Energy-loss scaling in Ar + D_2 collisions

S. J. Martin, V. Heckman, E. Pollack, and R. Snyder
Department of Physics, University of Connecticut, Storrs, Connecticut 06268
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The $Ar+D_2$ collision is studied in an energy range from 0.750 to 3.00 keV. At small angles the collision is primarily electronically elastic, but electronically inelastic processes are found to increase in importance with increasing scattering angle and become dominant. The electronically elastic results are compared to the predictions of Sigmund's scaling law, which suggests that the reduced energy loss f depends only on the reduced scattering angle $\tau=E\theta$. At sufficiently small values of θ the data do obey this scaling, but at larger values of θ, which fall outside the postulates of Sigmund's theorem, they do not. However, a generalization of the usual definition of f is presented which does retain the scaling property even at the larger values of θ. We also find that there is an interesting and systematic development of $f(\tau)$ in the sequence of collision systems $He+D_2$, $Ne+D_2$, $Ar+D_2$, in which vibrorotational excitation manifests itself at smaller and smaller values of τ as heavier rare-gas projectiles are used.

I. INTRODUCTION

Collisions between projectile atoms and target molecules generally result in the excitation of electronically and vibrorotationally inelastic processes. Studies of the vibrorotational excitation are particularly useful since they can provide information on the energy surfaces of the triatomic quasimolecule.[1] Although our quantitative understanding of collisional vibrorotational excitation is still at a rudimentary level, these energy-loss processes have received increasing attention recently, both experimental and theoretical,[1,2] and their underlying details are now beginning to be understood. As was previously found in the atom-atom case,[3] our progress in understanding atom-molecule collisions is facilitated by analyzing experimental results in terms of scaled variables. This paper is primarily concerned with energy-loss scaling for "quasielastic" collisions: the term "quasielastic" refers to channels in which *no* electronic excitation of the target or projectile occurs, although vibrorotational excitation of the molecule may occur. Thus they are *electronically* elastic, but the qualifying adjective "quasi" points up the possibility of vibrorotational excitation.

A very useful scaling technique for these quasielastic atom-molecule collisions results from the reduction of the measured energy losses in terms of an energy-loss function f which may be defined by

$$f=\tfrac{1}{2}\Delta E/\Delta E_{\rm elas}\ . \tag{1}$$

Here ΔE is the most probable energy loss in the quasielastic channel, and $\Delta E_{\rm elas}$ is the smaller energy loss which would result if the projectile scattered from the molecule purely elastically, without any vibrorotational excitation. Thus f is a dimensionless parameter which has an absolute minimum value of $\frac{1}{2}$, attained in the case of *purely* elastic scattering, without any vibrorotational excitation, so that the measured ΔE is equal to $\Delta E_{\rm elas}$. Any experimental data points having values below $f=\frac{1}{2}$ provide a measure of the experimental uncertainty, which has its maximum effect at small τ values. The value $f=1$ can also be interpreted physically. From Eq. (1), it corresponds to an actual energy loss twice as large as that which would occur in a purely elastic collision with the molecule as a whole; but simple kinematics requires (see Sec. III) that elastic energy losses vary inversely as the mass of the target in first order, so an $f=1$ energy loss is the same loss as would occur in an elastic collision with a mass half as large as that of the entire molecule. Therefore, $f=1$ collisions are suggestive of "hard" collisions with a single *atom* of the target molecule (assumed homonuclear). One might anticipate from this simple interpretation that empirical f values would usually fall between the purely elastic limit ($f=\frac{1}{2}$) and the "spectator" or "binary" limit ($f=1$), and indeed all experimental measurements of f to date do fall between these limits. Another very important advantage of this scaling procedure is that $f-\frac{1}{2}$ is interpretable as a natural, "reduced" measure of the vibrorotational excitation energy (often denoted by Q), and the reduction of results in terms of the f function allows excitation energy to be easily identified and separated in experimental data sets, as later examples will make clear.

These phenomenological features alone make f a valuable parameter for reducing experimental data, but its value is greatly enhanced by a scaling law due to Sigmund.[4] He proved that f will be a *universal* function of the reduced scattering angle τ for all projectile energies if certain assumptions are made. His derivation assumed classical scattering in a sudden (or impulse) approximation, i.e., the projectile's speed was assumed to be sufficiently fast that the motion of the nuclei in the target molecule could be neglected during the collision. On the other hand, it was also assumed that the projectile speed was low enough to allow the interaction to be described by a static atom-molecule potential. Sigmund pointed out that the validity of this assumption of adia-

baticity is measured by the relative absence of electronic excitations. The additional assumption was made that the relative change in the projectile velocity and the projectile scattering angle were small. In his second paper, Sigmund[4] generalized the scaling law from the homonuclear, diatomic case treated in his first paper to encompass polyatomic and heteronuclear targets, and also relaxed the restriction on the potential function.

By determining $f(\tau)$ at different collision energies, a number of subsequent papers[5–9] have confirmed the suggested universality in several collision systems and found it lacking in others. This paper reports on the third in a series of experiments which study these energy-loss effects in an orderly progression of relatively simple projectiles, the rare-gas atoms, on an important and relatively simple target, the hydrogen molecule. This family of collision partners is shown to be a useful grouping for uncovering systematic features in the evolution of the reduced energy loss as the rare-gas projectiles progress through the Periodic Table. The understanding thus gained can then point the way to the study of more complicated systems. Neon projectiles were historically the first in this sequence to be studied, by Andersen *et al.*,[5] who found that the universal scaling law predicted by Sigmund[4] was very well satisfied in these collisions. In $Ne + D_2$, the electronically excited channels were very much weaker than the quasielastic channels, in accordance with the assumption built into Sigmund's derivation; however, this was not the case for $He + D_2$, the second rare-gas-on-hydrogen system to be studied. Yet Jakacky *et al.*[8] found here too that f was a universal function of reduced scattering angle τ, even though electronic excitation was strong in those collisions. For this system *ab initio* theoretical calculations of the specific functional dependence of f on τ were also carried out[8] and were in excellent agreement with experiment.

This paper reports on a third member of this family, $Ar + D_2$. In this case molecular motion during the collision and electronically inelastic processes are not insignificant, as was required in Sigmund's proof, but we find that the f function is still universal here *if* its definition is generalized. Thus a central theme emerging in this research is the broad persistence of a universal f function in regimes beyond those originally envisioned. We will also show that the evolution of the $f(\tau)$ curve in the sequence He-, Ne-, Ar- D_2 is systematic, which suggests that this sequence provides a useful classification containing fundamental information.

II. EXPERIMENTAL TECHNIQUES

The experimental techniques have been previously described[8] and are only outlined here. Briefly, Ar is extracted from a glow discharge ion source, focused, and passed between two small plates where it is "chopped" by a voltage pulse (amplitude of 20 V, frequency of 100–300 kHz, and width of 0.05 μsec). The Ar beam then is velocity analyzed by a Wien filter and passes through a charge-exchange cell containing Ar gas. The residual Ar^+ leaving the charge-exchange cell is deflected and the remaining Ar beam then enters the scattering cell containing D_2 target gas. Following a collision the scattered Ar then traverses a 4-m-long drift tube positioned at an angle θ with respect to the incident beam direction and is energy analyzed using time-of-flight techniques. Figure 1 shows a spectrum of the scattered Ar from 3.0 keV, $\theta = 1.1°$ $Ar + D_2$ collisions. The peak labeled A corresponds to the quasielastic channel. The figure shows that there are also significant contributions from electronically inelastic collision channels.

III. ENERGY-LOSS KINEMATICS FOR HEAVY PROJECTILES

The purely elastic energy losses, ΔE_{elas} in Eq. (1), are of course determined by kinematics alone. The usual definition of f which has been used in the literature to date can be obtained from Eq. (1) by using the well-known "small-angle" elastic-loss result,

$$\Delta E_{\text{elas}} = EM/m\theta^2 , \tag{2}$$

where M and m are the masses of the projectile and target, respectively, E is the original projectile energy, and θ is the scattering angle in the laboratory frame of reference. However, we will show below that for collisions with heavy projectiles ($M/m \gg 1$) such as $Ar + D_2$, Eq. (2) can become inadequate at scattering angles of even a few degrees. We note that a much more general elastic-loss formula, of which Eq. (2) is a special case, can equally well be derived from the kinematics assuming only that $M > m$; it is

$$\Delta E_{\text{elas}} = E - [\cos\theta + (m^2/M^2 - \sin^2\theta)^{1/2}]^2 \times EM^2/(M+m)^2 . \tag{3}$$

In this paper we will investigate the effects of using the full expression, Eq. (3), without approximation in reducing ΔE to f.

Figure 2 illustrates these effects by showing the shift

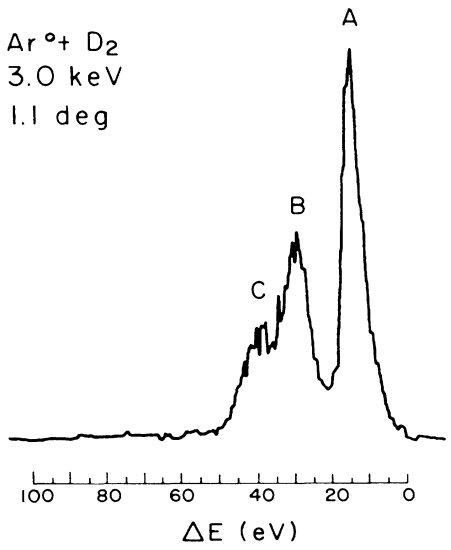

FIG. 1. Energy spectrum of the direct scattering of Ar by D_2. The 3-keV Ar projectile is scattered through a laboratory angle of 1.1°.

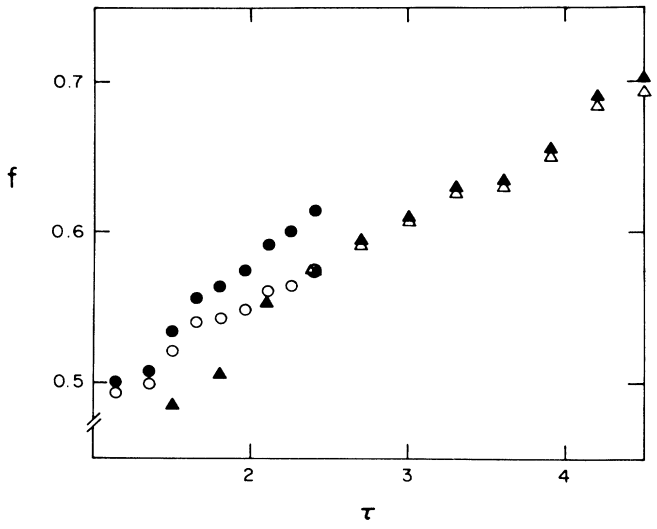

FIG. 2. Reduced energy-loss function f vs reduced scattering angle, $\tau = E\theta$, in keV deg. Circles, 0.750-keV data; triangles, 3.00-keV data. Open symbols are based on the full kinematics of Eq. (3); closed symbols are based on Eq. (2).

in f that results from using Eq. (3) instead of Eq. (2) to reduce our 750-eV and 3-keV data on Ar + D_2 scattering. The figure clearly shows that the shift is an important one, which will very much affect the interpretation of the results: when the "small-angle" result, Eq. (2), is used, the 750-eV and 3-keV data appear to fall on separate curves, but when Eq. (3) is substituted the data are reasonably consistent with a common curve. Thus we see that for the analysis of these data Eq. (2) is significantly different from Eq. (3), which we suggest as a natural extension into the heavy-projectile, large-angle regime. Using Eq. (3) precisely insures the desirable bound, $f > \frac{1}{2}$, which is lost if Eq. (2) is retained at large angles. And empirically Eq. (3) extends the universal scaling of f to smaller values of τ than does the use of Eq. (2); however, further work will be required to probe the theoretical underpinnings of this generalization.

It is useful to consider the expansion of Eq. (3),

$$\Delta E_{\text{elas}} = EM/m\theta^2 + (M^2/4m^2 - M/2m - \tfrac{1}{12})EM/m\theta^4 + \cdots \quad (4)$$

which shows explicitly that Eq. (3) does contain Eq. (2) as a limiting case and reveals that the fractional shift introduced by using $EM/m\theta^2$ alone is approximately $(M^2/4m^2 - M/2m - \frac{1}{12})\theta^2$. Thus for large projectile-target mass ratios, it is the parameter $M\theta/2m$ whose square determines the validity of Eq. (2), and thereby the significance of the phrase "small angle."

Next we will show that the shift in f caused by this effect is bounded in practice, and that we can obtain a simple estimate of that maximum shift in f due to including the higher-order terms. A study of the experimental literature[5-8] shows that in fact the largest observed scattering angles are only slightly larger than $m/2M$; this also occurs in the theoretical calculations of Snyder and Russek,[10] who discuss the significance of that angle. Thus for a collision between a projectile atom of mass M and a target molecule of mass m one anticipates maximum fractional shifts in f of slightly more than $(\frac{1}{16} - m/8M - m^2/48M^2)$. For Ar + D_2, this would suggest a 5% shift; the data of Fig. 2 have a maximum shift of 7%. Thus for even heavier projectiles and/or lighter targets, shifts of up to 8 or 9% could be obtained. The example of Fig. 2 has already made it clear that such shifts can be very significant in the interpretation of energy-loss scaling.

All f values in the remainder of this paper have been reduced using the full expression, Eq. (3), for ΔE_{elas}.

IV. RESULTS AND DISCUSSION

Figure 3 shows a plot of f versus τ for Ar + D_2 at five different beam energies in the range from 0.750 to 3.0 keV. The experimental results at all energies are reasonably well fit by a common $f(\tau)$ curve, in spite of strong electronically inelastic channels and significant molecular motion during the collision. Thus we find that universal scaling of the reduced energy loss is obtained if the definition of f is generalized. As an additional point of interest it should be noted that the center-of-mass energies lie in the range from 75 to 300 eV and within the collision model show that a common potential surface determines the scattering in this transition region between "low" and "high" energies.

Figure 3 also shows the empirical $f(\tau)$ for He + D_2 and for Ne + D_2 collisions, taken from earlier work,[5,8] for comparison with the present Ar + D_2 result. The figure shows that there is a very systematic development of $f(\tau)$ as the mass number of the rare-gas projectile in-

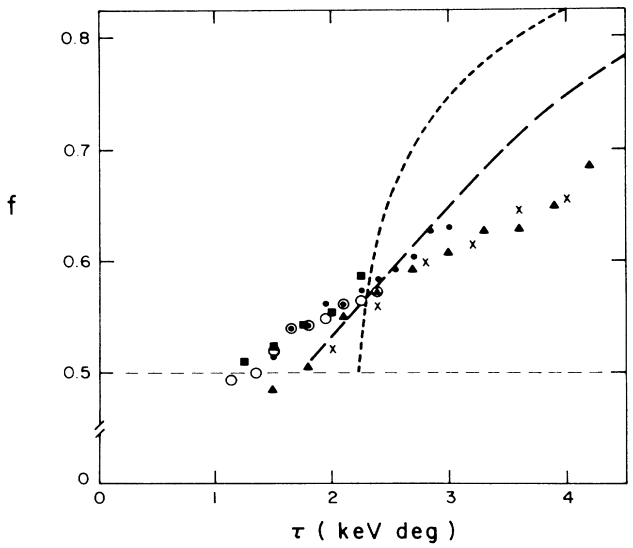

FIG. 3. Energy loss $f(\tau)$ at five different beam energies: 750 eV (○), 1.0 keV (■), 1.5 keV (●), 2.0 keV (×), and 3.0 keV (▲). All f values were reduced using the full Eq. (3) for ΔE_{elas}. Results from two earlier experiments are superimposed on the plot: Ne + D_2 (long-dash curve) and He + D_2 (short-dash curve).

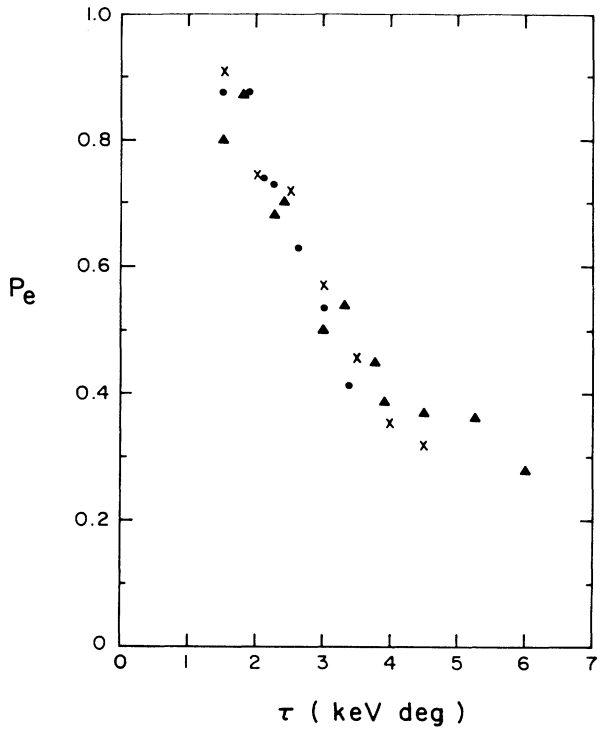

FIG. 4. The probability of electronically elastic scattering in the direct channel P_e as a function of τ for beam energies of 1.5 keV (●), 2.0 keV (×), and 3.0 keV (▲).

creases, in which $f(\tau)$ leaves its purely elastic limit of $\frac{1}{2}$ at progressively smaller values of τ, and then rises with a progressively smaller slope. The discovery of this previously unknown regularity for atom-molecule energy losses illustrates the possible usefulness of the f function in the rare-gas-hydrogen sequence. It also suggests that $Kr + D_2$ and $Xe + D_2$ experiments would be of interest to fill out the picture.

Although the present study primarily addresses the quasielastic channel, detailed energy-loss spectra showing the electronically inelastic channels were also obtained at energies of 1.5, 2.0, and 3.0 keV. Results of these measurements are plotted in Fig. 4, which shows P_e, the probability of a collision resulting in a quasielastic process, at these energies, as a function of τ. These results are also seen to be reasonably well fit by a common curve, showing that τ is generally a useful variable in this collision system. This scaling of the P_e versus τ is also consistent with an earlier model[8] in which the inelastic processes are predominantly excited when the distance of closest approach lies inside a critical value.

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