

bility of the scintillation spectrometer, a better knowledge of the collision quenching rate, and perhaps a more careful calculation of the angular distribution correction as regards averaging over the peak and valley energy regions. Furthermore, it was observed upon numerous occasions that the valley-to-peak ratio in freon would decrease with time over a period of several hours, suggesting some mechanism which was quenching positronium—perhaps a buildup of a gas impurity or of ionization due to the radioactivity. By sufficiently frequent changes of the gas this effect was believed to introduce no error in the determination of f to the

order of 2 percent, but for any greater accuracy the effect would be troublesome.

It might be worth mentioning that one motivation for a more precise measurement is that the presence of $2S$ orthopositronium might be exhibited as an apparent high value of the ratio λ_p/λ_0 . Indeed a 10^{90} increase in the apparent value of λ_p/λ_0 as calculated in this paper would result if the relative number of $2S$ positronium atoms to $1S$ positronium atoms is of the order of 1 to 30. A higher precision measurement of λ_p/λ_0 is being planned, and a measurement of the magnetic quenching effect at $\theta=0^\circ$ is under way.

Rotational Excitation by Slow Electrons. II*

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Theoretical cross sections for the rotational excitation of homonuclear molecules by slow electrons are applied to calculation of the fractional energy loss per collision (λ) in H_2 . The theoretical losses are not more than $2.5(2m/M)$ and except at the lowest energies studied (~ 0.1 ev) are smaller than observed.

It would be desirable to have more direct experimental evidence of rotational excitation. For this reason we have calculated λ at $77^\circ K$ in pure para-hydrogen and in normal hydrogen at that temperature. At electron energies ~ 0.075 ev, the two λ 's should differ by about 50 percent. Similarly, because of the altered rotational distribution, λ for deuterium differs from λ for H_2 . Such differences, if observed, could hardly be accounted for on any other basis than rotational excitation.

I. INTRODUCTION

IN a previous paper¹ cross sections were calculated for the rotational excitation of homonuclear diatomic molecules by very slow electrons. These cross sections were used to compute λ , the average fractional energy loss per collision. In nitrogen it was found that, at energies below the vibrational threshold, excitation of rotational levels easily accounted for the observed excess of λ' (λ in units of $2m/M$) above the purely elastic value of unity. The calculations of I are here applied to hydrogen for which recent swarm measurements are also available.²

In Fig. 1 are compared the theoretical and observed values of λ' for H_2 . The notation and procedure used to compute the curves are the same as in I. In hydrogen,^{3,4} $B=7.5 \times 10^{-3}$ ev, $Q=0.393$ in units of ea_0^2 , and we use a

total cross section⁵ $\sigma_i=13.5\pi a_0^2$, independent of energy. The calculations apply to H_2 at $290^\circ K$, with a Boltzmann distribution of rotational levels. The theoretical values of λ' are seen to be smaller than the experimental values even at average energies well below the vibrational threshold (0.54 ev). Our estimate of the energy loss due to rotational excitation accounts for only about half the observed excess of λ above $2m/M$. It is unlikely that these departures between the theory and observations are wholly due to vibrational excitation by higher energy electrons in the swarm.⁶ The significance of the discrepancy between the curves of Fig. 1 is difficult to

⁵ L. J. Varnerin, Jr., Phys. Rev. **84**, 563 (1951).

⁶ For average electron energies of about 0.1 ev and assuming a Maxwellian distribution in the swarm, the magnitude of the vibrational excitation cross section required to account for the difference between the theoretical and experimental curves of Fig. 1 is $\sim 0.3\pi a_0^2$. This probably is an underestimate of the required cross section since the tail of the electron energy distribution is expected to fall off more rapidly than Maxwellian. T. Holstein, Phys. Rev. **70**, 367 (1946); D. Barbiere, Phys. Rev. **84**, 633 (1951). Little is known about the value of the vibrational cross section near threshold, but the measured values at higher energies are much smaller than $0.3\pi a_0^2$. H. Ramien, Z. Physik **70**, 353 (1931); Chao, Wang, and Shen, Science Record (China) **2**, 358 (1949). Moreover, none of the somewhat disparate theoretical estimates are nearly this large. H. S. W. Massey, Trans. Faraday Soc. **31**, 556 (1935); T. Y. Wu, Phys. Rev. **71**, 111 (1947); P. M. Morse, Phys. Rev. **90**, 51 (1953); T. R. Carson, Proc. Phys. Soc. (London) **A67**, 909 (1954).

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¹ E. Gerjuoy and S. Stein, Phys. Rev. **97**, 1671 (1955); referred to as I.

² R. W. Crompton and D. J. Sutton, Proc. Roy. Soc. (London) **A215**, 467 (1952).

³ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand and Company, New York, 1950), second edition, p. 532.

⁴ N. J. Harrick and N. F. Ramsey, Phys. Rev. **88**, 228 (1952).

assess.† In H_2 , the theoretical and experimental uncertainties in λ' are qualitatively similar to those in N_2 (Appendix of this paper), as are the complications involved in comparing the theoretical and experimental curves of Fig. 1. These results in H_2 reinforce the conclusion, voiced in I, that it would be desirable to have more direct experimental evidence that rotational excitation is a significant mechanism in the energy loss of slow electrons in homonuclear diatomic molecules. The differences between the low temperature rotational distributions of ortho- and para- H_2 , and of D_2 , suggest an experiment (Sec. II) which may be able to elucidate this question.

II. LOW-TEMPERATURE LOSSES

If rotational excitation is important in the energy loss of slow electrons, it may be expected that at low gas temperatures, with only the lowest rotational levels populated, λ' will change sharply at mean energies near an excitation threshold and will be sensitive to changes in the rotational distribution. In H_2 , the lowest ($J=1$, and $J=2$) excited states lie at 0.015 and 0.045 ev above the ground ($J=0$) state. Thus at liquid air temperatures ($77^\circ K$, $kT=0.0066$ ev) only the lowest rotational states are appreciably occupied. Also, the first excitation threshold in para- H_2 ($J=0 \rightarrow J=2$) is 0.045 ev, while excitation of ortho- H_2 cannot occur below 0.075 ev ($J=1 \rightarrow J=3$).

These remarks motivate the calculations summarized in Fig. 2, which exhibits λ' as a function of electron

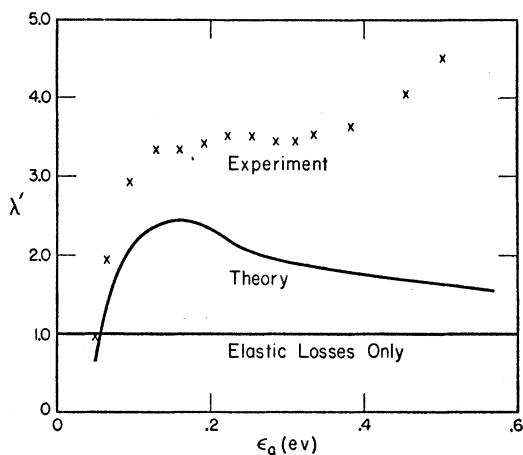


FIG. 1. Fractional energy loss per collision in H_2 (in units of $2m/M$), vs electron energy. ($T=290^\circ K$.)

†Note added in proof.—We have adopted Varnerin's value of σ_t since his electrons are very nearly in thermal equilibrium, so that there is no uncertainty concerning the electron distribution function. However, Phelps (private communication) has made electron drift velocity measurements at very low E/p , i.e., with electron swarms which also must be very nearly in thermal equilibrium, and obtains $\sigma_t=10.5\pi a_0^2$, in good agreement with Crompton and Sutton (see reference 2). With this value of σ_t the agreement between the theoretical and experimental curves of Fig. 1 is considerably improved, especially at $\epsilon_a < 0.2$ ev.

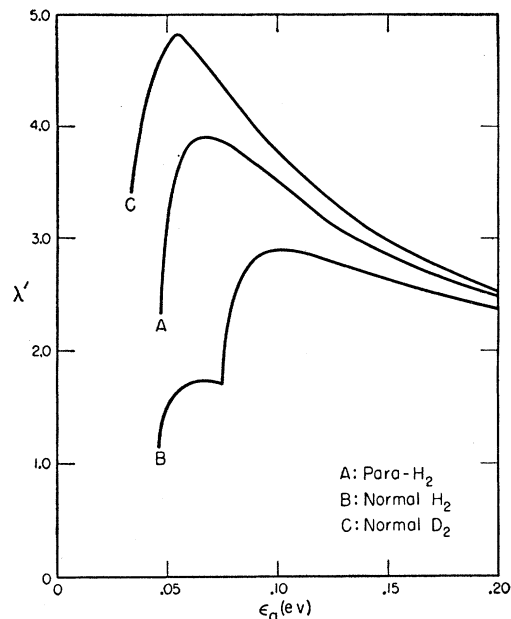


FIG. 2. Fractional energy loss per collision (in units of $2m/M$), vs electron energy. ($T=77^\circ K$.)

energy ϵ_a , in pure para- H_2 at $77^\circ K$ (curve A), and in normal⁸ H_2 at that temperature (curve B), using $\sigma_t=13.5\pi a_0^2$. The losses at $77^\circ K$ in normal D_2 (curve C) are also shown for comparison, again with $\sigma_t=13.5\pi a_0^2$. The assumption that σ_t is the same in ortho- and para- H_2 , and in D_2 , is discussed in Sec. III.

At higher energies, all three curves of Fig. 2 rapidly approach each other. This result may be understood from Eq. (26) of I, which is increasingly valid as the electron energy is increased, and which shows that the rotational losses at high energies are independent of the rotational distribution and depend on the nature of the molecule only through the factor Q^2MB/σ_t . The quadrupole moment, Q , must be virtually the same for H_2 and D_2 , while for these two gases the rotational constant, B , is inversely proportional^{8,9} to the mass M . At lower energies, there is a distinct difference between curve C and the hydrogen curves, mainly due to the smaller threshold energies in D_2 . The abrupt break in curve B occurs at the $J=1 \rightarrow J=3$ threshold. At this energy, where only 25 percent of the normal H_2 mole-

⁷ At electron energies above 0.045 ev, the calculated losses at $77^\circ K$ are negligibly smaller than for a gas at absolute zero.

⁸ At any temperature an ortho-para mixture in the ratio of the statistical weights is termed "normal;" i.e., the ortho-para ratio in normal H_2 is 3:1, and in normal D_2 is 2:1. In the absence of catalysts, the half-life for conversion of pure para- H_2 or of normal H_2 to the $77^\circ K$ equilibrium mixture is very large, of the order of years at atmospheric pressure. The same is true for D_2 , of course. In the swarm experiments, the electronic magnetic moment can catalyze the reaction. The electron densities are so low, however, that comparing with the known conversion by O_2 it is apparent that the half-life will not be seriously reduced in the presence of the swarm. See A. Farkas, *Ortho-hydrogen, Para-hydrogen, and Heavy Hydrogen* (Cambridge University Press, Cambridge, 1935), p. 79.

⁹ G. Herzberg, see reference 3, pp. 141-143.

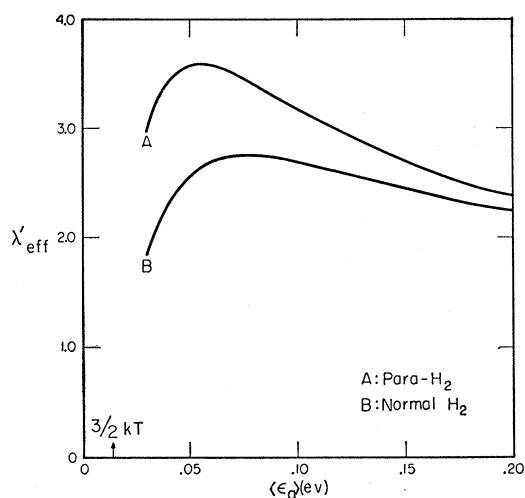


FIG. 3. Average low-temperature energy losses vs average energy.

cules can undergo inelastic collisions, the difference between curves *A* and *B* is most marked, the very large effect resulting in part from the somewhat fortuitous circumstance that the pure para- H_2 curve peaks at the same energy.

The curves in Fig. 2 are drawn for monoenergetic electrons and, as explained in Sec. III of I, must be averaged in some complicated fashion over the electron energy distribution in order to be directly comparable with the experimental fractional energy losses. That the averaging process is unlikely to wash out the differences between the curves of Fig. 2 is indicated by Fig. 3. Curves *A* and *B* of Fig. 3 are simple averages over a Maxwellian distribution of electron velocities of the corresponding curves of Fig. 2. Specifically, the quantity λ' plotted in Fig. 2 is given by Eq. (25) of I, namely

$$\lambda' = \frac{M}{2m} \frac{1}{N \sigma_i v_a \epsilon_a} \frac{dW}{dt},$$

whereas in Fig. 3 we plot as a function of $\langle \epsilon_a \rangle$ the quantity

$$\lambda_{\text{eff}}' = (M/2m) \langle \langle \epsilon_a \rangle \langle N \sigma_i v_a \rangle \rangle^{-1} \langle dW/dt \rangle,$$

where the angular braces indicate an average over the electron distribution. The average energy loss per collision is $\langle dW/dt \rangle / \langle N \sigma_i v_a \rangle$ and λ_{eff}' has been taken to be this quantity divided by $(2m/M) \langle \epsilon_a \rangle$, the expected average elastic energy transfer per collision. For constant σ_i this definition makes λ_{eff}' identical with the fractional energy loss factor η (in units of $2m/M$) which is customarily reported.¹⁰

It appears therefore that comparison of low temperature swarm experiments in para- H_2 , normal H_2 , and in D_2 , can yield significant information concerning the importance of rotational excitation in these homonuclear

molecules. A further advantage of these proposed measurements is that the comparison is to be made at electron energies so low that vibrational excitation, if it is important at room temperature (Fig. 1), is here reduced by several orders of magnitude. We conclude that distinct differences in the measured values of λ' in these proposed experiments will be strong evidence in favor of the importance of rotational excitation in these and other gases, while failure to observe any differences, though perhaps open to other interpretations, will suggest strongly that the calculations of I overestimate the rotational excitation cross sections.

III. TOTAL CROSS SECTIONS

In Fig. 2, we have computed λ' , the fractional energy loss per collision, on the presumption that the energy losses of slow electrons in H_2 are due largely to rotational excitation, i.e., to relatively infrequent inelastic collisions. It was also assumed that the total collision probability—inelastic plus elastic—is independent of the molecular rotational state. The observed differences between the values of λ' in para- and normal H_2 could prove very unlike the differences between curves *A* and *B* of Figs. 2 or 3, if the total cross sections σ_i actually were unequal in ortho- and para- H_2 . Of course, if there are no inelastic losses, $\lambda' = 1$, independent of σ_i . Thus, whether or not σ_i is the same for ortho- and para- H_2 , it remains true that distinct differences in the measured values of λ' in low temperature swarm experiments in para- and normal H_2 will be strong evidence in favor of the importance of rotational excitation. However, we are concerned with the possibility that differences in σ_i may fortuitously cause the values of λ' to be very nearly identical in para- and normal H_2 , so that the proposed experiments, when performed, might give the erroneous impression that rotational excitation is not a significant energy loss mechanism. Similar remarks pertain to the comparison of λ' for H_2 and D_2 .

For these reasons it is gratifying that theoretical justification can be given for the assumption that σ_i is the same in ortho- and para- H_2 , and in D_2 . The difference between H_2 and D_2 stems solely from the dissimilar vibrational wave functions in these two molecules, both molecules having the same equilibrium separation,³ but the D_2 oscillations being confined to a somewhat smaller region.⁹ However, the range of oscillation is small in either case, and between H_2 and D_2 the deviation in $[s - s_e]_{\text{Av}}/s_e$, where s_e is the equilibrium separation, is only a few percent.¹¹ The cross sections for these molecules can hardly fail to be about equally close, as is evidenced by the success to within a few percent of calculations using a rigid rotator in the very analogous problem¹² of the scattering of slow neutrons by ortho- and para- H_2 . Moreover, the inelastic cross sections, Eq. (20) of I, are very much smaller than the reported $\sigma_i = 13.5\pi a_0^2$; consequently, equality of the elastic cross

¹⁰ L. G. H. Huxley and A. A. Zaazou, Proc. Roy. Soc. (London) **A196**, 402 (1949), see p. 419.

¹¹ N. F. Ramsey, Phys. Rev. **87**, 1075 (1952).

¹² M. Hamermesh and J. Schwinger, Phys. Rev. **71**, 678 (1947).

sections σ_e implies equality of the total cross sections. Thus for the purposes of this paper it is sufficient that at low energies σ_e in H_2 be very nearly independent of the molecular rotational state. That this is indeed the case stems from the fact that, apart from the small contribution of long-range forces [comparable to the inelastic cross sections in Eq. (20) of I], the zero energy elastic cross section involves only incoming and outgoing s -waves, coupling through the spherical part of the interaction. At zero energy, consequently, the interaction, Eq. (12) of I, can be replaced by its spherical part, which part is readily seen to yield a scattering amplitude independent of J . A more detailed analysis¹³ shows that σ_e remains very nearly independent of rotational state at energies less than a few tenths of an electron volt.

In conclusion, we stress: (1) We have not found any experimental comparisons of the total cross sections, and therefore are forced to rely on a theoretical argument. (2) Since our argument is wholly theoretical, and in many respects qualitative, we feel it would be worth while to measure these total cross sections using some suitable and identical procedure, e.g., Varnerin's.⁵ (3) The swarm mobility and diffusion measurements² which yield λ' also yield a measurement of σ_t , so that the proposed swarm experiments can check, albeit somewhat equivocally¹⁴ our assumption about σ_t .

¹³ S. Stein, thesis, University of Pittsburgh, 1955 (unpublished).

¹⁴ Since the swarm experiments determine an effective σ_t from complicated averages over the electron distribution, and since the

We are happy to thank Dr. Arthur V. Phelps for his very helpful comments.

APPENDIX

The examination of the validity of the theory in H_2 parallels I, Sec. IV. Because both Q and the molecular radius r_0 are smaller in H_2 than in N_2 , and because we are here interested in even slower electrons than in the previous paper, the only question requiring detailed examination is the ratio A_1/A_2 of "near-" and "far-" field amplitudes. Using, much as in I, the Wang potential¹⁵ with the nuclei at their equilibrium separation to compute for H_2 the quantity $f_a(\theta)$, we obtain for small k_a

$$A_1 = 1.8(k_a a_0)^2 A_2. \quad (1)$$

Estimating $f_a(\theta)$ from the measured elastic cross section gives nearly the same result, the factor being 2.3 instead of 1.8. At the vibrational threshold, Eq. (1) makes $A_1/A_2 = 0.07$; at 0.075 ev, $A_1/A_2 = 0.01$. These numbers indicate that the cross sections of I are valid for H_2 at electron energies below the vibrational threshold, and are surely valid at the very low energies of interest in the proposed low-temperature experiments.

electron energy distribution is affected by inelastic losses, it is possible for the swarm experiments to indicate unequal σ_t even though the total cross sections in these gases actually are the same. Thus, for definitive experiments detailed knowledge of the distribution functions is required, but we may expect that there should be at least qualitative significance to comparing the magnitudes of $\sigma_{t, \text{eff}}$ in different gases.

¹⁵ S. C. Wang, Phys. Rev. **31**, 579 (1928).

Generation of Coulomb Wave Functions by Means of Recurrence Relations

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A discussion of the computation of Coulomb wave functions from their recurrence relations is given. Specifically, it is demonstrated that the regular solution F_L and the irregular solution G_L may be obtained recursively based on the knowledge of the functions for $L=0$.

THE present paper is concerned with the computation of the regular and irregular Coulomb wave functions F_L and G_L , for L a positive integer, with the aid of the recurrence relations satisfied by these functions. Thus if y_L stands for either $F_L(\eta, \rho)$ or $G_L(\eta, \rho)$ we have¹

$$L \frac{dy_L}{d\rho} = (L^2 + \eta^2)^{\frac{1}{2}} y_{L-1} - \left(\frac{L^2}{\rho} + \eta \right) y_L, \quad (1)$$

$$(L+1) \frac{dy_L}{d\rho} = \left[\frac{(L+1)^2}{\rho} + \eta \right] y_L - [(L+1)^2 + \eta^2]^{\frac{1}{2}} y_{L+1}, \quad (2)$$

$$L[(L+1)^2 + \eta^2]^{\frac{1}{2}} y_{L+1} = (2L+1) \left[\eta + \frac{L(L+1)}{\rho} \right] y_L - (L+1)[L^2 + \eta^2]^{\frac{1}{2}} y_{L-1}. \quad (3)$$

In addition, we have the Wronskian relations

$$F_L' G_L - F_L G_L' = 1, \quad (4)$$

$$F_{L-1} G_L - F_L G_{L-1} = L(L^2 + \eta^2)^{-\frac{1}{2}}. \quad (5)$$

The method is entirely similar to that employed for the generation of Bessel functions of integral order.² This is to be expected in view of the fact that the functions F_L and G_L bear the same relation to each other as the Bessel functions J_n and Y_n or the modified Bessel functions I_n and K_n ; namely, for $L \rightarrow \infty$, that F_L is a decreasing function of L while G_L is an increasing function of L . The recurrence relation (3) will be stable when applied in decreasing order to F_L and in increasing

² Bessel Functions, Part II (British Association for the Advancement of Science, Cambridge, 1952). The method is credited to J. C. P. Miller.

¹ J. L. Powell, Phys. Rev. **72**, 626-627 (1947).