

experiment. Taking into account both the H₂ and HD contribution to the line width, the required separation of components is found to be 52 ± 6 cps. The result can be considered in good agreement with the theoretical predictions, since relatively crude wave functions⁵ were used in predicting the separation.

We are indebted to Dr. Ramsey and Dr. Purcell⁶ for their invaluable suggestions and information and to Dr. O. C. Simpson of this laboratory who encouraged us to made these measurements.

¹ E. L. Hahn and D. E. Maxwell, Phys. Rev. **84**, 1246 (1951).

² McNeil, Slichter, and Gutowsky, Phys. Rev. **84**, 1245 (1951).

³ N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952).

⁴ B. Smaller, Phys. Rev. **83**, 812 (1951).

⁵ N. F. Ramsey, private communication.

⁶ We have been informed recently that H. Y. Carr, using pulse echo techniques in HD, has obtained results in substantial agreement with our own.

The Probability of Internal Conversion of *K* Series Radiation of Au Arising from the Interaction of the *L* Subshells*

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IF a vacancy is created in the *K* shell of an atom, for example, by a *K* capture event, an *L* electron can fall into this vacancy, losing energy either by emission of an x-ray photon or by transfer of energy to an outer electron (Auger effect). Calculations have been made by Massey and Burhop¹ for the probability of internal conversion of the *K* series radiation for gold arising from the interaction of the *L_IL_I*, *L_IL_{II}*, and *L_IL_{III}* shells. They used the Møller correspondence principle, employing Dirac wave functions, and treat the process as a transition between states of equal energy of the system comprised of the two electrons. Two approximations were made: (1) the treatment of the problem as a two-electron problem, neglecting the perturbation of the wave function of the atomic electrons due to the ionization of the atom; (2) the use of screened hydrogen-like wave functions for the atomic electrons. They obtained the probability of the Auger transitions *L_IL_I→K,∞*, *L_IL_{II}→K,∞*, and *L_IL_{III}→K,∞* for gold. These results for the relativistic theory were compared with those obtained in the nonrelativistic approximation of Burhop² (see Table I).

We have obtained an experimental value for the relative probability of the Auger transitions for which they made calculations, and in addition, we have obtained values for the transitions *L_{II}L_{II}→K,∞*, *L_{II}L_{III}→K,∞*, and *L_{III}L_{III}→K,∞*. The source, Hg^{197m}, which decays to Au^{197m} by *K* capture, was prepared by Dr. A. DeShalit by irradiating Au with protons in the Princeton cyclotron.³ The Auger electrons were analyzed in a 180° permanent magnet photographic spectrograph. The measured energies of the lines, along with the energies expected using a recent compilation of x-ray level energies,⁴ are listed in Table I. The measured intensities are compared with the two sets of theoretical calculations. It may be noted here that energy and intensity considerations eliminate the possibility of these Auger lines arising in Hg^{197m}.

TABLE I. Experimental and theoretical energies and intensities for Auger transitions in Au involving two *L* electrons.

Transition	Energy (keV)		Intensity			
	Meas.	Calc. ^a	Theoretical Nonrel. ^b	Theoretical Rel. ^c	Measured This work	Measured <i>Z</i> =83 ^d
<i>L_IL_I→K,∞</i>	51.87	52.00	1.0	1.0	1	1.0
<i>L_IL_{II}→K,∞</i>	52.51	52.62	1.14	5.5	1.7	1.83
<i>L_IL_{III}→K,∞</i>	54.26	54.43	2.28	5.3	1.2	1.33
<i>L_{II}L_{II}→K,∞</i>	53.10	53.24			~0.3	<0.2
<i>L_{II}L_{III}→K,∞</i>	54.89	55.05			1.4	2.33
<i>L_{III}L_{III}→K,∞</i>	56.64	56.86			0.8	1.25

^a Using x-ray critical absorption edge energies (see reference 4).

^b See reference 2.

^c See reference 1.

^d See reference 5.

In addition, Ellis⁵ has obtained similar data for Auger transitions in *Z*=83 [using Th(B+C)], which are listed in the table.

It is clear that the experimental data on intensities, which have an experimental uncertainty of about 25 percent, are incompatible with the relativistic results of Massey and Burhop, who suggested the experiment as a test for the extension of the Dirac equation to two bound electrons, believing it was not likely that the inaccuracies in the approximations discussed above would be great enough to mask the relativistic effect. However, it may be that a recalculation of this effect, using the Hartree self-consistent field method as suggested by Massey and Burhop, would modify the theoretical values. One would hesitate to question the validity of the Dirac equation on the basis of existing calculations for this Auger effect.

Two additional points are of interest. First, we observe the *L_{II}L_{II}→K,∞* transition which Ellis did not detect and for which he set an upper limit of 0.2 of the intensity of the other transition. Second, Ellis notes that the Auger electron energies were less (by ~0.2 keV) than the calculated values ($E_K - 2E_{L_I}$), etc., where E_K and E_{L_I} are the x-ray absorption edge energies for the *K* and *L_I* shells. This is a measure of the additional energy required to remove an *L* electron from an atom ionized in the *L* shell. Robinson and Cassie⁶ have noted a similar energy defect (~0.07 keV) for Cu, by directly comparing the energies of photoelectrons with the energies of Auger electrons. We also observe such an energy defect (~0.15 keV) which is just outside experimental error.

Thanks are due Dr. A. DeShalit, for preparation of the source, and Professor J. H. Bartlett, Dr. M. Goldhaber, and Dr. John Miskel for discussion.

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¹ H. S. W. Massey and E. H. S. Burhop, Proc. Roy. Soc. (London) **A153**, 661 (1936). See also *The Auger Effect and Other Radiationless Transitions*, E. H. S. Burhop (Cambridge University Press, London, 1952).

² E. H. S. Burhop, Proc. Roy. Soc. (London) **A148**, 272 (1935). Similar nonrelativistic results have been calculated by E. G. Ramberg and R. K. Richtmyer, Phys. Rev. **51**, 913 (1937). See also L. Pincherle, Nuovo cimento **12**, 81 (1935).

³ The source was prepared in connection with an investigation of the decay of Hg^{197m} and Au^{197m} [A. DeShalit and J. W. Mihelich (to be published)].

⁴ Hill, Church, and Mihelich, Rev. Sci. Instr. (to be published).

⁵ C. D. Ellis, Proc. Roy. Soc. (London) **139**, 336 (1933).

⁶ H. R. Robinson and A. M. Cassie, Proc. Roy. Soc. (London) **113**, 282 (1926).

Interaction between Nuclear Spins in HD Gas*

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A NUMBER of nuclear resonance experiments have disclosed effects that could be explained only by an internuclear interaction of the form $\mathbf{I}_1 \cdot \mathbf{I}_2$, I_1 and I_2 being the spins of the two nuclei involved.¹⁻³ Ramsey and Purcell⁴ have pointed out that such an interaction can arise from the indirect coupling of one nuclear spin to another via the exchange-coupled electrons of the molecule and that an especially clear test of this theory would be afforded by the molecule HD. In this molecule the interaction should split both the H and the D resonances into multiplets. The separation of the multiplets is calculable and should be field independent.

Fine structure in both the H and D resonances of HD gas has now been observed. Furthermore, the fine structure has been observed in the H resonance at both 30 Mc/sec and 5 Mc/sec and found to be field independent. According to the theoretical prediction, the H resonance should consist of three equally intense lines, equally spaced in frequency, the separation between the central line and the satellites being denoted δ cps. The D resonance should consist of two equally intense lines, δ cps apart. This is the structure observed. An approximate calculation based on Heitler-London wave functions gave 70 cps as the order of magnitude of δ . The observed δ is 43.5 ± 1 cps, which agrees with the theoretical prediction as well as one could expect.

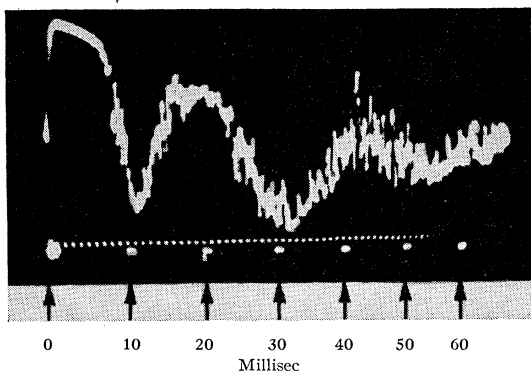


FIG. 1. Deuteron signal from HD.

The method of observation consisted of the application of an intense 15- μ sec rf pulse at the resonant frequency to a tuned coil containing the sample in the static magnetic field. The intensity and duration of the pulse were such as to cause the net nuclear magnetic moment vector to nutate 90° . This enabled the observation of maximum signal amplitude due to the free ringing or precession of the moment vector when the 15- μ sec pulse was removed.⁵ The homogeneity of the static field was good enough to allow the observation of the nuclear free-ringing signal or "tail" with its modulation pattern⁶ for 100,000 μ sec. The ultimate limitation on the observation of the fine structure modulation in the nuclear signal was the relaxation time.

The modulation pattern on the "tail" in the D resonance in HD at 4.4 Mc/sec is shown in Fig. 1. It is a simple beat pattern of two signals of equal amplitude. The two spin groups correspond to the two possible orientations of the neighboring H magnetic moment. Figure 2 shows the pattern observed in the H resonance at the same frequency. This is the slightly more complicated but typical beat pattern of three signals of equal frequency separation and amplitude. The three groups in this case correspond to the three possible orientations of the neighboring D magnetic moment. In addition to the fine structure modulation, both tails decay due to the normal relaxation processes.

The most accurate value for the separation δ , 43.5 ± 1 cps, was obtained from the fifth minimum on a picture of the H resonance at 4.4 Mc/sec. The ± 1 cps is the estimated maximum limit of error. The limits in the D resonance at 4.4 Mc/sec and the H resonance at 30.0 Mc/sec were somewhat greater. To within the latter limits, all separations observed in the D resonances and the H resonances agreed with the value quoted above.

The samples used consisted of substantially pure HD gas sealed in a glass bulb of 0.1 cc volume, in amount such that the pressure at room temperature would be about 300 atmospheres. The samples were prepared by admitting a known volume of the

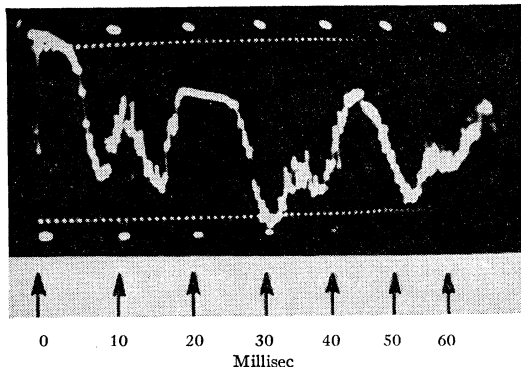


FIG. 2. Proton signal from HD.

gas at known pressure and temperature through 25 cm of capillary to the bulb where the gas was frozen by immersing in liquid helium. While the bulb was still immersed and the gas still frozen, the upper end of the capillary was sealed off. The observations were then made at liquid nitrogen temperature.

We are greatly indebted to Mr. David G. White of the Department of Chemistry for the preparation of the gas which was subsequently sealed off. The method of preparation involved the reaction of D_2O with lithium aluminum hydride in a manner similar to that described by Fookson, Pomerantz, and Rich.⁷ In the present work the final fractionation process was omitted. Two of their samples prepared by the same method as the present samples were analyzed mass spectrographically before fractionation and were found to contain 98.1 percent and 97.0 percent hydrogen deuteride, respectively.

* This work was partially supported by the joint program of the ONR and AEC.

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² McNeil, Slichter, and Gutowsky, Phys. Rev. **84**, 1245 (1951).

³ E. L. Hahn and D. E. Maxwell, Phys. Rev. **84**, 1246 (1951).

⁴ N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952).

⁵ E. L. Hahn, Phys. Rev. **77**, 297 (1950).

⁶ E. L. Hahn, Phys. Rev. **80**, 580 (1950), Part G.

⁷ Fookson, Pomerantz, and Rich, J. Research Natl. Bur. Standards **47**, 31 (1951).

The Theory of Secondary Emission*

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SEVERAL authors^{1,2} have treated the problem of the interaction between energetic primary electrons and the weakly-bound lattice electrons of a solid. However, owing to considerations involving the orthogonality of Bloch wave functions, certain conclusions based upon these theories are incorrect.

The differential cross section for the process in which a primary electron undergoes a transition from a state \mathbf{K} to a state \mathbf{K}' , within a solid angle $d\Omega'$, is given by

$$d\sigma(\mathbf{K} \rightarrow \mathbf{K}') = \sum_{\mathbf{q}} d\sigma_{\mathbf{q}}, \quad (1)$$

where

$$d\sigma_{\mathbf{q}} = [4m^2 e^4 K' / \hbar^4 S^4 K] \times |\sum_{\mathbf{m}} a_{\mathbf{m}+\mathbf{q}}(\mathbf{k}) a_{\mathbf{m}}^*(\mathbf{k}')|^2 d\Omega'. \quad (2)$$

Here, $\mathbf{S} = \mathbf{K} - \mathbf{K}'$, \mathbf{m} and \mathbf{q} are vectors with integer components, and \mathbf{k} and \mathbf{k}' are wave vectors corresponding to initial and final states of the lattice electron. The $a_{\mathbf{m}}$ are the coefficients in the Fourier expansion of the eigenfunctions for a cubic lattice of lattice constant a .

These have the form

$$\Psi_{\mathbf{k}}(\mathbf{r}) = V^{-1/2} \exp[i\mathbf{k} \cdot \mathbf{r}] \sum_{\mathbf{m}} a_{\mathbf{m}}(\mathbf{k}) \exp[i(2\pi/a)\mathbf{m} \cdot \mathbf{r}]. \quad (3)$$

It is found that for each \mathbf{q} the following conservation relation holds:

$$\mathbf{S} + \mathbf{k} - \mathbf{k}' + 2\pi\mathbf{q}/a = 0. \quad (4)$$

For given \mathbf{K} , \mathbf{K}' , \mathbf{k} , and \mathbf{q} , \mathbf{k}' is uniquely specified by Eq. (4), and the summation indicated in Eq. (1) is equivalent to an integration over final states \mathbf{k}' .

Because of the presence of S^4 in the denominator of Eq. (2) $d\sigma_{\mathbf{q}}$ is appreciable only when \mathbf{K}' has values for which S is near its minimum S_{\min} . For primary energies above several hundred ev, S_{\min} is considerably smaller than any of the other terms in Eq. (4), and, in the region of interest, \mathbf{k}' is given approximately by

$$\mathbf{k}' \approx \mathbf{k} + 2\pi\mathbf{q}/a. \quad (5)$$

It is consequently assumed for purposes of integration over Ω' that $a_{\mathbf{m}}(\mathbf{k}')$ can be replaced by $a_{\mathbf{m}}(\mathbf{k} + 2\pi\mathbf{q}/a)$. This approximation leads to the total cross section of the Wooldridge theory:

$$\sigma_{\mathbf{q}} = \frac{16\pi m^2 e^4}{\hbar^4} \frac{|\sum_{\mathbf{m}} a_{\mathbf{m}+\mathbf{q}}(\mathbf{k}) a_{\mathbf{m}}^*(\mathbf{k} + 2\pi\mathbf{q}/a)|^2}{[(2\pi\mathbf{q}/a) \cdot (2\pi\mathbf{q}/a + 2\mathbf{k})]^2}. \quad (6)$$

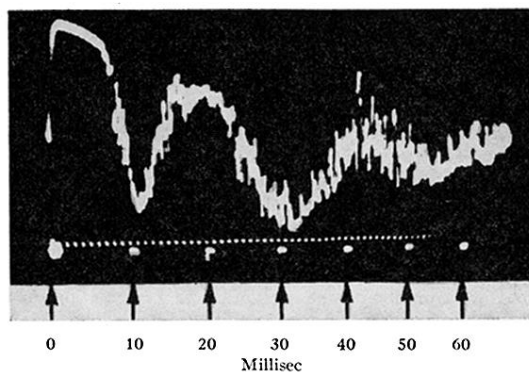


FIG. 1. Deuteron signal from HD.

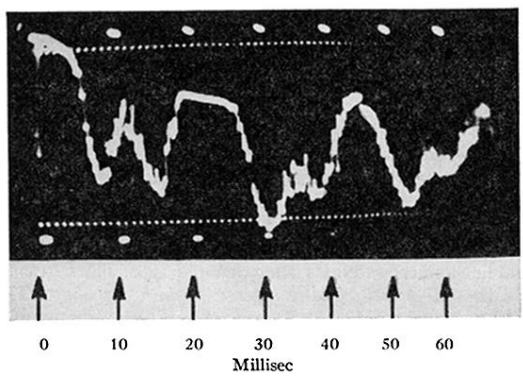


FIG. 2. Proton signal from HD.