Relaxation of gaseous spin-polarized ^{3}He targets due to ionizing radiation

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The theory of spin-polarized ^{3}He relaxation due to hyperfine coupling in ^{3}He$^+$ and due to spin-rotation coupling in ^{3}He$_2^+$ is presented. Comparison is made between the theory and recent experiments which utilized spin-polarized ^{3}He as a charged-particle beam target. The theory predicts that at low He pressures applying a magnetic field significantly reduces the ^{3}He depolarization rate due to formation of ^{3}He$_2^+$. At high He pressures the relaxation rate decreases with pressure. In addition, charge-transfer processes with foreign gases suppress ^{3}He depolarization by reducing the ^{3}He$^+$ and ^{3}He$_2^+$ concentrations.

I. INTRODUCTION

Recently there has been considerable interest in producing ^{3}He targets for nuclear accelerators. Interesting and fundamental experiments would become possible if a suitable density of highly-spin-polarized ^{3}He were produced. A dense gas of polarized ^{3}He would serve well as a polarizer or analyzer of neutron polarization.[1,2] The use of polarized ^{3}He as a target with muon or proton beams might produce measureable weak interaction effects.[3] There is interest in measuring the neutron form factor via e-^{3}He scattering experiments.[4]

Two groups are currently developing gaseous targets of spin-polarized ^{3}He gas. Milner *et al.*[5] used optical pumping of metastable He atoms while Chupp *et al.*[6] have used spin-exchange optical pumping of ^{3}He–alkali-metal-vapor mixtures. Both groups have shown that beams of charged particles passing through the ^{3}He targets accelerate the nuclear spin relaxation. This is to be expected since ionizing radiation creates an environment in which the ^{3}He nuclei are subject to many depolarizing interactions. The most important depolarizing mechanism is the Fermi contact hyperfine interaction between ^{3}He nuclei and unpaired electrons. This interaction is ubiquitous in the ionized ^{3}He gas. For example, it occurs when free electrons from the plasma collide with ^{3}He atoms, it occurs in the triplet states of excited ^{3}He atoms or ^{3}He$_2$ molecules, and it occurs in the ground and excited states of ^{3}He$^+$ atomic ions and of ^{3}He$_2^+$ molecular ions. Because of their abundance and long duration and because of their strong Fermi contact interactions, the ground states of the ^{3}He$^+$ atomic ion and the ^{3}He$_2^+$ molecular ion are expected to make the largest contribution to the depolarization of ^{3}He nuclei. We will therefore focus our attention on the depolarization due to these species in this paper.

We will find it convenient to introduce a depolarization number

$$n_d = n_a + n_m , \qquad (1)$$

which is defined as the mean number of nuclei depolarized for each atomic ion ^{3}He$^+$ created. As indicated in (1), the depolarization number is the sum of two terms, n_a, the number of nuclei depolarized by the ^{3}He$^+$ atomic ion, and n_m, the number of nuclei depolarized by any ^{3}He$_2^+$ molecular ions into which the atomic ion may be transformed. We will show that $n_a \leq 1$, i.e., an atomic ion can depolarize no more than one nucleus and n_a can be considerably less than 1 under some conditions. We will show that it is possible to have $n_m \gg 1$, i.e., a molecular ion can depolarize many nuclei. This is because the molecular ion can continuously dissipate nuclear spin angular momentum to the translational degrees of freedom of the gas by means of the Fermi contact and spin-rotation interactions, in conjunction with particle-exchange collisions with ^{3}He atoms. In this paper we show how this catalytic destruction of nuclear spin polarization by molecular ions occurs and we discuss ways to control these loss mechanisms in practice.

We show that the depolarization rate due to ^{3}He$_2^+$ can be substantially reduced at low ^{3}He gas pressures ($P \leq 30$ Torr) by applying a modest magnetic field ($B_0 \approx 200$ G) which decouples the rotational angular momentum $\mathbf{N}$ from the total molecular-ion spin $\mathbf{F}$. At higher pressures ($P \geq 100$ Torr) the depolarization rate is decreased because $\mathbf{F}$ does not precess very far about $\mathbf{N}$ before another collision occurs. Additionally, we emphasize that the number density of both ^{3}He$^+$ and ^{3}He$_2^+$ can be significantly reduced if a modest amount of foreign gas (H$_2$O, N$_2$, H$_2$, Ne, etc.) is present in the ^{3}He target. These gases have large cross sections for asymmetric charge-transfer processes[7-9] with ^{3}He$^+$ and ^{3}He$_2^+$. For example, a particularly effective reaction is

$$^3\text{He}_2^+ + \text{N}_2 \rightarrow \text{N}_2^+ + 2\text{He} . \qquad (2)$$
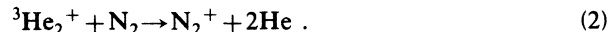
If experimental conditions allow it, introduction of such a gas will effectively eliminate depolarization of ^{3}He due to formation of ^{3}He$_2^+$.

II. PROPERTIES OF ^{3}He$^+$ AND ^{3}He$_2^+$

The hydrogenic ^{3}He$^+$ ion has a $^2S_{1/2}$ ground state with a Fermi contact hyperfine interaction

$$V_{\text{hfs}} = A_a \mathbf{I} \cdot \mathbf{S} \tag{3}$$

between the electron spin $\mathbf{S}$ and the nuclear spin $\mathbf{I}$. The magnitude of the coupling constant is[10] $A_a = 8.66$ GHz.

The ^{3}He$_2^+$ molecular ion has a $^2\Sigma_u^+$ electronic ground-state potential shown in Fig. 1. The equilibrium internuclear separation is[11] 1.08 Å and the dissociation energy is 2.39 eV. The rotational energy of the molecular ion is

$$V_{\text{rot}} = B_e N(N+1) , \tag{4}$$

where $N = 0, 1, 2, \ldots$ is the rotational angular momentum quantum number and the rotational constant is

$$B_e = \frac{\hbar^2}{2I} = (9.61 \text{ cm}^{-1})hc . \tag{5}$$

The homonuclear molecular ion ^{3}He ^{3}He$^+$ can exist in para states, with nuclear spin quantum number $K = 0$ and even values of N, or in ortho states, with $K = 1$ and odd values of N.

In the ortho states there is a strong hyperfine interaction

$$V_{\text{hfs}} = A_m \mathbf{K} \cdot \mathbf{S} \tag{6}$$

between the electronic spin $\mathbf{S}$ and the total nuclear spin

$$\mathbf{K} = \mathbf{I}_1 + \mathbf{I}_2 , \tag{7}$$

which is the sum of the nuclear spins $\mathbf{I}_1$ and $\mathbf{I}_2$ of the two nuclei. There seem to be no measurements of A_m, but we estimate that

$$\frac{A_m}{h} = \frac{8}{3h} \left[\frac{Z_{\text{eff}}}{a_B} \right]^3 \frac{\mu_B \mu_K}{K} = 2.6 \text{ GHz} . \tag{8}$$

This value is based on the approximation that A_m is due to the Fermi contact magnetic dipole hyperfine interaction of the ^{3}He nuclei with the unpaired electron of the $1\sigma_u$ molecular orbital. The orbital is constructed from an antisymmetric linear combination of $1s$ hydrogenic wave functions centered on the two nuclei. To obtain the numerical estimate 2.6 GHz for A_m/h, we have chosen
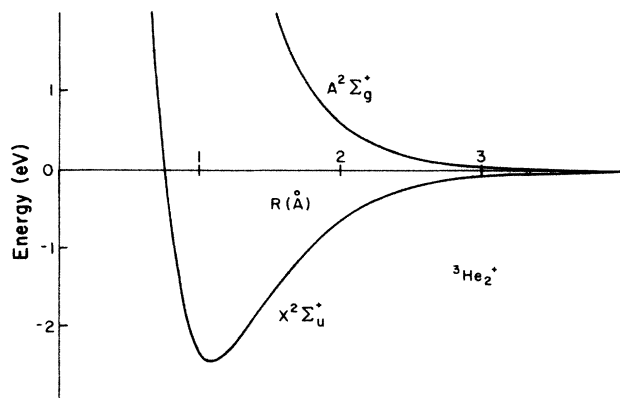

FIG. 1. Potential curves (Ref. 11) for the bound $X^2\Sigma_u^+$ state and the repulsive $A^2\Sigma_g^+$ state of ^{3}He$_2^+$. The equilibrium internuclear separation of the $X^2\Sigma_u^+$ state is 1.08 Å and the binding energy is 2.39 eV.

the same value for the effective charge, $Z_{\text{eff}} = \frac{27}{16}$, which minimizes the energy of the ground state of the He atom if both electrons are assumed to be in $1s$ hydrogenic orbitals. The estimates of the relaxation rates are insensitive to the value of A_m for the "low-pressure" conditions characteristic of the Milner et al. experiments,[5] and at the high-pressures characteristic of the Chupp et al.[6] experiments the molecular-ion lifetime is so short that the depolarization caused by molecules is negligible.

In both para and ortho states there will be a spin-rotation interaction

$$V_{s\text{-}r} = \gamma_m \mathbf{S} \cdot \mathbf{N} \tag{9}$$

between the electron spin $\mathbf{S}$ and the rotational angular momentum $\mathbf{N}$. The magnitude of γ_m does not seem to have been measured but the value

$$\frac{\gamma(a^3\Sigma_u^+)}{h} = 2.421 \text{ MHz} \tag{10}$$

has been measured for the $a^3\Sigma_u^+$ metastable state of He$_2$.[12] If we regard the spin-rotation interaction as the sum of single-particle operators

$$V_{s\text{-}r} = \gamma(1\sigma_u)\mathbf{S}_1 \cdot \mathbf{N} + \gamma(2\sigma_g)\mathbf{S}_2 \cdot \mathbf{N} \tag{11}$$

of the two unpaired electrons in the molecular orbitals $1\sigma_u$ and $2\sigma_g$ of He$_2(a^3\Sigma_u^+)$, we would have

$$\gamma(a^3\Sigma_u^+) = \tfrac{1}{2}[\gamma(1\sigma_u) + \gamma(2\sigma_g)] . \tag{12}$$

We also expect to find that the $1\sigma_u$ orbital has a substantially larger spin-rotation interaction than the much more loosely bound $2\sigma_g$ orbital, so one would have $|\gamma(1\sigma_u)| \gg |\gamma(2\sigma_g)|$. A reasonable estimate for $\gamma(1\sigma_u)$ would therefore be $\gamma(1\sigma_u)/h \approx 2\gamma(a^3\Sigma_u^+)/h = 4.8$ MHz. Since He$_2^+$ has its unpaired electron in the $1\sigma_u$ orbital we estimate that $\gamma_m/h \approx \gamma(1\sigma_u)/h = 4.8$ MHz for ^{4}He$_2^+$. Scaling this estimate for ^{4}He$_2^+$ by the ratio of the masses of the two different isotopes of He we obtain, for ^{3}He$_2^+$, that

$$\frac{\gamma_m}{h} = \tfrac{4}{3} \times 4.8 \text{ MHz} = 6.4 \text{ MHz} . \tag{13}$$

The gas may also be located in a magnetic field $\mathbf{B}_0$. We choose a coordinate system with its z axis along $\mathbf{B}_0$ so that the Zeeman interaction can be written

$$V_Z = g_S \mu_B B_0 S_z . \tag{14}$$

We will neglect the much smaller interaction of $\mathbf{K}$ and $\mathbf{N}$ with $\mathbf{B}_0$.

Thus the dominant terms of the spin Hamiltonians are

$$H = B_e \mathbf{N} \cdot \mathbf{N} + A_m \mathbf{K} \cdot \mathbf{S} + \gamma_m \mathbf{N} \cdot \mathbf{S} + g_S \mu_B B_0 S_z . \tag{15}$$

A qualitative sketch of the low-lying energy levels of the Hamiltonian for $B_0 = 0$ is given in Fig. 2. Note that the total longitudinal angular momentum

$$J_z = N_z + S_z + K_z \tag{16}$$
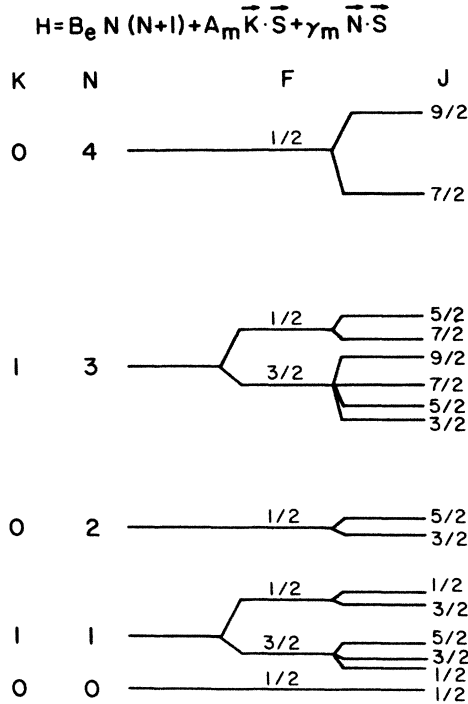
is a good quantum number. The mean-squared rotational

$$H = B_e\, N\,(N+1) + A_m\,\vec{K}\cdot\vec{S} + \gamma_m\,\vec{N}\cdot\vec{S}$$

FIG. 2. Energy levels of the $^3He_2{}^+$ molecular ion in the $X\,^2\Sigma_u^+$ state in zero magnetic field. Here the electronic spin $S = \frac{1}{2}$ and the total spin of the molecular ion is $J = F + N$, where $F = K + S$ and K is the total nuclear spin. The hyperfine and spin-rotation splittings are greatly exaggerated.

angular momentum is fairly large at a representative gas temperature of 300 °C,

$$\langle N(N+1) \rangle \simeq \frac{kT}{B_e} = 20.6 \ , \tag{17}$$

so we will treat N as a classical vector which does not change in direction or magnitude during the free evolution of the molecule. Only minor changes would occur in the final results if N is treated quantum mechanically.

III. RELAXATION DUE TO $^3He^+$ ATOMIC IONS

We assume that a beam (e.g., protons) of particle current density J_b $(cm^{-2}sec^{-1})$ passes through a cell containing nuclear-spin-polarized ^3He gas. Denote the energy loss per unit length of a beam particle by dE/dx. The energy loss for various ionizing particles (electrons, protons, α particles) passing through ^3He gas has been measured and can be found in convenient tables.[13,14] This energy loss is mainly due to the production of $^3He^+$ ions and free electrons. The mean energy ΔE expended by electrons, protons, or α particles in the creation of a $^3He^+$ ion has been measured to be $\Delta E \approx 32$ eV, a value somewhat higher than the 24.5-eV ionization potential of the He atom. The excess energy is presumably expended in the creation of excited states of helium atoms or ions or in imparting kinetic energy to atoms, ions, and free

electrons of the gas. For future reference we will find it convenient to define an ionization rate Γ_{ion} per He atom by

$$\Gamma_{ion}[He] = \frac{1}{\Delta E}\frac{dE}{dx}J_b \ , \tag{18}$$

where [He] is the atomic number density of the gas.

The direct ionization of a He atom by a charged particle will take place in a time on the order of 10^{-13} sec. This is much too short a time for the nuclear spin to precess appreciably under the influence of any hyperfine coupling, which cannot exceed $A_a = 8.66$ GHz in magnitude. After the $^3He^+$ ion has been formed, the nucleus will begin to precess about the free electron under the influence of the contact interaction (3). We will assume that the external magnetic field is small enough $(B_0 \ll A_a/2\mu_B \approx 1500$ G$)$ that we can ignore its influence compared to that of the contact interaction.

The free precession of I and S about each other will be interrupted by charge exchange collisions, i.e.,

$$He(2) + He^+(1) \rightarrow He^+(2) + He(1) \ . \tag{19}$$
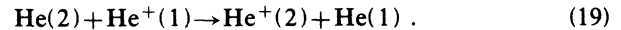
The mean time between charge exchange collisions (19) has been measured to be[15]

$$\tau_{ex} \approx \frac{60}{P_{He}}\text{nsec/Torr} \ , \tag{20}$$

where P_{He} is the He pressure. The charge exchange collision (19) takes place over such a short-time interval, on the order of 10^{-12} sec, that hyperfine interactions like (6) and spin-rotation interactions like (9) are not strong enough to cause appreciable changes of the electron or nuclear spin polarizations. In the relatively long periods between charge exchange collisions the hyperfine interaction (3) will transfer angular momentum from the "fresh" nucleus of $He^+(2)$ to the spin of the unpaired electron. If nothing limits its lifetime, the $^3He^+$ ion can undergo repeated charge exchange collisions with ^3He atoms, and angular momentum transfer to the spin of the unpaired electron will continue until saturation, that is, until the mean electron spin angular momentum $\langle S_z \rangle_a$ of the atomic ion becomes equal to the mean nuclear spin angular momentum $\langle I_z \rangle$ of the atoms. After saturation has occurred, there will be no further nuclear spin depolarization since the nuclear spin angular momentum of the atom which is formed by neutralization of an atomic ion in a charge exchange collision is equal to the nuclear spin angular momentum of the atom which was ionized to form a new atomic ion.

Under many experimental conditions the atomic ion does not live long enough for the electron spin to be saturated. Let $\langle S_z \rangle_a$ denote the mean electron spin of the atomic ion when it is destroyed by a charge exchange collision with the wall, with a gaseous impurity like an N_2 molecule, or by conversion into a molecular ion. The mean electron spin angular momentum $\langle S_z \rangle_a$ of the atomic ions at the time of their destruction will be irreversibly lost from the ensemble of ^3He atoms if the atomic ion is destroyed by charge exchange. If the atomic ion is destroyed by being converted into a molecular

ion, as described in Sec. IV, some of the electron spin $\langle S_z \rangle_a$ could in principle be returned to the ensemble of polarized nuclei. However, any return of angular momentum will ordinarily be negligible in comparison to the depolarization caused by the spin-rotation interaction in the molecular ion. We will therefore assume that the electron spin angular momentum is irreversibly lost whether the atomic ion is converted into a molecular ion or is destroyed by charge exchange. Thus the loss of angular momentum due to hyperfine interactions in the atomic ion is described by the rate equation

$$\frac{d^{(1)}}{dt}\langle I_z \rangle = -\Gamma_{\text{ion}}\langle S_z \rangle_a = -\Gamma_{\text{ion}}n_a\langle I_z \rangle = -\Gamma_1\langle I_z \rangle \ ,$$

$$\text{(21)}$$

where the atomic-ion depolarization number is

$$n_a = \frac{\langle S_z \rangle_a}{\langle I_z \rangle} \ . \tag{22}$$

The value of n_a lies between 0 and 1, and, for external magnetic fields which do not exceed a few hundred G, it depends on three factors, the hyperfine coupling constant A_a of (3), the mean spin exchange time τ_{ex} for the process (19), and the mean atomic-ion lifetime τ_a. Unfortunately, it is not possible to write down a formula for n_a which is valid for all ranges of the parameters A_a, τ_{ex}, and τ_a. However, a reasonably good approximation for n_a when $A_a\tau_{\text{ex}}/\hbar \gg 1$ and when $A_a\tau_a/\hbar \gg 1$, the experimental conditions of Milner et al.[5] and Chupp et al.,[6] is

$$n_a \approx \frac{\tau_{\text{ex}}+\tau_a}{2\tau_{\text{ex}}+\tau_a} \ . \tag{23}$$

We will not pause to derive a more general expression for n_a here since no very-high-pressure experiments, for which the simple formula (23) would be inapplicable, have yet been performed.
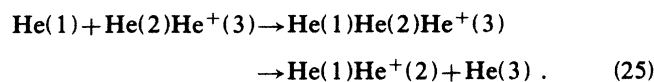
IV. RELAXATION DUE TO EXCHANGE COLLISIONS WITH ^{3}He$_2^+$ MOLECULAR IONS

The ^{3}He$^+$ atomic ions can be readily converted into molecular ions by three body collisions of the form

$$\text{He}^+ + \text{He} + \text{He} \rightarrow \text{He}_2^+ + \text{He} \ . \tag{24}$$
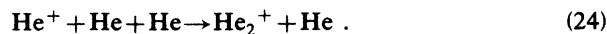
The rate constant for the three-body process (24) has been measured by several groups.[16-18]

The molecular ion ^{3}He$_2^+$ can undergo exchange collisions with He atoms, a process we represent as

$$\text{He}(1) + \text{He}(2)\text{He}^+(3) \rightarrow \text{He}(1)\text{He}(2)\text{He}^+(3)$$

$$\rightarrow \text{He}(1)\text{He}^+(2) + \text{He}(3) \ . \tag{25}$$

As indicated in (25), we assume that the exchange proceeds through a short-lived He$_3^+$ molecular ion, which may live no longer than a vibrational period.

The exchange process (25) will occur at a rate

$$\Gamma_{\text{ex}} = \langle \sigma_e v \rangle [^3\text{He}_2^+] \tag{26}$$

per He atom. Here [^{3}He$_2^+$] is the ^{3}He$_2^+$ number density and $\langle \sigma_e v \rangle$ is the rate constant. Similarly, the exchange rate per molecule will be

$$\frac{1}{\tau} = \langle \sigma_e v \rangle [\text{He}] \ . \tag{27}$$

Physically one would expect the exchange cross section σ_e to be approximately gas kinetic, and experimental data on the magnitude of σ_e seem to confirm this. Measurements of two different ion mobilities for two equal-mass ions have been interpreted[19] as being mobilities for ^{3}He$_2^+$ in the two different states $^2\Sigma_u^+$ and $^4\Sigma_u^+$. As a result of its symmetry, the quartet state is unable to exchange atoms. Hence the difference in mobility is attributed to the different atom-atom exchange probabilities of ^{3}He$_2^+$ molecules in the two different Σ_u^+ states. The exchange cross section which results from analysis of these mobility experiments is $\sigma_e = 1.1 \times 10^{-15}$ cm^2, which is nearly gas kinetic.

It is convenient to refer to the atom He(1) and the molecular ion He(2)He$^+$(3) of (25) as input particles. In like manner, refer to the atom He(3) and the molecular ion ion He(1)He$^+$(2) as output particles. As yet, there is no detailed information about the changes in angular momentum which occur during the exchange process (25). We thus make the following physically reasonable assumptions.

(1) The rotational angular momentum **N** will be approximated with a classical vector of magnitude $\sqrt{kT/B_e}$. The direction of N remains fixed during the free evolution of the molecule. After the exchange process (25), the direction of **N** in the output molecule is random and uncorrelated with the direction of **N** in the input molecule. This is a good assumption because of the isotropic nature of the gas-phase collisions and the very weak coupling of **N** to **S** during a collision.

(2) The mean electron spin $\langle S_z \rangle_o$ of the output molecule equals the mean electron spin $\langle S_z \rangle_i$ of the input molecule, i.e.,

$$\langle S_z \rangle_o = \langle S_z \rangle_i \ . \tag{28}$$

This is a good assumption since the hyperfine and spin rotation interactions are too small to change the direction of **S** much during the short duration $\tau_e \approx 10^{-12}$–10^{-13} sec of an exchange collision.

(3) The total nuclear spin angular momentum of the output particles, $\langle I_z \rangle_o + \langle K_z \rangle_o$, is equal to that of the input particles $\langle I_z \rangle_i + \langle K_z \rangle_i$. This is reasonable since $A_m\tau_e \ll \hbar$ and thus there is insufficient time for the hyperfine interaction to transfer much nuclear polarization to electronic polarization during the exchange collision. Furthermore, we assume the output molecule has $\frac{2}{3}$ of the nuclear spin,

$$\langle K_z \rangle_o = \tfrac{2}{3}(\langle K_z \rangle_i + \langle I_z \rangle_i) \ , \tag{29}$$

and the output atom has the remaining $\frac{1}{3}$,

$$\langle I_z \rangle_o = \tfrac{1}{3}(\langle K_z \rangle_i + \langle I_z \rangle_i) \ . \tag{30}$$

This partitioning ensures that $\langle K_z \rangle$ and $\langle I_z \rangle$ approach

the correct statistical ratio 2:1 if there are no angular momentum losses in the molecular ion.

From assumption (3), the nuclear spin polarization $\langle I_z \rangle = \langle I_z \rangle_i$ of the atom will evolve at the rate

$$\frac{d^{(2)}}{dt}\langle I_z \rangle = -\Gamma_{ex}(\langle I_z \rangle - \langle I_z \rangle_o)$$

$$= -\frac{2\Gamma_{ex}}{3}\langle I_z \rangle + \frac{\Gamma_{ex}}{3}\langle K_z \rangle_i . \tag{31}$$

Defining

$$r = \frac{\langle K_z \rangle_i}{\langle K_z \rangle_o} \tag{32}$$

as the ratio of the nuclear spin angular momenta of the input and output molecules, we can rewrite (29) as

$$\langle K_z \rangle_i = \frac{2r}{3-2r}\langle I_z \rangle . \tag{33}$$

Substituting (33) into (31) yields

$$\frac{d^{(2)}}{dt}\langle I_z \rangle = -\Gamma_2 \langle I_z \rangle , \tag{34}$$

where the depolarization rate is

$$\Gamma_2 = \frac{2-2r}{3-2r}\Gamma_{ex} = \lambda\Gamma_{ex} . \tag{35}$$

The depolarization rate Γ_2 is equal to the rate Γ_{ex} of the incorporation of ^{3}He atoms into ^{3}He$_2^+$ molecules times the average fraction λ of nuclear spin polarization lost while the nucleus is in a molecule.

To find an expression for r in terms of fundamental quantities such as molecular ion lifetime τ_m, magnetic field B_0, etc., we need to consider in detail the evolution of angular momentum in the molecular ion. We can think of the exchange collisions as converting input molecules to output molecules and the molecular evolution converts output molecules into input molecules.

A multipole expansion of the spin density operator can be written

$$\rho_0 = \tfrac{1}{8} + C_K \langle K_z \rangle_o K_z + C_S \langle S_z \rangle_o S_z + \cdots . \tag{36}$$

The term $\tfrac{1}{8}$ is the probability to find an unpolarized molecular ion in any one of the six sublevels of an ortho state or the two sublevels of a para state. The terms $C_K \langle K_z \rangle_o K_z$ and $C_S \langle S_z \rangle_o S_z$ describe the nuclear and electronic spin polarizations and the coefficients $C_K = \tfrac{1}{4}$ and $C_S = \tfrac{1}{2}$ are chosen to ensure that $\langle S_z \rangle_o = \mathrm{Tr}(S_z \rho_0)$ and $\langle K_z \rangle_o = \mathrm{Tr}(K_z \rho_0)$. We assume higher-order polarizations are small enough to be neglected.

After an exchange process the molecular ion evolves under the influence of the Hamiltonian (15) until the next exchange occurs. If the molecular ion evolves freely for a time t, the density operator ρ at the end of the period will be related to the initial density operator ρ_0 by

$$\rho_i = U\rho_0 U^{-1} , \tag{37}$$

where the time evolution operator is

$$U = \exp\left[\frac{-iHt}{\hbar}\right] . \tag{38}$$

Note that the spin Hamiltonian H does not cause transitions between ortho and para states and so it can be written as a sum of a para term ^1H and an ortho term ^3H

$$H = {}^1H + {}^3H . \tag{39}$$

The notation is chosen to represent the singlet character (multiplicity is 1) of the para states and the triplet character (multiplicity is 3) of the ortho states.

The time evolution operator can also be written as the sum of para and ortho terms

$$U = {}^1U + {}^3U \tag{40}$$

and the density operator becomes

$$\rho_i = U\rho_0 U^{-1}$$

$$= \tfrac{1}{8} + C_K \langle K_z \rangle_o \{{}^3U K_z\, {}^3U^{-1}\}$$

$$+ C_S \langle S_z \rangle_o \{{}^3U S_z\, {}^3U^{-1} + {}^1U S_z\, {}^1U^{-1}\} + \cdots . \tag{41}$$

The curly brackets denote an average over the free-evolution time t and the direction of $\mathbf{N}$. The mean values of the spins become

$$\langle K_z \rangle_i = \mathrm{Tr}(K_z \rho_i) = {}^3\eta_{KK}\langle K_z \rangle_o + {}^3\eta_{KS}\langle S_z \rangle_o , \tag{42}$$

$$\langle S_z \rangle_i = \mathrm{Tr}(S_z \rho_i) = {}^3\eta_{SK}\langle K_z \rangle_o + \bar{\eta}_{SS}\langle S_z \rangle_o , \tag{43}$$

where the coupling coefficients are given by the expression

$${}^3\eta_{VW} = C_W\{\mathrm{Tr}(V_z\, {}^3U W_z\, {}^3U^{-1})\} , \tag{44}$$

and V_z, W_z are spin operators from the set $\{S_z, K_z\}$, and

$$\bar{\eta}_{SS} = {}^3\eta_{SS} + {}^1\eta_{SS} \tag{45}$$

$${}^1\eta_{SS} = C_S\{\mathrm{Tr}(S_z\, {}^1U S_z\, {}^1U^{-1})\} . \tag{46}$$

Since we have assumed that $\langle S_z \rangle_o = \langle S_z \rangle_i$ we can write (43) as

$$\langle S_z \rangle_o = \frac{{}^3\eta_{SK}}{1-\bar{\eta}_{SS}}\langle K_z \rangle_o . \tag{47}$$

Substituting (47) into (42) gives

$$\langle K_z \rangle_i = r\langle K_z \rangle_o \tag{48}$$

and

$$r = {}^3\eta_{KK} + \frac{{}^3\eta_{KS}\, {}^3\eta_{SK}}{1-\bar{\eta}_{SS}} . \tag{49}$$

We now show how to calculate the coupling coefficients $^j\eta_{VW}$ of (44) and (46) where V,W can be chosen from the set $\{K,S\}$ and $j=1$ or 3 for the para and ortho states, respectively. The Hamiltonian is

$$H = A_m \mathbf{K}\cdot\mathbf{S} + g_S\mu_B B_0 S_z + \gamma_m \mathbf{N}\cdot\mathbf{S} . \tag{50}$$

It is clear the internal field of the molecular ion is too

small to decouple **K** and **S**, i.e.,

$$\gamma_m N \ll A_m \ . \tag{51}$$

Assume that this is also true for the external field, i.e.,

$$B_0 \ll \frac{A_m}{g_S \mu_B} \simeq 930 \text{ G} \ . \tag{52}$$

Because of (51) and (52) the total internal spin $\mathbf{F} = \mathbf{K} + \mathbf{S}$ will be a reasonably good quantum number. For ortho states $K = 1$ and $S = \frac{1}{2}$ and we can have $F = \frac{3}{2}, \frac{1}{2}$, while for para states $K = 0$ and $S = F = \frac{1}{2}$. Denote eigenstates of H by $| KFm \rangle$ and the corresponding eigenenergies $E(KFm)$. Then

$$H \, | KFm \rangle = E(KFm) | KFm \rangle \ . \tag{53}$$

We note that the states $| KFm \rangle$ are quantized along the

vector ω in Fig. 3, i.e.,

$$\omega \cdot \mathbf{F} \, | KFm \rangle = \omega m \, | KFm \rangle \ . \tag{54}$$

The vector ω is a sum of two frequencies

$$\omega = \omega_0 + \omega_1 \ , \tag{55}$$

where

$$\hbar \omega_0 = g_S \mu_B B_0 \hat{z} \ , \tag{56}$$

$$\hbar \omega_1 = \langle \gamma \mathbf{N} \rangle \ . \tag{57}$$

Here $\hat{z}$ is a unit vector along the z axis. All three frequencies are illustrated in Fig. 3.

To calculate the coefficients use the eigenstates $| KFm \rangle$ as basis states and write, for $^j\eta_{VW}$,

$$
\begin{aligned}
^j\eta_{VW} &= C_W \{ \text{Tr}(V^{\,j}UW^{\,j}U^{-1}) \} \\
&= C_W \left\{ \sum_{F,F',m,m'} \langle KFm \, | \, V_z \, | \, KF'm' \rangle \langle KF'm' \, | \, W_z \, | \, KFm \rangle \exp[-i\Omega(KF'm';KFm)t] \right\} \ ,
\end{aligned} \tag{58}
$$

where

$$\hbar \Omega(KFm;KF'm') = E(KFm) - E(KF'm') \ . \tag{59}$$

Since S_z, K_z, and U are all diagonal in the quantum number K we have omitted terms with $K' \neq K$ from (58).

We assume an exponential probability distribution of evolution times with a mean evolution time τ_m, where τ_m is the average lifetime of a $^3\text{He}_2{}^+$ molecule. We find that the time average of (58) is

$$^j\eta_{VW} = C_W \left[\sum_{F,F',m,m'} \frac{\langle KFm \, | \, V_z \, | \, KF'm' \rangle \langle KF'm' \, | \, W_z \, | \, KFm \rangle}{1 + i\Omega(KF'm';KFm)\tau_m} \right] \ . \tag{60}$$

We will ignore terms with $F \neq F'$. This is justified under the condition of long molecular lifetimes, where

$$\frac{A_m \tau_m}{\hbar} \gg 1 \ , \tag{61}$$

since these terms contribute little to the sum (60) in comparison to the terms with $F = F'$ because then $\Omega \tau_m \gg 1$. For the experiments on the nuclear spin relaxation of weakly ionized ^{3}He gas that have been done at low pressures (Milner et al.[5]) condition (61) holds. For example, at a ^{3}He pressure of 10 Torr we find that $A_m \tau_m / \hbar \approx 220$. Thus if $F \neq F'$ in (60) then

$$| \Omega(KF'm';KFm)\tau_m | \simeq \left| \frac{3\pi A_m \tau_m}{h} \right| \gg 1 \ . \tag{62}$$

For the experiments at high pressures (Chupp et al.[6]) the molecular lifetime is short enough that we can ignore relaxation due to molecules.

We now show how to account for the random direction of **N**. Denote a state $| KFm \rangle$ for which $\omega = \omega \hat{z}$ by $| KFm \}$. These states are quantized along the z axis of the laboratory coordinate system, i.e.,

$$F_z \, | KFm \} = m \, | KFm \} \ . \tag{63}$$

Since

$$| KFm \rangle = R \, | KFm \} \ , \tag{64}$$

where R is the rotation operator

$$R = \exp(-i\alpha F_z) \exp(-i\beta F_y) \ , \tag{65}$$

we may substitute (64) and (65) into (60) and obtain

$$
\begin{aligned}
^j\eta_{VW} = C_W \sum_{F,m,m',\mu,\mu'} & \{ KFm \, | \, V_\mu \, | \, KFm' \} \\
& \times \{ KFm' \, | \, W_{\mu'} \, | \, KFm \} \\
& \times \frac{d_{0\mu}^{(1)}(\beta) d_{0\mu'}^{(1)}(\beta)}{1 + i\Omega(KFm';KFm)\tau_m} \ ,
\end{aligned} \tag{66}
$$

where $d_{0\mu}^{(1)}(\beta)$ is the matrix representation of R, and the angle β between ω and the z axis is shown in Fig. 3.

Since we are interested in the matrix elements of the vector operators **S** and **K** between states $| KFm \}$ and $| KFm' \}$ which have the same quantum number F for the total angular momentum operator $\mathbf{F} = \mathbf{S} + \mathbf{K}$, we may use the projection theorem to write
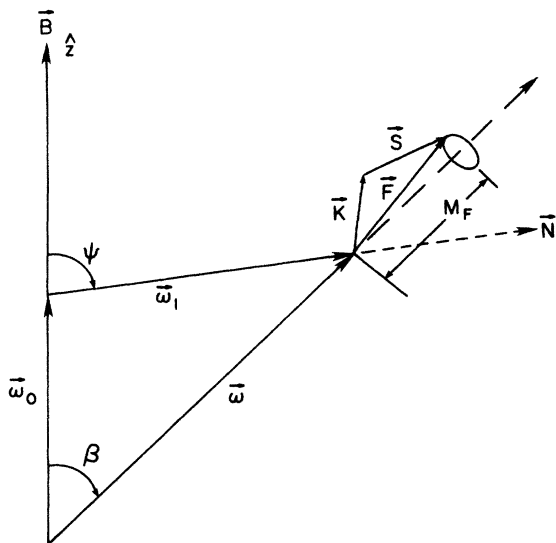
FIG. 3. Interacting spins of an $^3\mathrm{He_2}^+$ molecule in the presence of a magnetic field. The total nuclear spin of the molecule is denoted by $\mathbf{K}$, the electronic spin is $\mathbf{S}$, and the rotational angular momentum is $\mathbf{N}$. The total spin angular momentum, excluding $\mathbf{N}$, is $\mathbf{F}=\mathbf{K}+\mathbf{S}$. Note that $\omega=\omega_0+\omega_1$, where $\omega_0=g_S\mu_B B_o/\hbar$ and $\omega_1=\gamma_m N/\hbar$.

$$\mathbf{V}=\sum_F {}^j P_{VF}\mathbf{F} \ , \tag{67}$$

where the nonzero coefficients $^jP_{VF}$ are $^1P_{S1/2}=1$, $^3P_{K3/2}=\frac{2}{3}$, $^3P_{K1/2}=\frac{4}{3}$, $^3P_{S3/2}=\frac{1}{3}$, and $^3P_{S1/2}=-\frac{1}{3}$. In view of the projection theorem we may write

$$\hbar\Omega(KFm';KFm)=\hbar\omega\, ^jP_{SF}(m'-m) \ . \tag{68}$$

Then the coupling coefficient becomes

$$^j\eta_{VW}=\,^j\chi_{VW}(1-\,^jf) \ , \tag{69}$$

where

$$^j\chi_{VW}=\frac{C_W}{3}\sum_F {}^jP_{VF}\,^jP_{WF}F(F+1)(2F+1) \ , \tag{70}$$

and the fraction ^jf of angular momentum destroyed due to rotation about the vector sum of the external field and the internal field is

$$^jf=\frac{\omega_1}{4\omega_0}\left[2\,^jd+(1-\,^jd^2)\ln\left|\frac{1+\,^jd}{1-\,^jd}\right|\right] \ , \tag{71}$$

where

$$^jd=\frac{j^2+(\omega_0^2+\omega_1^2)\tau_m^2}{2\omega_0\omega_1\tau_m^2} \ . \tag{72}$$

Using (49) and the last few equations we can write an expression for the parameter λ,

$$\lambda=\left[\frac{4\,^1f+14\,^1f\,^3f+44\,^3f+10(^3f)^2}{16+13\,^1f+14\,^1f\,^3f+55\,^3f+10(^3f)^2}\right] \ . \tag{73}$$

V. DISCUSSION

Using the results of Secs. III and IV we can write the total rate of depolarization of the mean longitudinal atomic nuclear spin $\langle I_z \rangle$ as [cf. (21) and (34)]

$$\frac{d}{dt}\langle I_z\rangle=\frac{d^{(1)}}{dt}\langle I_z\rangle+\frac{d^{(2)}}{dt}\langle I_z\rangle=-\Gamma\langle I_z\rangle \ , \tag{74}$$

where

$$\Gamma=\Gamma_1+\Gamma_2=n_a\langle\Gamma_{\mathrm{ion}}\rangle+\lambda\langle\Gamma_{\mathrm{ex}}\rangle \ . \tag{75}$$

The angular brackets denote a volume average of the ionization rate Γ_{ion} and the exchange rate Γ_{ex}. A convenient way to express this rate is to define n_m as the number of $^3\mathrm{He}$ atoms depolarized per ion created due to formation of $^3\mathrm{He_2}^+$ molecules. Then we can write

$$\Gamma=\Gamma_{\mathrm{ion}}(n_a+n_m) \ , \tag{76}$$

where

$$n_m=\frac{\lambda\langle\Gamma_{\mathrm{ex}}\rangle}{\langle\Gamma_{\mathrm{ion}}\rangle}=\frac{\langle\Gamma_2\rangle}{\langle\Gamma_{\mathrm{ion}}\rangle} \ . \tag{77}$$

Note that $\Gamma_{\mathrm{ex}}\propto\Gamma_{\mathrm{ion}}$ in regimes dominated by diffusion or charge transfer, so that under many conditions n_m is independent of Γ_{ion}.

The relaxation rate due to atomic ions, $\Gamma_1=n_a\langle\Gamma_{\mathrm{ion}}\rangle$, depends on the helium number density [He] since n_a depends on [He] through τ_a and τ_{ex} [see (23)]. The dependence of τ_a on helium pressure depends on experimental conditions. For example, in the experiments of Milner et al.[5] the atomic-ion lifetime is determined by both diffusion and conversion to molecular ions which have very different He pressure dependences. In the experiments of Chupp et al.,[6] charge transfer with N_2 dominates the atomic-ion lifetime, and so τ_a is independent of He pressure. The pressure dependence of τ_{ex} is independent of experimental conditions. From a measurement of the charge exchange cross section for the process (19) at 1 eV energy and from theoretical calculations[18] we estimate that the time for free precession of a $^3\mathrm{He}^+$ ion between exchanges is about $\tau_{\mathrm{ex}}\approx 60/P_{\mathrm{He}}$ nsec Torr, where P_{He} is the partial pressure of He.

The relaxation rates predicted by Γ_2 are shown in Fig. 4. The relative relaxation rate Q, where

$$Q=\frac{\Gamma_2}{\left\langle\dfrac{\gamma_m N}{h}\right\rangle\phi} \ , \tag{78}$$

is plotted on the vertical axis. Here $\langle\gamma_m N\rangle/h$ is the mean electron spin rotation rate about $\mathbf{N}$. The ionization fraction of molecules is

$$\phi=\frac{[^3\mathrm{He_2}^+]}{[\mathrm{He}]} \ . \tag{79}$$

Along the horizontal axis we have plotted the relative number density d of He atoms,
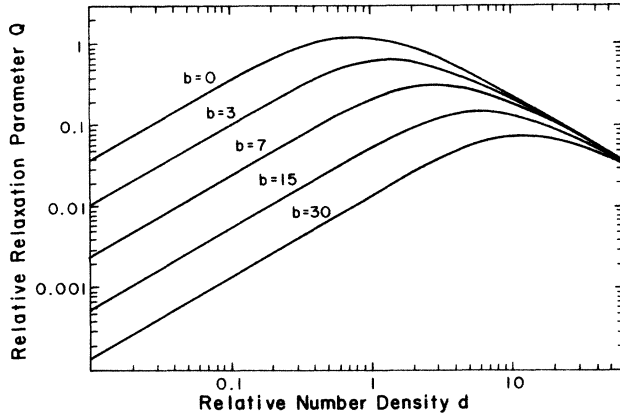
$$d=\frac{[\mathrm{He}]}{[\mathrm{He}]^*} \ . \tag{80}$$

FIG. 4. Plot of the relative relaxation rate Q vs relative number density d for various values of the relative magnetic field b. This plot enables one to estimate the expected relaxation rate due to ^{3}He$_2^+$. Take the best estimates for $\gamma_m N/h$ and σ_e and calculate [He]* and B^* from (81) and (84). Then determine Q from the graph for the experimental conditions of interest, and obtain the relaxation rate from (78).

At the *characteristic number density* [He]*, where

$$[\text{He}]^* = \frac{2\pi}{\sigma_e v}\left\langle \frac{\gamma_m N}{h}\right\rangle , \tag{81}$$

the product of the average molecular lifetime and the spin-rotation angular frequency is 1, i.e.,

$$2\pi\left\langle \frac{\gamma_m N}{h}\right\rangle \tau_m = 1 . \tag{82}$$

Predicted relative relaxation rates are plotted in Fig. 4 for several values of the *relative magnetic field b*, where

$$b = \frac{B_0}{B^*} . \tag{83}$$

At the *characteristic field B^**, where

$$B^* = \frac{\langle \gamma_m N\rangle}{g_s \mu_B} , \tag{84}$$

the Larmor frequency $g_s \mu_B B^*/\hbar$ of the electron spin is equal to $2\pi\langle \gamma_m N\rangle /h$.

For experiments where the nitrogen pressure is high enough to have asymmetric charge transfer with N_2 dominating both the atomic-ion lifetime τ_a and the molecular-ion lifetime, τ_m, a simple expression relating n_m to the relative relaxation rate Q can be written, viz.,

$$n_m = 6.31\times 10^{-14}\ \text{sec}\left\langle \frac{\gamma_m N}{h}\right\rangle \left[\frac{[\text{He}]}{[\text{N}_2]}\right]^2 Q . \tag{85}$$

For the value $\langle \gamma_m N/h\rangle = 29$ MHz we can write

$$n_m = 1.83\times 10^{-6}\left[\frac{[\text{He}]}{[\text{N}_2]}\right]^2 Q . \tag{86}$$

As can be seen from Fig. 4, the relative relaxation rate, which can be thought of as the rate at a fixed molecular ionization fraction ϕ, increases with pressure at low pressures, then reaches a maximum, and finally decreases with pressure at higher pressures. The figure also shows that modest magnetic fields (~ 200 G) will reduce the relaxation rate by about two orders of magnitude at low pressures. From Fig. 3 we see that if $\omega_0 \gg \omega_1$, the resultant frequency ω will be nearly longitudinal and unable to precess the longitudinal spin $\langle F_z\rangle$ very far from the z axis, even when the spin rotation frequency ω_1 is transverse and would completely randomize the direction of $\langle F_z\rangle$ in the absence of a magnetic field.

To conclude this section, we point out that the experiments of Milner *et al.* and Chupp *et al.* operate at two opposite extremes as far as which depolarization rate dominates, Γ_1 or Γ_2. For the former, the depolarization rate due to atomic ions, Γ_1, is negligible compared to that due to the molecular ions, i.e., $\Gamma_1 \ll \Gamma_2$. In the experiments of Chupp *et al.*, the opposite is true, i.e., $\Gamma_1 \gg \Gamma_2$. To be more quantitative, for the experiments of Milner *et al.* we estimate the number of nuclei depolarized per ^{3}He$^+$ atomic ion at all He pressures to be $n_a \simeq 1$, whereas the measurements indicate that the number of nuclei depolarized per ^{3}He$_2^+$ varies from $n_m \simeq 7$ at $P_{\text{He}} = 0.8$ Torr to $n_m \simeq 1200$ at $P_{\text{He}} = 4.5$ Torr. In the experiments of Chupp *et al.* the corresponding numbers are $n_a \simeq 0.7$ and $n_m \simeq 10^{-7}$.

VI. COMPARISON TO EXPERIMENT

To estimate a depolarization time for a given experiment a reliable value for the ionization fraction ϕ is necessary. For a cw experiment, an estimate of [^{3}He$_2^+$] can be obtained by assuming a balance between its production and destruction rates. The production rate depends on the production rate of He$^+$ and the conversion rate of He$^+$ to ^{3}He$_2^+$. The conversion rate has been measured to be[16–18] $103P_{\text{He}}^2$ sec^{-1}, where P_{He} is the He pressure in Torrs. The destruction rate has contributions from ambipolar diffusion and from recombination. At small pressures ($P_{\text{He}} \leq 10$ Torr) and in reasonably sized cells where the radius is on the order of a few cm, the diffusion rate dominates. At high pressures ($P_{\text{He}} \geq 100$ Torr) and significant electron densities ($n_e \geq 10^{10}$ cm^{-3}) recombination dominates. The recombination coefficient for He$_2^+$ for $P_{\text{He}} = 10$–100 Torr was measured to be[18]

$$\alpha = \alpha_d + \beta_n[\text{He}] + \beta_e[e^-]^*, \tag{87}$$

where the two-body recombination contribution was $\alpha_d = 5\times 10^{-10}$ cm^3/sec, $\beta_n = 2\times 10^{-27}$ cm^6/sec, and $\beta_e = 2\times 10^{-20}$ cm^6/sec.

The present calculation can be compared to experimental data taken using 3-MeV protons produced by the Caltech Pelletron accelerator.[5] Milner *et al.* measured relaxation times T for a 1-μA beam incident on targets with He pressures 0.8, 1.9, 3.5, and 4.5 Torr. To compare their results to the theory we estimate the relaxation times T for each of their pressures according to (78), where

$$\Gamma = \frac{1}{T} \simeq \Gamma_2 = \left\langle \frac{\gamma_m N}{h} \right\rangle \langle \phi \rangle Q \ , \tag{88}$$

and we have used the fact that here $\Gamma_1 \ll \Gamma_2$, as we shall later show. Here $\langle \phi \rangle$ is the spatial average of the space-dependent fractional ionization $\phi(r,z)$, where we have assumed cylindrical coordinates and, by symmetry, there is no azimuthal dependence. To estimate $\langle \phi \rangle$ at each He pressure we must review in detail the experiments of Milner et al.

A proton beam of radius[20] $R_0 = 0.25 \pm 0.12$ cm produced ^{3}He ions along the full length of the cell. The cell consisted of a central sphere of radius 1.9 cm with two cylindrical pieces, each 3.1 cm long and 0.71 cm in radius, attached to the sphere. The total cell length (along the beam axis) was 10 cm. The production rate per unit volume of ^{3}He ions is given by

$$S = \Gamma_{\text{ion}}[\text{He}] = \frac{1}{\Delta E} \frac{dE}{dx} \left\langle \frac{I}{e \pi R_0^2} \right\rangle \Theta(r - R_0) \ , \tag{89}$$

where the amount of energy removed from the beam per ion created is[13] $\Delta E = 32$ eV, $I/e\pi R_0^2 = J_b$ is the incident proton flux (I is the beam current, e is the proton charge, and πR_0^2 is the beam area), and the step function Θ is defined such that $\Theta(x) = 1$ if $x > 0$ and $\Theta(x) = 0$ otherwise. The energy loss per unit length for 3-MeV protons in ^{4}He gas of mass density ρ can be obtained by interpolation from standard tables[14] and is $dE/dx = 133\rho$ MeV cm^2/g. Scaling this result with atomic mass gives the value 177ρ MeV cm^2/g for 3-MeV protons incident on ^{3}He. The production rate per unit volume S can be written in this case as

$$S = S_0 \Theta(r - R_0) \ , \tag{90}$$

where $S_0 = 3.76 \times 10^{13} P_{\text{He}}$ cm^{-3} sec^{-1} Torr^{-1}.

At the low pressures used in the experiments, the loss of ^{3}He ions due to diffusion is important. In addition, the ^{3}He ions have a high conversion rate to ^{3}He$_2^+$. To find $[^3$He$^+]$, we must solve the rate equation under equilibrium conditions, i.e.,

$$\frac{\partial}{\partial t}[\text{He}^+] = S - \varepsilon[\text{He}^+] - \delta[A][\text{He}^+] + D\nabla^2[\text{He}^+] = 0 \ , \tag{91}$$

where S is the production rate of ^{3}He$^+$ in units of cm^{-3} sec^{-1}, the conversion rate of ^{3}He$^+$ to ^{3}He$_2^+$ is[16-18] $\varepsilon = 103 P_{\text{He}}^2$ sec^{-1} Torr^{-2}, δ is the rate constant for an asymmetric charge transfer reaction between He$^+$ and the atomic or molecular species A, and D is the diffusion constant

$$D = D_0 \frac{760}{P_{\text{He}}} \ , \tag{92}$$

where D_0 is the diffusion coefficient. The ambipolar diffusion coefficient of ^{3}He$^+$ in He is[18] $D_0 = 0.53$ cm^2/sec. The term due to asymmetric charge transfer is important both here and in the rate equation for ^{3}He$_2^+$. This is due to the fact that many common impurities, H_2O, N_2, O_2, etc. have substantial rate constants for charge transfer re-

actions. As an example, for the charge transfer process given by

$$\text{He}^+ + \text{N}_2 \rightarrow \text{He} + \text{N}_2^+ \ , \tag{93}$$

the rate constant has been measured to be[7] $\delta = 1.0 \times 10^{-9}$ cm^3/sec. The final result of the process (93) and of similar processes involving ^{3}He$_2^+$ [see (2) and Sec. V] is a significant reduction in the equilibrium density of ^{3}He$_2^+$, which will reduce the depolarization rate of ^{3}He.

It is difficult to solve (91) due to the complicated geometry of the cell. To find an approximate solution to (91) we assume an effective cell that is cylindrical with the radius chosen so that the effective cell volume matches the actual cell volume. The cell volume was 38.7 cm^3 and its length was 10 cm. This gives an effective radius of $R = 1.1$ cm. Under the assumption of a cylindrical cell we can solve (91) by expanding the number density of ^{3}He$^+$ as a sum of cylindrical diffusion modes,

$$[^3\text{He}^+] = \sum_{m,p=1}^{\infty} n_{mp} J_0 \left[x_{0m} \frac{r}{R} \right] \sin \left[\frac{\pi p z}{L} \right] \ , \tag{94}$$

where x_{0m} is the mth zero of the Bessel function J_0 and p is a positive integer. The diffusion modes of (94) are zero at the edges of the cylinder. Similarly the source, which we assume to be uniform out to the beam radius, can be written

$$S = \sum_{m,p=1}^{\infty} s_{mp} J_0 \left[x_{0m} \frac{r}{R} \right] \sin \left[\frac{\pi p z}{L} \right] \ . \tag{95}$$

It can be easily shown that for p odd,

$$s_{mp} = \frac{8 S_0}{\pi p x_{0m}} \frac{R_0}{R} \frac{J_1 \left[x_{0m} \dfrac{R_0}{R} \right]}{[J_1(x_{0m})]^2} \ , \tag{96}$$

and otherwise, $s_{mp} = 0$. Substitution of (94) and (95) into (91) gives the relation

$$n_{mp} = \frac{s_{mp} R^2}{x_{0m}^2 D + \varepsilon R^2 + \left[\dfrac{\pi R}{L} p \right]^2 D + \delta[A] R^2} \ . \tag{97}$$

To find $\langle \phi \rangle$ we estimate $[^3$He$_2^+]$ by solving the ^{3}He$_2^+$ rate equation under equilibrium conditions, i.e.,

$$\frac{\partial}{\partial t}[^3\text{He}_2^+] = \varepsilon[^3\text{He}^+] + D'\nabla^2[^3\text{He}_2^+] - \alpha[^3\text{He}_2^+]^2$$
$$- \delta'[A][^3\text{He}_2^+]$$
$$= 0 \ , \tag{98}$$

where the diffusion constant D' is given by an expression similar to (92), α is the recombination coefficient for ^{3}He$_2^+$, which includes three-body recombination with both He and electrons and two-body recombination [see (87)], and δ' is the rate constant for the asymmetric charge transfer reaction between ^{3}He$_2^+$ and an impurity species A (see Refs. 7–9 and Sec. V). Again, the last term included in (98) is important because many common impurities, e.g., N_2, H_2, etc. have substantial rate constants

for charge transfer reactions. As an example, for dissociative charge transfer between ^{3}He$_2{}^+$ and N$_2$ [see (2)] the rate constant has been measured to be[8] $\delta' = 1.3 \times 10^{-9}$ cm^3/sec. We ignore the recombination term since this rate is small compared to the diffusion rate at the low pressures encountered here. For instance, we estimate from (87) and (98) that the recombination term, with $P_{He} = 4.5$ Torr, electron number density $[e] = 5 \times 10^{10}$ cm^{-3}, and $[^3$He$_2{}^+] = 1 \times 10^{10}$ cm^{-3}, is

$$\alpha[^3\text{He}_2{}^+]^2 = 1.8 \times 10^{11} \text{ cm}^{-3} \text{sec}^{-1} ,$$

whereas, using notation that will be explained shortly, the diffusion term is (to within 20%)

$$D'\nabla^2[^3\text{He}_2{}^+] \approx D' \left[\frac{x_{01}^2}{R^2} + \left[\frac{\pi}{L} \right]^2 \right] n_{11}'$$

$$= 6.0 \times 10^{12} \text{ cm}^{-3} \text{sec}^{-1} . \qquad (99)$$

The ambipolar diffusion coefficient for ^{3}He$_2{}^+$ in He is[18] $D_0' = 0.81$ cm^2/sec. Again we make the expansion

$$[^3\text{He}_2{}^+] = \sum_{\substack{m,p=1 \\ p \text{ odd}}}^{\infty} n_{mp}' J_0 \left[x_{0m} \frac{r}{R} \right] \sin \left[\frac{\pi p z}{L} \right] , \qquad (100)$$

and substituting (94) and (100) into (98) we find

$$n_{mp}' = \left[\frac{\varepsilon R^2/D'}{x_{0m}^2 + \left[\frac{\pi R}{L} p \right]^2 + \delta'[A]R^2/D'} \right] n_{mp} . \qquad (101)$$

To obtain $\langle \phi \rangle$ we average $\phi(r,z)$ over the radial and axial coordinates,

$$\langle \phi \rangle = \frac{\int_0^L \int_0^R \phi(r,z) r \, dr \, dz}{LR^2/2}$$

$$= \frac{32\varepsilon R_0 R^3 S_0}{\pi^2[\text{He}]D'} \sum_{\substack{m,p=1 \\ p \text{ odd}}}^{\infty} \left[\frac{J_1 \left[x_{0m} \frac{R_0}{R} \right]}{p^2 x_{0m}^2 J_1(x_{0m})} \right] \left[\frac{1}{x_{0m}^2 + \left[\frac{\pi R}{L} p \right]^2 + \delta'[A]R^2/D'} \right] \left[\frac{1}{x_{0m}^2 D + \left[\frac{\pi R}{L} p \right]^2 D + \varepsilon R^2 + \delta[A]R^2} \right] .$$

$$(102)$$

At the low pressures encountered here 95% of the contribution to $\langle \phi \rangle$ is given by the first few terms ($m = 1,2$, $p = 1,3$) in the above sum.

Before comparing the theory to the measurements, note that the ionization rate is $\Gamma_{ion} = 5.6 \times 10^{-5}$ sec^{-1} so the depolarization rate due to atomic ions, $\Gamma_1 = n_a \Gamma_{ion} \simeq \Gamma_{ion}$, is significantly less than even the smallest observed rate of $\Gamma = 3.1 \times 10^{-4}$ sec^{-1}. We use two tables to compare the theory to the experiments. Table I compares the experimental relaxation times to those calculated for the case of pure helium in the cell, i.e., where there are no charge transfer reaction constitu-

ents present so $[A] = 0$ in (102). Column 1 contains the helium pressure and column 2 lists our estimates of the corresponding ^{3}He$_2{}^+$ number densities. Measured values for the relaxation time T at the various helium pressures are given in column 3. Using the magnetic field applied by Milner et al., $B_0 = 10$ G, we estimate the relaxation times T at the various pressures used in the experiments. Assuming $\langle \gamma_m N/h \rangle = 29$ MHz and $\sigma_e = 1.1 \times 10^{-15}$ cm^2, the value inferred from mobility experiments,[18,19] we obtain the values listed in column 4 of Table I. Under this assumption of a pure helium target the relaxation times in column 4 are in poor agreement with the mea-

TABLE I. Relaxation times for pure helium. The magnetic field is $B_0 = 10$ G.

P_{He} (Torr)	$[^3$He$_2{}^+]$ (cm^{-3})	T (sec) Measured[a]	T (sec) Calculated[b]	n_a Calculated	n_m Measured
0.8	1.3×10^7	3200 ± 850	680	1	7
1.9	7.3×10^8	700 ± 200	13	1	30
3.5	6.7×10^9	22 ± 7	1.4	1	1000
4.5	1.4×10^{10}	19 ± 6	0.74	1	1200

[a] See Milner et al. (Ref. 5).
[b] The value used was $\sigma_e = 1.1 \times 10^{-15}$ cm^2.

TABLE II. Relaxation times with background $[N_2] = 1.3 \times 10^{-4}$ Torr. The magnetic field is $B_0 = 10$ G.

P_{He} (Torr)	$[^3He_2^+]$ (cm^{-3})	T (sec) Measured[a]	T (sec) Calculated[b]
0.8	1.9×10^6	3200 ± 850	3700
1.9	4.3×10^7	700 ± 200	210
3.5	3.2×10^8	22 ± 7	30
4.5	6.8×10^8	19 ± 6	15

[a] See Milner et al. (Ref. 5).
[b] The value used was $\sigma_e = 1.1 \times 10^{-15}$ cm^2.

sured times of column 3. However, Milner et al. gave no indication of the purity of their helium. It is well known that water vapor is slowly released from the walls of glass cells. This outgassing could have been enhanced by the proton beam and by the operation of a discharge. The presence of contaminants in small quantities is important because they will significantly decrease the $^3He_2^+$ number density. As already mentioned, common gases such as H_2O, N_2, H_2, CO, etc. quench $^3He_2^+$ very effectively by various charge transfer mechanisms. To demonstrate how effectively depolarization is suppressed by even a small amount of such a gas, we calculated new values for both the relaxation times and the $^3He_2^+$ number densities, assuming a background nitrogen pressure in the cell of $[A] = [N_2] = 4.6 \times 10^{12}$ cm^{-3}. We list in Table II all the same quantities given in Table I but with these new values for the calculated relaxation times and the $^3He_2^+$ number densities. Under these conditions, the agreement between columns 3 and 4 is quite good and most of the calculated relaxation times now agree within error bars to the measured values.

To make a more definitive comparison between the theory and experiment, more carefully designed experiments must be carried out. The use of a getter in the cell would significantly reduce impurity levels. The experimental data could be more easily compared to theory by using a cell of convenient geometry, e.g., a cylinder. A better definition of the spatial profile of the proton beam is also essential. To conclude, it is difficult to make definitive comparisons but it seems the relaxation can be attributed to the spin-rotation interaction. The key to this interpretation is that the measured relaxation rates do qualitatively scale according to the $^3He_2^+$ number density.

Before proceeding we point out one other comparison that can be made to a depolarization measurement done at low pressure. Byerly[21] measured the depolarization rate of spin-polarized ^3He at 20 Torr of helium under two conditions: with about 10^{13} cm^{-3} of neon gas added as an impurity quencher of $^3He_2^+$ and without neon. Attributing the difference in the depolarization rates as that due to $^3He_2^+$ molecular ions, Byerly estimates that the depolarization rate constant due to molecular ions, taken as the difference of the two measured rate constants for the two different conditions, is $k = \Gamma_2/[^3He_2^+] \simeq 10^{-12}$ cm^3/sec. Using Fig. 4 to estimate a value for k from the theory gives $k \simeq 3 \times 10^{-12}$ cm^3/sec. Note that Byerly's

conditions were such that $B_0 \simeq 10$ G and $\phi \simeq 10^{-10}$. The agreement is very good considering the uncertainties associated with both the measurements and the critical parameters necessary to make the estimate.

VII. PROSPECTS FOR SUPPRESSING DEPOLARIZATION BY $^3He_2^+$

In this section we review methods for reducing depolarization by $^3He_2^+$ formation. We begin with a discussion of charge transfer destruction of $^3He_2^+$ by collision with a foreign gas atom or molecule because of its importance in suppressing the equilibrium $^3He_2^+$ concentration in target cells. The rate constants for various types of charge transfer processes with $^3He_2^+$ have been measured.[8,9] The rate constants are on the order of gas kinetic rates. For instance, it is known that $^3He_2^+$ will rapidly charge exchange and dissociate in the presence of N_2 by process (2). The rate constant for this reaction has been measured to be[8] 1.3×10^{-9} cm^3/sec. Other gases which have been measured include Ne, Ar, Xe, H_2O, CO, O_2, and H_2.

Recent experiments by Chupp et al.[6] clearly demonstrate the significance of such reactions. The experiments involved measuring ^3He spin relaxation due to 18-MeV α particles with a beam current of 0.336 μA. They used spin exchange with optically pumped Rb to polarize ^3He (see Chupp et al.[6]). The target cell, which consisted of 434 Torr of ^3He and 153 Torr of N_2, resulted in a spin-relaxation time of about $T = 1.4 \times 10^4$ sec. The nitrogen was included to prevent radiation trapping of the Rb $D1$ line used for optical pumping. The relaxation time attributable to atomic ions alone is calculated to be 2.2×10^4 sec. Therefore, little indication of depolarization due to $^3He_2^+$ was found. Due to the large concentration of nitrogen, $^3He_2^+$ was effectively eliminated. We estimate that under these conditions about 850 cm^{-3} of $^3He_2^+$ was present and so there was no significant relaxation of ^3He due to $^3He_2^+$, as observed. The shorter observed relaxation time could be due to depolarization effects we have ignored until now. For instance, we would expect a significant number of $2\ ^3S_1$ metastable ^3He neutral atoms to be created and the hyperfine interaction (between the nuclear spin and the electronic spin) to cause a loss of polarization of the nuclear spin to the electronic spin.

TABLE III. Nitrogen densities required to make the number of ^{3}He atoms depolarized per ^{3}He$_2{}^+$ equal to 1, i.e., $n_m = 1$ [see (77)]. These numbers assume $\sigma_e = 1.1 \times 10^{-15}$ cm^2.

P_{He} (Torr)	[N$_2$]/[^{3}He]	Ref.
0.8	0.44×10^{-3}	6
1.9	0.95×10^{-3}	6
3.5	1.3×10^{-3}	6
4.5	1.4×10^{-3}	6
434	8.3×10^{-5}	5

TABLE IV. Relaxation times for pure helium at $B_0 = 10$ G and $B_0 = 200$ G for low-pressure cells. These numbers assume $\sigma_e = 1.1 \times 10^{-15}$ cm^2.

P_{He} (Torr)	T (sec) $B_0 = 10$ G	$B_0 = 200$ G
0.8	680	1.4×10^4
1.9	13	1100
3.5	1.4	130
4.5	0.74	66

To show more quantitatively the importance of charge transfer processes, we estimate the concentrations of N$_2$ in ^{3}He that are sufficient to suppress depolarization arising from ^{3}He$_2{}^+$ molecules. Specifically, we calculate the N$_2$ concentrations necessary to make the depolarizing rate from ^{3}He$_2{}^+$ formation equal to the rate expected due to ^{3}He$^+$ atomic ions for both the Milner et al. and the Coulter et al. experimental conditions. Using the notation defined in (76), we evaluate the N$_2$ concentration necessary to have $n_m = 1$, i.e., the number of ^{3}He atoms depolarized per ^{3}He$_2{}^+$ molecule is 1. Table III summarizes the results. In column 1 we list the helium gas pressure and column 2 shows the fractional concentration of N$_2$ to ^{3}He that is required to make $n_m = 1$. The table indicates, in the case of two radically different sets of experimental conditions, that very modest foreign gas levels ([N$_2$]/[^{3}He] $\simeq 10^{-3}$) are sufficient to suppress depolarization by formation of ^{3}He$_2{}^+$. Thus, if experimental conditions allow it, introduction of one of the foreign gases that is effective at charge transfer reactions with ^{3}He$_2{}^+$ will reduce depolarization due to ^{3}He$_2{}^+$ molecules.

Since there are plans for future experiments using targets of much higher helium densities,[22] it is important to note that recent work[23] indicates that the termolecular asymmetric charge transfer process

$$^3\text{He}_2{}^+ + \text{N}_2 + \text{He} \rightarrow \text{N}_2{}^+ + 3\text{He} \tag{103}$$
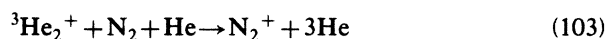
has a fairly high rate constant of $k_3 = 1.31 \times 10^{-29}$ cm^6/sec. At nitrogen densities of 5×10^{18} cm^{-3} and helium densities of about 10^{20} cm^{-3} the bimolecular [see (2)] and the termolecular asymmetric charge transfer rates become equal. Thus, at higher He pressures, conditions become even more favorable for suppression of depolarization by ^{3}He$_2{}^+$.

Finally, it is also clear that depolarization rates can be reduced in low-pressure cells by increasing the magnetic field. In the case of a cell of pure helium a magnetic field of 200 G would lengthen the relaxation times of Milner et al.[5] by a factor of about 100. A comparison of calculated relaxation times in fields of 10 and 200 G is given in Table IV.

VIII. CONCLUSIONS

We have presented a model which predicts the depolarization rate of ^{3}He due to atomic ions and due to formation of ^{3}He$_2{}^+$. The comparison between theory and the Milner et al. experiments is difficult and inconclusive due to the uncertainties in the gas purity, the cell cleanliness, the spatial profile of the proton beam, the value of the spin-rotation coupling constant γ_m, and the value of the exchange cross section σ_e. However, it does seem that the ^{3}He spin relaxation can be attributed to the spin-rotation interaction in the molecular ion ^{3}He$_2{}^+$.

There are several ways to overcome spin relaxation due to ^{3}He$_2{}^+$. The number density of ^{3}He$_2{}^+$ can be lowered by introducing a foreign gas, such as nitrogen, that will undergo a charge transfer reaction with ^{3}He$_2{}^+$. At low gas pressures ($P_{He} \leq 20$ Torr) ^{3}He depolarization by ^{3}He$_2{}^+$ is greatly reduced by applying a modest magnetic field $B_0 \simeq 200$ G. Operating at high target pressures also significantly reduces the relaxation rate. Through one or a combination of these techniques, the problem of relaxation of polarized ^{3}He by ^{3}He$_2{}^+$ can probably be solved.

ACKNOWLEDGMENTS

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