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Hyperfine Temperature Shift of Deuterium in Neon and Argon

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The temperature dependence of the hyperfine frequency of deuterium in neon and argon buffer gases has been measured over the range −100 to +300 °C. From a linear least-squares fit to the data, the shifts at constant buffer-gas density were found to be $(2.9 \pm 0.4) \times 10^{-3}$ Hz/°K Torr in neon and $(3.1 \pm 0.5) \times 10^{-3}$ Hz/°K Torr in argon.

In a previous paper[1] we presented the results of an optical-pumping experiment in which we measure the hyperfine temperature shift (HTS) of deuterium in the presence of a helium buffer gas over the range −135 to +400 °C. The results were in qualitative agreement with the theoretical predictions of Rao and Das[2] and are in better agreement with a more recent calculation by Kunik and Kaldor.[3] Rao, Ikenberry, and Das[4] have now calculated the HTS of hydrogen in all of the rare gases over the range 50–900 °K. Their calculations stimulated an extension of our previous work on the HTS of deuterium to include the rare gases Ne and Ar. Within the precision of present optical-pumping experiments, the fractional pressure shift for any one buffer gas is the same for all the hydrogen isotopes.[5] Deuterium was chosen because of the ease with which the rf field (hyperfine frequency) could be generated.

The deuterium hyperfine frequency was measured at constant density as a function of temperature in neon and argon. The pressure of Ne and Ar at 300 °K was 98.7 and 54.0 Torr, respectively. The estimated error in the pressure is ±1 Torr. The known pressure shift[6] and zero-pressure hyperfine frequency[7] were used as consistency checks on the pressure. The observed temperature dependences are shown in Fig. 1.

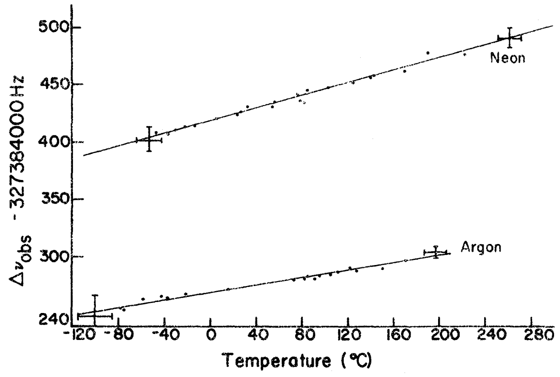

FIG. 1. Hyperfine frequency of deuterium as a function of temperature. The neon and argon pressures are 98.7 and 54.0 Torr, respectively, at a filling temperature of 300 °K.

The experimental technique has been previously described[1,8] and is essentially the same. As in the case of helium,[1] the signal amplitudes decreased with increasing temperature. No deuterium signals could be measured at temperatures over 300 and 250 °C for neon and argon buffer gases, respectively. There was strong evidence that below room temperature there were large temperature gradients in the sample. To obtain an estimate of the magnitude of these gradients, an Ar sample was made with three thermocouples inside and two cemented to the outside. The inside temperature could vary from the outside temperature by as much as 20 °C. This is because while the sample is being cooled a sidearm reservoir of Rb is being heated to drive Rb into the sample, and an rf discharge is in another sidearm to dissociate

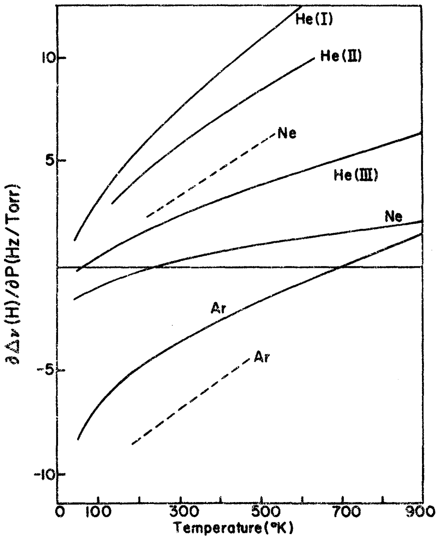

FIG. 2. Plot of $\partial\Delta\nu/\partial P$ for hydrogen as a function of temperature. The curves denoted as He(I) and He(III) are the theoretical calculations of Kunik and Kaldor (Ref. 3) and Rao *et al.* (Ref. 4), respectively. He(II) is the experimental results of Wright *et al.* (Ref. 1). The solid curves for Ne and Ar are the theoretical calculations of Rao *et al.* (Ref. 4), and the dashed curves represent the results of the present experiment.

TABLE I. Temperature shifts of the deuterium hyperfine frequency. The values listed are a linear least-squares fit to the data. The value for He is from Ref. 1 averaged over the range 300–600 °K.

Buffer gas	$\frac{\partial^2\langle\Delta\nu\rangle}{\partial P\partial T}\left(\frac{10^{-3}\text{ Hz}}{°\text{K Torr}}\right)$
He	2.8 ± 0.4
Ne	2.9 ± 0.4
Ar	3.1 ± 0.5

TABLE II. Temperature shifts of the hydrogen hyperfine frequency.

Buffer gas	$\frac{\partial^2\langle\Delta\nu\rangle}{\partial P\partial T}\left(\frac{\text{Hz}}{°\text{K Torr}}\right)$ Experiment	Theory[a]
He	$1.2\pm0.2\times10^{-2}$ [b]	0.7×10^{-2} [c]
Ne	$1.3\pm0.2\times10^{-2}$	1.5×10^{-2} [d]
Ar	$1.3\pm0.2\times10^{-2}$	0.4×10^{-2} [c]
	$1.2\pm0.3\times10^{-2}$ [e]	1.2×10^{-2} [c]

[a] These values are an average over the range 300–600 °K.

[b] From Ref. 1. This value is from a linear least-squares fit to the data over the range 300–600 °K.

[c] From Ref. 4.

[d] From Ref. 3.

[e] From Ref. 5.

the D_2 molecules. (The D atoms are then polarized via spin-exchange collisions with the optically pumped Rb). This situation produces not only temperature gradients but also density gradients in the sample. For lack of a better scheme, the temperature of the sample cell was taken as the average of two thermocouples cemented to the outside of the cell at hot and cold spots. The temperature and density gradients at the low temperatures and the weak signals at the high temperatures account for the rather large errors at these extremes which are shown in Fig. 1. The solid curves in Fig. 1 are a linear least-squares fit to the data.

From these measurements and data analysis we conclude that the temperature shift per Torr of the deuterium hyperfine frequency at constant neon and argon buffer gas density (defined as $\partial^2\langle\Delta\nu\rangle/\partial P\partial T$) is well approximated by a linear curve over the temperature range -100 to $+300$ °C. The results of the least-squares fit to the data are presented in Table I. Deduced values for hydrogen and the theoretical predictions of Rao *et al.*,[4] and Kunik and Kaldor[3] (averaged over the range 300–600 °K) are presented in Table II. The only other experimental datum is a measurement by Brown and Pipkin[5] for hydrogen in argon over the temperature range 30–45 °C and is also presented in Table II.

In Fig. 2 we compare our data to the theory of Rao *et al.*[4] and Kunik and Kaldor[3] for hydrogen. To make this reduction of the data, we substracted the zero-pressure hyperfine frequency of 327 284 352 Hz[7] from the experimentally determined frequency at each temperature, divided this shift by the buffer-gas pressure in the sample, and then multiplied by the ratio of the hydrogen to deuterium hyperfine frequencies. Figure 2 is perhaps deceptive in that the theoretical curves are based on calculated values for the pressure shifts themselves. This accounts for most of the vertical displacement of the theoretical curves. Comparison with Table II indicates that the theory is better equipped to predict the temperature dependence than the pressure shift. The fact that the slopes are positive is consistent with the theory in that as the temperature increases the effect of the short-range force (positive frequency shift) increases. It is interesting to note that, within experimental error, the temperature shifts in Table I are the same for all buffer gases. It was originally hoped that for both Ne and Ar the shift (Fig. 2) would go to zero at some temperature which would mean that the long-range van der Waals and short-range Pauli overlap forces were equal. Although this objective was not achieved, it is hoped that valuable information of this sort can be obtained from a quasiextrapolation to the zero-frequency-shift temperature.

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