AN INVESTIGATION OF THE EFFICIENCIES OF VARIOUS BUFFER GASES IN Na-Xe SPIN EXCHANGE

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Measurements of the efficiencies of He, Ne and Xe as buffer gases in Na-Xe spin exchange are presented, and earlier values determined for N_2 revised slightly. The spin-rotation coupling of Na-Xe van der Waals molecules is also measured and found to be consistent with recent theoretical work.

Bouchiat et al. [1] were the first to show that the dominant mechanism causing spin relaxation of alkali-metal atoms in the presence of heavy noble-gas atoms such as Ar, Kr and Xe was the formation of short lived ($\approx 10^{-7}$ s) van der Waals molecules. Later work by Volk et al. [2] and by Bhaskar et al. [3] showed that although the majority of alkali-atom spin was transferred to the rotation of the molecule, some could be transferred into the spin of the noble-gas nucleus. This was of interest for the purposes of creating large numbers of spin-polarized nuclei for use in other fields of physics.

These van der Waals molecules form in three-body collisions where the third body can be either a noble-gas atom or some other buffer-gas atom. The molecule endures until another collision overcomes the weak binding. The molecular lifetime is thus inversely proportional to the third-body pressure. While the molecule persists, the electron spin S of the alkali-metal atom is coupled to the nuclear spin K of the noble gas and to the rotation N of the molecule. The spin-transfer rates due to these interactions are described by the theory developed by Happer et al. [4].

The largest spin-interaction terms are

$$H = AI \cdot S + \gamma N \cdot S + \alpha K \cdot S + g_s \mu_B S \cdot H, \qquad (1)$$

where the first term is the alkali hyperfine interaction and the last term is the Zeeman interaction of the electron spin in the presence of an applied magnetic field. The term $\alpha K \cdot S$ can result in spin transfer

from the alkali-metal atom to the noble-gas nucleus. The term $\gamma N \cdot S$ (which dominates the alkali-metal spin relaxation) describes spin transfer between the alkali-metal atom and the rotational angular momentum of the molecule.

Interest here focuses on measuring the efficiencies of various buffer gases as third bodies, and on refining a previous experimental determination of the quantity γN for the sodium-xenon system [5]. Herman [6] worked out a theory for the determination of the coefficient γ that made γ proportional to the fine-structure splitting of the alkali-metal atom. However, subsequent experimental work [7] failed to detect the strong dependence on alkali atomic number that this theory predicts. Wu et al. [8] have derived an expression for γ more in keeping with experimental determinations. The value of γN inferred for the Na-Xe system in this experiment compares favorably with the prediction of this latter theory.

The quantity γN can be measured by either of two methods. Here, γN is determined (as originally done by Bouchiat [1]) from observation of the fast spin relaxation of the alkali-metal atom. It is also possible to determine γN by observing the slow relaxation of the noble-gas nuclear spin. In either case, what is actually measured is the value of γN averaged over all available rotational and vibrational states of the alkali-metal-noble-gas van der Waals molecule.

The experimental procedure is essentially identical to that described by MacKintosh et al. [5]. Cylin-

drical pyrex cells containing some Na metal, 3 Torr of Xe with natural isotopic content and various pressures of the different buffer gases were used. The cells were heated to around 190°C where the sodium number density is 1.6×10^{12} cm^{-3}. The variation of sodium density with temperature is fairly slow in this region and temperatures were maintained within one or two degrees Celsius. Hence we expect the observed relaxation of S to be unaffected by fluctuations in Na density, especially as these fluctuations have a very small influence on the observed spin-relaxation times via short duration Na–Na spin-exchange collisions [9].

The apparatus was the same as shown in fig. 1 of ref. [5]. A tunable dye laser using rhodamine 6G was employed both to optically pump and to probe the sodium vapor. Beam splitters separated and attenuated the probe beam, which was further attenuated by neutral density filters. The chopping cycle was so arranged that the pump and probe illumination alternated with a slight overlap at the beginning of the probe phase. The circular dichroism technique of monitoring absorption of circularly polarized resonant light could not produce a viable signal with this apparatus as the relatively large bandwidth of the dye laser produced too many off resonant photons. Instead, we observed the relaxation of S with crossed linear polarizers.

This was done by detuning the dye laser slightly away from resonance so that the linearly polarized probe beam becomes rotated and slightly elliptically polarized by an amount proportional to $\langle S_z \rangle$ as the two components σ_+ and σ_- propagate through the absorbing vapor with different phase velocities. The signal for this light passing through an exactly crossed linear polarizer is proportional to $\langle S_z \rangle^2$, which is easy to observe as the polarizer blocks much of the unwanted background. However, Faraday rotations also occur which in effect change the "exactly crossed" point of the polarizer as the applied magnetic field changes. To eliminate the sensitivity to this in our fitted rates, we rotated the polarizer away from the crossed configuration by a small angle δ. This introduces a small term linear in $\langle S_z \rangle$ via $\sin^2(\theta + \delta) \approx \theta^2 + 2\theta\delta + \delta^2$. Rotating the polarizer to the other side by an equal angle gives a signal proportional to $\sin^2(\theta - \delta)$ so that the difference of these two eliminates the quadratic term and leaves only a
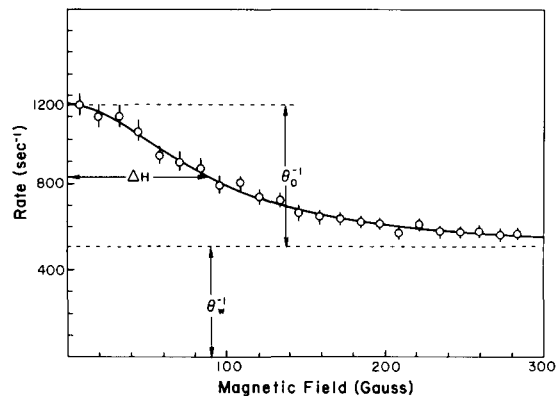

Fig. 1. Typical sodium spin-relaxation rate versus applied magnetic field.

term linearly proportional to $\langle S_z \rangle$ which we found to be relatively insensitive to polarizer setting.

Each signal was detected with a photomultiplier tube and averaged over 1024 sweeps with a Nicolet 2100 analyzer. The difference of the opposing polarizer settings (a total of 2048 sweeps) was recorded by an IBM PC/XT. This was subsequently used to fit a single exponential to the data to determine the decay rate.

As the applied magnetic field is increased, N becomes decoupled from S. For sufficiently large external fields the Zeeman interaction dominates the spin–rotation interaction and S remains locked around H for the lifetime of the van der Waals molecule. This results in a slowing down of the Na spin relaxation induced by Xe. A plot of relaxation rate versus magnetic field closely resembles a lorentzian curve with full width at half maximum ΔH. We fitted these slowing down curves to a function of the form

$$\Theta^{-1} = \Theta_w^{-1} + \Theta_0^{-1} / [1 + (H/\Delta H)^2] \qquad (2)$$

(see fig. 1). Here Θ^{-1} is the observed decay, Θ_w^{-1} is the baseline rate caused by binary collisions and wall diffusion, Θ_0^{-1} is the zero-field rate attributable to Na–Xe van der Waals molecules, ΔH is the magnetic halfwidth and H is the applied magnetic field. The magnetic halfwidth ΔH increases with the buffer gas pressure P. ΔH contains information about the molecular lifetime τ and about the spin–rotation coupling.

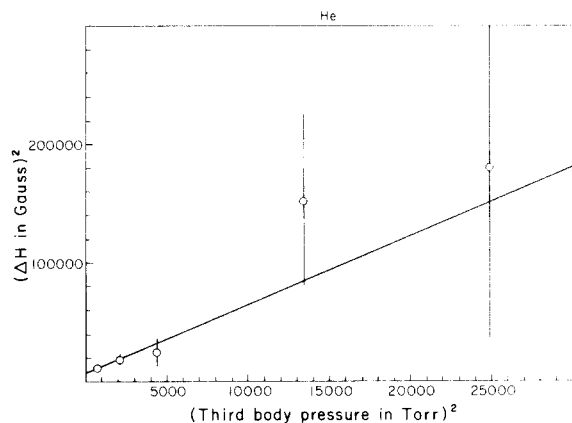According to the theory of Happer et al. [4], ΔH

Fig. 2. Magnetic halfwidth squared versus third-body pressure squared for He buffer gas with fit parameters $\Delta H_0 = 81 \pm 19$ G and $\beta = 2.4 \pm 0.6$ G/Torr.
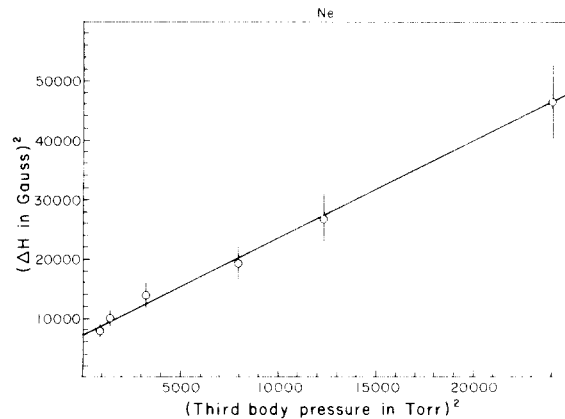

Fig. 3. Magnetic halfwidth squared versus third-body pressure squared for Ne buffer gas with fit parameters $\Delta H_0 = 84 \pm 10$ G and $\beta = 1.3 \pm 0.1$ G/Torr.

is linearly proportional to P at high pressure, i.e.

$$\Delta H = (2I+1)\hbar/\mu_B g_s \tau = \beta P, \tag{3}$$

where β is given by

$$\beta = (2I+1)\hbar/\mu_B g_s \tau P. \tag{4}$$

The efficiency of the third body at breaking up the van der Waals molecules is proportional to β and different buffer gases have different β. For small P, ΔH approaches a nonzero constant ΔH_0 which is characteristic of the molecule and hence independent of buffer gas. The simple formula

$$(\Delta H)^2 = (\Delta H_0)^2 + \beta^2 P^2 \tag{5}$$

was used to interpolate between low and high third-body pressures.

Figs. 2–5 show our data plotted in this form. Table 1 summarizes the results of the measurements of ΔH_0 and β for the various buffer gases. Note that heavier gases are progressively more efficient at causing molecular breakup (larger β) with the exception of helium. The final result for He is less certain because it was necessary to add N_2 in the He cells to facilitate optical pumping. We also attempted to measure β for H_2 and D_2 to obtain more information in this mas range, but these molecules form sodium hydrides so that the partial pressure of H_2 in the cells changes with time, making it difficult to know what is being measured.

Since Xe can act as a third body as well as any other

gas, its effects must be accounted for. Indeed, it is substantially more efficient than the other gases studied, so that the presence of 3 Torr of Xe in every cell makes a difference to the fitting for ΔH_0. In the work of MacKintosh et al. [5] N_2 was the buffer gas, and a value for the relative effectiveness of Xe to N_2 had to be guessed. This value was taken to be $\beta_{Xe}/\beta_{N_2} \approx 3$, based on work on the Rb–Xe system [10]. This contributed to the uncertainty of that measurement.

Considerable effort was subsequently placed on directly determining β_{Xe}. This was difficult to do for two reasons. At low pressure, pure Xe cells without
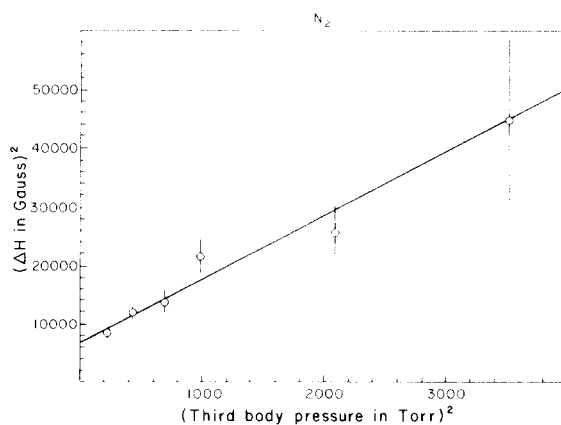

Fig. 4. Magnetic halfwidth squared versus third-body pressure squared for N_2 buffer gas with fit parameters $\Delta H_0 = 82 \pm 8$ G and $\beta = 3.3 \pm 0.3$ G/Torr.
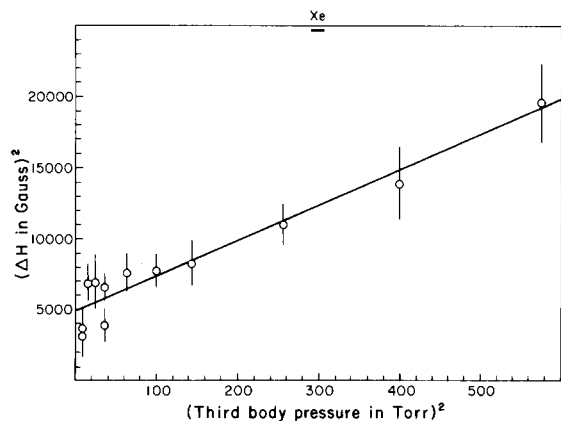
Fig. 5. Magnetic halfwidth squared versus third-body pressure squared for Xe self-buffer gas with fit parameters $\Delta H_0 = 70 \pm 8$ G and $\beta = 5.0 \pm 0.4$ G/Torr.

N_2 to enhance optical pumping had low polarization efficiencies resulting in poor signal and substantial scatter of the data from these low pressure cells. At high pressure, the spin-relaxation times were shorter than the response time of our electronics. We tried one cell with 50 Torr of Xe, but found it produced poor and highly uncertain data. The highest Xe pressure data point in fig. 5 is a cell containing 24 Torr of Xe.

The number finally found for β_{Xe} (see table 1) is somewhat smaller than originally assumed, i.e. $\beta_{Xe}/\beta_{N_2} = 1.5 \pm 0.3$. This has only a slight effect on the fitting but lessens the uncertainty. ΔH_0 is a number characteristic of the van der Waals molecule and is independent of buffer-gas type. In comparing this value to theory, the weighted average of ΔH_0 for all buffer gases tested is used:

$$(\Delta H_0)_{ave} = 78 \pm 5 \text{ G} .$$

ΔH_0 is related to γN by [4]

Table 1
A summary of results, showing ΔH_0 and breakup efficiency β as determined for each buffer gas.

Buffer gas	ΔH_0 (G)	β (G/Torr)
He	81 ± 19	2.4 ± 0.6
Ne	84 ± 10	1.3 ± 0.1
N_2	82 ± 8	3.3 ± 0.3
Xe	70 ± 8	5.0 ± 0.4

$$\Delta H_0 = \gamma N / \mu_B g_s h_0 , \qquad (6)$$

where h_0 is the halfwidth of the alkali spin-transfer coefficient, which depends only weakly on the Breit–Rabi parameter $x = \gamma N / \alpha$. A reasonable estimate [5] is $h_0 = 1.35 \pm 0.05$. With this, we measure

$$\gamma N / h = 163 \pm 11 \text{ MHz} .$$

By the method of Bouchiat et al. [1] we get $N_{rms} = 42$. So, we find

$$\gamma_{exp} / h = 3.8 \pm 0.3 \text{ MHz} ,$$

where $\gamma N \pm \gamma_{exp} N_{rms}$.

The value of γ_{exp} is somewhat larger than the value γ_{th} predicted by the theory of ref. [8],

$$\gamma_{th} \approx 2 \text{ MHz} ,$$

where γ_{th} is an appropriate average over available molecular states. This average is approximated by taking the value of the theoretical expression for $\gamma(R)$ at equilibrium internuclear separation R_0 and multiplying by a scaling factor of 0.522 [8]. The values used for R_0 are 5.03 [11], 5.06 [12] and 4.91 Å [13]. However, the theory predicts an exponential dependence of $\gamma(R)$ on the internuclear separation. This makes the predicted value extremely sensitive to the precise value of the equilibrium separation R_0 – a value just 5% lower (within the uncertainty of the measurements) doubles γ_{th}. Simply taking $\gamma(R_0 = 5.03 \text{ Å})$ gives 4 MHz. In contrast, the theory of Herman [6] predicts that γ should be proportional to the fine-structure splitting of the alkali. Scaling from the Rb–Xe system [7], this would imply that

$$\gamma(\text{Na–Xe}) \approx [\Delta\nu_{fs}(\text{Na})/\Delta\nu_{fs}(\text{Rb})]\gamma(\text{Rb–Xe})$$

$$= 0.11 \text{ MHz} .$$

This is so far from the experimental value that it is clear there is no fine-structure dependence as in Herman's theory. Indeed, $\gamma(\text{Na–Xe})$ is larger than $\gamma(\text{Rb–Xe}) = 1.6$ MHz. These things considered, the experimental results seem consistent with the theory of Wu et al. [8].

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