\rangle}{\langle^2l|H_{nr}|^2l\rangle-\langle^4P|H_{nr}|^4P\rangle}\ ,$$

where H_{nr} is the nonrelativistic Hamiltonian. Except for the $3s^2\epsilon l$ configuration, all matrix elements were computed using the ^4P radial functions. For β_J, we obtained for $^2l_J=^2S_{1/2},^2D_{3/2},^2D_{5/2}$ the values 1.055×10^{-3}, 3.896×10^{-4}, 9.720×10^{-4}, and for the off-diagonal H_{nr} matrix elements, the corresponding values $+0.021\,033$, $-0.050\,95$, and $-0.050\,95$ a.u. It may be noted that the estimate for Be^- $^4P_{5/2}$ using this method is 370 μs. Such short lifetimes may make the species difficult to detect under certain sets of conditions.

A much more thorough treatment of this lifetime and the analogous one in Be^- by C. A. Nicolaides, G. Aspromallis, and the author should be available shortly.

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