Comparison of the Landau-Zener Theory with Measurements of Electron Capture in B^{3+} + He Collisions

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An experimental total cross section for single-electron capture by heliumlike B^{3+} from He has been measured at relative velocities between 0.7 and 7.4×10^7 cm/sec (300-eV to 31.5-keV B^{3+} laboratory energy), and has been compared with a cross section calculated via the Landau-Zener theory. In the velocity range considered, the dominant crossing of the $(B+He)^{3+}$ system is between s states and the often-neglected conditions for applicability of the theory are met. The velocity positions of the cross-section maxima are in agreement, but the experimental magnitude at maximum is greater by a factor of 2.

I. INTRODUCTION

Single-electron capture by a multiply charged ion in collision with a neutral atom has been used for many years as a model for investigating the effects of pseudocrossing of adiabatic potential-energy curves. Unfortunately, most of the systems studied experimentally involved numerous electrons, a multiplicity of nonisolated crossings, and effective crossings between other than s states. The problem of deducing from cross-section data the influence of each crossing in a complex system can be formidable. In such situations, qualitative or semiempirical arguments may be the only practical recourse in analyzing the effects of crossings.

For the understanding of pseudocrossing processes, the phenomenological theory of Landau[1] and Zener[2] (LZ) and the more detailed Jeffries, Wentzel, Kramer, Brillouin (JWKB) treatment of Stueckelberg[3] provide quantitative, but greatly idealized and simplified, descriptions of electron transition behavior. In addition, recent extensions and developments of the Landau-Zener-Stueckelberg (LZS) formulations have been effective in explaining observed oscillatory structure in both differential and total cross sections.

Although various estimates of the limitations of the LZS theory and of improved treatments have been obtained,[4] the range of validity of the LZS model and the worth of LZS calculations remain quite uncertain for even the best of conditions. Briefly, the present situation is that, with few exceptions, quantitative predictions of the LZS theory and bounds on its range of validity have not been tested by direct comparison with experiment.

In view of the variety of physical processes affected by pseudocrossings and because of the difficulty of performing detailed calculations for complex situations, it is important to determine the quantitative usefulness of the relatively simple LZS theory applied to specific interactions. One approach would be a series of experimental investigations of pseudocrossing systems that are simple enough to permit detailed application of the LZS theory and justifiable comparisons of experimental and theoretical results. Hopefully, the systems studied would also be amenable to calculations more rigorous than the LZS theory. The goal of such comparisons would be the development of criteria for the applicability of the LZS theory to complicated situations where more detailed calculations are not practical.

In regard to previous studies of exothermic electron capture by multiply charged ions, Bates and his co-workers[5] presented a series of cross-section calculations using the LZ theory. Hasted and his co-workers[6] have measured a number of others and made some calculations. There has not been a great deal of overlap between theory and experiment in this area. Often comparisons of theory and experiment have used one or two adjustable parameters to position and/or normalize the computed and observed cross sections. Such procedures amount to comparing only the forms of cross sections and are qualitative at best. Furthermore, in some instances even the qualitative usefulness of the comparison is questionable because of possible contributions by electronic states not included in the calculations.

This paper summarizes a direct comparison (not involving cross-section positioning or normalization) between a LZ calculation and the experimental absolute cross section for the exothermic process

$$B^{3+} + He \rightarrow B^{2+} + He^{+} . \qquad (1)$$

For this reaction there are two final states

$$B^{2+}(2s) + He^{+} + 13.34 \text{ eV}$$

and

$$B^{2+}(2p) + He^{+} + 7.35 \text{ eV},$$

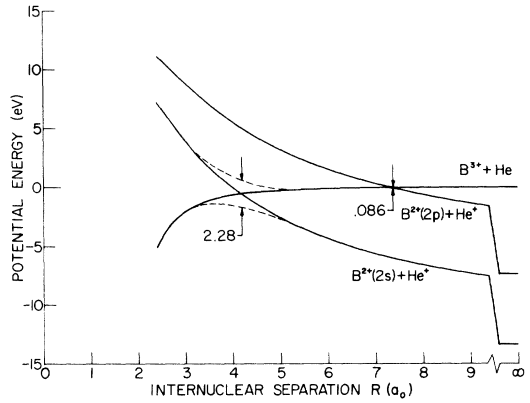

FIG. 1. Pseudocrossing potential-energy curves for $(B+He)^{3+}$ system.

which are exothermic and which pseudocross the initial state at $4.18a_0$ and $7.37a_0$, respectively, (Fig. 1). Since at these internuclear separations only long-range forces are appreciable and since the potential coefficients are calculable in this case, the computed crossing distances are quite accurate. Other final states are endothermic by more than 9 eV, do not have pseudocrossings, and hence can be neglected. The separation of the $2s$ and $2p$ states is sufficiently large to permit individual treatment of the crossings and classical combination of the resultant transition probabilities. Furthermore, the $2s$ state meets the requirement of spherical symmetry inherent in the LZ theory. Good analytic wave functions are available for the initial and final electron configurations.

II. THEORY

For a process such as (1), the probability of a transition between adiabatic potential-energy curves in the vicinity of a pseudocrossing of states i and f is given by the LZ formula

$$P_{if} = e^{-W_{if}/v}, \tag{2}$$

where v is the radial velocity at the crossing point and

$$W_{if} = \frac{\pi}{2\hbar} \frac{\Delta U(R_x)^2}{|U_i'(R_x) - U_f'(R_x)|}. \tag{3}$$

Here R_x is the crossing distance, $\Delta U(R_x)$ is the separation of the curves at R_x, and U_i' and U_f' are the first derivatives of the diabatic potential-energy curves U_i and U_f with respect to R at R_x. Neglecting interference effects and combining probabilities classically, the total transition probability for process (1) is

$$P = 2p_{sp}(1-p_{sp}) + 2p_{sp}^2 p_{ss}(1-p_{ss}), \tag{4}$$

where p_{ss} and p_{sp} are the transition probabilities at the inner $(1s-2s)$ and outer $(1s-2p)$ crossing.

Although the LZ formula is strictly applicable only to s-s transitions, we use Eq. (2) to calculate both p_{ss} and p_{sp}. The error caused by neglecting rotational coupling terms in calculating p_{sp} will be at most of the order of the calculated $(1-p_{sp})$. Since p_{sp} is close to unity in the velocity region of comparison with experiment, the inner $(1s-2s)$ crossing is dominant.

The total electron capture cross section is obtained by integration over the impact parameter b,

$$\sigma_{LZ} = 4\pi \int_0^{R_{xp}} p_{sp}(1-p_{sp})\, b\, db + 4\pi \int_0^{R_{xs}} p_{sp}^2 p_{ss}(1-p_{ss})\, b\, db, \tag{5}$$

where R_{xs} and R_{xp} are the crossing distances of the initial curve and the curves associated with capture into the $2s$ and $2p$ levels, respectively. Assuming motion in a straight line, the first integral in Eq. (5) can be expressed in terms of tabulated exponential integrals, but the second cannot be performed in closed form. The latter integral was evaluated numerically by expanding p_{sp}^2 in a power series in b and integrating term by term. For the parameters appropriate to the process and the range of relative velocities considered, it was sufficient to include two terms of the series to obtain better than 1% accuracy.

The matrix elements occuring in the formula of Eq. (2) were evaluated following Bates and others.[5] For this purpose the $B^{2+}(2s)$ and $B^{2+}(2p)$ wave functions were chosen to be of the Morse, Young, and Haurwitz[7] type. Owing to errors[8] in their original calculations the variational parameters appearing in the wave functions were recomputed. For $He(1s)$ the variational wave function determined by Green *et al.*[9] was used. The B^{2+} polarizabilities appearing in the potential energies were computed by a method owing to Hylleras[10] and were found to be approximately $4a_0^3$. The He polarizability was taken to be $1.37a_0^3$ and the He^+ polarizability to be $0.28a_0^3$. The coefficient of the inverse cube term in the $B^{2+}(2p)$ potential was calculated to be $1.1a_0^2$. Calculated values of $\Delta U(R_x)$ are given in Fig. 1.

The computed total cross section is shown in Fig. 2 as a solid line. The broad maximum near 10 keV is predominantly a result of capture into the $2s$ state, while the rise near 100 eV is associated with capture into the $2p$ state. Computed values for each final state, assuming complete diabatic behavior at one or the other crossing, are also shown.

We mention, also, a detailed study of the LZ theory by Bates *et al.*,[11] which included the effect of transitions occuring away from the crossing point; their numerical solutions of the two-state approximation for a process having a crossing at moderate distance $(5.8a_0)$ indicate that the LZ predictions, while preserving the qualitative behavior, tend to

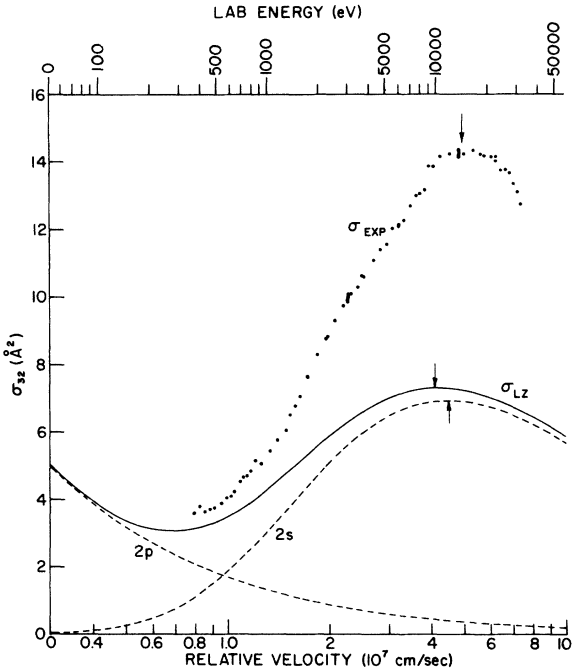

FIG. 2. Experimental and theoretical cross sections for single-electron capture by B^{3+} in He.

underestimate the cross section. For large crossing distances, their results exhibited a second cross-section maximum not predicted by the LZ theory (cf. Ref. 12).

III. EXPERIMENT

The ion beam apparatus, except for the ion source, has been described elsewhere.[12] For these measurements, we used an electron-impact ion source having a variable electron energy (0–800 eV) to control the metastable ion contamination and to increase the absolute cross-section accuracy. Boron trifluoride was used as a source gas, and the natural mixture of the two boron isotopes permitted a definite identification of the B^{3+} ions. Experimental errors and corrections are described below.

A beam of 10^3 ground-state B^{3+} ions per second was produced using 190-eV electrons in the ion source. This electron energy is below the 198 eV required for excitation of the ions. The B^{3+} current was about 3×10^{-6} times the B^+ current and 10^{-10} times the total extracted ion current. Since the useful B^{3+} current was eight times larger at 550-eV electron energy, it was convenient to operate above the threshold for metastable B^{3+} production. Therefore, a correction for the metastable contamination was required. We can assume that the charge-changing cross sections for metastable B^{3+} incident on helium are negligible at these velocities because the exothermic energy defects are quite large. Under that assumption, the fraction k of incident metastable B^{3+} was determined by measuring the electron-capture cross sections at ion energies of 3 and 13.5 keV as a function of electron-impact energy in the ion source. A value of k equal to 0.037 ± 0.015 for 500-eV electrons was measured. Thus, the corrected number of ground-state B^{3+} was $N^c_{3+}=N_{3+}-k(N_{3+}+N_{2+})$, and the cross section was proportional to the logarithm of $N_{2+}/(N^c_{3+}+N_{2+})$. The relative counting efficiency for the detectors of the respective ions was measured, and a 2.1% correction was applied.

At low energies some of the B^{2+} ions were lost before detection, due to the upper limit on the angle θ_m through which an ion can scatter and still be collected. The fraction lost is given by

$$F_L=\tfrac{1}{2}(b_m^i/R_x)^2+\tfrac{1}{2}[1-(b_m^0/R_x)^2]\,, \tag{6}$$

where b_m^i and b_m^0 are the respective impact parameters, corresponding to θ_m for electron capture occuring on the ingoing or outgoing crossing, and where the LZ probability has been taken to be independent of b for $b\leq R_x$. The value of θ_m, which depends on the point of scattering and other experimental parameters, range between 1.7 and 4 deg. The estimated loss of B^{2+} ions from capture occuring at $R_x=4.18a_0$ is 20% at $E_{LAB}=500$ eV, and 5% at 1000 eV; for $R_x=7.37a_0$ it is only 5% at 500 eV. A correction for this systematic error was not made because an assumption about where the capture occurs would be required.

The estimated limit of error on the corrected absolute cross section is ±7% (pressure calibration ±2%; cell-end correction ±3%; detector efficiency correction ±0.5%; metastable correction ±1.5%), in addition to the low-energy collection error mentioned above. Also, each data point has a typical scatter of 1% (standard deviation of the curve fit of capture ratio versus pressure).

IV. RESULTS AND DISCUSSION

General qualitative agreement between the absolute experimental (σ_{exp}) and theoretical (σ_{LZ}) cross sections and their quantitative difference can be observed in Fig. 2. An increasing contribution from capture into the $2p$ state at low velocities is indicated by the shape of σ_{exp}. Above 10^7 cm/sec, capture into the $2s$ state should be dominant. The velocity positions of the maxima agree within about 20%, which is perhaps better than might be expected considering the approximations of the LZ model and its sensitivity to the value of the calculated $\Delta U(R_x)$. On the other hand, the magnitude of σ_{exp} is a factor of 2 greater than σ_{LZ}. This difference is similar to recent mutual neutralization results.[13]

To demonstrate how superficial agreement can be obtained by normalization, we substituted $R_x(2s)=1.41\,R_x(2s)$ and $v=1.27v$. The recalculated cross

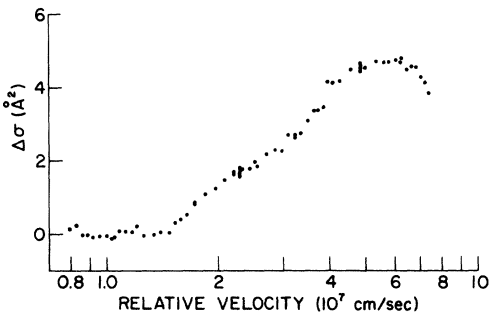

FIG. 3. Difference between experimental and corrected LZ cross sections.

section matches the data to several percent, except above 6.5×10^7 cm/sec where the data is significantly lower.

In the following discussion, we examine qualitatively the difference between σ_{exp} and σ_{LZ}. As noted in early work,[5] the magnitude of σ_{LZ} should be reasonably accurate because $\sigma_{LZ}=\pi R_x^2 p(v)$, where the maximum of $p(v)$ is approximately one-half, owing to the reversibility of the transition, and where R_x is accurately determined. This dependency on R_x is a result of the LZ assumption that transitions occur only at a well-defined crossing point, and a larger magnitude obviously means that transitions also occur at separations greater than R_x. As noted above, the work of Bates *et al.*[11] reveals that transitions away from R_x are likely, with the size of the transition region dependent upon the magnitude of R_x. The results of Bates *et al.* applied qualitatively to the $(B+He)^{3+}$ system indicate that one might expect (a) transitions to the $2s$ state just outside of $R_x(2s)$ and (b) transitions to the $2p$ state well inside of $R_x(2p)$. The first effect would primarily increase the LZ cross section, whereas the second would produce a second maximum. A rough estimate of the first effect is made by taking $R_x^c(2s) = R_x(2s)+\Delta R$, where $\Delta R \approx \Delta U(R_x)/|U_i' - U_f'|_{R_x} = 0.67a_0$ is one-half the width of the transition region (cf. Refs. 3, 14, 4). This is reasonable since ΔR is a measure of the region outside of R_x, where the separation of the adiabatic curves is approximately constant. The corresponding ΔR for the $2p$ crossing is only 1.2% of $R_x(2p)$. Adding these ΔR to the crossing distances as first-order corrections gives a σ_{LZ}^c that is very close to the data below 1.5×10^7 cm/sec. The difference at higher velocities is shown in Fig. 3 and might be largely due to the second effect.

As a final point, we note that the data appear to exhibit oscillations, which we tentatively identify as Stueckelberg-Olson oscillations[15] due to a maximum in the difference between the initial and final $(2s)$ adiabatic potentials inside of R_x. The characteristics of this structure are being further studied.

We conclude that, for at least one system which meets the required conditions, the LZ theory gives a cross section having a reasonably good velocity dependence and a magnitude within a factor of 2. The difference is very likely due to transitions occuring away from R_x, and improved models to include these transitions may provide alternatives to numerical solutions of the coupled-state equations. Furthermore, the factor-of-two discrepancy should not be considered general, but dependent on the values of the R_x involved.

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