Kinematic Isotope Effects in Low Energy Electron Capture

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The replacement of hydrogen with its isotope deuterium, in collisions with multiply charged ions, is shown to lead to a suppression of total charge transfer cross sections at collision energies much higher than previously thought. We demonstrate, using a fully quantal calculation of electron capture in collisions of $N^{4+}(2s)$ with $H(1s)$ and $D(1s)$, that this isotope effect is significant for capture into the $N^{3+}(3d)$ states at collision energies approaching 10 eV/amu. Estimates of the magnitude of the effect, using the semiclassical Landau-Zener-Stueckelberg model, are made for several multiply charged systems.

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Electron capture by ions during collisions with neutral atoms is an atomic process that plays an important role in the physics of both laboratory and astrophysical plasmas [1]. Because of its importance in applications, electron capture has received much attention as a fundamental physical process in its own right [2,3]. Merged-beams experiments have been able to measure total charge transfer cross sections in collisions of hydrogen with heavier ions over a range of charge states down to relative collision energies of around 1 eV/amu [4,5]. Advances in, and availability of, computing machines have allowed increasingly sophisticated, fully quantal, calculations of the cross sections for electron capture in collisions at this energy range [3]. Because of their predominant abundance in astrophysical and tokomak plasmas, most attention has focused on electron capture in systems involving collisions of H and He with heavier ions.

Trajectory effects have been known to lead to isotope effects in K-vacancy production in ion-atom collisions [6] and in differential cross sections in charge exchange and formation of negative ions [7]. In recent merged-beams experiments, H and D were used interchangeably as a means for relative velocity selection, to decrease angular scattering and improve angular collection of products [4,5]. At collision energies $\gtrsim 1$ eV/amu it is generally believed that the replacement of the hydrogen target with its isotope deuterium does not affect the total charge transfer cross sections at a given relative collision velocity.

Most theoretical studies of isotope effects have focused on the resonant charge capture process involving the collisions of protons with hydrogen and deuterium [8,9]. In that system, symmetry considerations, the identity of the nuclei, and the 0.0037 eV isotopic shift of the deuterium ionization potential are known to contribute to an isotope effect at extremely low collision energies [10,11]. However, it is generally assumed that significant isotope effects, in asymmetric systems, are due to the difference in the ionization potentials of the isotopes, i.e., an atomic mass shift effect. It has been suggested [11] that, if the 0.0037 eV isotopic atomic mass shift is neglected, the two processes $H^+ + H(D) \rightarrow H + H^+(D^+)$ should be identical. So for collision energies $E \gg 0.0056$ eV/amu, it is generally taken for granted that any isotope effect is negligible.

In this Letter we show that there is an important, additional isotopic effect, independent of the atomic shift effect, which significantly affects total charge transfer cross sections at collision energies much higher than previously thought. Although this effect has not been fully discussed in the literature [12,13], we demonstrate here, using a full quantal calculation of electron capture for the process

$$N^{4+}(2s) + H(D) \rightarrow N^{3+}(3\ell) + H^+(D^+), \quad (1)$$

the reality of this isotope effect. We show that the kinematic isotope effect is significant for capture into the $N^{3+}(3d)$ state at collision energies on the order of 10 eV/amu, well within the range available in merged-beams experiments. We provide a physical explanation for this effect and, using the semiclassical Landau-Zener-Stueckelberg (LZS) model, we make estimates for other systems. The LZS calculations suggest that this effect is significant in other, highly charged, collision systems at energies approaching 1 keV/amu.

In general, for a given interaction potential, scattering solutions to the Schrödinger equation may be parametrized by the mass and collision energy or, alternatively, the relative velocity and de Broglie wavelength of the collision system. If one of the collision partners is replaced by its isotope, and we ignore the small atomic shift effect, the scattering solutions at a given collision velocity are characterized by different de Broglie wavelengths. Furthermore, if the interaction potential has some characteristic range, or scale, then the cross section may be sensitive to the value of the de Broglie wavelength at a given relative collision velocity.

In the case of electron capture we can give a concise statement of this effect by employing the LZS model. In this picture the probability for a system, with reduced

mass μ, to undergo a charge transfer transition at the impact parameter b and collision velocity v, is [14]

$$P_b = \exp(-2u/v_b), \quad (2)$$

where the critical velocity $u = \pi V_{12}^2/\hbar|V_{11}' - V_{22}'|$, V_{12} is the diabatic interaction energy, V_{11},V_{22} are the diabatic potentials corresponding to the incoming and outgoing channels, respectively, and V_{11}',V_{22}' are their radial derivatives. All quantities are evaluated at the internuclear distance R^*, where the diabatic potential curves cross. u is independent of the nuclear masses but the relative radial velocity $v_b = v\sqrt{1 - 2V_{11}/\mu v^2 - b^2/R^{*2}}$ at the crossing is not. If the ratio $2V_{11}/\mu v^2$ is comparable to the quantity $1 - b^2/R^{*2}$, then P_b is sensitive to the mass of the isotope at a given collision velocity.

Though considerable experimental and theoretical attention has been given to process (1) for a hydrogen target [5,15–18], the results cannot be scaled since the coupled scattering equations have an explicit mass dependence. The method employed for the present calculation is described in Zygelman *et al.* [17], while further details including state-dependent cross sections and rate coefficients will be given elsewhere [19]. The deuterium ionization potential shift is neglected.

Figure 1 displays the quantum mechanically determined cross sections for reaction (1) with D for capture into the $^1\Sigma$ and $^3\Sigma$ states of ND^{4+} compared to the calculations of Zygelman *et al.* [17,18] for H. For the singlet manifold, a significant difference in the cross sections is apparent for $E \lesssim 8$ eV/amu and this difference increases with decreasing energy. Below 5 eV/amu an oscillatory structure is present in both systems. These are a manifestation of Stueckelberg oscillations, and the location of the peaks can be reproduced by a two-channel semiclassical approximation [17]. The semiclassical approximation also predicts the two additional oscillations computed for a deuterium target. Above 5 eV/amu slight differences in the cross sections persist and again there are two additional oscillations for D. At collision energies of ~50 eV/amu the H

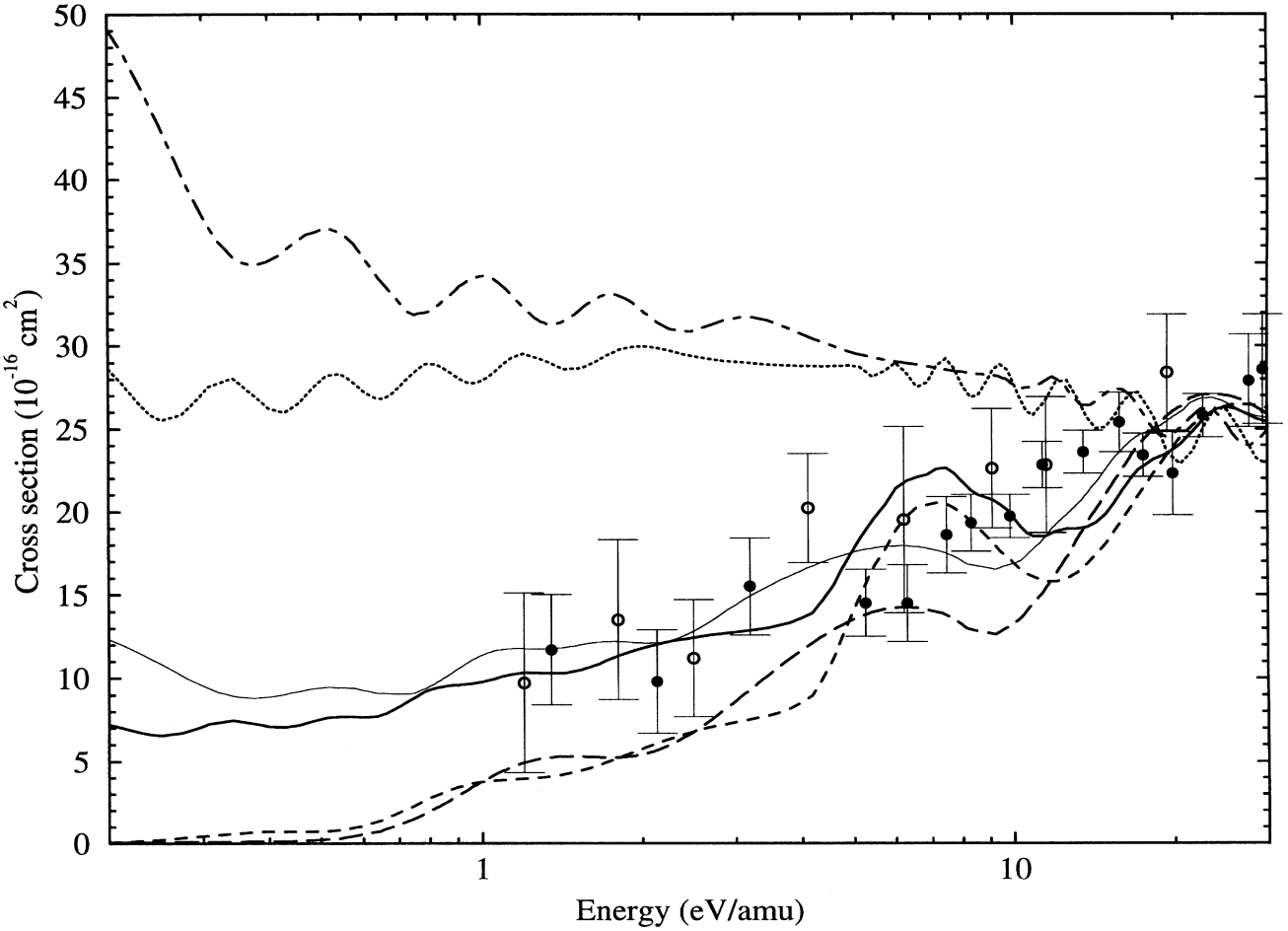

FIG. 1. Charge transfer cross sections for $N^{4+} + H(D) \rightarrow N^{3+} + H^+(D^+)$. Theoretical with hydrogen target: $^1\Sigma$ manifold (dot-dashed line), Ref. [17]; $^3\Sigma$ manifold (long dashed line), Ref. [18]; and total (thin solid line), Ref. [18]. Theoretical with D target, from this work and Ref. [19], $^1\Sigma$ manifold (dotted line), $^3\Sigma$ manifold (short dashed line), and total (thick solid line). Total experimental: H or D targets (empty circles), Ref. [5], and D targets (filled circles), Ref. [16].

and D cross sections become quantitatively indistinguishable. In the triplet manifold oscillations in the total cross sections are also prominent. Between 5 and 10 eV/amu there is $\sim 180°$ phase shift in the oscillations of the H and D cross sections, resulting in a considerable enhancement in the D cross section. In this manifold slight differences between the H and D cross sections persist for collision energies up to 50 eV/amu.

Unfortunately for this system, spin-selective cross sections cannot be observed with current experimental techniques. The total cross section is a weighted sum of the singlet and triplet manifolds and is presented in Fig. 1. The decreasing behavior of the triplet manifold with decreasing energy effectively damps out any isotopic effects in the total cross section within observable experimental uncertainty. While this system is unsuitable for experimental searches of isotope effects, the calculations suggest that in multiply charged systems a reduction in the cross section for D may appear at larger energies than previously believed. Some previous measurements and calculations that have disregarded this effect may need to be reevaluated.

Reasonable qualitative predictions of the magnitude of the kinematic isotope effect can be made with the LZS approximation for other multiply charged systems. The LZS cross section is given by [14]

$$\sigma(v) = 4\pi \int_0^{b_{\max}} db\, bP_b(1 - P_b), \qquad (3)$$

where we have replaced a sum over partial waves with an integral over the impact parameter b, a phase factor with its average value, and where $b_{\max} = R^*\sqrt{1 - 2V_{11}/\mu v^2}$. Given the ionic state energies from Bashkin and Stoner [20], the required Landau-Zenner parameters can be estimated following the procedures of Butler and Dalgarno [21]. In Table I we present some results for a variety of multiply charged systems. The seventh column gives the collision energy for a 2% enhancement in the H cross section compared to the D result. We view this as an upper energy threshold E_{th} for the kinematic isotope effect. The value obtained for N^{4+} agrees with the full quantal calculation of the $^1\Sigma$ manifold as shown in Fig. 1. The last column is the ratio of the H to D cross sections at 0.1 eV/amu. We choose this energy since it is the lower limit of current experimental efforts. The value of 3.8 is in qualitative agreement with the quantal value of 1.74 for the N^{4+} $^1\Sigma$ manifold. While the LZS results for the triplet manifold appear to indicate a significant isotope effect, the cross section falls off rapidly with decreasing energy below 20 eV/amu, giving a negligible contribution in agreement with the quantal calculation.

Havener *et al.* [12] have performed a LZS calculation for the O^{5+} + H(D) system and find a similar enhancement for H. Our estimates for both the singlet and triplet manifolds are in agreement with Havener *et al.* [12]. In contrast to the system of Eq. (1), both triplet and singlet cross sections increase with decreasing energy, suggesting the possibility of experimentally verifying this prediction. In addition, this system represents the only other we are aware of for which a full quantum-mechanical calculation has been performed for deuterium targets [13]. Gargaud's [13] computations extend down to only 0.87 eV/amu, but show an enhancement for H of a few percent. Our LZS calculation gives a comparable result.

The N^{5+} system may also be suitable for investigation, since its cross section increases with decreasing energy and is quite large: $\sim 0.8 \times 10^{-14}$ cm^2 at 1 eV/amu. The remaining systems given in Table I have not been previously studied. To estimate which final capture state dominates the cross section, LZS calculations were performed in the energy region where the isotope effect becomes important. In general, E_{th} increases with the charge of the initial ion. It is rather surprising in light of traditional views on electron capture isotope effects that this occurs near 1.4 keV/amu for Ti^{22+}.

If we make a change in variables $x = \sqrt{(1 - 2V_{11}/\mu v^2)/(1 - 2V_{11}/\mu v^2 - b^2/R^{*2})}$, then Eq. (3) may be rewritten

$$\sigma(v) = 4\pi R^{*2}(1 - 2V_{11}/\mu v^2) \times \int_1^\infty \mathcal{P}(x)[1 - \mathcal{P}(x)]x^{-3}dx, \qquad (4)$$

where $\mathcal{P}(x) \equiv P_b$. Assuming that any isotope effect is negligible in the integral, the LZS theory predicts the ratio of the H to D cross section, at the collision velocity v, to be

$$\frac{\sigma_{\text{H}}}{\sigma_{\text{D}}} \approx \frac{1 - 2V_{11}/\mu_{\text{H}} v^2}{1 - 2V_{11}/\mu_{\text{D}} v^2}. \qquad (5)$$

Equation (5) gives a simple relation for predicting the magnitude of the kinematic isotope effect provided the dominant capture channel is known. Equation (5) is in general agreement with the values given in Table I determined with the semiclassical LZS relation (3) justifying the neglect of the integral. The reader is forewarned that results obtained from Eqs. (3) or (5) are only estimates, but they may be useful for the selection of systems for further study.

Finally, in tokamak fusion devices, neutral H or D beams are injected for plasma heating or diagnostics [22]. The neutral beams may interact with the ambient plasma or with heavy, highly stripped, impurity ions usually of heliumlike or neonlike configurations with energies in the 1–200 keV/amu range [23]. The last row of Table I suggests that kinematic isotope effects may be important for interactions with heavy impurity ions. In the analysis of fusion plasmas, H charge transfer cross sections are currently incorporated irrespective of whether the beam is H or D [22].

TABLE I. Estimates of kinematic electron capture isotope effects and Landau-Zener parameters for various multiply charged systems.

Initial ion	Final ion	Term	ΔE [a] (a.u.)	R^* [b] (a.u.)	V_{11} [b] (a.u.)	E_{th} [c] (eV/amu) at 0.1 eV/amu	σ_H/σ_D [c]
$N^{4+}(2s)$	$N^{3+}(2s3d)$	$^1\Sigma$	0.4016	7.47	−0.01142	8	3.8
		$^3\Sigma$	0.4431	6.77	−0.01662	17	10
$N^{5+}(1s^2)$	$N^{4+}(1s^24s)$	$^2\Sigma$	0.3340	11.98	−0.00273	2	1.2
$O^{5+}(2s)$	$O^{4+}(2s4s)$	$^1\Sigma$	0.3519	11.37	−0.00337	2	1.3
		$^3\Sigma$	0.3938	10.16	−0.00528	3	1.4
$O^{6+}(1s^2)$	$O^{5+}(1s^24d)$	$^2\Sigma$	0.6258	7.99	−0.01979	13	2.0
$Ne^{8+}(1s^2)$	$Ne^{7+}(1s^25s)$	$^2\Sigma$	0.8258	8.48	−0.02784	17	1.6
$Al^{11+}(1s^2)$	$Al^{10+}(1s^25\ell)$	$^2\Sigma$	1.9239	5.20	−0.34900	250	...
$Cl^{7+}(2p^6)$	$Cl^{6+}(2p^65s)$	$^2\Sigma$	0.7456	8.05	−0.0262	17	2.0
$Ar^{8+}(2p^6)$	$Ar^{7+}(2p^65p)$	$^2\Sigma$	0.9801	7.14	−0.05482	30	2.6
Ar^{18+}	$Ar^{17+}(6\ell)$	$^2\Sigma$	4.0111	4.24	−2.0406	1300	...
Ti^{22+}	$Ti^{21+}(7\ell)$	$^2\Sigma$	4.4548	4.71	−2.0917	1400	...

[a] Asymptotic atomic energy defects from Ref. [17].
[b] Estimated following the procedures of Ref. [18].
[c] Determined using Eq. (3).

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