Measurement of the spin-exchange cross section in the collision of H atoms with O_2 and NO by means of stored atomic-beam spectroscopy

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The spin-exchange cross section σ for the collision of hydrogen atoms with O_2 and NO have been measured by means of stored atomic-beam spectroscopy. Average values at room temperature are $\sigma(\text{H-O}_2) = (10 \pm 1) \times 10^{-16}$ cm^2 and $\sigma(\text{H-NO}) = (13 \pm 1) \times 10^{-16}$ cm^2. A comparison between our data and pulsed-maser measurements is presented. The development of a passive hydrogen maser based on our bolometric detection technique is proposed.

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INTRODUCTION

The experimental methods available for the study of the influence of collisions on the electronic spin polarization of gaseous atoms are several and differ widely with respect to their technical difficulty and amount of information delivered.

The most direct method involves the performance of crossed-beam scattering experiments with polarized atoms with or without the analysis of the scattered particles' polarization. This method has been applied so far only to alkali atoms because of the very high sensitivity with which these atoms can be detected.[1,2] A second class of experiments involves the perturbation of the thermal distribution over spin states of a gas contained in a cell and the monitoring of the level populations while equilibrium is restored. Classical examples belonging to this second class are optical pumping experiments,[3,4] where population inversion is obtained when the sample absorbs radiation of the proper frequency, and experiments involving masers,[5-11] where population inversion is achieved by physically separating the different spin states in inhomogeneous magnetic fields prior to emission into the interaction region.[12] In the latter category of experiments two further options are open for the monitoring of the time behavior of the spin populations. In the "active" mode the sample cell is located in an electromagnetic cavity and an analysis of the power emitted by it together with a series of collateral assumptions allows for the derivation of the desired information.[5,6] In the "passive" mode, the spin state of the atoms under study when remitted from the cell, after having spent a variable amount of time in it, is measured, again using physical separation of the spin states by inhomogeneous magnetic fields and normal atomic-beam-detection techniques.[13] In spite of the fact that both for the maser operation as a frequency standard, and for the study of spin-changing collisions, the passive mode has definite advantages,[14,15] its use has been, until now, very limited because of beam-detection difficulties. Indeed the easily detectible alkali atoms have a too large polarizability (and therefore interact too strongly with the walls of the storage bulb) while the weakly interacting H atoms ("the natural choice for these kind of experiments"[15]) are notoriously difficult to detect. Nevertheless the introduction, little more than ten years ago, of low-temperature bolometers as atomic-beam detectors[16] has drastically changed the level of sensitivity with which H atoms can be detected. Fluxes as low as 10^8 atoms cm^{-2} sec^{-1} have been detected, and quite sophisticated scattering experiments involving H atoms have been performed.[17-20] Because of the above experimental considerations and because of our interest in spin-perturbating collisions (see below) we have decided to revive the stored atomic-beam resonance method and study the possibility of applying it to a wide range of physical phenomena. Apart from their immediate interest for maser operation[5,21-23] and astrophysical reasons[24] spin-perturbing collisions are interesting because they depend directly and primarily on the exchange interactions.[25] Indeed, considering the basic atom-wall interaction, it is easy to understand that measuring only its exchange-interaction part opens up the possibility of sensitively studying (a) the surface concentration of atoms for which "activity" for exchange interaction with the H atoms is known and (b) the nature of the interaction of the same atom with unknown surfaces. In other words polarized atomic hydrogen acts like a sensitive probe for the presence of unpaired electrons on the solid surface. In this note we report the operation of such an apparatus with good signal-to-noise performance and at the same time we give its first example of application

by measuring the spin-exchange cross section for the scattering of H atoms with O_2 and NO at room temperature.

EXPERIMENTAL

The experimental setup is shown in Fig. 1(a) and consists of two high-vacuum chambers pumped by oil diffusion pumps and one ultrahigh-vacuum chamber pumped by a 500-l sec^{-1} turbomolecular pump. The atomic hydrogen beam is produced in the first chamber by means of a radiofrequency discharge (s) with a source gas pressure of about 1 Torr and a source diameter of 0.05 cm. The beam can be chopped by means of a rotating blade device (CH) located in the second chamber. Spin selection also happens in this chamber by means of a hexapolar magnet (H_1) (0.31-cm diameter, maximum field of 9600 G which, with reference to Fig. 1(b), acts as a focusing lens for $|1\rangle$ and $|2\rangle$ and as a defocusing lens for states $|3\rangle$ and $|4\rangle$. When the atoms leave the hexapole they move adiabatically to a low-field region where a transition unit (AW) of the Abragam-Winter-type[26,27] is located. This unit consists in an 18-MHz radiofrequency field acting in a region of space where the magnetic field varies slowly around 12 G and produces two-photon dressed atom transitions[26,28] which result in a population inversion between states $|1\rangle$ and $|3\rangle$, thereby depolarizing the beam. The efficiency of this process can be checked by rearranging the experimental setup as indicated in Fig. 2(a) using a second hexapole to defocus state $|3\rangle$ and refocus state $|2\rangle$ on the detector D. The total beam intensity for unit transition probability is decreased by a factor of 2 at saturation. A saturation plot for the transition probability as a function of the radiofrequency field measured in arbitrary units is shown in Fig. 2(b). When the atoms leave the Abragam-Winter transition unit they pass into the third-vacuum chamber where they enter, through a 0.3-cm hole, a Teflon cavity (C) in which they are stored for a short time with respect to the chopping period. The cavities used have a cylindrical form with a height equal to the diameter and 1 or 2 cm. After less than 10^{-3} sec (i.e., about 100 collisions with the walls) some atoms are reemitted at right angles to the primary beam, and in the upwards direction, through another 0.3-cm hole located in the ceiling on top of the storage cavity. This vertical beam is analyzed by means of a second hexapolar (H_2) focusing magnet, identical to the first, and is finally detected by a liquid-He-cooled doped Si bolometer (D) which has an area of 0.3×0.3 cm^2, a responsivity of 5×10^4 V W^{-1} and a noise-equivalent power of 10^{-12} W $Hz^{-1/2}$ (when operated at a modulation frequency of 30 Hz).

The signal analysis can be developed assuming, in first approximation, the hexapoles to be perfect filters for states $|1\rangle$ and $|2\rangle$ and defining a beam polarization P given by

$$P = 2(\rho_1 + \rho_2 - \tfrac{1}{2}) , \qquad (1)$$

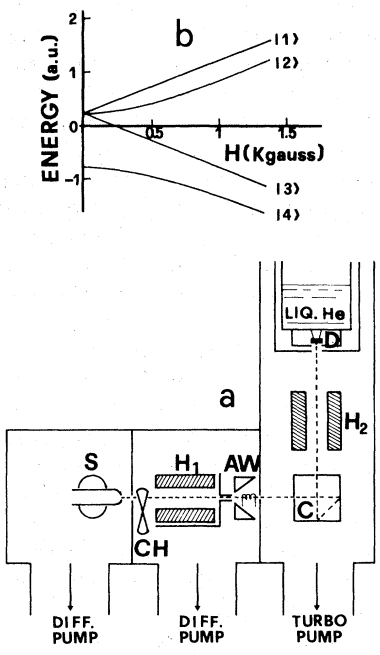

FIG. 1. (a) Experimental apparatus: S atomic-hydrogen source; CH chopper; H_1 and H_2 hexapolar magnets; AW Abragam-Winter transition unit; C Teflon cavity; D bolometric detector; (b) Hydrogen hyperfine energy levels as a function of magnetic field H.

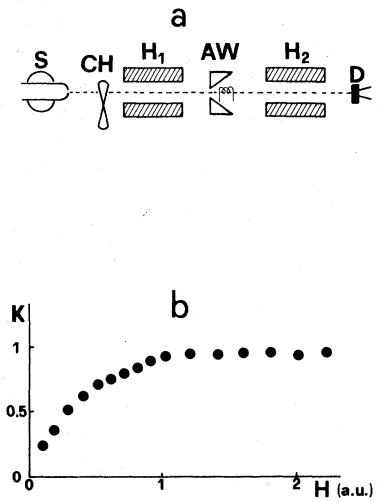

FIG. 2. (a) Experimental setup for testing the Abragam-Winter transition unit (the same symbols of Fig. 1(a) are used); (b) Transition efficiency K as a function of the radio-frequency field amplitude H.

where ρ_i indicates the population of hyperfine level $|i\rangle$. The normalization condition

$$\sum_1^4 {}_i\rho_i = 1$$

is implicitly assumed in Eq. (1). The polarization P is not the electron-spin polarization, unless the atom is placed in a high magnetic field where the z component of electron spin is a good quantum number.

The detector signal is a function of the polarization P_c of the beam emitted by the Teflon cavity and is given by

$$S = G\phi\left(\frac{1+P_c}{2}\right), \tag{2}$$

where ϕ is the atomic flux emitted by the cavity and G is a proportionality constant which takes into account geometric factors. If the beam polarization is P_0 after the first hexapole and P_1 before entering the Teflon cavity we have

$$P_1 = P_0(1-K), \tag{3}$$

where K is the $|1\rangle$ to $|3\rangle$ transition probability in the Abragam-Winter unit. Assuming that the atoms are not depolarized by collisions with the cavity Teflon walls[6,22,29] and neglecting the H-H exchange interaction (the H pressure inside the cavity is less than 10^{-6} Torr) the only way to change the beam polarization is to admit a gas with density n into the cavity. Indicating with σ the corresponding depolarization cross section we have

$$P_c = P_1\langle\exp(-nl\sigma)\rangle, \tag{4}$$

where l is the path of an atom inside the cell and the average is taken over all atoms entering the cavity. If the foreign gas has unpaired electrons the depolarization process is governed by the electron-spin exchange. We note that in general the quantity σ is not exactly the spin-exchange cross section because in our rough analysis we have not considered the detailed evolution of hyperfine level populations for hydrogen atoms and the interacting gas. An example of such a calculation is reported in Ref. 31 where the theory developed by Balling *et al.*[25] has been applied to the system H-D. We have not used such detailed data analysis because the actual difference between σ and the exact spin-exchange cross section has the same order of magnitude as our experimental standard error. To calculate the average in Eq. (4) we need the probability per unit time P for an atom inside the cavity to find the exit hole and be reemitted,

$$p = (2U/A)(\bar{v}/\lambda), \tag{5}$$

where U is the area of each hole, A the total cavity surface, $\bar{v}$ the average velocity of the atoms and

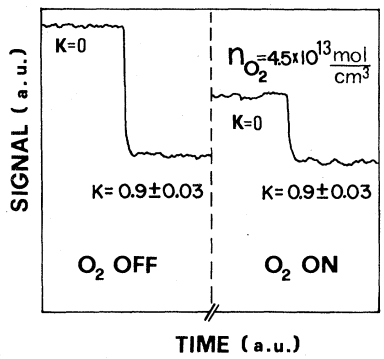

FIG. 3. Detector signals are shown for different values of transition efficiency K and gas density n. In this experiment a 1-cm cavity was used.

λ is the mean path of the atoms between two successive wall collisions and is equal to[12] $4VA^{-1}$ with V being the volume of the cavity. Carrying out the averaging, keeping into account that the time of storage is much shorter than the chopping period we obtain

$$P_c = P_0(1-K)\frac{1}{1+n\langle\sigma\rangle L}, \tag{6}$$

where $L = 2VU^{-1}$ is the average path of the atoms inside the cell and $\langle\sigma\rangle$ is the integral depolarization cross section averaged over the velocity distributions of the atoms at the temperature of the cell. Because L is much larger than the cell dimensions, the effect of the finite density of partner gas just outside the entrance and exit holes can be neglected. From (1) we see that the detector signal is related to P_c and therefore, taking data at different values of K and n (the latter measured with a mks baratron pressure gauge), one can derive $\langle\sigma\rangle$. An example of experimental data is shown in Fig. 3.

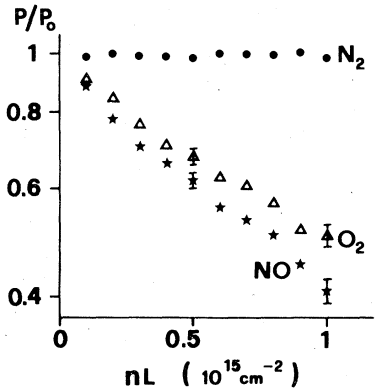

FIG. 4. Experimental results for N_2 (circles); O_2 (triangles) and NO (stars). The behavior of the hydrogen relative polarization P/P_0 as a function of the attenuation factor nL is shown.

TABLE I. Average spin-depolarization cross section at room temperature (units 10^{-16} cm^2). Results of Fleming *et al.* (Ref. 32) have been recently obtained for the collision of muonium with O_2 and NO.

System	This work	Berg [a]	Gordon *et al.* [b]	Fleming *et al.* [c]
H-O_2	10 ± 1	21 ± 2	9 ±1	(8 ± 1.2)
H-NO	13 ± 1	25 ± 2	10.6 ± 0.9	(11 ± 1.2)

[a] Reference 6.
[b] Reference 9.
[c] Reference 32.

RESULTS AND DISCUSSION

Experimental results with N_2, O_2, and NO as depolarizing gas are shown in Fig. 4. It appears that the depolarization cross section for H-N_2 collisions is negligible as one should expect because of the closed-shell nature of the N_2 molecule. Numerical values of the spin-flip cross section for H-O_2 and H-NO encounters are reported in Table I where they are compared with previous values obtained by Berg[6] and Gordon *et al.*[9] using pulsed-maser techniques. The last column in Table I shows results for muonium collision with O_2 and NO recently obtained by Fleming *et al.*[32] Before drawing any conclusions from Table I it is useful to examine the consequences of the existence, in the pulsed-maser technique, of two relaxation times (T_1 and T_2)[6] and their relationship to the spin-depolarization cross section as measured by both groups. In both experiments it has been verified that for both H-O_2 and H-NO systems

$$T_{2g}\,T_{1g}^{-1} = \tfrac{4}{3}\,, \tag{7}$$

where T_{2g} and T_{1g} are the contribution to the relaxation times due to the addition of the foreign gas. For a partner gas made of spin $\frac{1}{2}$ and spin 1 particles we have (from Ref. 6)

$$T_{1g}^{-1} = n\langle\sigma v\rangle$$

and (8)

$$T_{1g}^{-1} = 1.18\,n\langle\sigma v\rangle\,,$$

respectively. The data presented in Table I all derive from T_{2g} measurements, but while in Ref. 6 σ is derived using Eqs. (7) and (8), in Ref. 9 the spin-flip cross section is operatively defined as

$$\sigma = (n\bar{v}\,T_{2g})^{-1}\,. \tag{9}$$

A reanalysis of the data of Ref. 9 using Eq. (7) and (8) yields for the two spin-flip cross sections at room temperature the values of 10 ± 1 Å^2 and 14 ± 1 Å for O_2 and NO, respectively.

The difference between the cross sections measured by Berg and Gordon *et al.* remains large while the agreement between our data and those of Ref. 9 can be considered quite satisfactory. The most likely origin of the above-mentioned discrepancy is a possible error by Berg in the measurement of the absolute value of the maser storage-bulb pressure. In conclusion we have shown the viability of the stored-beam method for atomic-hydrogen-beam spectroscopy and we have measured the spin-flip integral cross sections for H-O_2 and H-NO collisions reducing the error with which these quantities are known. A comparison of our data and Ref. 9 with Ref. 32 enable us to exclude the existence of a large isotope effect in the spin-exchange cross sections of hydrogen and muonium with paramagnetic gases.

The basic technology described in the present paper can be refined and applied in several different directions. First, there are no reasons why the method should not work with free radicals other than atomic hydrogen. Second, using a geometry as indicated in Fig. 5 one can construct a very compact frequency standard of the "passive maser" type. We have tested in practice the feasibility of detecting the beam reemitted in the backward direction using an annular bolometer located very near the primary beam source. The signal-to-noise level achieved in this way was better than 100 to 1 and therefore quite satisfactory.[30] Third, instead of a gas one can introduce a different solid surface into the Teflon cavity thereby studying the exchange interaction between the H atoms and the new surface. Work in progress in our laboratory

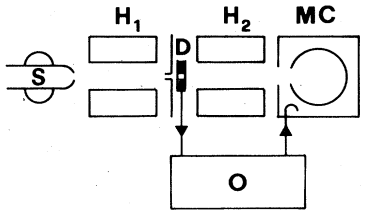

FIG. 5. A possible configuration for a passive hydrogen maser. The signal on the annular detector D depends on the polarization of hydrogen atoms coming out of the microwave cavity MC. This signal can be used to feed back the oscillator O. (H_1 and H_2 are hexapolar magnets.)

is aimed to the clarification of difficulties and possibilities in the third direction.

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