so that at high energies, the ratio of this cross section to that for electron ionization (see Ref. 4) is

$$\frac{\sigma_{\text{ion}}(\text{protons},E_1)}{\sigma_{\text{ion}}(\text{electrons},E_1)}=\frac{1}{\lambda}=\frac{m_1}{m_e},$$

or for the same velocity

$$\sigma_{\text{ion}}(v_1,\text{ protons})/\sigma_{\text{ion}}(v_1,\text{ electrons})=1\,.$$

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Classical Calculations of Charge-Transfer Cross Sections*

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The utility of Gryzinski's classical procedure for estimating charge-transfer cross sections is examined. The essential content of the method is that charge transfer occurs whenever the energy transferred in a Coulomb collision between the incident ion and the transferring electron lies between specified limits. For protons incident on noble-gas and alkali atoms, it is found that the procedure in its present form is not as reliable for predicting charge-transfer cross sections as for ionization, though individual examples of remarkable agreement are found. Nevertheless, it remains possible that a more sophisticated classical approach can reasonably account for charge transfer.

I. INTRODUCTION

THE classical binary-encounter approximation has been found to be remarkably successful at predicting atomic ionization cross sections due to electron[1] and proton[2] impact. Its present form is due to Gryzinski.[3] In later papers,[4] Gryzinski proposed a procedure for applying this approximation to charge-transfer processes. It is this procedure which we have examined.

Section II describes the procedure. In Sec. III we present some results for charge transfer to incident protons from noble gases and from alkali atoms. Wherever possible, we have compared our results with existing data. Our study indicates that Gryzinski's prescription does not provide a generally reliable quantitative, or even qualitative, guide to the energy dependence of these cross sections, though some exceptional agreements with experiment are found. For the noble-gas series, where adequate data exist, it appears that the theory is best: (a) when $U_A > U_B$, where U_A and U_B are the binding energies of the electron before and after capture, respectively; (b) at incident energies $E > \sim 2E_{\max}$, where $E_{\max} \sim (M/m)U_A = 1836\ U_A$ is the incident energy at which the cross section peaks on the Gryzinski theory. Some possible simple modifications of the Gryzinski procedure, which do not notably improve the agreement with experiment, however, are described in Sec. IV. Section IV also discusses some formal aspects of the Gryzinski procedure; this discussion is concluded in Sec. V.

The failure of the Gryzinski theory at low incident energies is understandable, because for slow collisions the assumption (basic to the Gryzinski theory) that the electron is deflected only by the incident ion is untenable. There is evidence[5] for the viewpoint that a different classical approximation can correctly predict charge-transfer cross sections at low energies. Moreover, the Gryzinski theory seems to quite successfully predict[6] the cross sections for capture into the $2s$ state by protons impinging on H, H_2, and He. Therefore, though our results do indicate that Gryzinski's approximations are too simple, it remains possible that charge transfer can be understood on the basis of a classical approach more sophisticated than Gryzinski's.

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[1] See, e.g., E. Bauer and C. D. Bartky, J. Chem. Phys. **43**, 2466 (1965).

[2] J. D. Garcia, E. Gerjuoy, and J. E. Welker, preceding paper, Phys. Rev. **165**, 66 (1968).

[3] M. Gryzinski, Phys. Rev. **115**, 374 (1959).

[4] M. Gryzinski, Phys. Rev. **138**, A336 (1965).

[5] D. R. Bates and R. Mapleton, Proc. Phys. Soc. (London) **87**, 657 (1966).

[6] J. D. Garcia and E. Gerjuoy, Phys. Rev. Letters **18**, 944 (1967).

II. ENERGY-EXCHANGE METHOD

The classical binary-encounter approximation is based upon a knowledge of the cross section for energy transfer, $\sigma_{\Delta E}{}^{\rm eff}(v_1,v_2)$, in the laboratory frame, resulting from a collision of two charged particles of masses m_1 and m_2 (in charge transfer the masses, respectively, of the incident ion and of the electron), moving with arbitrary velocities $\mathbf{v}_1,\mathbf{v}_2$ in the laboratory system, averaged over all orientations of $\mathbf{v}_2$, for fixed speeds v_1,v_2. As proposed by Gryzinski,[4] the charge-transfer cross section is then calculated by integrating $\sigma_{\Delta E}{}^{\rm eff}$ over the range of values of ΔE for which there is a significant probability of electron capture;

$$\sigma_{10}=\int_{\Delta E_l}^{\Delta E_u}\sigma_{\Delta E}{}^{\rm eff}(v_1,v_2)d\Delta E. \tag{1}$$

The resultant cross section should be averaged over the speed distribution for the bound electron, $f(v_2)dv_2$, and multiplied by the number of equivalent electrons involved. Gryzinski[4] proposed that the limits in (1) should be

$$\Delta E_l=\tfrac{1}{2}m_e v_1^2+U_A-U_B, \tag{2a}$$

$$\Delta E_u=\tfrac{1}{2}m_e v_1^2+U_A+U_B, \tag{2b}$$

where U_A, U_B are as defined above, and m_e is the electron mass.

A number of cases were calculated on the basis of the above model by Gryzinski.[4] However, he used a number of approximations in arriving at his results, some of which are unnecessary. Because the classical binary approximation provides a reasonable tool for ionization cross-section prediction,[1,2,7] we have undertaken an examination of the usefulness of the above model in providing general estimates for charge-transfer cross sections. We list here the modifications to Gryzinski's procedure which we have used, and defer a critique of this procedure until Sec. IV

(a) We use the correct expression, without any approximation, for $\sigma_{\Delta E}{}^{\rm eff}$, which has been given recently by Gerjuoy.[8] His expressions are readily integrated and result in the following (for singly charged ions):

$$\int^{\Delta E}\sigma_{\Delta}{}^{\rm eff}d\Delta E$$

$$=\frac{\pi e^4}{3v_1^2v_2}\left[-\frac{2v_2^3}{\Delta E^2}-\frac{6v_2/m_2}{\Delta E}\right],\quad \text{if}\quad 0<\Delta E<b$$

$$=\frac{\pi}{3}\frac{e^4}{v_1^2v_2}\left[3\frac{v_1/m_1-v_2/m_2}{\Delta E}+\frac{(v_2'^3-v_2^3)-(v_1'^3+v_1^3)}{\Delta E^2}\right],$$

$$\text{if}\quad b<\Delta E<a$$

$$=\frac{\pi}{3}\frac{e^4}{v_1^2v_2}\left(-\frac{2v_1'^3}{\Delta E^2}\right),\quad \text{if}\quad \Delta E>a,\ m_e v_2>(m_1-m_e)v_1$$

$$=0,\quad \text{if}\quad \Delta E>a,\ m_e v_2<(m_1-m_e)v_1,$$

where (3)

$$b=\frac{4m_1m_e}{(m_1+m_e)^2}\left[E_1-E_2-\frac{v_1v_2}{2}(m_1-m_e)\right],$$

$$a=\frac{4m_1m_e}{(m_1+m_e)^2}\left[E_1-E_2+\frac{v_1v_2}{2}(m_1-m_e)\right],$$

$$v_1'=(v_1^2-2\Delta E/m_1)^{1/2},\quad v_2'=(v_2^2+2\Delta E/m_e)^{1/2}.$$

(b) We have not adopted Gryzinski's use of exponential velocity distributions for the bound electron because we could find no justification for this assumption. However, this should have no major effect on the results. All of our calculations were done by replacing v_2 by $(2U_A/m_e)^{1/2}$, corresponding to a δ-function distribution consistent with the classical virial theorem for Coulomb forces.

The calculations we report in Sec. III are then the result of using (3) in (1) with limits as given by (2), and with $v_2=(2U_A/m_e)^{1/2}$. It can be seen that (3) will lead to divergent expressions for some $v_1>0$ if $U_A<U_B$; if $U_A=U_B$, then the cross section diverges at $v_1=0$. For these cases, Gryzinski[4] proposed a geometrical upper bound; it is not clear that this proposal is well founded or generally useful. The procedures discussed in Sec. IV avoid this difficulty of divergent cross sections.

Unlike the results for ionization cross sections, the Gryzinski charge transfer cross sections—with the limits as given by (2)—in general do not scale with the bound electron energy. However, scalable expressions are obtained at high incident energies. In particular, consider the cross section for the case $U_A>U_B$ and $v_1\gtrsim 2v_2$, in which events (letting $m_e/m_1=\lambda\ll 1)(\Delta E)_u$ from Eq. (2) are $<b$, so that (per equivalent electron in the target atom)

$$\sigma_{10}=\frac{\pi}{3}\frac{e^4}{U_A}\frac{1}{\lambda E_1}\left\{-\frac{2U_A{}^2}{\Delta E^2}-\frac{3U_A}{\Delta E}\right\}_{\Delta E=\Delta E_l}^{\Delta E=\Delta E_u}. \tag{4}$$

Now, if in addition $U_B\ll\lambda E_1+U_A$, then Eq. (4) yields

$$\sigma_{10}\cong\frac{2\pi}{3}\frac{e^4}{\lambda U_A{}^3}\frac{U_B}{(E_1/U_A)}\times\left[\frac{4}{(\lambda E_1/U_A+1)^3}+\frac{3}{(\lambda E_1/U_A+1)^2}\right]. \tag{5}$$

Equation (5) is scalable in the sense that for a given impinging ion (fixed U_B) the resulting cross sections per electron at high incident energies for different target atoms A,A' are related by

$$\sigma_{10}(U_A,E_1)\cong(U_{A'}{}^3/U_A{}^3)\sigma_{10}(U_{A'},E_1'),\qquad E_1'=(U_{A'}/U_A)E_1. \tag{6}$$

Another question which arises in the Gryzinski procedure is the convergence of the cross section when

[7] J. D. Garcia, Phys. Rev. 159, 39 (1967).
[8] E. Gerjuoy, Phys. Rev. 148, 54 (1966).

summed over all possible capture states. Our numerical results indicate that the total capture cross section, summed over all possible final states, does indeed remain finite when the ground state $U_B < U_A$. The convergence readily can be demonstrated analytically for protons incident on ground-state hydrogen atoms at energies E_1 such that (5) is the cross section. For given principal quantum number n_B, $U_B/U_A = 1/2$ in (5). Thus the explicit sum over all n_B of the terms in (5) is merely proportional to the sum of $1/n^2$ over all integers $n \geqslant 1$. Hence we obtain

$$\sum_{n_B=1} \sigma_{10} \cong \frac{\pi^3}{9} \frac{e^4}{\lambda E_1 U_A} \left[\frac{3\lambda E_1/U_A + 7}{(\lambda E_1/U_A + 1)^3} \right], \tag{7}$$

where U_A is the ionization energy of the ground-state hydrogen atom.

In connection with the above result (7), we note that the $\sigma_{\Delta E}{}^{\text{eff}}$ appearing in (3) has been integrated over all final angular momenta consistent with given energy transfer ΔE. For this reason, in performing the sum over U_B in (5), we do not multiply by the statistical weight $n_B{}^2$ of the capturing energy level U_B. Including the statistical weight would cause the sum over final capturing states to diverge. We also remark that the Gryzinski theory predicts that the capture cross section into the nth hydrogenic level is proportional to n^{-2} at high incident energies, whereas the quantum mechanical Born or Kramers-Brinkman approximations yield a capture cross section having about an n^{-3} dependence.[9]

III. RESULTS

A. Noble Gases

A large amount of data[10–14] is available for total charge-transfer cross sections of protons on the noble gases. Figures 1–4 show comparisons with the Gryzinski theory for He, Ne, Ar, and Kr. The theoretical curves labeled G are the cross sections for capture into the H(1s) state only, computed as described in Sec. II. Plotting capture into just the H(1s) state facilitates comparison between the Gryzinski prescription (curves G) and possible alternatives (curves Gm and DB) described in Sec. IV. In the energy range of the plots in Figs. 1–4, inclusion of the sum over all excited states has a negligible effect on the theoretical curves G at low energies, but it increases them about 25% at their high-energy ends. In the very high-energy limit where

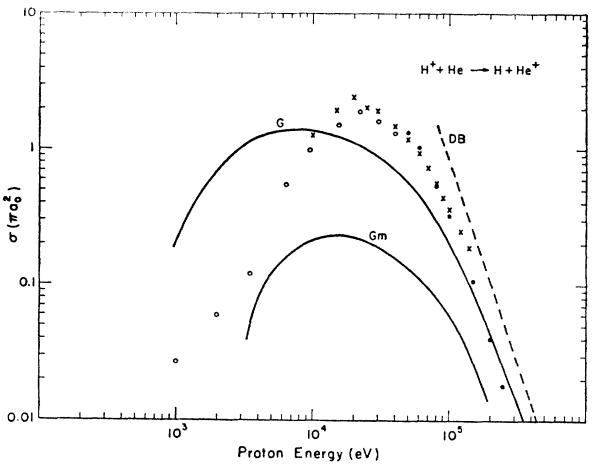

FIG. 1. Charge capture by protons in helium. Curves G, Gm, and DB, present results. Experiment: Crosses, De Heer (Ref. 10); open circles, Stedeford and Hasted (Ref. 11); full circles, Stier and Barnett (Ref. 12).

(5) holds, the H(1s) capture cross section is about 60% of the total capture cross section.

At energies past the peak in the curves G, the agreement between theory and experiment is surprisingly good, particularly in Ar. However, it is evident, especially in Kr, that while the Gryzinski predictions are adequate at some impact energies, large discrepancies occur at energies near to and below the energies at which the curves G peak. On the other hand, it is likely that such very large discrepancies near the maximum mainly are a consequence of the particular choice of $(\Delta E)_l$ [namely, Eq. (2a)] that Gryzinski prescribes, and thus are not a necessary outcome of the binary-encounter approximation. In case of Kr, for which the discrepancy near the maximum is largest, the ionization potential is almost equal to that of hydrogen,

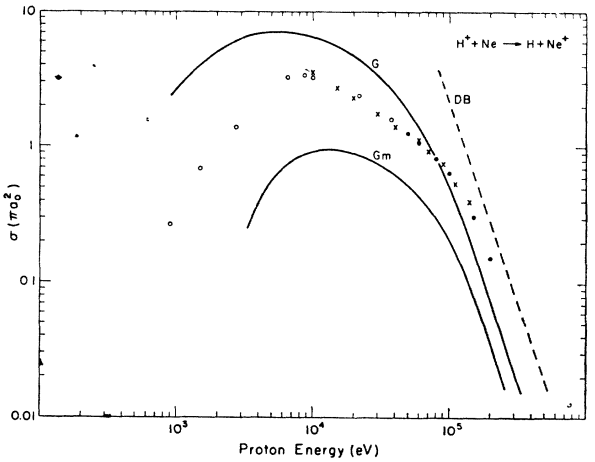

FIG. 2. Charge capture by protons in neon. Curves G, Gm, and DB, present results. Experiment: Crosses, De Heer (Ref. 10); open circles, Stedeford and Hasted (Ref. 11); full circles, Stier and Barnett (Ref. 12).

[9] J. D. Jackson and H. Schiff, Phys. Rev. **89**, 359 (1953).
[10] F. J. De Heer, J. Schutten, and H. Moustafa, Physica **32**, 1766 (1966).
[11] J. B. H. Stedeford and J. B. Hasted, Proc. Roy. Soc. (London) **A227**, 466 (1955).
[12] P. M. Stier and C. F. Barnett, Phys. Rev. **103**, 896 (1956).
[13] C. F. Barnett and H. K. Reynolds, Phys. Rev. **109**, 355 (1958).
[14] V. V. Afrosimov, R. N. Ilin, and E. S. Solovev, Zh. Techn. Fiz. **30**, 705 (1960) [English transl. Soviet Phys.—Tech. Phys. **5**, 661 (1960)].

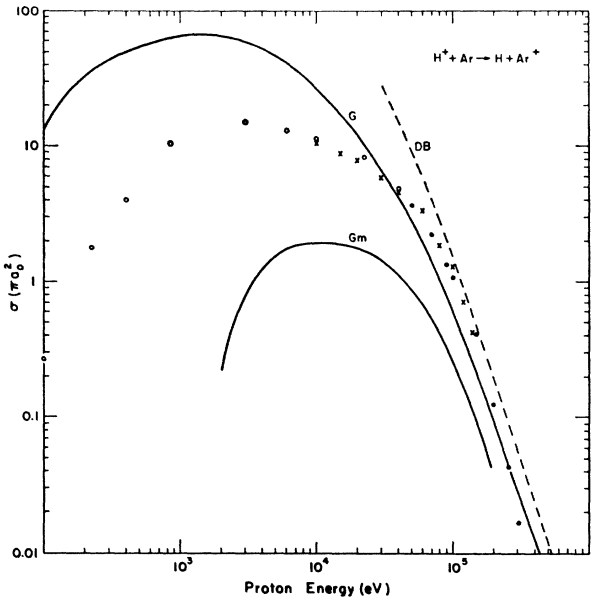

FIG. 3. Charge capture by protons in argon. Curves G, Gm, and DB, present results. Experiment: Crosses, De Heer (Ref. 10); open circles, Stedeford and Hasted (Ref. 11); full circles, Stier and Barnett (Ref. 12) or Barnett and Reynolds (Ref. 13).

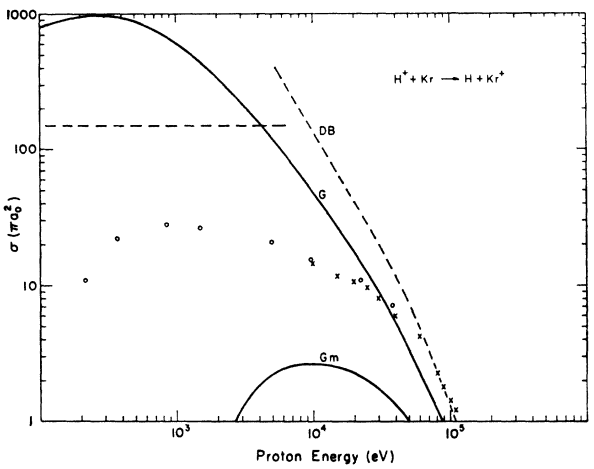

FIG. 4. Charge capture by protons in krypton. Curves G, Gm, and DB, present results. Experiment: Crosses, De Heer, (Ref. 10); open circles, Stedeford and Hasted (Ref. 11). The horizontal dashed curve is the Gryzinski cutoff.

giving an almost divergent expression for σ_{10} (recall Sec. II). In Fig. 5, for protons incident on Xe, $U_A < U_B$ and the divergence is manifest. The cross-section curve G becomes infinite at the velocity $(v_1)_{\text{crit}}$ making $(\Delta E)_l = 0$ in (2a), and remains infinite for incident $v_1 < (v_1)_{\text{crit}}$. The horizontal dashed lines in Figs. 4 and 5 show the Gryzinski geometrical upper bounds (off scale on Figs. 1–3). According to Gryzinski,

$$(\sigma_{10})_{\max} \cong \pi a_0^2 (r_A/a_0 + 27.2/U_A)^2 \qquad (8)$$

per equivalent electron, where r_A is the atomic radius of the target atom. The values of r_A used are semi-empirical values.[15]

B. Alkali Atoms

There are relatively little data for charge transfer to incident protons from alkali atoms. Figure 6 compares theory and experiment[16] for potassium target atoms; as previously, the G curves are the Gryzinski pre-

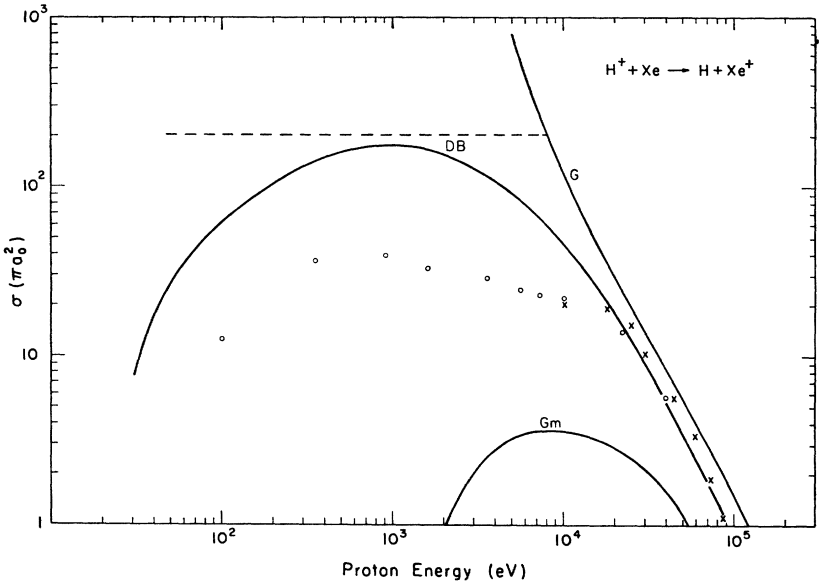

FIG. 5. Charge capture by protons in xenon. Curves G, Gm, and DB, present results. Experiment: Crosses, Afrosimov (Ref. 14); open circles, Stedeford and Hasted (Ref. 11). The dashed curve is the cutoff proposed by Gryzinski.

[15] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1956), 35th ed., p. 3089.
[16] The experimental total charge-transfer cross sections for protons on potassium were kindly furnished us by T. M. Donahue and R. Nieman prior to publication.

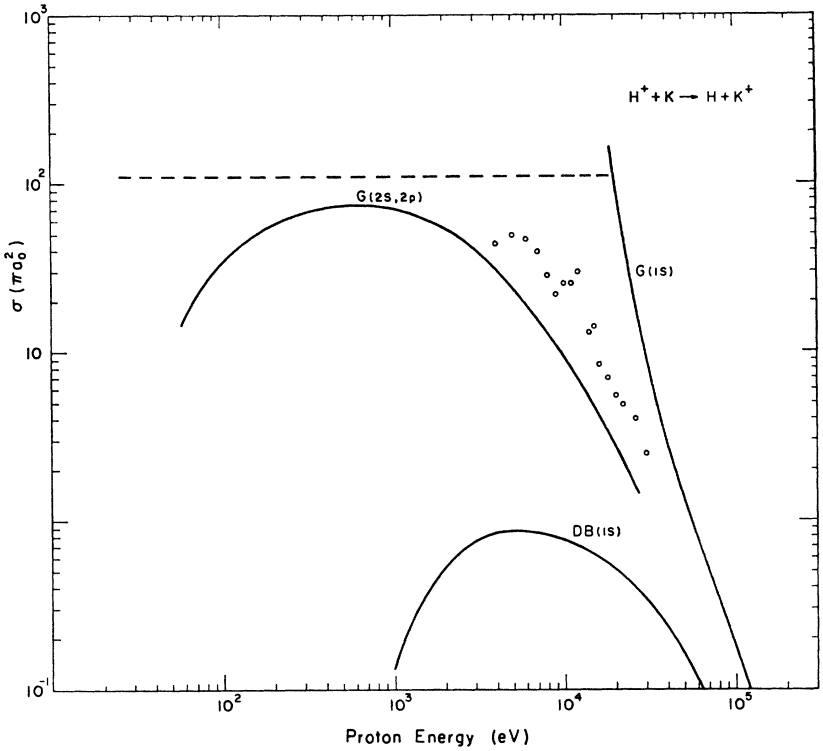

FIG. 6. Charge-transfer cross section for protons on potassium. Curves G(1s), DB(1s), and G(2s,2p), present results. Circles, experiment (Ref. 16). The dashed curve is the Gryzinski cutoff.

scriptions described in Sec. II. Again—as for all the alkalis with incident protons—for capture into the H(1s) level, $U_A < U_B$. Thus the Gryzinski prediction [labeled G(1s)] diverges at incident velocities $v_1 < (v_1)_{\text{crit}}$; as previously, the horizontal dashed line in Fig. 6 is the Gryzinski upper bound (8).

The theoretical curves in Fig. 7 show the Gryzinski predictions, including the upper bounds (8), for capture into the H(1s) state using Li, Na, and Rb as targets; in these cases no data could be found. In Fig. 8 are shown the corresponding Gryzinski predictions for capture into the $n=2$ levels of hydrogen. Although these theoretical $n=2$ cross sections lie below the corresponding $n=1$ cross sections of Fig. 7, they are very large at maximum. We note that the upper bound (8) is independent of final U_B, i.e., (8) presumably is the upper bound on the total capture cross section summed over all final states. In Fig. 6, the line labeled G(2s,2p) is the predicted σ_{10} for capture into the hydrogen $n=2$ levels.

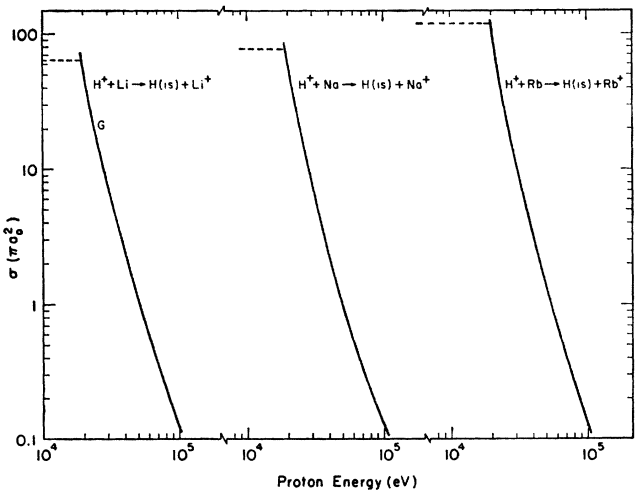

FIG. 7. Charge capture by protons into the $n=1$ state: (a) lithium-atom cross section; (b) sodium-atom cross section; (c) rubidium-atom cross section. Dashed curves represent the Gryzinski cutoff.

We remark that so far we have made no mention of charge transfer from inner shells of the target atom. We have computed the Gryzinski inner-shell charge transfer in a few alkalis, and found it to be utterly negligible. We would expect the inner-shell contribution to be even more negligible in the rare gases, where the outermost shell contains many electrons, not merely one (as in the alkalis). For these reasons, all the theoretical curves we show, in Figs. 1–9, neglect charge transfer from inner shells.

IV. AVOIDANCE OF DIVERGENCES

The results presented in Sec. III indicate that the Gryzinski prescriptions are considerably less useful for charge-transfer reactions than for ionization, whether by incident heavy ions or by electrons. The circumstance that the Gryzinski procedure described in Sec. II yields divergent cross sections for $U_A < U_B$ and very large cross sections for U_A only slightly greater than

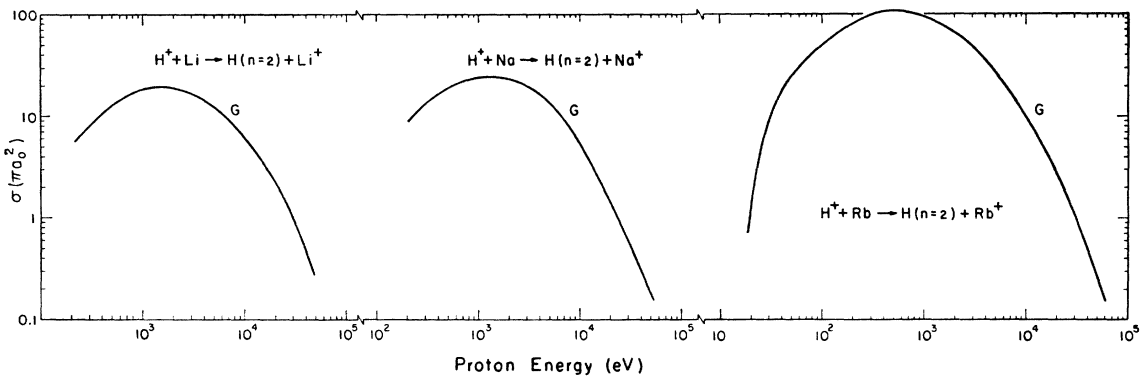

FIG. 8. Charge capture by protons into $n=2$ states: (a) protons on lithium; (b) protons on sodium; (c) protons on rubidium.

U_B, is especially troublesome. Evidently, the difficulty arises from the fact[8] that the function $\sigma_{\Delta E}{}^{\text{eff}}$, which is the integrand in (1), is proportional to $(\Delta E)^{-3}$ for small ΔE. Thus σ_{10} from (1) necessarily diverges whenever $(\Delta E)_l \leqslant 0$, and is very large if $(\Delta E)_l$ only slightly exceeds zero.

A. Modified $(\Delta E)_l$

One obvious way of avoiding divergent cross sections, therefore, is to modify the Gryzinski prescription (2a) so as to ensure that $(\Delta E)_l$ never is very small. The possible modifications are myriad; the simplest try, just to get some idea of the effect of altering $(\Delta E)_l$, is to replace (2a) by

$$(\Delta E)_l = \tfrac{1}{2} m_e v_1^2 + U_A, \tag{9}$$

leaving $(\Delta E)_u$ unchanged. Equation (9) is perhaps not as well founded as (2a) when $U_A > U_B$, but has the desired virtue that even when $U_A < U_B$, (9) does not permit charge transfer unless the transferring electron gains energy in its binary Coulomb collision with the incident ion.

The curves labeled Gm (Gryzinski modified) in Figs. 1–5 are the H(1s) capture cross sections using $(\Delta E)_l$ from (9). As anticipated, the Gm curves remain finite in Xe and reduce the discrepancies between theory and experiment near the peak. At higher energies, however, the Gm curves in Figs. 1–5 are a poorer fit to the data than the G curves. The fact that the Gm curves lie a factor of about 2 below the G curves at higher energies is obvious from Eq. (1). When $U_B \ll \lambda E_1 + U_A$, Eq. (1) is approximated by

$$\sigma_{10} = [(\sigma_{\Delta E}{}^{\text{eff}})_{\text{av}}][(\Delta E)_u - (\Delta E)_l], \tag{10a}$$

where $(\sigma_{\Delta E}{}^{\text{eff}})_{\text{av}}$ is $\sigma_{\Delta E}{}^{\text{eff}}$ evaluated at

$$\Delta E = (\Delta E)_{\text{av}} = \tfrac{1}{2} m_e v_1^2 + U_A. \tag{10b}$$

With Eq. (9) for $(\Delta E)_l$, the difference $(\Delta E)_u - (\Delta E)_l$ is only half as large as when $(\Delta E)_l$ is given by Eq. (2a).

These comparisons between the G and Gm curves suggest that a superior alternative to (2) would retain

$$(\Delta E)_u - (\Delta E)_l = 2U_B \tag{11}$$

at high incident energies, though keeping $(\Delta E)_l$ positive at low incident energies. Again, there are myriad means of so modifying Eqs. (2). Because we have no sound theoretical basis for any such modifications, and because it is understandable that the binary-encounter approximation fails at low incident energies (recall Sec. I), we have not tried any other alternative [than (9)] to Eqs. (2). It seems likely, however, that one could find empirical formulas for $(\Delta E)_l$, $(\Delta E)_u$ yielding modified Gryzinski charge-transfer predictions in agreement with noble-gas data at both high and low energies. The question whether or not such empirical formulas would have any utility for targets other than noble gases is not easily answerable *a priori*, and must be left up to future studies.

B. Detailed Balance

Gryzinski's prescription for computing σ_{10} has one obvious fundamental theoretical defect: His prescription is not generally consistent with detailed balancing. This deficiency arises from the unsymmetric way in which he treats the incident and target particles. The unsymmetric treatment occurs at several points in Gryzinski's prescription, but is most apparent in his formula for $(\Delta E)_l$, Eq. (2a). In fact, Eq. (2a) implies that when $(\Delta E)_l$ is negative in the reaction

$$B^+ + A \rightarrow B + A^+, \tag{12a}$$

then $(\Delta E)_l$ remains positive in the reverse reaction

$$A^+ + B \rightarrow A + B^+. \tag{12b}$$

In particular, for the reaction (12b), at the same relative velocity v_1 as in (12a), Eqs. (2) are replaced by

$$(\Delta E)_l = \tfrac{1}{2} m_e v_1^2 + U_B - U_A, \tag{13a}$$

$$(\Delta E)_u = \tfrac{1}{2} m_e v_1^2 + U_B + U_A, \tag{13b}$$

where U_A, U_B have the same values as in Eqs. (2) and (12a), i.e., where U_A, U_B are the ionization potentials of the neutral atoms A,B, respectively. It follows that Gryzinski's prescription surely makes one or the other of the charge-transfer cross sections (12a), (12b) infinite, in obvous violation of detailed balance.

The foregoing remarks, taken together with the results of Figs. 1–5 discussed above, suggest the following hypothesis: within the confines of the classical binary-encounter approximation, Gryzinski may have hit on very nearly the right formulas for $(\Delta E)_l$, $(\Delta E)_u$ under the circumstance that the initial binding energy of the electron exceeds its final binding energy. On this basis, it is not necessarily a defect that his prescription violates detailed balance and makes σ_{10} infinite whenever the final binding energy of the electron exceeds its initial binding energy. Rather, one can postualte that Gryzinski's prescription is to be used only when the initial binding energy of the electron exceeds its final binding energy; if the initial binding energy is less than the final binding energy, the desired cross section is to be calculated via detailed balance from the Gryzinski procedure for the reverse reaction.

The curve marked DB in Fig. 5 is the theoretical cross section for charge transfer into H(1s) from ground-state Xe atoms, computed via this detailed balancing modification of Gryzinski's prescription. Specifically, at each energy E in Fig. 5, the DB curve is computed from

$$\sigma_{DB}(E)=\sigma_{10}[H^+, Xe(^1S_0)\rightarrow H(1s), Xe^+(^2P); E]$$
$$=(\omega_f/\omega_i)\sigma_{10}[Xe^+(^2P), H(1s)\rightarrow Xe(^1S_0), H^+; \tau E], \quad (14)$$

where $\tau=M_{Xe}/M_p=131$, and σ_{10} on the right side of (14) is the Gryzinski theoretical cross section for the reaction

$$Xe^+(^2P)+H(1s)\rightarrow Xe(^1S_0)+H^+ \quad (15)$$

at incident ion energy τE, computed in accordance with Sec. II; note that the equivalent number of electrons now is $\frac{1}{2}$, because for any given incident Xe^+ ion, half the target H(1s) atoms will have their electron spins wrongly aligned for capture. Ignoring nuclear spins, $\omega_f=12$ is the statistical weight of the reactants on the left side of (15); $\omega_i=1$ is the statistical weight of the reactants on the right side of (15).

The agreement in Fig. 5 between curve DB and experiment is not particularly good. However, the ionization potentials of Xe and of H are very nearly equal, so that the Gryzinski computed cross section for the reaction (15) tends to be much too large at energies near its peak, for reasons previously discussed. Correspondingly, the $\sigma_{DB}(E)$ computed via (14) will be too large at energies near its peak. Charge transfer to H(1s) from alkali atoms should offer a much better opportunity for useful exploitation of this detailed-balancing approach. The curve labeled DB(1s) in Fig. 6 is the detailed-balancing prediction for capture into H(1s) from potassium, using the appropriate analog of Eq. (14). Figure 9, to be compared with Fig. 7, shows the detailed-balancing predictions for capture into H(1s) from other alkali targets. For all alkali targets, the ratio $\omega_f/\omega_i=1$ in the analog of (14). The DB curves for He, Ne, Ar, and Kr diverge, as shown in Figs. 1–4 and are explained following Eqs. (13).

V. CONCLUDING REMARKS

Even at high energies, where the Gryzinski predictions remain finite for both reactions (12a) and (12b), Gryzinski's theory is not formally consistent with detailed balance. For example, consider again capture into H(1s) from Xe($^1S_0$). Then in the very-high-energy

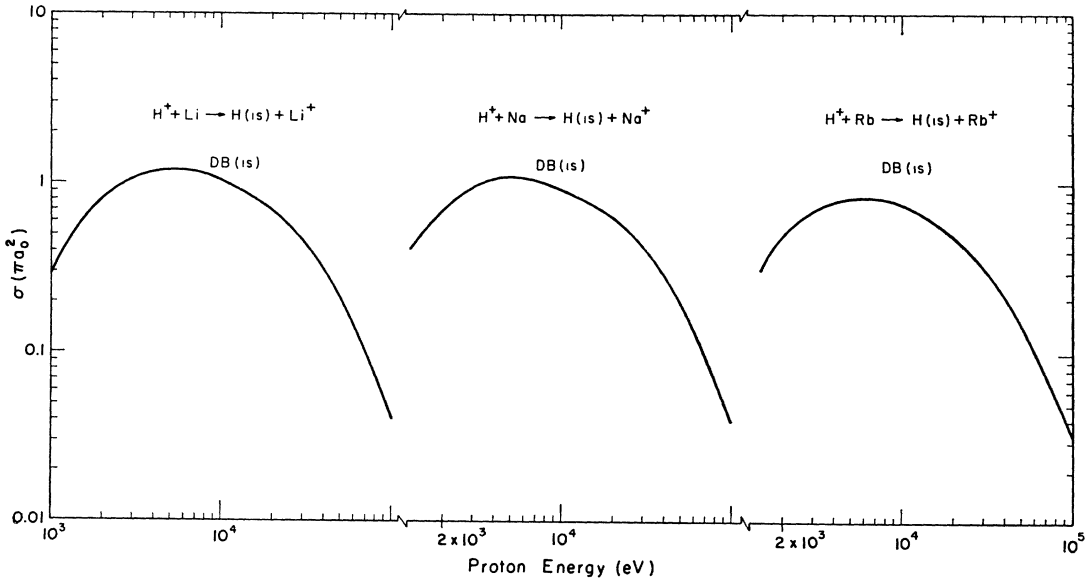

FIG. 9. Charge capture by protons into the $n=1$ state computed by detailed balancing: (a) protons on lithium; (b) protons on sodium; (c) protons on rubidium.

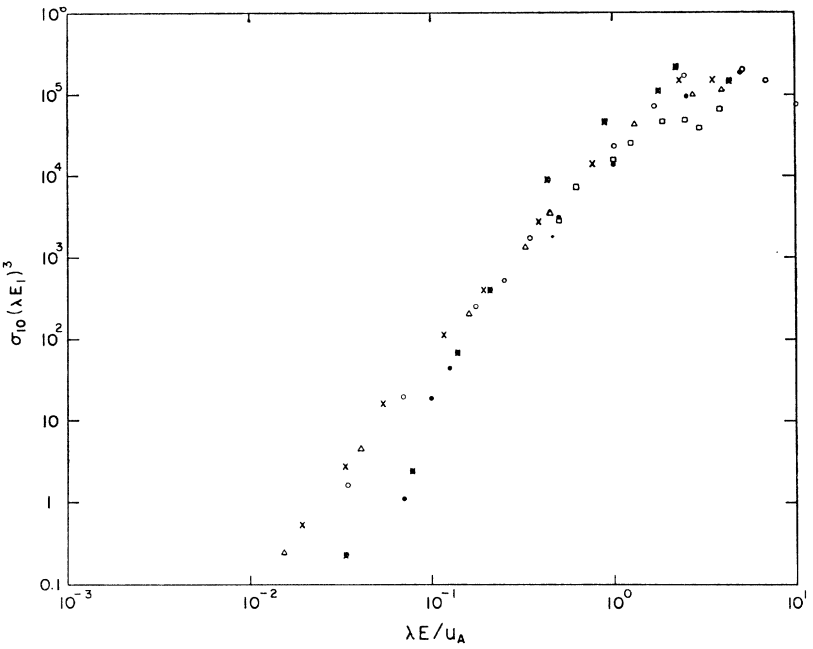

FIG. 10. Scaled experimental charge-transfer cross sections. Crossed circles, helium; full circles, neon; open circles, agron; crosses, krypton; triangles, xenon; open squares, potassium. Data are from Figs. 1–6.

limit, Eq. (5) yields

$$\sigma_{10}[H^+, Xe(^1S_0) \rightarrow H(1s), Xe^+(^2P); E] = 6[2\pi e^4/(\lambda E)^3]U_B \quad (16a)$$

$$\sigma_{10}[Xe^+(^2P), H(1s) \rightarrow Xe(^1S_0), H^+; \tau E] = \tfrac{1}{2}[2\pi e^4/(\lambda E)^3]U_A, \quad (16b)$$

where $\lambda = 1/1836$, $U_B = 13.6$, and $U_A = 12.13$. The ratio of (16a) to (16b) differs by the factor U_B/U_A from the ratio $\omega_f/\omega_i = 12$ required by detailed balance, Eq. (14). This result carries the further implication that modifying Gryzinski's procedure, so as to make $(\Delta E)_l$ positive at low energies while retaining (11) at high energies, cannot yield results consistent with detailed balancing.

On the other hand, U_B/U_A is close to unity for $H(1s)$ capture from $Xe(^1S_0)$, so that in effect Gryzinski's high energy predictions (16) do obey detailed balance. Even when U_B is not so close to U_A—or when the numbers of classically "equivalent" electrons on the left sides of (12a) and (12b) are not as wonderfully consistent with quantum-mechanical statistical weights as in the case of $H(1s)$ capture from ground-state Xe—the high-energy Gryzinski predictions will deviate from detailed balance merely by a constant factor, generally of the order of unity. This remark may help make it believable that the Gryzinski charge-transfer cross sections turn out to have approximately the correct high-energy behavior, in the noble gases at any rate (Figs. 1–5).

As Eqs. (16) show, the Gryzinski charge-transfer cross sections are proportional to E^{-3} at high incident E. Bates and Mapleton[5] have pointed out that Thomas's classical theory[17] predicts a high energy $\sigma_{10}(E) \sim E^{-11/4}$ for charge transfer to protons from "heavy" atoms, which should include all target atoms examined in this paper, except perhaps He and Li. Thomas's theory involves an important statistical assumption concerning the velocity distribution of the target bound electrons; also (we think) the $E^{-11/4}$ dependence should not persist to incident proton velocities which are very large compared to all reasonably probable bound-electron velocities. The essential distinction between the Thomas and Gryzinski theories, however, is that Thomas assumes that capture takes place as the result of not one but rather two binary encounters: first between the oncoming proton and a bound electron proton, and second between the scattered electron and the nucleus of the atom to which it originally was bound.

Certainly at high energies, Thomas's double binary-encounter model makes more sense than Gryzinski's single binary-encounter model. Moreover, Thomas does not *postulate* an energy range $(\Delta E)_l$ to $(\Delta E)_u$ for significant probability of electron capture; he *computes* the probability of capture for all initial (first binary encounter) energy transfers ΔE and scattering angles. Indeed, it is clear that the probability of electron capture can not depend only on ΔE; especially at high incident energies, to have any chance of being captured, the electron must end up moving almost parallel to the incident proton. Now the energies past the peak displayed in Figs. 1–5 are not so high as to make Thomas's $E^{-11/4}$ dependence questionable; moreover, an $E^{-11/4}$ dependence is practically indistinguishable from E^{-3}. It is possible, therefore, that Gryzinski succeeds at the higher energies in Figs. 1–5 because at those energies his postulated limits on ΔE, Eqs. (2), happen to nearly coincide with the actually effective range of ΔE in

[17] L. H. Thomas, Proc. Roy. Soc. (London) **A114**, 561 (1927).

Thomas's double binary-encounter integrals. Explicit verification of this possibility would considerably elucidate the theoretical foundation of Gryzinski's prescriptions for predicting charge-transfer cross sections.

In much of this paper we have criticized Gryzinski's prescriptions, on both formal and pragmatic grounds. Gryzinski's prescriptions do have one very important practical virtue, however: Compared with most other theories, Gryzinski cross sections—in their original form or modified as suggested in Sec. IV—are very easy to compute. It is interesting, therefore, that at high energies, using Eq. (5), Gryzinski predicts

$$\frac{\sigma_{10}E^3\lambda^3}{U_B}=\frac{2\pi e^4}{3}\frac{\lambda^2E^2}{U_A^2}\left[\frac{7+3\lambda E/U_A}{(\lambda E/U_A+1)^3}\right]=F\left(\frac{\lambda E}{U_A}\right). \quad (17)$$

Equation (17), which asserts $\sigma_{10}E^3\lambda^3/U_B$ is a function of $\lambda E/U_A$, is surprisingly close to the scaling law inferred by Bates and Mapleton[5] from their modification of the Thomas theory. Therefore, in the spirit of their paper, in Fig. 10, we have plotted the experimental values of $\sigma_{10}E^3\lambda^3$ against $\lambda E/U_A$, for the noble gases and potasium from Figs. 1–6. (We have multiplied the values for He and K by 3 and 6, respectively, to obtain six equivalent electrons in each case.) It can be seen that the heavy noble gases scale exceptionally well; however, all points lie close together in the region $10^{-1}<\lambda E/U_A<10$. The fact that potassium agrees so well with a curve obtained from scaling only noble-gas data may be construed to mean that this curve can be used for predicting other charge-transfer reactions in this range of values of $\lambda E/U_A$.

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Alignment of the H_2^+ Molecular Ion by Selective Photodissociation. II. Experiments on the Radio-Frequency Spectrum*

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Magnetic resonance transitions have been observed among several Zeeman sublevels of the hyperfine states of H_2^+ in magnetic fields from 50 to 115 mG. The following g-factor ratios $g(KF_2F)/g(K'F_2'F')$ have been determined: $g(1\,\frac{1}{2}\,\frac{3}{2})/g(1\,\frac{3}{2}\,\frac{5}{2})=0.584(3)$; $g(1\,\frac{1}{2}\,\frac{3}{2})/g(1\,\frac{3}{2}\,\frac{5}{2})=1.241(6)$; $g(1\,\frac{1}{2}\,\frac{3}{2})/g(3\,\frac{3}{2}\,\frac{9}{2})=1.051(5)$. An analysis using the ratios yields equations relating the hyperfine interaction constants b, c, and d in the Hamiltonian $H=b\mathbf{I}\cdot\mathbf{S}+cI_zS_z+d\mathbf{K}\cdot\mathbf{S}$, such as $(\sqrt{2}c/6-\sqrt{2}d/3)/(3b/2+23c/30-d/6)=(8/\sqrt{5})\{[g(1\,\frac{1}{2}\,\frac{3}{2})/g(3\,\frac{3}{2}\,\frac{9}{2})]-1\}$. When nuclear contributions to the g factors are included and a weighted average of the measured ratios is used with theoretical values of b and c from the literature, a value for d may be obtained. The result is $d=32.2\pm5.1$ MHz. With this it is possible to predict the H_2^+ hfs spectrum in the 20-cm region with an error estimate of a few MHz. $(1\,\frac{3}{2}\,\frac{3}{2})-(1\,\frac{1}{2}\,\frac{3}{2})=1415.3$ MHz; $(1\,\frac{3}{2}\,\frac{3}{2})-(1\,\frac{1}{2}\,\frac{1}{2})=1400.9$ MHz; $(1\,\frac{3}{2}\,\frac{5}{2})-(1\,\frac{1}{2}\,\frac{3}{2})=1398.1$ MHz; $(1\,\frac{3}{2}\,\frac{1}{2})-(1\,\frac{1}{2}\,\frac{3}{2})=1322.4$ MHz; $(1\,\frac{3}{2}\,\frac{1}{2})-(1\,\frac{1}{2}\,\frac{1}{2})=1308.2$ MHz. The ion sample is contained electrically in an rf quadrupole trap where production and analysis of alignment is by selective optical excitation by linearly polarized light of the transition $1s\sigma$-$2p\sigma$ leading to dissociation. The mechanism is briefly reviewed. A description is given of the trap and apparatus for the detection of the trapped ions and magnetic resonance.

INTRODUCTION

IN an earlier paper,[1] herein called I, a discussion was presented of the feasibility of alignment of a sample of free hydrogen molecule ions by optical means to permit observation of the rf spectrum of this simplest of all molecules. The source of the level splittings are the several magnetic interactions in the ion which depend differently on the average positions of the electron and protons, so that a measurement of the spectrum provides a very exacting test of the ground-state molecular wave function, which is believed known to very high precision.[2] Interesting small effects such as unknown electron-proton radiative corrections, centrifugal stretching, vibrational effects, rotational mixing of excited states,[3] and electron slippage should be revealed. Further, H_2^+ has been discussed as a possible interstellar radio source.[4] A laboratory measurement of the spectrum would aid in a search for this radiation.

The method discussed in I for detection of magnetic resonance in H_2^+ is akin to the optical-pumping method

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