Approximate scaling formula for collisional angular-momentum mixing of Rydberg atoms

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(Received 27 June 1980)

An approximate scaling formula has been determined that permits the rapid estimation of cross sections for angular-momentum-changing collisions of Rydberg atoms with a variety of targets, using information about low-energy-electron scattering from the target. The formula is obtained by fitting the results of coupled-channel and Born-approximation calculations to functions of reduced parameters. Application to Na(nd) + He, Ne, Ar, N_2, CH_4, C_3H_8; Rb(nf) + He, Ar, Xe; and Xe(nf) + CO_2, suggests that the accuracy is about a factor of 2.

I. INTRODUCTION

Considerable attention has been devoted recently to collisions involving Rydberg atoms, especially the "l mixing" or angular-momentum-changing process[1-12]

$$R^*(nl)+X \rightarrow R^*(nl')+X, \quad l' \neq l \tag{1}$$

where R^* is the Rydberg atom and X is the collision partner. It has generally been argued that one should be able to analyze this process in terms of the cross section for low-energy-electron scattering from X. In this paper we present a very simple scaling formula that can be used to estimate the cross section for reaction (1) to about a factor of 2, starting from information about e-X scattering. This degree of accuracy is useful because the cross sections may vary by as much as an order of magnitude over the range of n considered.

The scaling formula was determined by fitting the results of coupled-channel and Born-approximation calculations to functions of reduced parameters. These parameters have a reasonable physical interpretation in terms of the "nearly free-electron" picture. The determination of the formula and its physical interpretation are discussed in Sec. II. Section III contains the results of calculations for several systems, including molecular targets. The accuracy of the results for more complicated targets suggests that their internal structure may play only a minor role in the collisions studied.

II. THE SCALING FORMULA

A. Determination

Our previous calculations[6,8] of angular-momentum mixing may be characterized as exact or approximate solutions of a specific, well-defined model problem. We will begin by summarizing this problem, and then show how one might expect to estimate the desired cross sections using empirical functions of reduced parameters. Then one additional approximation is introduced to tie the model problem to the physical system involving the Rydberg atom and an arbitrary collision partner.

The model problem may be posed as follows. Consider the system $Na^* + X$ indicated in Fig. 1. The Rydberg atom Na^* has principal quantum number n, and we consider only the initial level $l=2$ and other levels $l=3,4,\ldots,n-1$. Assume

$$E_{nl} - E_{nd} = \Delta E, \quad l=3,4,\ldots,n-1. \tag{2}$$

This is approximately true for sodium since the d quantum defect δ_d is much larger than δ_l for $l>2$. The interaction potential is given by a Fermi pseudopotential

$$V(\vec{R},\vec{r}) = 2\pi A \delta(\vec{r}-\vec{R}). \tag{3}$$

For the present discussion, A is to be considered an arbitrary constant. We wish to calculate $\sigma_{l\,\mathrm{mix}}$, defined by

$$\sigma_{l\,\mathrm{mix}} = \sum_{l=3}^{n-1} \sigma(nd \rightarrow nl), \tag{4}$$

using the quantum-mechanical Arthurs and Dalgarno[13] formalism or the Born approximation as discussed previously.[6,8] We expect that $\sigma_{l\,\mathrm{mix}}$ will depend on n, A, ΔE, and v, the relative velocity of Na^+ and X. That is,

$$\sigma_{l\,\mathrm{mix}} = \sigma_{l\,\mathrm{mix}}(n, A, \Delta E, v). \tag{5}$$

We wish to find a functional form for $\sigma_{l\,\mathrm{mix}}$. Previously, we showed[8] that if $\Delta E = 0$, the results of the Born approximation may be well fitted by

$$\sigma_{l\,\mathrm{mix}} \propto \left(\frac{A}{v}\right)^2 n^{-2.733}, \quad \Delta E = 0. \tag{6}$$

We can write this in a slightly different form by separating out a factor $\pi n^4 a_0^2$ (the so-called geometrical cross section of the Rydberg atom), and

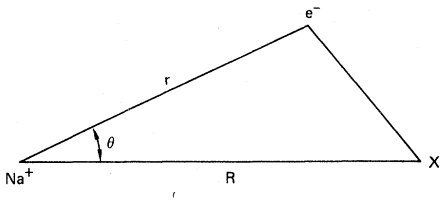

FIG. 1. Schematic diagram of coordinates used to describe the Rydberg atom and its collision partner.

making A/v dimensionless by dividing by the unit length and velocity in atomic units:

$$\sigma_{l\,\mathrm{mix}} \propto \pi n^4 a_0^2 \beta^2 , \quad \Delta E = 0 \tag{7}$$

where

$$\beta^2 = \frac{\hbar^2}{m_e^2 a_0^4} \frac{A^2}{v^2 n^{6.733}} . \tag{8}$$

The constant m_e is the electron mass in atomic units. If $\Delta E \neq 0$ our previous results[8] suggested that in the weak coupling limit a more general formula could be written

$$\sigma_{l\,\mathrm{mix}} \propto \pi n^4 a_0 \beta^2 f(\gamma) , \tag{9}$$

where

$$\gamma = \frac{n^2 a_0 \Delta E}{\hbar v} ; \tag{10}$$

$f(\gamma)$ is an approximation to the family of functions shown in Fig. 2 of Ref. 8 that depend weakly on the parameter n. In neglecting the dependence on n we simplify the functional form but introduce some ambiguity into the determination of f. Equation (9) is expected to be a reasonable approximation in the weak-coupling (small A or large n) limit. We now postulate that a more general formula can be obtained by writing

$$\sigma_{l\,\mathrm{mix}} = \pi n^4 a_0^2 g(\beta) f(\gamma) , \tag{11}$$

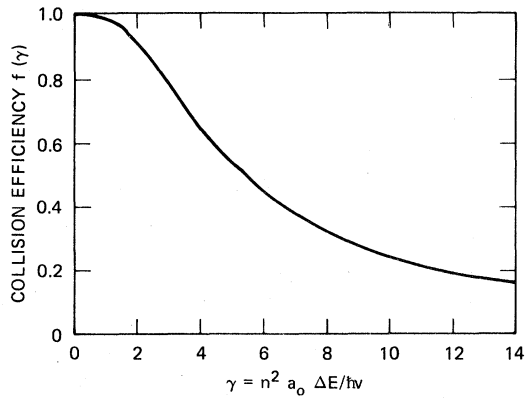

FIG. 2. The function $f(\gamma)$, which we interpret as the probability that a collision between the electron and the collision partner will cause a change of angular-momentum level of the electron.

where

$$g(\beta) \to \lambda \beta^2 \quad \text{as} \quad \beta \to 0 . \tag{12}$$

We will find later the constant λ has the value 0.715. We performed a number of calculations using the coupled-channel method and Born approximation to test the usefulness of Eq. (11). For the situations previously considered, the Born approximation could be applied only when n was large, and the coupled-channel method was feasible only when n and the number of channels was small. However, by varying A and v, we have been able to probe a wider region of β-γ space and still keep the number of channels small. The results of these calculations are listed in Table I.

It was possible to find, empirically, functions $f(\gamma)$ and $g(\beta)$ such that the results of the coupled-channel and Born-approximation calculations were approximated by Eq. (11) to about a factor of 2. These functions are shown in Figs. 2 and 3 and tabulated in Tables II and III.

At this point we have obtained an approximate scaling rule that can be used to estimate the results of a model problem involving a Fermi pseudopotential with arbitrary constant A. We now make an additional approximation to relate A to the low-energy-electron scattering by X. Let

$$4\pi A^2 = \sigma_{\mathrm{el}}\left(\frac{1}{2n^2}\right) . \tag{13}$$

σ_{el} is the e-X scattering cross section at the electron energy $1/2n^2$, which is the average kinetic energy of the electron in the quantum level n. As $n \to \infty$, $A \to L$, the scattering length. Some justifi-

TABLE I. Values of $\sigma_{l\,\mathrm{mix}}$ as a function of n, v, and L obtained by coupled-channel calculations.

n	v (a.u.)	L (a.u.)	γ	β	$\sigma_{l\,\mathrm{mix}}/\pi n^4 a_0^2$
4	6.867×10^{-4}	1.19	4.75	16.21	0.192
5	6.867×10^{-4}	1.19	3.82	7.64	0.387
6	6.867×10^{-4}	1.19	3.20	4.14	0.440
7	6.867×10^{-4}	1.19	2.75	2.46	0.402
8	6.867×10^{-4}	1.19	2.41	1.56	0.352
6	6.867×10^{-4}	0.595	3.20	2.07	0.324
6	6.867×10^{-4}	0.3	3.20	1.05	0.200
6	6.867×10^{-4}	0.15	3.20	0.523	0.082
6	6.867×10^{-4}	0.075	3.20	0.260	0.025
6	1.373×10^{-3}	1.19	1.60	2.07	0.535
6	4.856×10^{-4}	0.841	4.53	4.14	0.217
6	3.140×10^{-4}	0.544	7.00	4.14	0.102
6	3.140×10^{-4}	0.272	7.00	2.07	0.085
6	3.140×10^{-4}	0.137	7.00	1.04	0.055
6	3.140×10^{-4}	0.0686	7.00	0.523	0.024
6	3.140×10^{-4}	0.0343	7.00	0.260	0.0078
6	4.856×10^{-4}	0.421	4.53	2.07	0.171
6	1.717×10^{-3}	1.488	1.28	2.07	0.567
6	1.030×10^{-3}	0.892	2.14	2.07	0.462

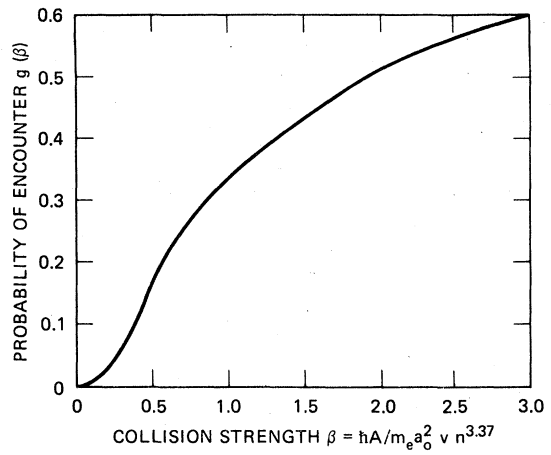

FIG. 3. The function $g(\beta)$, which we interpret as the probability of encounter between the Rydberg electron and a collision partner.

cation is given for Eq. (13) in Ref. 8. In this work we find, *a posteriori*, that it is reasonably successful.

With the substitution defined by Eq. (13), the final form of the scaling rule is given by Eqs. (10), (11), and

$$\beta = \frac{\hbar}{m_e a_0^2} \frac{1}{v n^{3.337}} \left(\frac{\sigma_{el}(1/2n^2)}{4\pi} \right)^{1/2} . \tag{14}$$

Although the scaling rule is empirical, it can be related to a natural physical interpretation of the scattering process. This interpretation will be discussed in the next section. Finally, note that although the preceding discussion has assumed that the Rydberg atom was sodium, we find that the formula may be applied to other atoms as well. The essential feature of the model is that the initial level is separated by ΔE from a nearly degenerate set of possible final levels. For large n, the difference in the number of final states for an initial $l = 2$ or 3 is small. Hence we will test the formula for collisions involving Na (nd), Rb(nf), and Xe(nf).

TABLE II. Values of the collision strength g as a function of β. For $\beta \leq 0.5$, $g = 0.715\,\beta^2$. For $\beta \geq 3.0$, we arbitrarily set $g = 0.60$.

β	g
0	0
0.5	0.18
1.0	0.33
1.5	0.43
2.0	0.51
2.5	0.56
3.0	0.60

TABLE III. Values of the collision efficiency.

$n^2 a_0 \Delta E/\hbar v$	f
0	1.00
1	0.99
2	0.91
3	0.78
4	0.65
5	0.54
6	0.45
7	0.38
8	0.32
9	0.28
10	0.25
11	0.22
12	0.19
13	0.18
14	0.17

B. Physical interpretation and discussion

The approximate scaling formula is a product of three factors. The geometrical factor $\pi n^4 a_0^2$ shows that the cross section scales with the overall size of the atom. We interpret the parameter β as a coupling strength, and $g(\beta)$ as the probability that the collison partner will encounter the orbiting Rydberg electron. β increases with σ_{el}, which gives an effective size of the collision partner, and decreases with n, because for larger n the electron "cloud" is more diffuse. We interpret the function $f(\gamma)$ as the probability that an elastic collision between the orbiting electron and the collision partner will cause a transition into a new energy level. It is interesting to note that the parameter γ may be rewritten as

$$\gamma \cong (\Delta\delta)\frac{v_e}{v} , \tag{15}$$

where $\Delta\delta$ is the difference in the quantum defects of initial and final states, and $v_e = 1/n$ (atomic units), the velocity corresponding to the average kinetic energy of an electron with principle quantum number n. This formula is obtained by expanding

$$\Delta E = \frac{1}{2(n+\delta_{l'})^2} - \frac{1}{2(n+\delta_l)^2} \tag{16}$$

in the limit $\delta_l \ll n$ and substituting into Eq. (10). When γ is large, $f(\gamma) \to 0$ and hence the l mixing will be small. Equation (15) shows that this can occur because the inelasticity is large, or because v_e is large compared to v, and hence it is less likely that a collison will deflect the electron enough to change the shape of its orbit. Conversely, the l mixing will be larger when γ is small. This may occur either because the energy difference between initial and final states is small,

or because the electron is moving slowly relative to the collision partner and a collision tends seriously to perturb its orbit.

It is instructive to consider various limiting values of the scaling functions g and f. We have already noted that the function g is parabolic as the argument approaches zero. For large values of the argument, g tends to saturate at a value of 0.5 to 0.6. This number is somewhat arbitrary since the prefactor $\pi n^4 a_0^2$ could equally well have been $2\pi n^4 a_0^2$ or $4\pi n^4 a_0^2$. Appropriate limiting values of $f(\gamma)$ are more easily defined. As $\Delta E \to 0$ (or $v \to \infty$), $\gamma \to 0$, and $f(\gamma) \to 1$. We can thus draw the following conclusions about the general behavior of l-mixing cross sections. For large n, $f \to 1$, and the angular momentum levels nd and $nl' \geq 2$) are effectively degenerate. The decrease of $\sigma_{l\,\mathrm{mix}}(n)$ with increasing n is due to the reduced coupling strength of the diffuse electron cloud. On the other hand, the (inelastic) cross section tends to be small for small n because of the smaller geometrical cross section and the increased importance of the energy-level splitting ΔE.

We now consider how the velocity dependence of the l-mixing cross section is controlled by the functions f and g. At large n, γ will generally be sufficiently small so that $f \approx 1$ for typical (thermal) value of v. (Note that $\Delta E \propto n^{-3}$.) Then the behavior of $g(\beta)$ shows that $\sigma_{l\,\mathrm{mix}}$ decreases for larger values of v. In the limit $v \to \infty$, $\sigma_{l\,\mathrm{mix}} \propto 1/v^2$ but for smaller values of v the dependence may go as $1/v$ or weaker. The $1/v$ dependence corresponds to the intuitive notion that a slower projectile spends more time passing through the Rydberg atom, and consequently has a higher probability of encountering the electron. The opposite may be true for small n when the coupling is stronger. In this case, $g(\beta)$ may achieve a saturated value of ~0.5–0.6 for a range of thermal velocities, so that the velocity dependence of $\sigma_{l\,\mathrm{mix}}$ will be determined by $f(\gamma)$. Examination of Fig. 2 shows that $\sigma_{l\,\mathrm{mix}}$ will then increase with larger values of v, because increasing v has the same effect as decreasing ΔE. Similar behavior has been analyzed theoretically in other inelastic collisions by Olson.[14]

III. RESULTS AND DISCUSSION

A. General comments

The approximate scaling formula determined in the previous section has been used to estimate angular-momentum-changing cross sections for collisions of Na(nd) with He, Ne, Ar, N_2, CH_4, and C_3H_8, for collisions of Rb(nf) + He, Ar, and Xe, and for collisions of Xe(nf) + CO_2. The collision velocities used were the mean thermal velocities at the temperatures of the experiments with which the results are compared. This velocity is given by

$$v = \left(\frac{8kT}{\pi\mu}\right)^{1/2}, \tag{17}$$

where k is Boltzmann's constant and μ is the reduced mass of the collision system. For collisions involving Na, we used $T = 430$ K, for Rb $T = 520$ K, and for Xe, $T = 300$ K.

The electron scattering cross sections were determined as follows. For the rare gases Ne, Ar, and Xe, we used the formulas for the s, p, and higher phase shifts given by O'Malley[15] and computed the total elastic scattering cross section in the standard way. For He, we used at every n the value $A = 1.19a_0$ (the scattering length) as the constant term in the Fermi potential [Eq. (3)]. For N_2, following Gallagher *et al.*,[3] we used $A = 0.7a_0$ at every n. For low-energy-electron scattering ($E \leq 0.5$ eV) from He and N_2 there is not a strong energy dependence of the cross section. For e-CO_2 and e-CH_4, we used the scattering data compiled by Itikawa.[16] These data are the total-momentum-transfer cross sections, which may include inelastic processes, rather than the elastic cross sections required by the theory. For the CH_4 data, Itikawa estimates an uncertainty in the data of about a factor of 2. At this level of accuracy, and at the very low electron energies involved, the substitution of the momentum-transfer cross section for the elastic cross section is probably not too serious an approximation. This view is supported by Itikawa. The CO_2 data are more accurate, but the uncertainty in the scaling formula probably renders the distinction

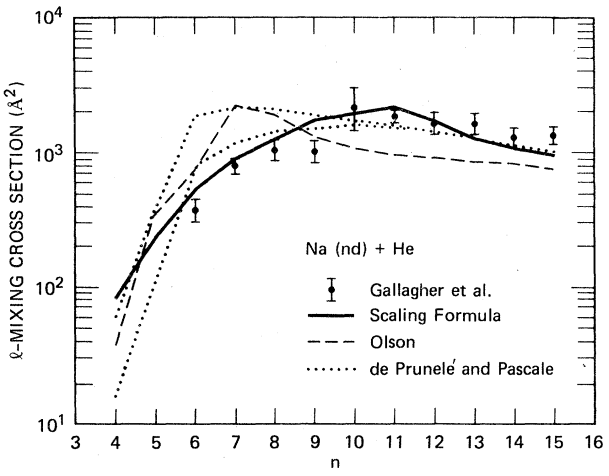

FIG. 4. The l-mixing cross sections for Na(nd)+ He. The calculation of de Prunelé and Pascale obtained upper and lower limits to the cross sections.

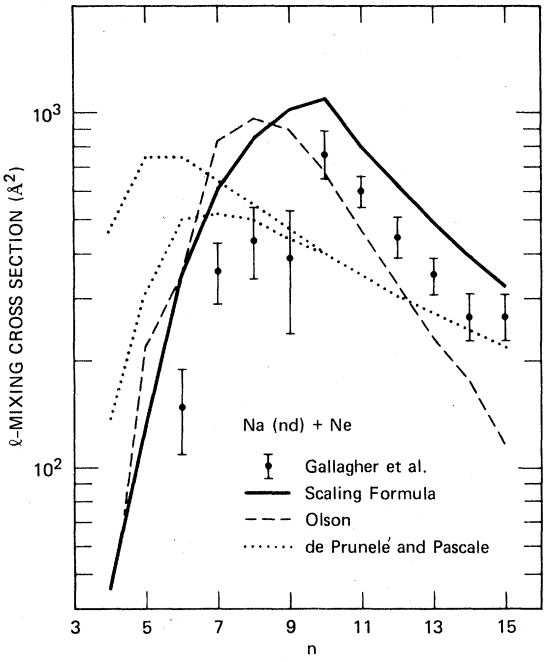

FIG. 5. The l-mixing cross sections for Na(nd)+ Ne. The calculation of de Prunelé and Pascale obtained upper and lower limits to the cross sections.

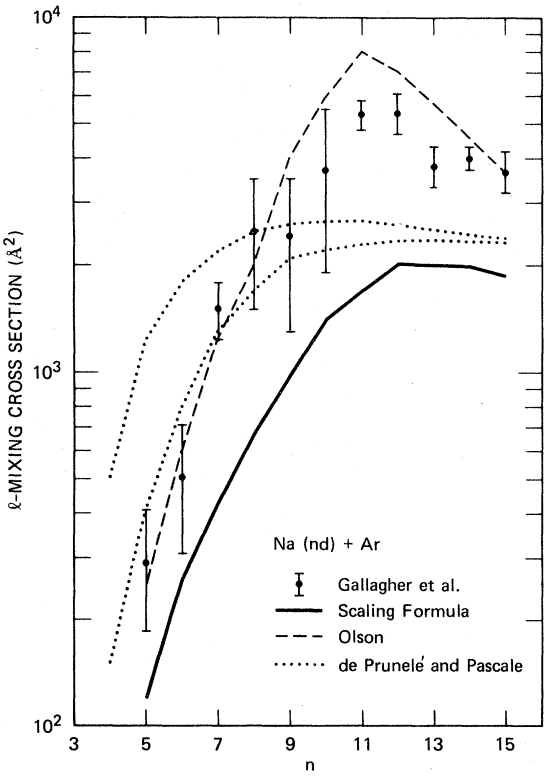

FIG. 6. The l-mixing cross sections for Na(nd)+ Ar. The calculation of de Prunelé and Pascale obtained upper and lower limits to the cross section.

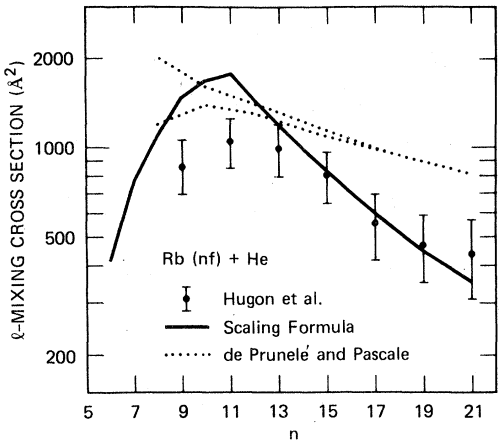

FIG. 7. The l-mixing cross sections for Rb(nf)+ He. The calculation of de Prunelé and Pascale obtained upper and lower limits to the cross sections.

between momentum-transfer cross section and elastic cross section irrelevant. Finally, the e-C_3H_8 scattering data of McCorkle *et al.*[17] were used. In this case also, the momentum-transfer cross sections were measured.

The energy differences ΔE of Na were taken to be the d-f splittings measured by Gallagher *et al.*[18] The parameter γ in the Rb and Xe collisions were determined from Eq. (15), assuming

$$\Delta\delta \approx \delta_f , \tag{18}$$

where $\delta_f = 0.02$ for Rb and 0.055 for Xe.

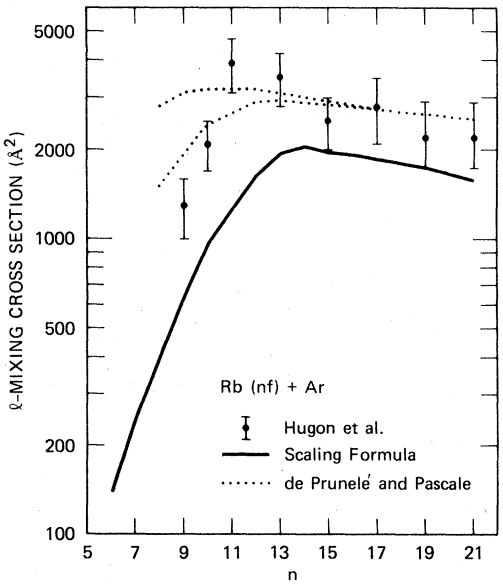

FIG. 8. The l-mixing cross sections for Rb(nf)+ Ar. The calculation of de Prunelé and Pascale obtained upper and lower limits to the cross sections.

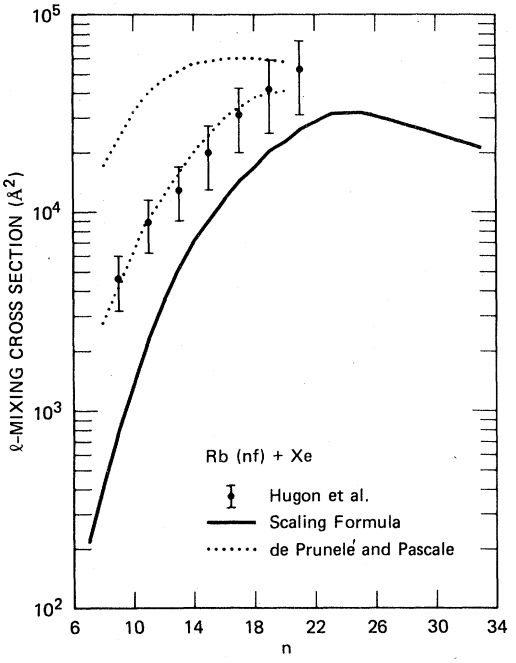

FIG. 9. The l-mixing cross sections for Rb(nf)+Xe. The calculation of de Prunelé and Pascale obtained upper and lower limits to the cross sections.

B. Cross sections

Results for collisions of Na and Rb Rydberg atoms with rare gases are presented in Figs. 4–9. The agreement for the case that the collision partner is He is especially good. Note that the present results for Na(nd)+He are determined using the scaling formula; they differ only slightly from the coupled-channel and Born-approximation results presented previously. The good agreement for He suggests that the Fermi pseudopotential is a rather good approximation when the low-energy-electron scattering has a weak dependence on energy. Also, the small polarizability of He supports the use of a short-range (delta-function) approximation to the e-He potential. For the collisions involving Ar and Ne the energy dependence of the electron scattering cross section does influence the predicted result for $n \sim 10$–20. The calculated cross sections are in reasonable agreement with the data in this range, suggesting that the approximate method of including the energy dependence [Eq. (13)] is at least qualitatively correct.

We have also applied the scaling formula to collisions involving more complicated partners. In these calculations the internal structure of the target is neglected, although it may of course influence the electron scattering cross sections used. The qualitative agreement observed between the calculations and experiment tends to suggest that the elastic scattering of the electron by the target is the dominant mechanism of l mixing in these collisions as well as in those involving rare gases. Note that the formula is not in-

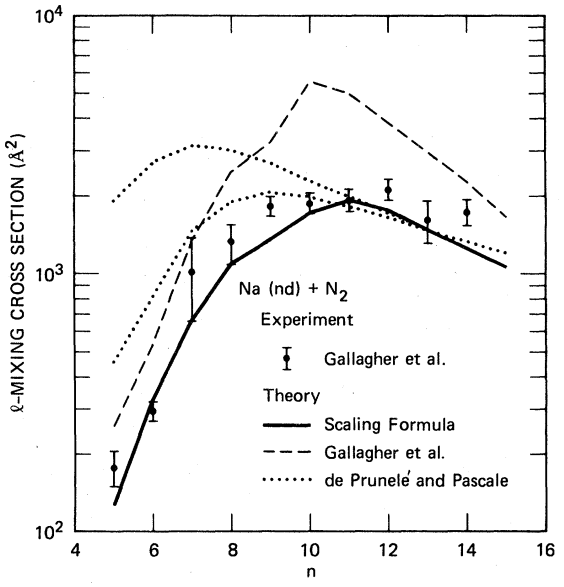

FIG. 10. The l-mixing cross sections for Na(nd)+N_2. The calculation of de Prunelé and Pascale obtained upper and lower limits to the cross sections.

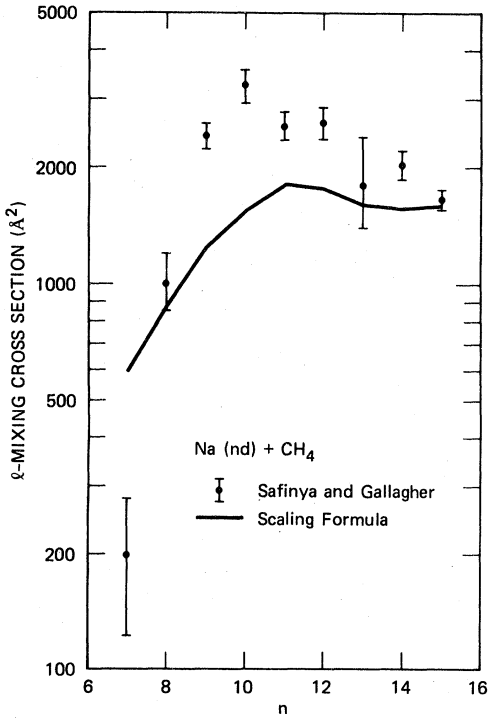

FIG. 11. The l-mixing cross sections for Na(nd)+CH_4.

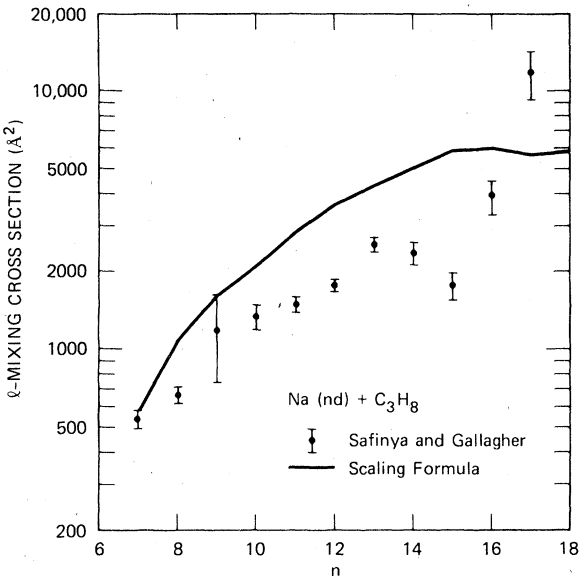

FIG. 12. The l-mixing cross sections for Na(nd) + C_3H_8. The unusual dip at $n=15$ is discussed in the text.

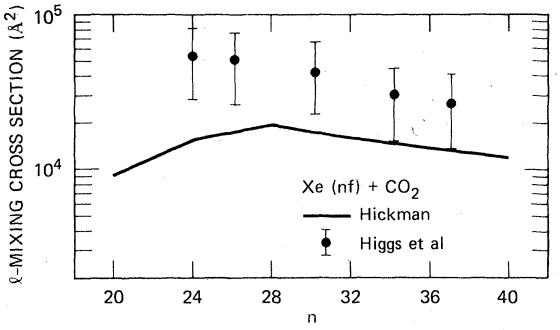

FIG. 13. The l-mixing cross sections for Xe(nf)+ CO_2.

tended to be used for a collision partner that has a charge or large dipole moment.

Figures 10–13 show the calculated results for a number of molecular targets. The agreement with experiment is generally reasonable. The excellent results for Na(nd) + N_2 tend to confirm, as in the case of He, the reliability of the Fermi pseudopotential when the low-energy-electron scattering does not have a strong energy dependence.

It is interesting to consider the structure observed in the experimental data[19] near $n=15$ for Na(nd) + C_3H_8. We have considered what form of the elastic cross section σ_{el} would be necessary to lead to the observed form of $\sigma_{l\,mix}(n)$, assuming the validity of Eq. (11). We found that the unusual structure in $\sigma_{l\,mix}(n)$ for $n\sim13$–16 could be fit by assuming an electron-propane elastic scattering cross section that exhibits a strong change of slope, but not a dip, at an electron energy 0.060 eV, which is the average electron kinetic energy for $n=15$. This effective elastic cross section is about a factor of 2 less than σ_m of McCorkle *et al.*[17] for $E>0.060$ eV, but rises more sharply for $E<0.060$ eV. In this region ($n\sim15$–17) the size of the coupling strength parameter β is sensitive to two competing factors. As n increases, A increases because of the rapid increase in σ_{el} as the electron energy goes to zero. However, this is nearly counteracted by the factor $n^{-3.37}$ that reflects the weaker effect of the increasingly more diffuse electron cloud. The net effect is that the coupling strength teeters between these competing influences. The results of this analysis are only qualitative, of course, but they indicate that the unusual structure in the Rydberg cross section can be related to a plausible behavior of the corresponding electron scattering cross section.

Very recently Higgs *et al.*[20] have measured rate constants for the angular-momentum mixing of Xe(nf) by CO_2 at 300 K. Effective cross sections are obtained from their data by dividing by the mean thermal velocity. Figure 13 shows the data and the calculations, which are in reasonable agreement. It is noteworthy that the scaling formula appears to be useful for n as high as 40.

IV. CONCLUDING REMARKS

An approximate scaling formula for collisional angular-momentum mixing of low-l Rydberg atoms has been determined that gives reasonable results for a wide variety of systems. Although the formula was determined using calculations that assumed the collision partner was a rare gas, qualitative agreement is also obtained for targets with internal structure. All the cross sections exhibit a maximum as a function of n, but the shape and position of the peak may vary considerably. For example, Rb + He has a sharp peak at $n=11$, while Xe + CO_2 has a very broad maximum for $n\sim28$. The formulas obtained here show how such contrasting behavior may be qualitatively related to the energy-level splittings of the Rydberg atom, the energy dependence of the electron scattering from the collision partner, and the relative velocity of the collision.

This work was supported by the Air Force Office of Scientific Research.

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