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Hyperfine Pressure Shift and Van der Waals Interaction. III. Temperature Dependence[*]

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A theoretical study of the temperature dependence of the pressure shifts of the hyperfine constants (HPS) for hydrogen-helium and nitrogen-helium systems over the temperature range 30 to 1000° K indicates that the temperature variations are well above the limits of detectability. An interesting peak is observed for the HPS in the hydrogen-helium system at 325° K and it is suggested that the occurrence of such peaks provides an experimental handle on the relative signs of the long-range and short-range contributions to HPS.

Accurate data on pressure shifts of hyperfine constants in rare-gas atmosphere are presently available from optical-pumping experiments[1] for a number of atoms. The interpretation of the origin of these hyperfine pressure shifts (HPS) involves a knowledge of both the interaction potential between the atoms as well as the wave functions of the perturbed atoms, and thus provides a comprehensive test of theories for interacting atoms.

There are two mechanisms[2] involved in the origin of the HPS, a long-range mechanism involving the mutual polarization of the atoms and a short-range mechanism associated with the overlap of their electronic orbitals. First-principle quantitative calculations on both these mechanisms have recently been performed for the H-He and the N-He systems.[3] In the H-He system the long-range HPS is found to be negative because the spin density at the nucleus decreases when there is an admixture of p character to the $1s$ orbital by the van der Waals interaction. The short-range HPS, on the other hand, is positive since the Pauli repulsion between the electronic orbitals of the atoms at short range pushes the electrons closer to the nuclei. While both these opposing effects are of the same order of magnitude as experiment, the short-range effect predominates, leading to a positive HPS. In the N-He system, the long-range and the short-range effects are both positive. Here the long-range effect, involving a polarization of the $2p$ orbitals by the van der Waals interaction, leads to an admixture of s character and positive spin density. The Pauli repulsion at short-range increases the density of the valence $2p$ orbitals in the neighborhood of the nucleus and at first sight would not be expected to influence the HPS, since the density from p orbitals vanishes at the nucleus. However, one can get a finite HPS from the alteration of the exchange interaction[4] between the valence $2p$ and core $2s$ (also $1s$) orbitals through their overlaps with the helium electrons. Again both the calculated long-range and short-range effects are found to be of the same order as experiment, their sum being about a factor of 2 larger.

Recently, experimental techniques[5] have been developed for carrying out optical-pumping experiments over an extensive range of temperatures. This advance in technology permits an additional test of the theory by making possible the measurement of the temperature dependence of HPS. The purpose of the present note is twofold. First we want to show that the temperature variations of the HPS in the two systems, as expected theoretically, are large enough to be experimentally detectable. Second, and more important, is the fact that the temperature variation is predicted to be characteristically different in nature when long-range and short-range contributions are of the same sign than when they oppose each other. In particular, a peak is predicted in the HPS for the H-He system around 50°C while the HPS in the N-He system shows a monotonic variation with temperature. The temperature variation of the HPS thus provides an experimental handle for determining the relative signs of the long-range and short-range effects. This feature is expected to be very useful in connection with the HPS of those atoms[6] where, like in the case of nitrogen, the sign of the effect cannot be predicted without actual calculations of the polarization effect involving the core and valence electrons.

The pressure shift at a particular temperature T can be calculated from the relation

$$a_p = \frac{\partial}{\partial p} (\langle \Delta a(R) \rangle)$$

$$= \frac{4\pi a_0^3}{kT} \frac{10^6}{760} \int \Delta a(R) e^{-V(R)/kT} R^2 dR, \qquad (1)$$

where $$\Delta a(R) = a(R) - a(\infty) \ . \tag{2}$$

In Eq. (2), $a(R)$ is the hyperfine constant for the magnetic atom when it is at a distance R from the buffer gas atom and $a(\infty)$ is the hyperfine constant for infinite separation, that is, for the isolated atom. The procedures for the evaluation of $a(R)$ for both the short-range and long-range regions have been described in earlier papers[3] and will not be repeated here.

The integration in Eq. (1) was carried out for a number of different temperatures over a range T = 30 to T = 1000°K for both H-He and N-He systems. The temperature 30°K should be accessible for measurements in the H-He system, because both hydrogen and helium are in gaseous phase at this temperature. Under standard pressure, nitrogen liquifies at 77°K. But under the experimental conditions in the optical-pumping experiments, the partial pressure of nitrogen is low and the consequent depression of boiling point might make the region near 30°K accessible experimentally. The temperature range of 300–1000°K has already been reported to be within the reach of newly developed temperature-variation technique.[5] In carrying out the integrations over R in Eq. (1), proper care was taken as in the earlier papers[3] to avoid the regions where the calculated long-range and the short-range results for $\Delta a(R)$ were not valid.

Our results for the temperature dependence of a_p are plotted in Figs. 1 and 2, respectively, for the H-He and N-He systems. The short-range and long-range contributions are plotted separately, along with total results, to provide a better understanding of the origin of the temperature variation.

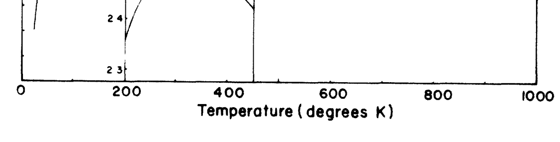

FIG. 1. Plot of the variation of long-range $[(a_p)_{\rm LR}]$, short-range $[(a_p)_{\rm SR}]$, and total (a_p) HPS with temperature for H-He system. The insert shows the region in the neighborhood of 50°C suitably amplified to show the peak in a_p.

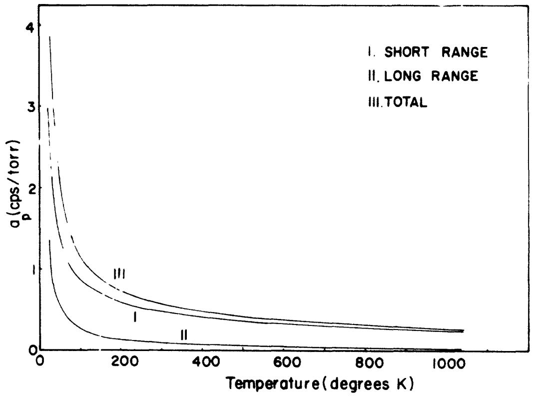

FIG. 2. Plot of the variation of long-range $[(a_p)_{\rm LR}]$, short-range $[(a_p)_{\rm SR}]$, and total (a_p) HPS with temperature for N-He system.

First, we would like to discuss the observability of the magnitudes of the changes we have obtained for the hyperfine constant due to change in temperature. Considering the N-He system first, the change in a_p over the range 300–1000°K is found from Fig. 2 to be 0.310 cps/Torr, while for the range 30–300°K the corresponding value is 2.964 cps/Torr. In the optical-pumping experiments on this system at 300°K, measurements of a_p were carried out at pressures up to 65 Torr. Assuming that this pressure can be used at other temperatures, the expected changes in the hyperfine constant over the ranges 30–300°K and 300–1000°K are 192.66 and 20.15 cps, respectively. For this system, the theoretical value of a_p at 300°K is found to be about a factor of 2 larger than the experiment. Even after scaling our predicted variations in hyperfine constants by this factor, the expected changes in frequencies are still sizable. This observation is in contradiction to conclusions arrived at by Adrian,[7] who expected the frequency variation with temperature to be negligible. However, his conclusions are based upon an approximate treatment of long-range contribution and neglecting of short-range contribution and the use of the long-range form in a region where it is not valid.

For the H-He system, again assuming a pressure of 65 Torr, the changes in the hyperfine constants for the temperature ranges 30–300° and 300–1000°K are predicted to be 368.74 and 24.57 cps, respectively. The changes in frequencies associated with the changes in the hyperfine constants should thus be well above the limits of detectability.

The other interesting feature of our results is the apparent peak in a_p for the H-He system at 325°K, in contrast with the monotonic variation predicted for the N-He system. The occurrence of this peak and the nature of the variations in

$(a_p)_{\rm LR}$ and $(a_p)_{\rm SR}$ with temperature can be understood qualitatively by examining the integrand in Eq. (1). The values of $(a_p)_{\rm LR}$ in Figs. 1 and 2 are found to be decreasing in magnitude for both H-He and N-He systems. This behavior occurs because the long-range HPS derives its contribution from large R where $V(R)$ is attractive and thus has a negative sign. Consequently, the term $\exp[-V(R)/kT]$ in the integrand in Eq. (1) decreases with increase of temperature. The short-range HPS, on the other hand, derives its contribution partially from the attractive and also from the repulsive regions of $V(R)$. The contribution to a_p from the attractive region of R will again be expected to show a decrease in magnitude with increase in temperature. The contribution to $(a_p)_{\rm SR}$ from the repulsive region of $V(R)$, on the other hand, is expected to show an increase due to the negative exponent in $\exp[-V(R)/kT]$. We have found, however, that for the temperature ranges considered, the relative contribution to HPS from the repulsive region was quite small and could be ignored except at the lowest temperatures chosen. Thus a trend of decreasing magnitude for $(a_p)_{\rm SR}$ with increasing temperature is predicted as in Figs. 1 and 2. If the short-range and long-range contributions have the same sign (as in N-He system), then the decreases in the magnitudes of $(a_p)_{\rm SR}$ and $(a_p)_{\rm LR}$ with increasing temperature assist each other and an over-all decrease in a_p with increasing temperature is expected. If on the other hand $(a_p)_{\rm SR}$ is positive and $(a_p)_{\rm LR}$ is negative, as in the H-He system, a decrease in the slope of the total a_p curve as the temperature is decreased from the high-temperature side, and the eventual turning over to a region of negative a_p after passing through a peak, becomes understandable.

It is hoped that the measurements of these predicted frequency changes with temperature will be possible in the near future in both the systems considered here, as well as in additional systems. Such studies can establish whether the relative signs of the long-range and short-range hyperfine effects can be distinguished purely by experiment, as expected from our analysis. In addition, a quantitative comparison between the results of experiment and current theoretical methods should provide stimulus for further refinement of the theory of interacting atoms.

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[6] Examples are other fifth-group atoms, such as phosphorous and arsenic, oxygen (O^{17}) and iron-group atoms.

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