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New Value for the Metastability Exchange Cross Section in Helium

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We have investigated the angular aspect of metastability exchange collisions between ground-state and 2^3S_1 metastable ^{3}He atoms theoretically and experimentally. Coupling between the orientations of the two 2^3S_1 hyperfine levels and partial coherence survival after a collision are shown to be important. We propose a different interpretation of previous experiments, and we suggest a new value of the metastability exchange cross section: $\sigma = (7.6 \pm 0.4) \times 10^{-16}$ cm^2. The case of ^{3}He-^{4}He mixtures is also studied.

Metastability exchange collisions play an important role in optical pumping of ^{3}He. The 1^1S_0 ground state ($I = \frac{1}{2}$) of this atom cannot easily be polarized directly through the far-uv resonance line. A nuclear orientation is indirectly achieved by optically pumping the 2^3S_1 metastable state populated by a weak discharge in the helium sample.[1] Orientation transfer between the two 2^3S_1 hyperfine metastable levels ($F = \frac{3}{2}$ and $F' = \frac{1}{2}$) and the ground state is provided by metastability exchange collisions. In this paper, we report the conclusions of a detailed study concerning the evolution of the orientations in these three levels under the influence of metastability exchange collisions. In our opinion, this process has not been treated carefully enough in previous publications, and the interpretation of some experiments ought to be modified. A much more detailed paper on this subject will be published elsewhere.[2]

The well-known scheme of a metastability exchange collision is summarized in Table I. The net result of this kind of collision between a ground-state atom (density matrix ρ_g) and a metastable atom (density matrix ρ_m) is a transfer of the electron clouds from one nucleus to the other: The metastable atom after the collision has the same electronic density matrix as the one before the collision. This spin-conservation law is due to the electrostatic character of the interaction between the two atoms (which does not involve directly the electronic spin variables). During the collision, the nuclear spin variables of the two atoms do not have time to evolve appreciably [(collision time)× (hyperfine coupling constant) $\ll \hbar$]. After the collision, the electrons and the nucleus of the metastable atom are uncorrelated and are described by the density matrix ρ_m'. Subsequent evolution due to the hyperfine coupling destroys hyperfine coherences and leads to the final density matrix ρ_m''.

From this basic analysis, we derive the equa-

TABLE I. Summary of the density-matrix evolution of two ^{3}He atoms undergoing a metastability exchange collision. Tr$_e$ and Tr$_n$ refer respectively to partial tracing over the electronic and nuclear variables; P_F is the projection operator onto the F hyperfine level.

	Ground state atom	Metastable atom
Before collision	ρ_g	ρ_m
After collision	$\rho_g' = \mathrm{Tr}_e \rho_m$	$\rho_m' = \rho_g \otimes \mathrm{Tr}_n \rho_m$
After hyperfine coupling	$\rho_g'' = \rho_g'$	$\rho_m'' = \sum_F \boldsymbol{P}_F \rho_m' \boldsymbol{P}_F$

tions which describe the evolution of the orientations[5] under metastability exchange collisions; if $\langle\vec{\mathbf{F}}\rangle$, $\langle\vec{\mathbf{F}}'\rangle$, and $\langle\vec{\mathbf{I}}\rangle$ are the orientations in the $F=\frac{3}{2}$ and $F'=\frac{1}{2}$ metastable hyperfine levels and in the ground state, we obtain

$$\tau d\langle\vec{\mathbf{F}}\rangle/dt=-\langle\vec{\mathbf{F}}\rangle+[\tfrac{5}{9}\langle\vec{\mathbf{F}}\rangle+\tfrac{10}{9}\langle\vec{\mathbf{F}}'\rangle+\tfrac{10}{9}\langle\vec{\mathbf{I}}\rangle], \qquad (1a)$$

$$\tau d\langle\vec{\mathbf{F}}'\rangle/dt=-\langle\vec{\mathbf{F}}'\rangle+[\tfrac{2}{9}\langle\vec{\mathbf{F}}'\rangle+\tfrac{1}{9}\langle\vec{\mathbf{F}}\rangle-\tfrac{1}{9}\langle\vec{\mathbf{I}}\rangle], \qquad (1b)$$

$$Td\langle\vec{\mathbf{I}}\rangle/dt=-\langle\vec{\mathbf{I}}\rangle+[\tfrac{1}{3}\langle\vec{\mathbf{F}}\rangle-\tfrac{1}{3}\langle\vec{\mathbf{F}}'\rangle]. \qquad (2)$$

$1/\tau$ is the rate at which metastable atoms undergo exchange collisions and $1/T$ is the corresponding rate for ground-state atoms. These two quantities are related by $n/\tau=N/T$ where n and N are the densities of metastable and ground-state atoms, respectively.

Only the first term in Eqs. (1a) and (1b) would exist if the metastable atom orientation were zero after the collision. This, however, is not the case. We must in addition consider not only the term in $\langle\vec{\mathbf{I}}\rangle$ which describes the well-known orientation transfer from the ground state, but also the two other terms in the brackets, which arise from the conservation of the electronic spin orientation during the collision. In other words, a certain amount of the $\langle\vec{\mathbf{F}}\rangle$ and $\langle\vec{\mathbf{F}}'\rangle$ orientations remains in each hyperfine level after metastability exchange; another part is directly transferred from one hyperfine level to the other. This fact has two important consequences: (a) The lifetime of the coherences in the two hyperfine levels are *different* and *longer than* τ: $\frac{9}{4}\tau$ in the F level and $\frac{9}{7}\tau$ in the F' level.[6] (b) There is a strong and direct coupling between the orientations of the two hyperfine levels, with a time constant of the order of τ.

We have performed experiments which entirely confirm these results. We have measured the magnetic resonance linewidths of the two ^{3}He hyperfine metastable levels, for pressures ranging from 0.1 to 3 Torr, in a magnetic field of order 10 G. The experiment is similar to that of Colegrove, Schearer, and Walters,[7] except for the detection technique. Instead of monitoring the 1.08-μm pumping-light absorption, we detected the circular polarization of the 6678-Å line emitted by the discharge.[8] In the upper level (3^1D) of this transition, the electronic orientation is proportional to the ground-state nuclear polarization which itself is strongly coupled to the metastable orientation. This method gives a good signal-to-noise ratio, and the observed signals can be entirely calculated (it does not suffer from any ambiguity concerning the spectral profile of the lamps[4,9,10]).

The results are given in Fig. 1. The linewidths extrapolated to zero rf power are proportional to the pressure. For the $F=\frac{3}{2}$ level our results are in very good agreement with those of Colegrove, Schearer, and Walters.[1,7] The ratio of the widths ΔB (in gauss) for the two hyperfine levels is constant over the entire pressure range and is found to be

$$\Delta B(F=\tfrac{3}{2})/\Delta B(F'=\tfrac{1}{2})=1.158\pm0.023. \qquad (3)$$

Taking into account the Landé g factors ($g_F=\frac{4}{3}$, $g_{F'}=\frac{8}{3}$), we obtain for the ratio of the widths $\Delta\nu$ (in hertz)

$$\Delta\nu_F/\Delta\nu_{F'}=0.579\pm0.012, \qquad (4)$$

which is in very good agreement with the theoretical value,

$$\Delta\nu_F/\Delta\nu_{F'}=\tfrac{4}{9}(\pi\tau)^{-1}/\tfrac{7}{9}(\pi\tau)^{-1}=\tfrac{4}{7}=0.572. \qquad (5)$$

From the slope of these two curves we extract

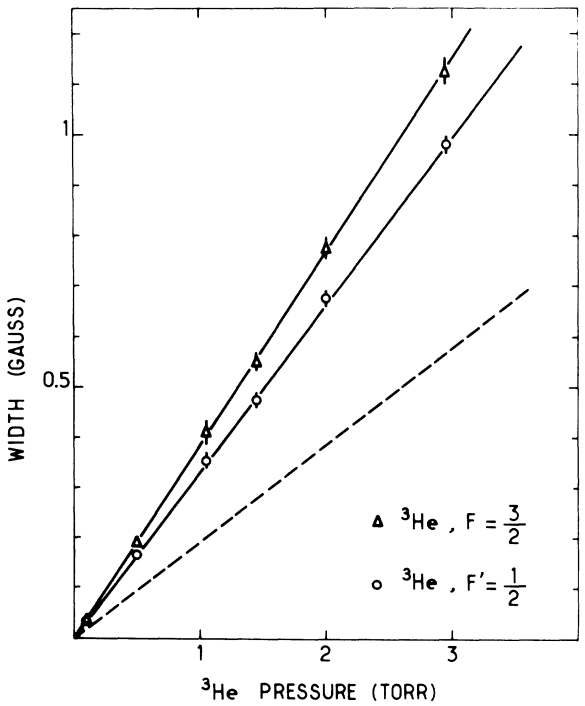

FIG. 1. Experimental magnetic resonance linewidths plotted versus pressure for the two 2^3S_1 hyperfine metastable levels ($F=\frac{3}{2}$ and $F'=\frac{1}{2}$) of ^{3}He. At a given pressure, the ratio of the two widths is 1.16, in good agreement with theoretical predictions. The ratio would be 2 if the coherences were destroyed in each collision, in which case the experimental points concerning the $F'=\frac{1}{2}$ level would lie on the dashed line.

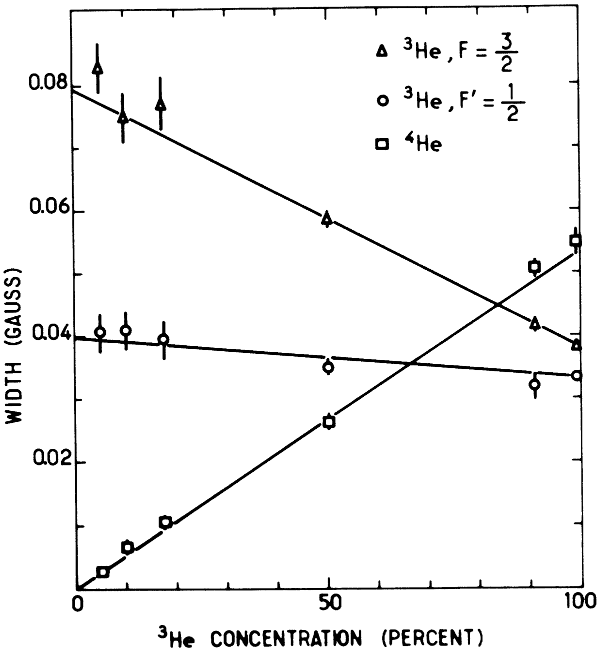

FIG. 2. The 2^3S_1 metastable state resonance linewidths for ^{3}He-^{4}He mixtures. ^{3}He concentration is varied from 0 to 100%, total pressure being kept constant and equal to 0.1 Torr. Points are experimental; straight lines are theoretical and fitted at one experimental point (pure ^{3}He, $F'=\frac{1}{2}$ level).

the exchange rate at room temperature:

$$1/\tau=(50.3\pm1.8)\times10^5\,\mathrm{sec}^{-1}\,\mathrm{Torr}^{-1}. \qquad (6)$$

It is worth noting that if the factors $\frac{4}{9}$ and $\frac{7}{9}$ are neglected, the exchange times derived from the widths of the two hyperfine levels *are different.* This point has not been considered up to now probably because previous experiments were concerned primarily with the $F=\frac{3}{2}$ level.

The same kind of analysis can also be applied to a ^{3}He-^{4}He metastability exchange collision. The nuclear spin variables do not take part in the collision, so that the cross sections $\sigma(^3\mathrm{He}$-$^3\mathrm{He})$ and $\sigma(^3\mathrm{He}$-$^4\mathrm{He})$ are supposed equal. The magnetic resonance linewidths of ^{4}He and ^{3}He metastable states in a mixture have been calculated under this hypothesis. Figure 2 shows the theoretical linewidths in gauss plotted versus the relative proportion of the two species in the mixture for a constant total pressure (0.1 Torr). The difference in the thermal velocities of the two isotopes has been taken into account (a 7% correction).

In almost pure ^{3}He, the linewidths of the two ^{3}He hyperfine levels are those determined above [cf. (3)]. For the few ^{4}He metastable atoms, every collision occurs with a ^{3}He atom and results in a loss of the coherences. Consequently the ^{4}He linewidth (in hertz) is rather large.

Conversely, if ^{3}He is present as a trace in ^{4}He, ^{3}He coherences are lost at every collision and the linewidths of the two ^{3}He resonances are equal. Taking into account the Landé g factors, we obtain the ratio of the widths:

$$\Delta B(^3\mathrm{He},\ F=\tfrac{3}{2})/\Delta B(^3\mathrm{He},\ F'=\tfrac{1}{2})=2. \qquad (7)$$

When ^{3}He concentration in the mixture varies from 0 to 100%, this ratio decreases from 2 to 1.15 [cf. formulas (3) and (7)].

Experimental points on Fig. 2 are in reasonable agreement with the theoretical curves. These results do show that, within a 10% uncertainty, $\sigma(^3\mathrm{He}$-$^3\mathrm{He})$ and $\sigma(^3\mathrm{He}$-$^4\mathrm{He})$ are equal.

To conclude, the coupling between the various orientations in metastability exchange collisions must be carefully treated to interpret the experimental data correctly. Especially for pure ^{3}He, factors of $\frac{7}{9}$ and $\frac{4}{9}$ are to be considered to relate the magnetic resonance linewidths to cross sections. With this precaution, we obtain for the metastability exchange cross section[13] at 300°K

$$\sigma(^3\mathrm{He}\text{-}^3\mathrm{He})=(7.6\pm0.4)\times10^{-16}\ \mathrm{cm}^2. \qquad (8)$$

This value agrees with Greenhow's result,[9]

$$\sigma(^3\mathrm{He}\text{-}^3\mathrm{He})=(7.9\pm2)\times10^{-16}\ \mathrm{cm}^2, \qquad (9)$$

determined by a different method, involving measurements of the ground-state linewidth, which is not affected (in high enough magnetic fields) by the coherence circulation among the metastable states.

Multiplying Colegrove's results[1] by $\frac{9}{4}$, and also by another factor 1.3 in order to use the same definition of the cross section,[13] one obtains

$$\sigma(^3\mathrm{He}\text{-}^3\mathrm{He})=(7.35\pm0.9)\times10^{-16}\ \mathrm{cm}^2, \qquad (10)$$

which agrees well with our value.

Metastability exchange collisions produce another well-known effect,[14-16], the shift of the ground-state magnetic resonance line. This shift, due to coherence circulation between the ground and metastable states, is proportional to the metastable atom density. Schearer quotes a calculation, performed by Bender,[14] apparently under the hypothesis that after a collision all the metastable atom orientation comes from the nuclear ground-state polarization. Starting from Eqs. (1) and (2), we obtain a new expression for this shift:

$$\Delta\omega_g = \frac{4}{3T}\,\frac{\omega_e\tau(2+7\omega_e^2\tau^2)}{(1+\omega_e^2\tau^2)(1+16\omega_e^2\tau^2)}, \tag{11}$$

where $\omega_e = -2\mu_B B$ (with μ_B the Bohr magneton, B the static magnetic field). This formula (11) is similar to Bender's one[14] in the high-field region ($\omega_e\tau \gg 1$), but is very different in low fields. We have performed an experimental verification of this effect which confirms the theoretical result (11) and which will be published soon.[17,2] This gives another experimental test of the validity of Eqs. (1) and (2).

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[2] J. Dupont-Roc, F. Laloë, and M. Leduc, to be published.

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[5] We neglect the influence of the metastable state alignment predicted by the theory (Ref. 2). This approximation can be justified for current optical pumping experiments where the ground-state polarization is not too high ($\lesssim$10%).

[6] Rigorously, this conclusion holds only in fields sufficiently high that the coherence circulation between F and F' levels can be neglected.

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[10] R. S. Timsit and J. M. Daniels, Can. J. Phys. 49, 545 (1971).

[11] At room temperature, the energy difference between ^{3}He and ^{4}He 2^3S_1 metastable states is negligible compared to kT.

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[13] We use the following definition: $1/\tau = N\sigma\langle v\rangle$, where N is the atomic density and $\langle v\rangle$ the mean relative velocity (2060 m/sec). In Ref. 1, the thermal velocity is used (1600 m/sec).

[14] L. D. Schearer, F. D. Colegrove, and G. K. Walters, Rev. Sci. Instrum. 35, 767 (1964).

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Gaugeless Diamagnetism of Atoms and Molecules

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It is shown that the second-order perturbation expression for the diamagnetic susceptibility of electrically neutral atoms and molecules can be put in a completely gauge-independent form, even when the susceptibility is expressed in terms of *approximate* zeroth-order wave functions. It is further shown that the natural choice of the origin of electronic coordinates is the center of nuclear charge of the molecule.

As early as 1932, Van Vleck obtained a quantum mechanical expression for the diamagnetic susceptibility of atoms and molecules.[1] Using second-order perturbation theory, he calculated the change in ground-state energy, ΔE_0, of the molecule when it is subjected to a homogeneous constant magnetic field $\vec{B}$:

$$\Delta E_0 = \frac{e^2}{2mc^2}\sum_j \langle 0|A_j^2|0\rangle - \frac{e^2\hbar^2}{m^2c^2}\sum_{k\neq 0}\frac{|\langle k|\sum_j \vec{A}_j\cdot\vec{\nabla}_j|0\rangle|^2}{E_k - E_0}. \tag{1}$$

Here, E_0 is the energy of the unperturbed ground state $|0\rangle$. The vector potential $\vec{A}_j$ describes the magnetic field $\vec{B}$ at the position of electron j.

Although the derivation of Eq. (1) is straightforward and simple, its actual application to atoms and molecules is beset with a difficulty of fundamental nature. ΔE_0 is independent of the choice of gauge, provided the states $|0\rangle$ and $|k\rangle$ are *exact* solutions of the Schrödinger equation for the molecule in the absence of the magnetic field.[2] In practice, however, these states are not known exactly. Consequently, an approximate ΔE_0, obtained by using approximate states $|0\rangle$ and $|k\rangle$, will be gauge dependent. One is therefore faced with the possibility that reasonably accurate unperturbed states could result in a completely inaccurate value for ΔE_0, simply by choosing the "wrong" gauge. A significant manifesta-