

Measurements of the rate constant for orientation transfer in the $H(1^2S_{1/2})$ - $He(2^3S_1)$ system and determination of the rate constant for spin exchange

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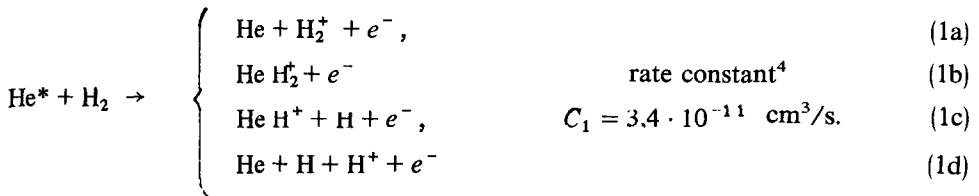
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The rate constant for the transfer of electronic orientation from H atoms to $He^*(2^3S_1)$ atoms has been determined by optical detection of the magnetic resonance of H atoms polarized in a helium-hydrogen plasma. As a result, a first experimental value has been found for the rate constant for spin exchange in collisions of He^* and H atoms.

Collisions of helium atoms in the metastable 2^3S_1 state with hydrogen atoms in the $1^2S_{1/2}$ ground state may be accompanied by a spin exchange and a chemical ionization, also called "Penning ionization." While the chemical ionization has been studied extremely thoroughly,^{1,2} no information is available on the rate constant for spin exchange, because of the difficulty in separating these two processes. In the present study we make use of the possibility of determining the rate constant for spin exchange which arises upon the polarization of He^* and H atoms in a helium-hydrogen plasma.³ The method is essentially one of analyzing the magnetic-resonance signals of the polarized H and He^* atoms which are observed under identical experimental conditions.

A gas discharge was excited in an absorption chamber filled with a mixture of He^4 (0.36 Torr at 300 K) and H_2 (0.01–0.02 Torr), and the metastable He^* atoms (spin $S = 1$) were optically oriented in the longitudinal magnetic field; H_0 by circularly polarized resonant radiation (the $2^3S_1 \rightarrow 2^3P_{0,1,2}$ transition, $\lambda = 1.08 \mu m$).

The orientation of the 2^3S_1 helium atoms, $\langle S_{He} \rangle = \text{Tr}(S_{He} \rho_{He})$ [ρ_{He} is the (3×3) density matrix of the He^* atoms, and $\text{Tr} \rho_{He} = 1$], depends on the pumping conditions and the relaxation conditions. The relaxation is determined primarily by



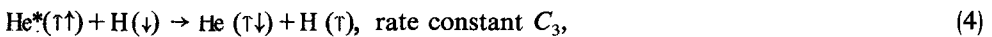
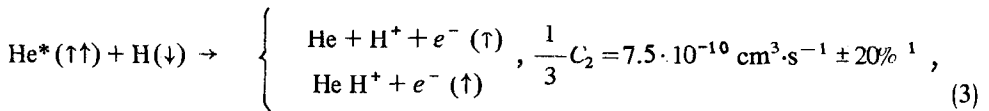
As a result of this process, primarily the chemical dissociation (1c), angular momentum is transferred from polarized He* atoms to H atoms. The angular momentum transferred per unit time is

$$\mathbf{q} = \frac{1}{2} \alpha N_{\text{He}^*} N_{\text{H}_2} C_1 \langle \mathbf{S}_{\text{He}} \rangle, \quad (2)$$

where α is the fraction of the orientation which is transferred to the H atoms (0.2, according to Ref. 3), and the N_i are the densities of the corresponding particles.

The electronic orientation of the hydrogen atoms, $\langle \mathbf{S}_{\text{H}} \rangle = \text{Tr}(S_{\text{H}} \rho_{\text{H}}) [\rho_{\text{H}}$ is the electronic part of the (2×2) density matrix of the H atoms; $\text{Tr} \rho_{\text{H}} = 1]$, arises primarily from process³ (1) and is determined by the value of \mathbf{q} and by the relaxation processes, the most important of which is the diffusion of hydrogen atoms to the walls of the absorption chamber.

In the experiments we observed a change in the absorption by He* atoms of pump light at a wavelength of $1.08 \mu\text{m}$ when a resonant magnetic field $H_1 \cos \omega t$ was applied. Optical detection of the magnetic resonance of the H atoms is possible because the $\langle \mathbf{S}_{\text{H}} \rangle$ and $\langle \mathbf{S}_{\text{He}} \rangle$ orientations are coupled by the processes



where the arrows specify the orientations of the electron spins.

The resonance signals observed are proportional to the changes in the orientation $\langle \mathbf{S}_{\text{He}} \rangle$ upon the magnetic resonance of the He* or H atoms, and in a steady-state plasma ($N_{\text{He}^*} = \text{const}$, $N_{\text{H}} = \text{const}$) these signals are given by the following expressions, according to expressions (20) and (21) of Ref. 3:

$$A^{\text{H}} = |\Delta \langle \mathbf{S}_{\text{He}} \rangle^{\text{H}}| = \frac{\phi_p r_1 r_2}{p_1 d} \omega_1^2 \frac{p_1 p_2 / d}{p_2^2 + \Delta \omega^2 + \omega_1^2 p_1 p_2 / d}, \quad (5)$$

$$A^{\text{He}} = |\Delta \langle \mathbf{S}_{\text{He}} \rangle^{\text{He}}| = \frac{\phi_p p_2}{d} (2\omega_1)^2 \frac{p_1 p_2 / d}{p_1^2 + \Delta \omega^2 + (2\omega_1)^2 p_1 p_2 / d}, \quad (6)$$

where ϕ_p is determined by the pumping conditions; p_1 and p_2 are determined by the loss of He* and H orientations; r_1 and r_2 are determined by the transfer of electronic

orientation from the H atoms to the He* atoms and vice versa; $d = p_1 p_2 - r_1 r_2$, $\Delta\omega = \omega - \omega_0$, $\omega_0 = \gamma H_0$, $\omega_1 = \gamma H_1$, and γ is the gyromagnetic ratio of the He* atoms.

In the case at hand we have $p_1 = N_{H_2} C_1 + \pi \Delta f_{He^4}$, $p_2 = \pi \Delta f_H$, $r_1 = \frac{4}{9} N_H C_2 + \frac{4}{3} N_H C_3$, and $r_2 = \alpha N_{He^*} N_{H_2} C_1 / 2N_H$, where Δf_H and Δf_{He^4} are the widths of the resonant lines of the H atoms (in the mixture He⁴-H₂) and the He* atoms (in the pure isotope He⁴), extrapolated to a zero value of H₁. Substitution of these expressions into (5) and (6) yields the following ratio of signal amplitudes in the limit $\omega_1^2 \rightarrow \infty$:

$$\frac{A_{\max}^H}{A_{\max}^{He}} = \frac{r_1 r_2}{p_1 p_2} = \frac{\alpha N_{He^*} C_{H-He^*}}{2\pi \Delta f_H (1 + \pi \Delta f_{He^4} / N_{H_2} C_1)}, \quad (7)$$

where $C_{H-He^*} = (4/9)C_2 + (4/3)C_3$.

The density of hydrogen atoms does not appear in (7), because the angular momentum acquired by the ensemble of atoms does not depend on N_H , according to (2). This independence makes it possible to find the rate constant C_{H-He^*} in an extremely simple way. For this purpose we need to measure A_{\max}^H and A_{\max}^{He} under conditions near rf saturation (at identical intensities of the pump light, in identical discharges, and at the same gain of the measurement system) and also Δf_H , Δf_{He^4} , and N_{He^*} . The density of metastable helium atoms is determined from the absorption of the helium line at 3888 Å (the $2^3S_1 \rightarrow 3^3P$ transition). This value was greater than 10^{11} cm^{-3} in all cases, so that the change in the density of the He* atoms at the time of the resonance makes a small contribution to the resonance signal of the H atoms.

In the experiments we analyzed the derivative of the absorption signal. We should thus take into account the possibility that the two resonant lines will have different widths. The corresponding correction is not necessary in the case of identical widths, and identical widths could be achieved easily by varying the amplitude of the rf magnetic field. Another point which must be taken into account is that in the case of a resonance in a system of Zeeman sublevels of the H atoms two transitions occur between sublevels with different values of the quantum number m_F ($\Delta m_F = 1$, $\Delta F = 0$).

The measurements were taken at various values of the densities He* and H₂. As a result, we determined the rate constant for the transfer of electronic orientation from H atoms ($1^2S_{1/2}$) to He* (2^3S_1) at $T = 295 \text{ K}$: $C_{H-He^*} = (2.35 \pm) \times 10^{-9} \text{ cm}^3/\text{s}$.

From this value we can single out the part due to spin exchange by making use of the rate constant given above for the Penning process, (3), from Ref. 1. This value is the same as that which we have calculated from the interaction potentials,⁵ and it agrees with the experimental data of Ref. 2. As a result, we find the following value for the rate constant for the spin exchange in the system He*-H at $T = 295 \text{ K}$: $C_3 = (1.01 \pm 0.37) \times 10^{-9} \text{ cm}^3/\text{s}$.

¹K. L. Bell, J. Phys. B 3, 1308 (1970).

²M. J. Shaw, R. S. Bolden, R. S. Hensworth, and N. D. Twiddy, Chem. Phys. Lett. 8, 148 (1971).

³S. P. Dmitriev, R. A. Zhitnikov, V. A. Kartoshkin, G. V. Klement'ev, and V. D. Mel'nikov, Zh. Eksp. Teor. Fiz. 85, 840 (1983) [Sov. Phys. JETP, to be published].

⁴R. A. Zhitnikov, V. A. Kartoshkin, and G. V. Klement'ev, *Pis'ma Zh. Eksp. Teor. Fiz.* **26**, 651 (1977) [JETP Lett. **26**, 624 (1977)].

⁵A. P. Hickman, A. D. Isaacson, and W. H. Miller, *J. Chem. Phys.* **66**, 1483 (1977).

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