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Collisional Quenching of Metastable Hydrogen Atoms by Rare Gases

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The collisional quenching of slow metastable hydrogen atoms by rare-gas targets is analyzed in the framework of a pseudopotential method. We find that the experimental results of Kass and Williams are in full agreement with theory if the anomalously large elastic scattering is taken into account.

Recent experiments by Kass and Williams[1] on the collisional quenching of metastable hydrogen atoms by noble gases led those authors to conclude that there is at the present time a discrepancy between their experimental results for He and the theoretical calculation of Byron and Gersten.[2] In this Letter we point out that, in fact, the theory and experiment are in full agreement. We trace the apparent discrepancy to the neglect of the contribution of large-angle elastic scattering. In their experiment metastables scattered through angles larger than 30 mrad were undetected and hence produced an effect equivalent to quenching. We show that a proper inclusion of this wide-angle scattering contribution brings theory and experiment into satisfactory agreement, although it would certainly be desirable to have experiments available which would separate the contribution of elastic and inelastic scattering. We also extend our previous theoretical work to include the other noble gases.

We propose to study this process using the formulation developed in Ref. 2, but with several important modifications. In Ref. 2 we reduced the problem of finding the quenching cross section to solving the set of coupled equations

$$\frac{d\alpha_n^{(2s)}}{dz}=\frac{i}{v}\sum_{n'\in I} M_{nn'}\alpha_{n'}^{(2s)}, \tag{1}$$

for all $n\in I$, I being the collection of degenerate states $2s$, $2p_+$, $2p_0$, and $2p_-$, subject to the boundary condition $\alpha^{(2s)}(z=-\infty)=\delta_{2s,n}$. The matrix elements were given by

$$M_{nn'}=(\varphi_n, V\varphi_{n'})+\sum_{m\notin I}\frac{(\varphi_n, V\varphi_m)(\varphi_m, V\varphi_{n'})}{\epsilon_{2s}-\epsilon_m}, \tag{2}$$

and φ_m and ϵ_m were the eigenvectors and eigenvalues, respectively, of the internal system. In this work we propose to eliminate the noble-gas target in favor of a pseudopotential obtained from low-energy electron scattering data, so we will use φ_m and ϵ_m to denote the eigenvectors and eigenvalues of the hydrogen atom; thus V will represent an electron and a proton interacting with a target whose effects are simulated by a pseudopotential. We use

$$V(\vec{r},\vec{R})=V^e(\vec{r}-\vec{R})+V^p(\vec{R})+\vec{R}\cdot(\vec{R}-\vec{r})\alpha/R^3|\vec{R}-\vec{r}|^3, \tag{3}$$

where α is the dipole polarizability of the noble gas, $\vec{r}$ denotes the internal coordinate of the hydrogen atom, and $\vec{R}$ represents the internuclear variable. V^e is the electron–noble-gas pseudopotential,[3] and V^p is the proton–noble-gas pseudopotential. The remaining term in Eq. (3) is present to take into account the induced nature of the long-range part of the atom-atom potential, thus guaranteeing the proper Van der Waals behavior of the interatomic potentials. Obviously, at small distances in both R and $|\vec{R}-\vec{r}|$ this term should be cut off appropriately.

A final modification which we shall make concerns Eq. (2). Since for many noble gases the pseudopotentials will be quite strong at small distances, we shall extend Eq. (2) to all orders of perturbation theory via

$$M_{nn'}=(\varphi_n, V\varphi_{n'})+(\varphi_n, VG_0V\varphi_{n'})+(\varphi_n, VG_0VG_0V\varphi_{n'})+\cdots, \tag{4}$$

where G_0 is given by

$$G_0=\sum_{m\in I}\frac{|m\rangle\langle m|}{\epsilon_{2s}-\epsilon_m}. \tag{5}$$

To evaluate Eq. (4) let us divide V into a short-range part and a long-range part, $V=V_{SR}+V_{LR}$. Here V_{LR} will contain the "tails" of V^e and V^p and the interference term in Eq. (3). This term will be weak and hence shall be treated to lowest order only:

$$M_{nn'}^{(1)}=(\varphi_n, V_{LR}\varphi_{n'}). \tag{6}$$

V_{SR} will be large at small distances and hence must be treated beyond first order:

$$M_{nn'}^{(2)}=(\varphi_n, V_{SR}\varphi_{n'})+(\varphi_n, V_{SR}G_0V_{SR}\varphi_{n'})+\cdots. \tag{7}$$

Since $V^p(\vec{R})$ cannot contribute to inelastic transitions, we will not consider it as a part of V_{SR}. With $M^{(1)}$ and $M^{(2)}$ determined in this manner, we then set $M=M^{(1)}+M^{(2)}$.

Now the short-range part of V^e (defined to be equal to V^e inside some radius R_c and zero outside R_c) will be sharply peaked about $\vec{r}=\vec{R}$, so we rewrite Eq. (7) as

$$M_{nn'}^{(2)}=\varphi_n^*(\vec{R})\varphi_{n'}(\vec{R})\left[\int d^3r\, V_{SR}^e(\vec{r}-\vec{R})+\int d^3r\int d^3r'\, V_{SR}^e(\vec{r}-\vec{R})G_0(\vec{r},\vec{r}')V_{SR}^e(\vec{r}-\vec{R})+\cdots\right],$$

where in the vicinity of $\vec{r}=\vec{r}'$, $G_0(\vec{r},\vec{r}')$ can be written approximately as

$$G_0(\vec{r},\vec{r}')\simeq-\frac{1}{2\pi}\frac{1}{|\vec{r}-\vec{r}'|}.$$

Thus,

$$M_{nn'}^{(2)}=4\pi\varphi_n^*(\vec{R})\varphi_{n'}(\vec{R})\int_0^\infty V_{SR}^e(\rho)\tau_{SR}(\rho)\rho^2\,d\rho, \tag{8}$$

where $\tau_{SR}(\rho)$ satisfies the integral equation

$$\tau_{SR}(\rho)=1-2\int_0^\infty(\rho^>)^{-1}V_{SR}^e\tau_{SR}(\rho')\rho'^2\,d\rho',\quad \rho^>\equiv\max(\rho,\rho'). \tag{9}$$

The function τ_{SR} will be recognized as the zero-energy, s-wave scattering wave function. If we define a_{SR} to be the scattering length due to the short range potential V_{SR}^e, then $M^{(2)}$ is given simply by

$$M_{nn'}^{(2)}=2\pi a_{SR}\varphi_n^*(\vec{R})\varphi_{n'}(\vec{R}), \tag{10}$$

where

$$a_{SR}=2\int_0^\infty V_{SR}^e(\rho)\tau_{SR}(\rho)\rho^2\,d\rho. \tag{11}$$

If the long-range part of V^e is negligible, then $a_{SR}\simeq a$, where a is the scattering length for the full potential V^e, and our result of Eq. (10) reduces to the Breit-Fermi results obtained previously.[2] However, the neglect of V_{LR}^e is fairly well justified only in the case of helium, where the polarizability is very small while the scattering length is of order of unity. Already for neon the assumption $a_{SR}\simeq a$ fails badly.

For some of the noble gases (argon, krypton, and xenon) V^e is not available so in this case we proceed as follows: We note that the scattering length due to V^e is given by $a=2\int_0^\infty V^e(\rho)\tau(\rho)\rho^2\,d\rho$, where

$\tau(\rho)$ is the zero-energy, s-wave function for scattering by the full potential V^e. We rewrite this as

$$a = 2\int_0^{R_c} V_{SR}{}^e(\rho)\tau(\rho)\rho^2 d\rho + 2\int_{R_c}^{\infty} V_{LR}{}^e(\rho)\tau(\rho)\rho^2 d\rho.$$

In the second integral, we write $V_{LR}{}^e(\rho) \simeq -\alpha/2\rho^4$ and $\tau(\rho)\simeq I$, i.e., we replace them by their asymptotic values. Also, if we assume that in the small-distance region $\tau(\rho)\simeq\tau_{SR}(\rho)$, then we have

$$a \simeq a_{SR} - \alpha\int_{R_c}^{\infty} d\rho/\rho^2 = a_{SR} - \alpha/R_c,$$

so we may write

$$a_{SR} \simeq a + \alpha/R_c. \tag{12}$$

Thus, if the basic parameters a and α are known experimentally (as they are for helium, neon, and argon), then a_{SR} may be readily estimated. In the cases of helium and neon, where we have pseudopotentials in addition to a and α, a_{SR} as determined by Eq. (12) agrees satisfactorily with a_{SR} as determined by Eqs. (9) and (11). As we should hope, the full matrix element $M_{nn'}$ is not particularly sensitive to the choice of R_c for R_c in the range 2–5 a.u., $M^{(1)}$ being obtained from Eq. (6) by numerical integration.

With the matrix elements evaluated, the set of four coupled equations [Eq. (1)] may be solved by standard numerical methods for the $\alpha_n{}^{(2s)}$. The quenching cross section is given by

$$\sigma_Q = 2\pi\int_0^{\infty}\sum |\alpha_{2pm}{}^{(2s)}(b, z=\infty)|^2 b\, db. \tag{13}$$

The quantities $\alpha_n{}^{(2)}(b, z=\infty)$ oscillate rapidly as b becomes less than some characteristic impact parameter b_c. Inside b_c, Eq. (13) was evaluated by Monte Carlo methods; outside b_c, ordinary numerical integration was performed.

In comparing the results for σ_Q with experiment in the range of velocities covered by Kass and Williams,[1] that is, from $v\simeq 8\times10^5$ cm/sec to $v\simeq 12\times10^5$ cm/sec, we find that our results are consistently too low. Since the experiment of Kass and Williams treated any atom scattered through angles greater than about 31 mrad as being quenched,[4] we are led to suspect that perhaps the effects of elastic scattering are not negligible. To investigate the effects of elastic scattering, we proceeded as follows. The elastic amplitude was evaluated in the eikonal approximation,[5] that is,

$$f_{\mathrm{el}} = (k/i)\int_0^{\infty} J_0(\Delta b)[\alpha_{2s}{}^{(2s)}(b, z=\infty) - 1]\, b\, db. \tag{14}$$

The total cross section σ_T was obtained from the optical theorem, and the total elastic cross section σ_{el} was found by subtracting σ_Q from σ_T. The eikonal amplitude was used to calculate the small-angle scattering for $\theta \le 31$ mrad. The difference between σ_{el} and the small-angle elastic scattering was added to σ_Q to give a total effective quenching cross section $\sigma_Q{}^{\mathrm{eff}}$.

Direct experimental verification of our elastic-scattering results is not possible at the present time. Kass and Williams[1] felt that elastic scattering did not affect their results, basing their assertion on the fact that they were able to follow their scattered beam shape out to a point where it had fallen by an order of magnitude from its central value. However, it is characteristic of the hard-sphere type of results we find that the elastic differential cross section has a large central peak which contains the bulk of σ_{el}, but there is a long tail which falls off very slowly and contains the rest of the elastic scattering. It is unlikely that Kass and Williams would have detected such a tail. It is hoped that in future experimental work attempts will be made to see elastic effects. This could be accomplished by making a careful study of large-angle differential cross sections. Alternatively, a less complete experiment might involve the direct observation of the Lyman quench radiation and its polarization. A typical elastic differential cross section is shown in Fig. 1.

When the elastic contribution is added to σ_Q, the resulting values of $\sigma_Q{}^{\mathrm{eff}}$ are in good agreement with experiment, as is seen from Fig. 2. The results for helium and neon were obtained by using the pseudopotentials of Bottcher,[3] although the use of Eq. (12) would have sufficed. The results for argon were obtained by taking $a = -1.65$ a.u. and $\alpha = 11.1$ a.u. in Eq. (12). For krypton, we are not aware of any experimental scattering length, although the polarizability is known to be 16.8 a.u. We decided to use values of $M_{nn'}$ in this case given by multiplying $M_{nn'}$ for argon by the ratio of the polarizabilities, $16.8/11.1 = 1.5$. This is probably not too bad an as-

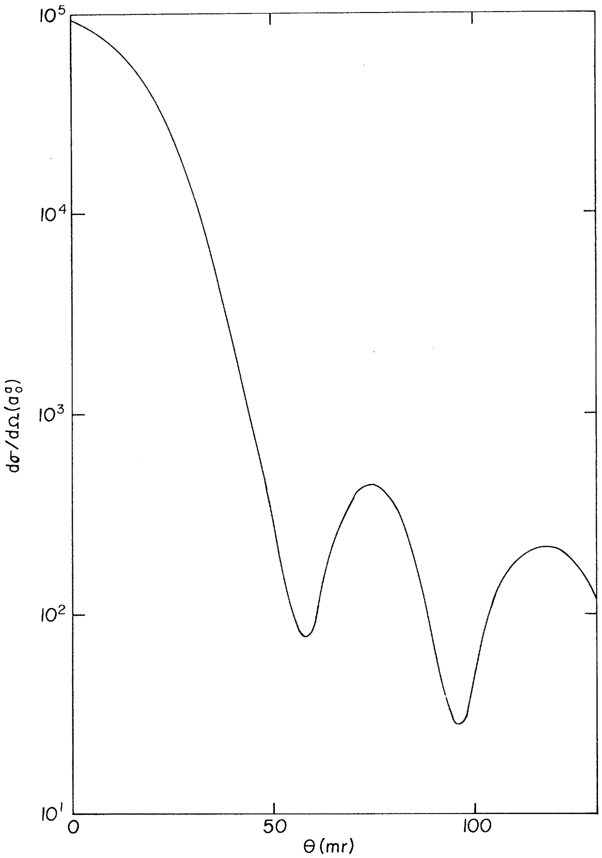

FIG. 1. Differential cross section for the elastic scattering of H(2S) by helium. The scattering angle is in milliradians.

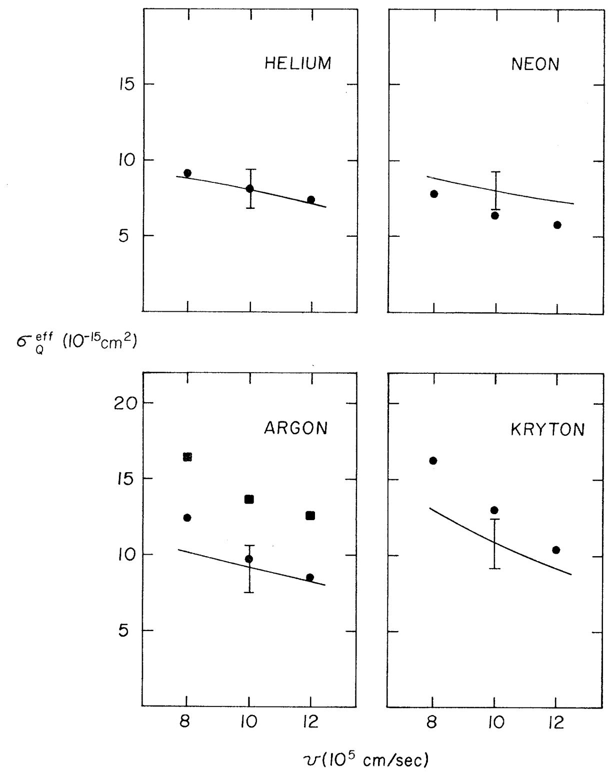

FIG. 2. Effective cross sections for the quenching of H(2S) by helium, neon, argon, and krypton. Solid curves, experimental results of Ref. 1; circles, results of this paper. Each curve has an error bar to give an idea of the experimental error. The figure for argon also shows (solid squares) the results obtained by using only the "long range" part of the matrix elements.

sumption since the results for argon are predominantly controlled by the polarizability. This is illustrated in Fig. 2 where we show for argon, in addition to our results based on the full $M_{nn'}$, the results obtained by using just $M_{nn'}^{(1)}$, the "long-range" part of $M_{nn'}$. The values of σ_Q so obtained are only about 30% larger than those obtained with the full $M_{nn'}$. This is in contradistinction with the case of helium, where because of the smallness of α the quenching is dominated by $M^{(2)}$, the "short-range" part of M. Finally it is worth mentioning that at the lowest velocities shown in Fig. 2, the contributions of elastic scattering are nearly the same as the contributions of pure quenching in the cases of neon, argon, and krypton.

[1]R. S. Kass and W. L. Williams, Phys. Rev. Lett. 27, 473 (1971).

[2]F. W. Byron, Jr., and J. I. Gersten, Phys. Rev. A 3, 620 (1971).

[3]For a discussion of pseudopotentials and the details of how the pseudopotentials used in this paper were obtained see C. Bottcher, J. Phys. B: Proc. Phys. Soc., London 4, 1140 (1971).

[4]R. S. Kass, private communication.

[5]F. W. Byron, Jr., Phys. Rev. A 4, 1907 (1971).