Physical state effects on the mean excitation energy of water as determined from α particle stopping-power measurements

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Recent measurements of the stopping powers of liquid water and water vapor for 2.0-to 5.5-MeV α particles have been analyzed with Bethe-Bloch theory including a Barkas-effect correction term in order to extract mean excitation energies reflecting the two physical states of the target substance. The resulting value of the mean excitation energy of liquid water, 68 eV, exceeds that characteristic of water vapor by about 13%. Although the difference in values is consistent with expectation in both magnitude and direction, the mean excitation energy of liquid water lies some 10% below a recent theoretical prediction.

I. INTRODUCTION

Measurements of the stopping powers of liquid water and water vapor for α particles have recently been made in an attempt to discern physical state effects.[1] Since the projectile energies lay within the interval of validity of Bethe-Bloch theory, preliminary calculations were performed so as to compare predictions of the theory with the measurements in a general sense. The purpose of the present study was to provide a detailed analysis of the data with Bethe-Bloch theory[2] modified by inclusion of a low velocity projectile-z^3 correction term[3-5] and the Bloch projectile-z^4 correction term.[6] The method of analysis employed was essentially that of a recent investigation of the stopping power of polystyrene for 2.2- to 5.9-MeV protons, where two parameters of the theory were simultaneously extracted from fits to the measurements.[7]

The theory of the stopping power of matter for charged particles is not complete. Even when the target material is an element, several parameters in the Bethe-Bloch formula cannot be calculated from first principles except for a few cases of very low atomic number, Z. Consequently, the various parameters are often determined by fits of theory to experimental data insofar as feasible. Unfortunately, when there are two or more parameters to be thus determined, the accuracy of extant measurements rarely supports the extraction of a unique set of values. Aggregation effects serve to

exacerbate the problem. Indeed, whenever one must treat a molecule of a given target element as a composite of its constituent atoms, one must deal with aggregation effects.[8] Further complicated ramifications of the problem are posed by mixtures and compounds, and by differences between vapor and condensed states of a particular material. The initial approach to management of aggregation effects in mixtures and compounds is to invoke the tenuous rule called "Bragg's rule of additivity,"[9] and to define appropriate averages for use in the Bethe-Bloch formula.[10] The situation for both types of aggregation effects has been reviewed recently.[11] The projectile-z^3 correction term for composite target materials[3,4] was incorporated into a general computer code designed for analysis of measurements[12] some time ago.[13] The same code was subsequently modified to include the Bloch projectile-z^4 correction term,[6] and applied to the aforementioned study of polystyrene.[7] The present investigation represents an attempt to characterize physical state effects for a given compound by means of different values of one important parameter of the theory known as the mean excitation energy.

II. METHOD AND RESULTS

The formalism utilized was essentially that described previously.[7] However, a minor controversy has developed over the correct form of the

projectile-z^3 correction term to be included in the Bethe-Bloch formula. When Lindhard reintroduced the Bloch term,[6] he suggested retention of the Ashley et al. z^3-effect term,[3-5] but with a multiplier of value somewhat less than 2.[14] An alternative selected by Ritchie and Brandt was to revise[15] the recommended values of the single free parameter of the formalism[3-5] upon inclusion of the z^4 term and fitting of some recent accurate measurements.[16] The Lindhard suggestion[14] has been quite literally implemented in a few cases[17,18] whereas another analysis[7] has followed the Ritchie and Brandt example. Still another analysis of three independent sets of data has explored the consequences of both the former[19] and latter[20] suggestions. The present study was undertaken with the intent to try both approaches[14,15] to the z^3-correction term. The method employed was to fix all but two of the parameters appearing in the modified Bethe-Bloch formula[7] and to search simultaneously for the remaining pair.

In order to minimize the number of parameters whose values were ill known at the outset, only those measurements taken with α particle projectile energies above 2.0 MeV were included in the analysis. (These data appear in Table I.) This measure precluded use of a charge-state parameter[2,21] whose evaluation for α-particle projectiles traversing low-Z targets proved most difficult in an earlier study.[22] Shell corrections were obtained for the K and L shells of the water molecule from

theoretical calculations[23] and the molecule simulation described previously.[7] The notation of Ref. 7 will be followed herein. Thus only three parameters were subject to evaluation through fits to the data[1]: the mean excitation energy I; the free parameter of the projectile z^3-correction term, b; and the multiplier of the z^3-correction term, ξ. Initially ξ was fixed at 1.0 and the two parameters I and b were varied simultaneously in order to find best-fit values, as established by attainment of a minimum in the root-mean-square relative deviation of calculated from measured stopping-power values, σ. In the case of liquid water σ achieved a minimum value of 0.27 for $I = 64.7$ eV and $b = 2.32$, but in the case of water vapor the minimum value of σ of 0.62 occurred for $I = 52.0$ eV and $b = 19.4$. Yet b, a composite parameter of the projectile-z^3 effect formalism,[3-5] is a product of three parameters of the statistical model of the atom, essentially independent of target atomic number, so that plausible values are roughly of order unity. Whereas the value of b initially recommended[3-5] on the basis of fits to accurate measurements was 1.8 ± 0.2, the number was revised to 1.4 ± 0.1 upon inclusion of the Bloch term.[6] An independent study[20] of earlier analyses[22,24] led to a recommendation of $b = 1.3 \pm 0.1$ for seven elements with atomic numbers in the closed interval, [13,79]. In another analysis,[7] of the stopping power of polystyrene for 2.2 to 5.9 MeV protons, the value of b extracted from the measurements

TABLE I. Measurements of the stopping power of water in both liquid and vapor phases for 2.0−5.5-MeV α particles, from Ref. 1.

| E_α(MeV) | Liquid water | | Water vapor | |
	S(MeVcm^2/g)	ΔS(MeV cm^2/g)	S(MeVcm^2/g)	ΔS(MeVcm^2/g)
2.00	1598	43	1652	16
2.25	1504	38	1548	15
2.50	1418	35	1458	15
2.75	1337	35	1381	14
3.00	1267	33	1310	13
3.25	1207	33	1250	12
3.50	1150	33	1194	12
3.75	1107	33	1143	11
4.00	1066	37	1100	11
4.25	1036	43	1060	11
4.50	1016	60	1023	10
4.75	1003	100	990	10
5.00			960	10
5.25			929	9
5.48			906	9

was 1.90 ± 0.05. Thus the best-fit value of b obtained from the water-vapor data $b=19.4$ was rejected as a value reflecting shortcomings in the theory or errors in the measurements or both. The experimental measurement techniques have been tested on other gases, showing good agreement with other published results.[25] For the particular case of water vapor, the presence of dimers has been discussed as a cause of discrepancies between theory and experiment.[26]

The next step was to fix the value of b at 1.90—the result obtained in the aforementioned analysis[7] of polystyrene data— and to search simultaneously for the best-fit values of I and ξ. Liquid-water measurements yielded $I=63.4$ eV with $\xi=0.58$ and $\sigma=0.27$, whereas corresponding results for water-vapor data were that $I=49.8$ eV with $\xi=-0.29$ and $\sigma=0.60$. Since the Lindhard suggestion[14] places ξ at a value somewhat less than 2 and the Ritchie and Brandt prescription[15] leaves ξ at 1.0, it seemed eminently reasonable to exclude negative values of ξ from fits to the measurements. Hence only the liquid-water results were acceptable in this facet of the study, too. Results of the analysis to this point appear in Table II.

In view of the difficulties encountered with the water-vapor data, in particular, in the foregoing approaches, yet another gambit was employed. The value of b was permanently set at 1.90, and a best-fit value of I was sought for several trial values of ξ within the interval of plausibility. Results of these searches are displayed in Table III, where σ achieves a minimum for $\xi=0.58$ in the case of liquid water but achieves no minimum in the permitted ξ interval in the case of water vapor, as discovered in the previously described two-parameter fits. The significance of the present approach lies chiefly in provision of an I-ξ grid for both physical states of water. The difference between I values for liquid and vapor cases, increasing monotonically with increasing ξ, averages about 8 eV for the ξ values shown. A good compromise selection for ξ appears to be about 1.0, in agreement with the Ritchie and Brandt approach.[15]

The measurements currently analyzed will support the simultaneous determination of at most two parameters, and even so not with unambiguous results. The source of this difficulty resides in the nature of both ξ and b, which are parameters characteristic of a generally small correction term. However, the results of the present investigation were unacceptable in both the I-ξ and I-b searches with water-vapor data, whereas the less accurate liquid-water measurements furnished plausible values of the searched parameters in both searches. The compelling reason for selecting the $\xi=1.0$ compromise is the fact that for water vapor σ decreases monotonically with decreasing ξ in the interval studied. Although σ reaches a minimum actually at $\xi=0.58$ for liquid water, the compromise choice comforms to one of the two major approaches[14,15] to the z^3-effect inclusion. Moreover, an attempt to accommodate the Lindhard suggestion[14] by fixing ξ at 2.0 apparently would drive b to implausibly high values.

III. CONCLUSIONS

Measurements of the stopping power of water[1] for α particles yield mean excitation energies which reflect the physical states of the target. The mean excitation energy for liquid water thus estab-

TABLE II. Results of two-parameter searches, I and b or I and ξ, for both phases of the water target. I represents the mean excitation energy, b the free parameter of the z^3-effect formalism, ξ the amplitude of the z^3-correction term, and σ the root-mean-square relative deviation of calculated from measured stopping powers. (The underlined quantity is that one fixed for a particular search.)

Target	Phase	I(eV)	b	ξ	σ
H_2O	Liquid	63.4	1.90	0.58	0.27
		64.7	2.32	1.00	0.27
H_2O	Vapor	49.8	1.90	−0.29	0.60
		52.0	19.4	1.00	0.62
		52.6	8.36	2.00	0.62

TABLE III. Results of one-parameter searches, with b (the free parameter of the z^3-effect formalism) fixed at 1.90. I represents the mean excitation energy, ξ the amplitude of the z^3-correction term, and σ the root-mean-square relative deviation of calculated from measured stopping powers.

Target	Phase	ξ	I(eV)	σ
H_2O	Liquid	0.5	63	0.28
		1.0	68	0.29
		1.5	74	0.38
		2.0	80	0.49
H_2O	Vapor	0.5	56	0.92
		1.0	60	1.38
		1.5	65	1.85
		2.0	70	2.35

lished is about 68 eV, and the value for water vapor is some 8 eV lower. These findings can be compared with a Bragg's rule prediction[10] for a mean excitation energy of 67.5 eV based on the constituent I values of Ref. 8. The water-vapor value falls short considerably of the 71.6-eV theoretical value recently published,[27] and the liquid-water value similarly lies well below the prediction based on energy-level shifts of 1.127 times the Bragg value[28] and below the recent theoretical value of 75 eV.[29] Measurements by Matteson *et al.*,[30] which overlap those currently analyzed[1] at energies below 2.0 MeV, featured higher stopping powers for both vapor and condensed phases from 1.0 to 2.0 MeV, so that an even lower mean excitation energy would characterize these data[30] in the 1.0−2.0-MeV interval. The measurements by Palmer and Akhavan-Rezayat,[26] overlapping the presently analyzed data[1] over the full energy interval considered herein for water vapor, also featured generally higher stopping powers but with nearly equal values at the largest energies; liquid-water stopping power curves for the two cases[1,26] crossed at about a 3.5-MeV projectile energy, with the present data lying lower at the smaller projectile energies and higher at the greater energies. On the average these previous measurements[26] would also be represented by lower mean excitation energies than those reported herein.

This analysis supports a difference in mean excitation energies for vapor and liquid states of water of some 12%, with that of the condensed phase being larger as expected. The absolute value of the mean excitation energy for liquid water is tentatively accepted as 68 eV. Further accurate measurements are needed to resolve differences among extant data sets[1,26,30] and to establish more convincing values of the mean excitation energy for both phases of water in order to furnish a better basis for comparison with a Bragg's rule prediction.[8,10]

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