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Alkali-Metal Hyperfine Shift in the Van der Waals Molecule KAr

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The hyperfine interaction of K in KAr has been measured in several vibrational states of KAr. The results yield a value for the hyperfine shift α as a function of internuclear separation R given by $\alpha = -115(R-R_0)$ kHz, where R is in bohrs and $R_0 = 12.0$ bohr, valid over the range 10.25 bohr $< R < 12.0$ bohr.

The problem of how the hyperfine interaction in an alkali atom is modified by the proximity of a rare-gas atom has been the subject of lively theoretical interest ever since the experimental discovery that the inert gas used as a buffer in optical-pumping experiments causes a shift in the alkali hyperfine separation.[1] This so-called "pressure shift" arises from two competing interactions; long-range polarization effects that reduce the density of the alkali valence electron at the nucleus, decreasing the hyperfine interaction, and short-range overlap effects that tend to concentrate the valence electron near the alkali nucleus, increasing the hyperfine interaction. With light rare gases, such as He and Ne, the short-range forces dominate and produce a positive pressure shift; for the heavier rare gases, such as Kr or Xe, the pressure shifts are generally negative. This suggests that the competition between the long- and short-range effects may cause a rapid change in the hyperfine coupling constant with internuclear separation. Unfortunately, a precise comparison between experiment and theoretical predictions of the dependence of the hyperfine shift on internuclear separation has not, so far, been possible because optical-pumping measurements necessarily involve a broad thermal average over angular momenta and energy that obscures many of the details of the interaction.

We report here the observation of the hyperfine shift in the bound alkali-rare-gas molecule KAr by molecular-beam magnetic resonance.[2] KAr is a particularly interesting system to study because the polarization and overlap effects are approximately equal, yielding an anomalously small pressure shift.[3] The experimental results (see Fig. 1) have a well-resolved structure which can be identified with the vibrational states of the molecule. The observed strong variation of the hyperfine shift with vibrational level is an indication of a rapid variation of hyperfine interaction with internuclear separation, and offers the possibility of determining the hyperfine interaction strength as a function of the internuclear separation R.

The principle magnetic interactions in an alkali-rare-gas Van der Waals molecule immersed in an external magnetic field H_0 are described by the Hamiltonian

$$\mathcal{H} = h[a + \alpha(R)]\,\vec{I}\cdot\vec{S} + g_s \mu_B \vec{S}\cdot\vec{H}_0 + h\gamma(R)\vec{S}\cdot\vec{N}, \qquad (1)$$

where $\hbar I$, $\hbar S$, and $\hbar N$ are, respectively, the angular momenta of the alkali nuclear spin, the alkali valence electron spin, and the molecular rotation. $g_s \mu_B \vec{S}$ is the magnetic dipole moment of the valence electron; a is the hyperfine coupling constant of the free atom; $\alpha(R)$ is the shift in the

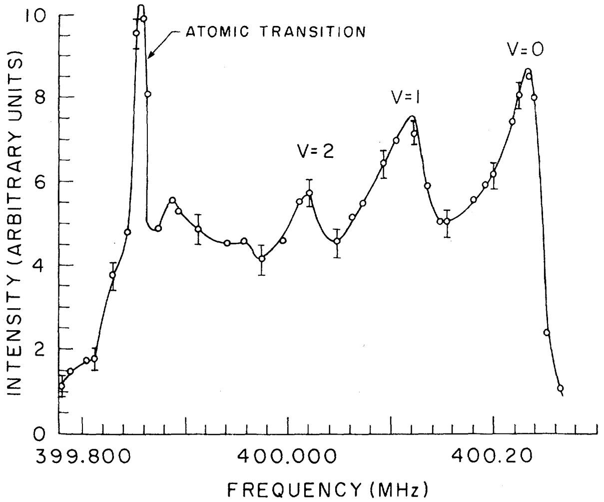

FIG. 1. Magnetic resonance curve for the transition $(F=2, m_F=-1)\rightarrow(F=1, m_F=-1)$ in KAr at a field of 82.5 G, where structure due to the spin-rotation interaction vanishes to first order. If there were no shift in a, the molecular and atomic resonance curves would be identical. The atomic resonance, due to residual atoms in the molecular beam, appears at the left; the peaks identified with the first three vibrational states of the molecule are marked $v=0,1,2$.

alkali hyperfine constant a; R is the internuclear separation, and $\gamma(R)$ is the molecular spin-rotation coupling strength.

The energy levels of Eq. (1) are similar to those of atomic potassium, but have an additional fine structure due to the spin-rotation interaction and the hyperfine shift. In zero magnetic field the hyperfine interactions couples $\vec{I}$ and $\vec{S}$ to form $\vec{F}=\vec{I}+\vec{S}$; in the fields used in this experiment the condition $g_s\mu_BH_0 \gg N\gamma$ holds, so m_F is still an approximately good quantum number, and the molecular states may be labeled (F, m_F, m_N). The spin-rotation interaction splits the observable transitions of KAr by separating states of different m_N, broadening the spectrum, and reducing the signal intensity.[2] In addition, the strong state dependence of the spin-rotation constant $\gamma(R)$ obscures the contribution of $\alpha(R)$, whose measurement is the aim of this experiment. Fortunately, in a magnetic field given by

$$H_0 = ah/2\mu_B \tag{2}$$

the frequency of the hyperfine transition $(F=2, m_F=-1)\rightarrow(F=1, m_F=-1)$ is independent of field, the spin-rotation splitting is eliminated to first order, and the quantum number m_N can be ignored. Under this condition, any displacement or broadening of the KAr spectrum relative to the atomic-potassium spectrum is due to the hyperfine shift $\alpha(R)$.

Figure 1 is the observed spectrum for the transition $(2,-1)\rightarrow(1,-1)$ in a field that satisfies Eq. (2) for potassium, 82.5 G. The peak marked "atomic transition" is due to residual potassium atoms not removed from the beam; its width is characteristic of the apparatus resolution. The peaks marked $v=0$, 1, and 2 are caused by KAr molecules in the lowest three vibrational states, while the smearing on the low-frequency side of each peak is due to the rotational structure of the vibrational level.

To determine the R dependence of α, we have compared the experimental data with a spectrum computed from a simple analytic model for α. Eigenvalues and wave functions were computed using Baylis's potential,[4] and expectation values of R were computed numerically. In an initial attempt we approximated $\alpha(R)$ by a straight line, shown in Fig. 2(a) (solid line). The relative populations of the molecular states were assumed to be described by vibrational and rotational temperatures $T_{\rm vib}=25$ K, $T_{\rm rot}=15$ K, values which are consistent with our most recent data on the spin-rotation interaction. The resulting line spectrum [Fig. 2(b)] agrees well with the observed spectrum in the region of positive shift. This suggests that for 10.25 bohr $<R<$ 12.0 bohr, $\alpha(R)$ can be described by

$$\alpha(R) = -M(R-R_0) \tag{3}$$

where $M=115$ kHz/bohr, and $R_0=12.0$ bohr.

Clearly the linear model for $\alpha(R)$ cannot be valid for all interatomic separations: While the hyperfine interaction is expected to be negative at large R, eventually it must vanish, implying a negative shift that decreases to zero for very large R. The dashed curve in Fig. 2(a) shows the expected form for $\alpha(R)$ for large R. The minimum in α has two implications: It sets a lower limit on the possible KAr hyperfine seperation, and it produces a bandhead in the spectrum arising from states with negative shifts. The experimental spectrum has a cutoff approximately 50 kHz below the atomic value, confirming the existence of a minimum value of α at least 25 kHz deep. Unfortunately, the vibrational levels giving rise to the negative shifts are the highest-lying states, which are weakly populated, so the signal drops rapidly near the bandhead. In addition, the unwanted atomic line further obscures the structure of the bandhead.

More detailed analysis of our data and experi-

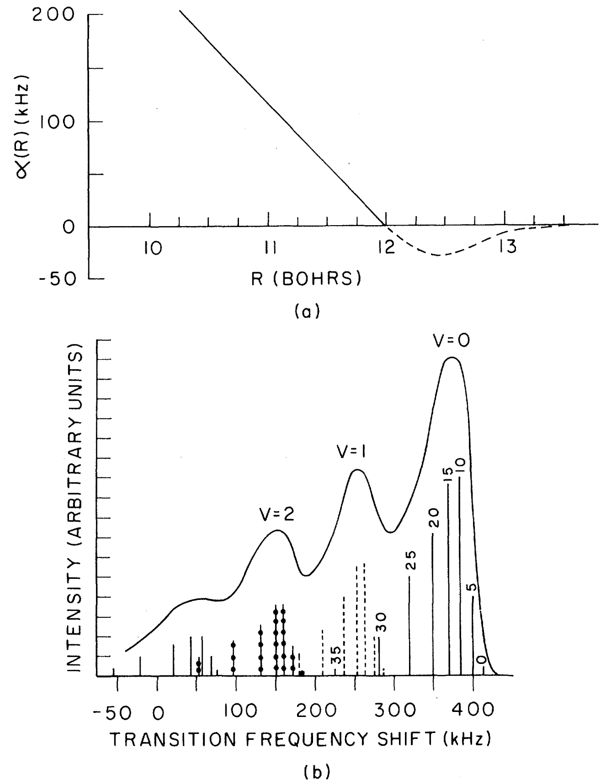

FIG. 2. (a) The functional form of $\alpha(R)$ used to calculate the spectrum in (b). The solid line corresponds to internuclear separations well resolved in this experiment. The dashed line is an indication of the form for $\alpha(R)$ for large R extracted from the cutoff bandhead near zero shift shown in Fig. 1. (b) Calculated line spectrum assuming $\alpha(R)$ given by solid line in (a). The lines in each grouping are rotational structure of each vibrational level. The rotational number N is labeled for the $v=0$ state. The solid curve shows the result of integrating the line spectrum over the apparatus resolution (approximately 25 kHz). The populations of the vibrational and rotational levels are taken to be given by $T_{\text{vib}}=25$ K, $T_{\text{rot}}=15$ K.

ments in progress on the large-R contribution to α should determine $\alpha(R)$ with sufficient accuracy that the size and temperature dependence of the KAr pressure shift can be calculated. At present, the pressure shift in KAr is known only approximately (-0.4 ± 1.4 Hz/Torr),[3] and its temperature dependence has not been determined. We hope that these results will encourage more detailed measurements of the pressure shift in KAr, and more detailed theoretical calculations on the radial dependence of the pressure shift.

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[1] An extensive review of the literature through 1971 is given by W. Happer, Rev. Mod. Phys. 44, 169 (1972). See also W. D. Davison and Y. C. Liew, J. Phys. B: Proc. Phys. Soc., London 5, 309 (1972); B. K. Rao, D. Ikenberry, and T. P. Das, Phys. Rev. A 8, 1673 (1973); C. M. Dutta, N. C. Dutta, and T. P. Das, Phys. Rev. A 7, 60 (1973); P. J. Fortune and P. R. Certain, J. Phys. B: Proc. Phys. Soc., London 6, L39 (1973).

[2] E. M. Mattison, D. E. Pritchard, and D. Kleppner, Phys. Rev. Lett. 32, 507 (1974).

[3] A. L. Bloom and J. B. Carr, Phys. Rev. 119, 1946 (1960).

[4] W. E. Baylis, Joint Institute for Laboratory Astrophysics Report No. 100, available from Scientific Reports Editor, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colorado 90302. Some corrections to these potentials have been calculated (W. E. Baylis, private communication).