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Comment on the dipole polarizability of the Zn^+ ion

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In a recent paper Kompitsas *et al.* [J. Opt. Soc. Am. B **11,** 697–702 (1994)] presented new spectroscopic measurements for the $4snf$ levels in neutral Zn and used these results to deduce a value for the dipole polarizability α_d of the Zn^+ ion. We point out other data sources that are relevant to this determination and present additional analyses and computations that test the value that they reported. In this manner we have obtained the value $\alpha_d(Zn^+) = 15.4 \pm 0.5 a_0^3$, which confirms with reduced uncertainties the value reported by Kompitsas *et al.*

1. INTRODUCTION

In a recent paper Kompitsas *et al.*[1] reported new spectroscopic measurements of the excitation energies of the $4snf$ ($n = 8$–26) Rydberg series in neutral zinc. By coupling the investigation of Ref. 1 with earlier measurements of the ionization potential by Brown *et al.*,[2] Kompitsas *et al.* also deduced the dipole polarizability α_d of the Zn^+ core. This was done with an early and restricted version of the core polarization model as proposed by Van Vleck and Whitelaw,[3] which neglects quadrupole polarization and penetration effects. A comparison was also made with the lower limit of this value deduced from a 1976 lifetime measurement by Andersen *et al.*[4]

We report here an extension of the determination of this quantity made through a variety of additional considerations. First, we have analyzed the data of Ref. 1 together with earlier measurements for lower n by Johansson and Contreras[5] in the context of a more comprehensive version of the core polarization model.[6,7] Studies using this model (Refs. 8–12) have indicated that the quadrupole polarizability α_q, the nonadiabatic correlation β, and the core penetration can strongly affect this analysis and should be considered in a determination of α_d. Second, we used predictions of α_d, α_q, and β for Zn^+ that already exist in the literature[13,14] to estimate these effects and to make comparisons with extracted results. Third, we note that the lifetime measurement[4] cited in Ref. 1 was superseded and substantially revised in a recent measurement by Bergeson and Lawler,[15] which permits an additional test. Fourth, owing to a previously reported[16,17] set of fortuitous cancellations in the $4s$–np oscillator strengths for $n \geq 5$, we show that it is possible to deduce a reliable value for α_d from experimental measurements of the $4p$ lifetimes alone. Finally, we report a value for α_d that is deduced from the lifetime measurements of Ref. 15, existing theoretical computations,[18] and new calculations demonstrating the severity of the cancellation effects. This value is in agreement with the result reported in Ref. 1.

2. CORE POLARIZATION MODEL

For states of sufficiently high principal and orbital angular momentum quantum numbers n and l, the active electron and the passive core are essentially coupled only by central electrostatic interactions, and the term values (freed of magnetic fine-structure and exchange effects by an appropriate configuration average) can be approximated by a model in which the inner electrons are represented by a deformable charged core. Thus, in terms of the excitation energy E_{nl} and the ionization potential IP,

$$\mathrm{IP} - E_{nl} = T_{nl}{}^H + A\langle r^{-4}\rangle_{nl} + B\langle r^{-6}\rangle_{nl}\,, \tag{1}$$

where $T_{nl}{}^H$ is the corresponding energy in a hydrogenlike system,

$$T_{nl}{}^H = R\left(\frac{\zeta}{n}\right)^2\left[1 + \left(\frac{\alpha\zeta}{n}\right)^2\left(\frac{n}{l+1/2} - \frac{3}{4}\right)\right], \tag{2}$$

and $\langle r^{-k}\rangle_{nl}$ denotes the expectation values of the radial coordinate in a hydrogenlike system. Here R is the Rydberg energy and ζe is the net charge of the nucleus and core electrons. In the limit of vanishing penetration of the core (high n and l),

$$A \Rightarrow R a_0 \alpha_d\,, \tag{3}$$

$$B \Rightarrow R a_0(\alpha_q - 6\beta)\,. \tag{4}$$

Here α_d is in units of $a_0{}^3$ and α_q and β are in units of $a_0{}^5$, where a_0 is the Bohr radius.

Analysis of spectroscopic data has traditionally[6,7] consisted of reducing the measurements for IP and E_{nl} to the form

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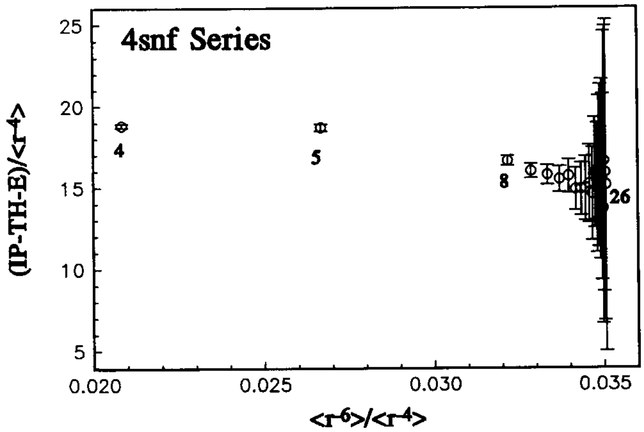

Fig. 1. Plot of y versus x in Eq. (5) for the $4snf$ Rydberg series, with labels denoting specific values of n.

$$y = A + Bx, \tag{5}$$

where

$$y \equiv (\mathrm{IP} - E_{nl} - T_{nl}{}^H)/Ra_0\langle r^{-4}\rangle_{nl}, \tag{6}$$

$$x \equiv \langle r^{-6}\rangle_{nl}/\langle r^{-4}\rangle_{nl}. \tag{7}$$

Thus, if effects of penetration are either absent or independent of n for a given value of l, a plot of y versus x for a single Rydberg series will be nearly linear. However, the values of the intercept A and the slope B tend to vary with l, stabilizing only when penetration effects become totally negligible at a rather high l value.[11] It has been noted[12] that penetration effects tend primarily to distort the quantity B, which has been successfully parameterized by use of an extension of relation (4) of the form[12]

$$B \Rightarrow Ra_0(\alpha_q - 6\beta + f_l). \tag{8}$$

Here f_l is an empirical parameter introduced to account for penetration that is approximately constant for each Rydberg series; f_l decreases with increasing l. Thus the value of B switches from positive to negative as l increases [corresponding to the dominance of the nonadiabatic correlation term β in relation (8)]. Thus, if the determination were based only on spectroscopic data, the values of A and B could be confidently associated with the core polarizabilities only when successively higher values of l yield the same slope and intercept. Unfortunately, spectroscopic data for zinc with $l > 3$ are not currently available, but other nonspectroscopic tests of these results can be made.

3. GRAPHIC EXPOSITION OF SPECTROSCOPIC DATA

A plot of this type for the $4snf$ Rydberg series data from Refs. 1 and 5 and the ionization potential from Ref. 2 is shown in Fig. 1. Labels indicate the points corresponding to $n = 4$, 5, 8, 26. The error bars were obtained from the quoted experimental uncertainties, or, where available, the singlet–triplet splitting. Clearly this plot does not exhibit the linearity that would be expected if the behavior were dominated by core polarization effects, and penetration effects are apparently present in at least some of the points.

The analysis applied in Ref. 1 is equivalent to assuming that B is zero and taking the simple (unweighted) average of the points with $n = 8$–26 (the $n = 4$–5 points are from Ref. 5). Such an analysis would succeed if the penetration correction in relation (8) corresponded for large n to $f_3 \cong 6\beta - \alpha_q = 169a_0{}^5$ (for the theoretical values $\alpha_q = 72.9a_0{}^5$ and $\beta = 40.4a_0{}^5$ from Ref. 14). To test this possibility, we have extended the analysis to the examination of transition probability information.

4. ANALYSIS OF LIFETIME DATA AND CANCELLATION EFFECTS

The recent measurements of the lifetimes of the $4p\,{}^2P_{1/2}$ and $P_{3/2}$ lifetimes in Zn^+ by Bergeson and Lawler[15] provide an independent means for deducing the dipole polarizability of this ion. Moreover, these measurements (2.5 ± 0.5 ns for both $4p$ levels) provide strong confirmation for our earlier semiempirical calculations[18] (2.524 and 2.385 ns for the $4p$ $J = 1/2$ and $J = 3/2$ levels). Reference 18 uses the Coulomb approximation with a Hartree–Slater core (CAHS), which has been found to produce highly reliable results for a wide class of alkalilike systems (see Table 1 of Ref. 19).

Since α_d is connected to the oscillator strengths $f_{4s,np}$ and the np excitation energies E_{np} through the relationship

$$\alpha_d = \sum_n f_{4s,np}(2R/E_{np})^2, \tag{9}$$

a computation based on experimental oscillator strengths that is truncated at some value of n provides a lower limit to α_d. Furthermore, it has been shown[17] that for the Zn^+ system there are almost complete cancellations of the Cooper minimum type for all of the $4s$–np transitions with $n \geq 5$ (see Fig. 4 of Ref. 17). Calculated values for the oscillator strengths for $n = 4$–8 have been published[16] and indicate that the $4s$–np transitions with $n \geq 5$ are several orders of magnitude smaller than the values for $n = 4$.

Table 1 lists CAHS calculations for the $4s$–np oscillator strengths, combining the values for $n = 4$ already reported in Ref. 18 with new calculations for $n = 5$–15 reported here. The calculations for $n = 4$–9 were made with the energy-level measurements of Martin and Kaufman,[20] and the values for $n = 10$–15 are based on a Ritz parameterized quantum-defect extrapolation[7] of the $n = 4$–6 levels (the $n = 7$–9 levels were perturbed by plunging configurations and were not included in the parameterization). Table 1 also lists the excitation energies and the contributions to Eq. (9) for each of these 24 levels. These contributions are then summed to obtain α_d.

Since the contribution from levels with $n \geq 5$ is less than 0.2% and the lifetimes of the $4p$ levels have been measured to within 8%, the experimental uncertainties for this determination are also 8%. However, the CAHS calculations have been confirmed to within 1–2% in many alkalilike systems,[19] so this value is probably reliable to a similar accuracy. A prediction for α_d of $18.1a_0{}^3$ made in Ref. 13 used a simpler version of the Coulomb

Table 1. Ground-State Oscillator Strengths and Excitation Energies of the np series in Zn^+ and Their Relationship to the Dipole Polarizability

Transition	$f_{4s,np}$	E_{np} (cm^{-1})	$f_{4s,np}\,(2R/E_{np})^2$
$4s\,^2S_{1/2}$ to			
$4p\,^2P_{1/2}$	2.5265×10^{-1}[a]	48 481.00[b]	5.1776
$4p\,^2P_{3/2}$	5.1593×10^{-1}[a]	49 355.04[b]	1.0202×10
$5p\,^2P_{1/2}$	2.0628×10^{-5}[c]	101 365.9[b]	9.6704×10^{-5}
$5p\,^2P_{3/2}$	1.2996×10^{-5}[c]	101 611.4[b]	6.0630×10^{-5}
$6p\,^2P_{1/2}$	1.9685×10^{-4}[c]	119 888.51[b]	6.5969×10^{-4}
$6p\,^2P_{3/2}$	2.5831×10^{-4}[c]	119 959.34[b]	8.6463×10^{-4}
$7p\,^2P_{1/2}$	3.2526×10^{-4}[c]	128 518.5[b]	9.4854×10^{-4}
$7p\,^2P_{3/2}$	1.3888×10^{-3}[c]	128 343.44[b]	4.0611×10^{-3}
$8p\,^2P_{1/2}$	4.0555×10^{-3}[c]	132 414.9[b]	1.1141×10^{-2}
$8p\,^2P_{3/2}$	2.7992×10^{-6}[c]	133 622.1[b]	7.5517×10^{-6}
$9p\,^2P_{1/2}$	6.8429×10^{-5}[c]	136 432[d]	1.7708×10^{-4}
$9p\,^2P_{3/2}$	1.6914×10^{-5}[c]	136 447[b]	4.3722×10^{-5}
$10p\,^2P_{1/2}$	4.8099×10^{-5}[c]	138 372[d]	1.2100×10^{-4}
$10p\,^2P_{3/2}$	7.3772×10^{-5}[c]	138 382[d]	1.8557×10^{-4}
$11p\,^2P_{1/2}$	3.4862×10^{-5}[c]	139 713[d]	8.6028×10^{-5}
$11p\,^2P_{3/2}$	5.3907×10^{-5}[c]	139 208[d]	1.3301×10^{-4}
$12p\,^2P_{1/2}$	2.5955×10^{-5}[c]	140 679[d]	6.3171×10^{-5}
$12p\,^2P_{3/2}$	4.0444×10^{-5}[c]	140 684[d]	9.8429×10^{-5}
$13p\,^2P_{1/2}$	1.9851×10^{-5}[c]	141 398[d]	4.7824×10^{-5}
$13p\,^2P_{3/2}$	3.0986×10^{-5}[c]	141 401[d]	7.4649×10^{-5}
$14p\,^2P_{1/2}$	1.5566×10^{-5}[c]	141 947[d]	3.7211×10^{-5}
$14p\,^2P_{3/2}$	2.4244×10^{-5}[c]	141 950[d]	5.7954×10^{-5}
$15p\,^2P_{1/2}$	1.2368×10^{-5}[c]	142 376[d]	2.9389×10^{-5}
$15p\,^2P_{3/2}$	1.9449×10^{-5}[c]	142 379[d]	4.6213×10^{-5}
Total	$\alpha_d = 15.399 a_0{}^3$		

[a] CAHS, Ref. 18.
[b] Ref. 20.
[c] CAHS, this study.
[d] Ritz parameter quantum-defect extrapolation.

approximation, which employed a simple cutoff radius in the core region. This prediction is superseded by these CAHS calculations, which employ a realistic potential in the core region.

Our experimental confidence in the determination of α_d could be enhanced by, e.g., measurements of improved accuracy for the $4p$ lifetimes in Zn^+ or by spectroscopic measurements of energy levels for high l states in neutral zinc. However, a critical examination of available energy-level and lifetime measurements made in the context of the CAHS calculations also provides a high degree of confidence in this determination and leads us to recommend the value $\alpha_d = 15.4 \pm 0.5 a_0{}^3$. This is in excellent agreement with the value reported in Ref. 1 and suggests that quadrupole polarization and nonadiabatic correlation in relation (8) are effectively offset by core penetration effects.

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