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Precision and accuracy of lifetimes of metastable levels using the Kingdon trap technique

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Abstract

The accuracy of measurements of the lifetimes of metastable levels using a Kingdon ion trap technique is discussed with reference to the recent measurement of the transition rate from the excited $2s2p\ ^3P_2$ level of AR XV. Particular attention focused on the aspects of the Kingdon trap technique, which differed from competing alternatives and might apply differently to ground and excited terms. These differences are related to the corrections for quenching of the metastable level by ion–atom collisions, to the possible quenching by Stark mixing due to the higher electric field of the Kingdon trap, and to optical effects associated with the charging of a lens in the light collection system. No significant systematic corrections to present excited level measurements were identified. (Int J Mass Spectrom 192 (1999) 149–155) © 1999 Elsevier Science B.V.

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1. Introduction

Since 1993, four techniques for measuring the lifetimes of metastable levels of ions, especially including ions in high charge states, have been introduced. These techniques include (1) the capture of metastable beam ions from an external ion source operated at low extraction voltage into a Kingdon ion trap, followed by collection of the decay fluorescence [1,2]; (2) the use of a heavy ion storage ring to confine fast metastable ions, with the collection of fluorescence [3,4]; (3) production of metastable ions in the electron beam ion trap (EBIT), with collection of fluorescence after the accelerating potential of the electron beam is switched to a nonexciting value [5]; or (4) with the electron beam switched off completely (the Penning confinement mode) [6,7]. The four techniques are based on the collection of fluorescence from levels of confined ions, which were previously excited, during the evolution of a long motional path in a limited region of space. They rely on the distribution of emitting ions remaining constant during the measurement, low probability for collisional quenching, and some means for isolating the wavelength of the decay of interest. The employment of these techniques has resulted in demonstrable lifetime measurement precisions better than 1%, and in certain cases significantly better [3,4,8], making metastable lifetime measurements competitive in precision with

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some of the best measurements on levels decaying by electric dipole ($E1$) transitions [9,10].

With the high precision now established, the question of measurement accuracy assumes renewed importance. In the case of the storage ring measurements, the precision result for the lifetime of the intercombination $E1$ transition from the $2s2p\ ^3P_1$ level to the ground state of Be-like C [4], which agrees with several recent detailed calculations [11,12], provides evidence of accuracy as well. Further, the measured lifetime of the He-like intercombination magnetic dipole ($M1$) transition from the C V $1s2s\ ^3S_1$ level to the ground state [3] agrees with the theory of Johnson et al. [13] within the measurement uncertainty of 0.13%. Two other measurements made on this same transition, but in different charge states, using EBIT [5,8] also agree with this same theory, with the O VII measurement having about 0.5% uncertainty. The agreement of similar measurements on different charge states with well-developed theory lends weight to the accuracy of both techniques near these levels of precision.

In this article, factors possibly affecting the accuracy of measurements in the Kingdon ion trap are considered. The accuracy of measurements using this trap was initially established by comparing several measurements with earlier independent measurements using similar techniques [14], and with theory. Unfortunately, in cases other than ions with fewer than five electrons, the theory, even for $M1$ transitions, is not thought to be accurate to better than about 10%. Earlier measurements of metastable lifetimes typically were limited to ions with one or two units of charge, with the results having typically 5% uncertainties [14].

Using captured highly charged ions, measurements of the lifetime of the $2p^5\ ^2P_{1/2}$ level of Ar X, measured in different Kingdon traps [1,15], and using different techniques to account for quenching, were found to agree within 2%. This demonstrates that measurements using similar, but different, traps are precise and reproducible, although still not necessarily accurate. A measurement [15] of the lifetime of the Ar XI $2s^22p^4\ ^3P_1$ level, with about 7% precision, agreed with three calculations well within the measurement uncertainty. An intercomparison of current data with results for the Ar XIV $2s^22p^2\ ^2P_{3/2}$ level lifetime, measured with a 2% uncertainty in the Kingdon trap [16], and also measured using EBIT [17] is now possible. Unfortunately, in this case the precision of this EBIT measurement is only about 5%. The lifetimes obtained with the two different trap types agree within this level of uncertainty. Theoretical decay rates for this level are 106.8 s^{-1} from a nonrelativistic calculation, and 104 s^{-1} from two relativistic calculations [16]. If it is assumed that the theoretical results for the decay rate of this level are accurate to within 2%, then the accuracy of the Kingdon trap technique would also be established within about 2%. To summarize, the accuracy of the Kingdon trap technique is at this point less well-established than the accuracies of the competing methods. Two main features distinguishing the Kingdon trap technique from the other techniques are the relatively high electric field associated with the ion confinement using the present apparatus, and the methods associated with corrections for collisional quenching.

Recently, Kingdon trap measurements of the decay rate of the Ar XV $2s2p\ ^3P_2$ level were published [16]. This level decays primarily by a $M1$ transition to the $^3P_1$ level, with the magnetic quadrupole ($M2$) decay to the ground state contributing near the 1% level, and with the electric quadrupole ($E2$) transition rates to lower P levels negligible. The experimental decay rate was found to lie about 15% (nearly 3 standard deviations σ of the experimental error) higher than two non-relativistic [18,19], and one relativistic [20], calculations. This experimental result has been questioned by Safronova and Johnson [21], who believe that the theory for both the $M1$ and $M2$ transitions is accurate to within a few percent. This opinion is supported by a new relativistic multiconfiguration Hartree–Fock-configuration interaction (MCHF-CI) calculation, based on the complete set of basis states created from the single-particle core orbitals. This calculation includes many more relativistic configurations than the earlier relativistic calculation by Idrees and Das [20]. A lowest order decay rate of 73 s^{-1} is obtained before the Breit and quantum electro-

dynamic (QED) corrections are included as first order perturbations, but the final result gives a spontaneous transition rate of 62.7 s^{-1}, in excellent agreement with the previous relativistic and nonrelativistic results.

Experimental inaccuracy at the 3σ level, although not statistically unreasonable, appears improbable enough in the light of the theoretical agreement to make useful a further consideration of the experimental technique, to ascertain if possible systematic effects associated with this particular measurement may come into play.

2. Experimental technique

With the present Kingdon trap technique, ion charge states and excited metastable levels are produced together in an electron cyclotron resonance ion source (ECRIS) [2]. The ions are extracted from the source and analyzed on a charge-to-momentum basis using an electromagnet. The analyzed ions are slowed as they enter the Kingdon trap, and are captured by pulsing the potential of the central wire to a low value relative to the potential of the cylinder and end electrodes (see Fig. 1). The present trap has a cylinder diameter $2a = 7.62$ cm, a length $L = 7.62$ cm, and a wire diameter $2b = 0.06$ mm. Once captured, the ions orbit in the confining potential. Near the trap midplane, this potential can be approximated as (neglecting end effects) $V(r) = V_0 \ln(r/b)/\ln(a/b)$, plus the space charge of the confined ion cloud. Since the trap is relatively large, with a volume exceeding 300 cm^3, and since the confined ion number usually does not exceed 3×10^7 (depending on the current from the ion source), the ion density is $\leq 10^5$ cm^{-3}. For the Ar XV measurement, the density calculated this way was $<10^3$ cm^{-3}. This low density, associated with the relatively high ion kinetic energy, means that the probability for ion-ion collisions is small, even for high charge states. This means that ion–ion collisions are not responsible for significant relaxation of the stored ion cloud during a measurement, even when the ion number is changing because of electron transfer collisions with residual gas. When the ions are initially confined, a short transient with a time

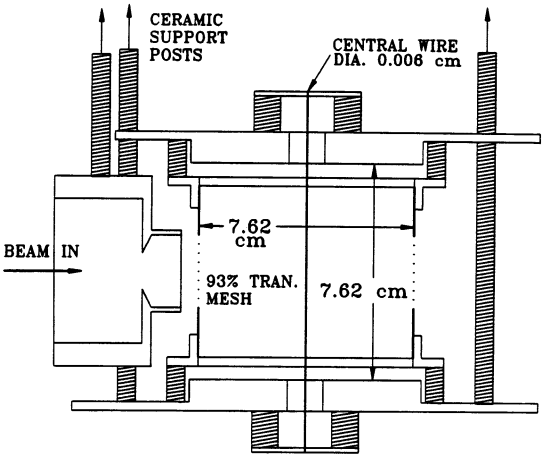

Fig. 1. A section of the Kingdon ion trap used for the Ar XV lifetime measurement. The cylinder, central wire, final ion lens and trap support structure are shown. The cylinder electrode is perforated by apertures covered with a highly-transmitting mesh. The ions are decelerated between the lens on the left and the cylinder, as they enter the trap. A Faraday cup mounted behind the aperture on the right collects transmitted ions. Fluorescence from the metastable levels is collected using a quartz lens mounted just behind a perpendicular aperture. A CaF_2 plate and a biased grid protect the lens from optical effects associated with charging.

constant near 1 ms is observed in all fluorescent decays. This is interpreted as due to ion settling in the trap, but in view of the long ion–ion collision time constant, settling is probably associated with the prompt loss of ions with marginally stable orbits. Following this transient, ion fluorescence from a metastable level of an ion of Mn, which was not susceptible to cascading, has been observed to decay with a single exponential behavior over at least six decay constants [2]. This demonstrates that the spatial distribution of ions from which the fluorescence is collected remains constant, at least when electron capture collisions are rare.

Ion–molecule electron capture collisions, which destroy the ion charge state, are a major quenching mechanism for multiply charged ion metastable levels in a vacuum environment. The charge transfer rate increases linearly with ion charge q, but is not strongly energy dependent for the ion energies considered here. The product ions from these multiply charged ion electron transfer collisions are not significantly confined in the Kingdon trap. This conclusion

arises from the following observations and logic. To detect the trapped ions, the wire potential is allowed to rise adiabatically back to the cylinder potential at the end of the measurement cycle. Some ions emerge from an aperture in the cylinder wall as the confining potential drops, and are accelerated to a microchannel plate (MCP) ion detector. There is no charge or mass selection employed. The area under the signal pulse is quantified and measured versus ion storage time. If all product ions from electron capture were confined, and proportionally detected, the observed signal would increase with time. However, it is unlikely that slow charged product ions will have sufficient angular momentum to be stably confined. But if only fast charged product ions were confined, the signal would still remain constant with storage time. Since the decrease in ion number with storage time is well-fitted with a single exponential, this implies that few product ions are stored, and hence that the measured storage time constant is related to the charge transfer rate. This conclusion is in accord with the measured magnitudes of the ion storage time constants and electron capture rates at a known residual gas pressure [22]. Some fast product ion storage is nevertheless theoretically possible [23].

The correction to the measured lifetime of the metastable level τ_m, due to electron capture collisions, to obtain the experimental lifetime τ_e, is given by the relation $\tau_e^{-1} = \tau_m^{-1} - \tau_s^{-1}$, where τ_s is the measured storage time constant of the ion cloud, limited by electron capture collisions. Note that this is a simplified approach applicable primarily to cases where the ion storage time constant is much longer than the level lifetime. In the original Kingdon trap measurements, the quenching of the decay was measured at several pressures, and extrapolated to zero pressure [1,15]. For the Ar XV measurements, the ion beam had poor stability, and the ion storage time constant was measured to be $\tau_s = 307(34)$ ms. A measurement of the stored Ar^{14+} decrease is shown in Fig. 2. In other research, carried out in superior vacuum, storage time constants as long as 2.5 s were measured [2]. The argument made in the previous paragraph was used to associate level quenching with ion charge-state changing. The quenching correction in the present

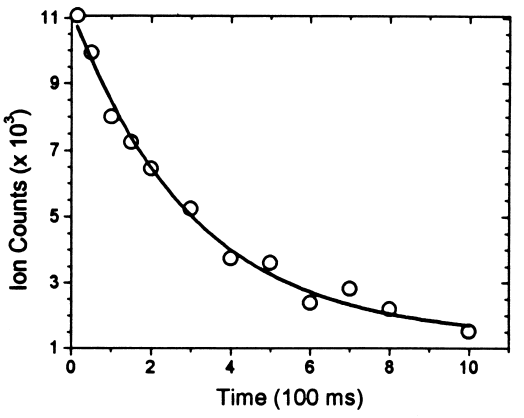

Fig. 2. A measurement of the decay of the captured Ar^{14+} ions with storage time is shown. Ions released from the trap at the end of the variable storage interval were counted using a multichannel plate detector.

case was relatively large due to a higher residual pressure of argon gas. The correction is comparable to the uncertainty in the level lifetime measurement.

In all previous measurements of the lifetimes of metastable levels using the present Kingdon trap technique, the levels were in the ground terms of the ions. The Ar XV $2s2p\ ^3P_2$ level is in an excited term, and so deserves special consideration. At very low ion energies, and low charge states, ions in metastable levels can have significantly higher electron capture rates from neutrals than ground state levels [24], since the metastable level wave function extends farther from the nucleus. This effect results in different avoided crossings of the potential surfaces of the quasimolecule formed during the collision, which can lead to higher capture rates. If τ_s were reduced for excited states, compared to ground states, in the Ar XV measurement, the effect would not be apparent in the ion storage time data, since only about 5% of the ions were in excited metastable levels, and the storage time data uncertainty was near 10%. Opposing this possibility, the probability of a different electron capture rate for metastables is reduced for higher ion charge states, since the metastable excitation becomes a much smaller fraction of the total potential energy involved in the collision. The effect is also reduced in higher kinetic-energy collisions for the same reason.

In the absorbing sphere model [25], which applies to the kinetic energy range of the ions studied here, only the binding energy of the target atom electron enters the calculation. The wave functions of the populated lower ion levels occupy a smaller volume because of the relatively high nuclear charge, whereas the capture radius for Ar^{14+} is near 8×10^{-8} cm [26]. Thus, a hypothesized different quenching rate due to electron capture collisions to Ar XV ions with metastable $^3P_2$ levels, rather than ground state levels, appears unlikely.

In the Landau-Zener model of electron capture, at a particular avoided crossing the capture probability peaks when the probability of an electron jump becomes $\frac{1}{2}$. Thus there could be a significant number of close collisions which do not result in electron capture, but could perturb the excited metastable level, resulting in quenching. When an additional quenching time constant τ_q is added as a correction, the revised equation for the experimental lifetime becomes $\tau_e^{-1} = \tau_m^{-1} - \tau_s^{-1} - \tau_q^{-1}$. If this equation is used, in order to reduce τ_e to the mean of the theoretical values, τ_q must have a magnitude near 100 ms, or about $\tau_s/3$. This is the minimum time constant that would be possible, consistent with a single Landau-Zener avoided crossing. However, in the spirit of the absorbing sphere model, many avoided crossings are hypothesized for the levels of ions in high charge states making collisions with neutrals, that make electron capture essentially inevitable in a single collision. Consequently, a significant amount of quenching, in collisions without electron capture, also seems unlikely.

A further consideration is the comparatively large electric field employed in the present Kingdon trap technique. The Stark effect could mix the $2s2p\ ^3P_2$ metastable level with close-lying higher levels which decay promptly by $E1$ transitions, effectively decreasing the lifetime of the metastable level. The maximum field $E_{max} = V_0/b\ \ln(a/b) = 6 \times 10^6$ V/m at the central wire, but the field drops linearly with distance from the wire. If a hypothetical eccentric orbit with a closest approach to the wire near $10b$ is assumed, then a mean field over the ion orbit of about $\langle E \rangle = 3 \times 10^5$ V/m seems to be a reasonable estimate. The first-order perturbation $\Psi_k^{(1)}$ to the wave function Ψ_k can be written in terms of unperturbed wavefunctions Ψ_m as

$$\Psi_k^{(1)} = \Sigma_m\,[H_{mk}/(U_k - U_m)]\Psi_m \tag{1}$$

where U denotes the unperturbed level energy and $H_{mk} = E\langle\Psi_m|ez|\Psi_k\rangle$ is the perturbation due to the mean electric field E. The matrix elements mix levels of opposite parity only. Since the $2s2p\ ^3P_2$ level has odd parity, the lowest-lying even parity levels with $J = 1$, 2, or 3 are the $2p^2\ ^1D_2$ level and the $2p^2\ ^3P_J$ levels. These levels have energy separations from the $2s2p\ ^3P_2$ level near 2 a.u. All $n = 3$ levels have energy separations about a factor of 10 larger. The new matrix elements used to compute the perturbed transition rate are given by

$$|\langle M1\rangle_{12}|^2 = |\Sigma_k(\langle\Psi_k|M1|\Psi_2\rangle + E\Sigma_m a_m\langle\Psi_k|E1|\Psi_m\rangle)|^2 \tag{2}$$

where the subscripts 1 and 2 denote the $^3P_1$ and $^3P_2$ (odd parity) levels and $M1$ and $E1$ denote the type of decays. The coefficient $a_m = \langle\Psi_m|E1|\Psi_k\rangle/(U_k - U_m)$, from Eq. (1). In the sum over k, only the term with $k = 1$ results in a matrix element which, when squared, has a term linear in the electric field E, and hence potentially large, since only for $k = 1$ are both terms in Eq. (2) nonzero. The calculations of the contributions to the perturbing terms are summarized in Table 1. Assuming that the mean electric field has the magnitude of 3×10^5 V/m $\approx 6 \times 10^{-7}$ a.u., the ratio of the difference between the perturbed and

Table 1
Calculations of the contributions of even parity levels to the magnetic dipole matrix element for the transition from the $2s2p\ ^3P_2$ level of Ar XV perturbed due to Stark mixing; relative level energies and matrix elements are in atomic units (a.u.)

Level m	$\langle\Psi_m\|E1\|\Psi_1\rangle \times 10^2$	ΔU_m (a.u.)	$\langle\Psi_1\|E1\|\Psi_m\rangle \times (10^2)$
$2p^2\ ^3P_1$	17.47	1.659	17.59
$2p^2\ ^3P_2$	30.06	1.720	−23.03
$2p^2\ ^1D_2$	5.476	2.024	−1.322
$2s3s\ ^3S_1$	6.070	16.818	−5.976
$2s3d\ ^3D_1$	3.297	17.581	16.38
$2s3d\ ^3D_2$	−12.76	17.584	−28.40
$2s3d\ ^3D_3$	−30.18	17.589	−1.018

unperturbed matrix elements to the original matrix element is about 10^{-5}, a minor change. This shows that the perturbation of the $^3P_1$–$^3P_2$ $M1$ decay rate, by electric fields even much higher than presently used, will be negligible. Consequently, in a general measurement, the Kingdon trap technique should not be less effective for excited levels, than for ground term metastable levels.

Another characteristic of the present Kingdon trap technique is that there is a possibility of charging of the quartz light collection lens, which is mounted close to the trap. The subsequent delayed discharging was observed to occur with a time constant up to eight milliseconds, and is thought to be associated with small sparks [27], which emit broadband radiation observed in the visible region of the spectrum. This observation is pertinent, since the $2s2p\ ^3P_1$–$^3P_2$ transition of Ar XV occurs near 593 nm. Because of the relatively low population of the $2s2p\ ^3P_2$ level, effects of this type on the decay would be magnified. Before the measurement, charging effects were suppressed by placing a CaF_2 plate, which has a higher conductivity than quartz, before the lens; by biasing a grid before the lens to suppress ion impact; and by pulsing the ion beam so that ions pass through the trap only for about 100 μs, when the central wire is pulsed to capture the ions [2]. Tests showed that these procedures removed the effect. During the Ar XV measurements, no background was observed at 440, 550, or 640 nm. Also, contemporaneous measurements on the 442 nm transition from the $2s^22p\ ^2P_{3/2}$ ground term level of Ar XIV agree well with theory and an independent measurement (see previous discussions).

In view of the conclusions, the best remedy to address the discrepancy between existing theory and measurement for the Ar XV $2s2p\ ^3P_2$ level appears to be an independent measurement. Steps toward this goal are in progress.

3. Summary

Possible systematic effects that might degrade the accuracy of metastable level lifetime measurements on excited ions captured into a Kingdon ion trap have been discussed and approximately evaluated. Particular attention was devoted to the excited $2s2p\ ^3P_2$ level of Be-like Ar XV. Theoretical lifetimes for this level were thought to be accurate to about 2%, and an improved relativistic calculation which agrees with earlier calculations for this level is presented. Recent Kingdon trap measurements differed by about 3 standard deviations of the experimental error from the theoretical lifetime results. Through examination of the characteristics of the Kingdon trap technique, differences from other techniques were noted to be in the method of correcting for collisional quenching of the excited level during the measurement, in the higher electric field associated with Kingdon trap operation, and in the observation of charging effects on the optical system employed (where corrective action was taken). Examination of these differences indicate that electric field effects and possible errors in the collisional quenching correction cannot be clearly identified with any systematic effect of sufficient magnitude to affect measurement accuracy. Charging effects resulting in a spurious optical signal were corrected. Thus, the discrepancy between present theory and experiment remains unexplained. The major differences between this Ar XV measurement and other measurements in the Kingdon trap are a lower data collection rate due to the excited state, poorer ion beam stability, and worse vacuum. These were thought to be accounted for in the statistical error of the measurement. At this point, a second experimental measurement, preferably by a different technique, appears to be the best way to address the present discrepancy.

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References

[1] L. Yang, D.A. Church, Phys. Rev. Lett. 70 (1993) 3860.
[2] D.P. Moehs, D.A. Church, R.A. Phaneuf, Rev. Sci. Instrum. 69 (1998) 1991.
[3] H.T. Schmidt, P. Forch, M. Grieser, D. Habs, J. Kenntner, G. Miersch, R. Repnow, U. Schramm, T. Schuessler, D. Schwalm, A. Wolf, Phys. Rev. Lett. 72 (1994) 1616.
[4] L. Doerfert, E. Traebert, A. Wolf, D. Schwalm, O. Uwira, Phys. Rev. Lett. 78 (1997) 4355.
[5] B.J. Wargelin, P. Beiersdorfer, S.M. Kahn, Phys. Rev. Lett. 71 (1993) 2196.
[6] P. Beiersdorfer, L. Schweikhard, J. Crespo Lopez-Urrutia, K. Widmann, Rev. Sci. Instrum. 67 (1996) 3818.
[7] F.G. Serpa, C.A. Morgan, E.S. Meyer, J.D. Gillaspy, E. Traebert, D.A. Church, E. Takacs, Phys. Rev. A 55 (1997) 4196.
[8] J. Crespo Lopez-Urrutia, P. Beiersdorfer, D.W. Savin, K. Widmann, Phys. Rev. A 58 (1998) 238.
[9] D. Marger, H. Schmoranzer, Phys. Lett. A 150 (1990) 1996.
[10] J. Jin, D.A. Church, Phys. Rev. A 49 (1994) 3463.
[11] J. Fleming, A. Hibbert, R.P. Stafford, Phys. Scr. 49 (1994) 316.
[12] C. Froese Fischer, Phys. Scr. 49 (1994) 323.
[13] W.R. Johnson, D.R. Plante, J. Sapirstein, Advances in Atomic and Molecular Physics, B. Bederson and H. Walther (Eds.), Academic, San Diego, 1995, Vol. 35, p. 255.
[14] D.A. Church, Phys. Rep. 228 (1993) 254 (see especially Refs. 247 and 248 in this article).
[15] L. Yang, D.A. Church, S. Tu, J. Jin, Phys. Rev. A 50 (1994) 177.
[16] D.P. Moehs, D.A. Church, Phys. Rev. A 58 (1998) 1111.
[17] F.G. Serpa, J.D. Gillaspy, E. Traebert, J. Phys. B: At. Molec. Opt. Phys. 31 (1998) 3345.
[18] A.K. Bhatia, U. Feldman, J.F. Seely, At. Data Nucl. Data Tables 35 (1986) 449.
[19] V. Kaufman, J. Sugar, J. Phys. Chem. Ref. Data 15 (1986) 321.
[20] M. Idrees, B.P. Das, J. Phys. B: At. Mol. Opt. Phys. 22 (1989) 3609. Upward transition rates for Ar XV were incorrectly presented in [16]. Correcting for the statistical weights, the calculated decay rate for the Ar XV $2s2p\ ^3P_2$ level is 63 s^{-1}.
[21] U. Safronova, W. Johnson, private communications, 1998.
[22] D.A. Church, L. Yang, S. Tu, Phys. Rev. A 50 (1994) 3151.
[23] C.E. Johnson, J. Appl. Phys. 55 (1984) 3207.
[24] D.A. Church, H.M. Holzscheiter, Phys. Rev. A 40 (1989) 54.
[25] R.E. Olson, A. Salop, Phys. Rev. A 14 (1976) 579.
[26] G. Weinberg, B.R. Beck, J. Steiger, D.A. Church, J. McDonald, D. Schneider, Phys. Rev. A 57 (1998) 4452.
[27] W.S. Bickel, private communication, 1994.