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Comments and Addenda

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Argon-induced hyperfine frequency shift in potassium*

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The hyperfine spectrum of the Van der Waals molecule KAr is analyzed assuming an isotropic perturbation of the potassium hyperfine constant. The analysis yields the hyperfine frequency shift in KAr as a function of the internuclear separation between 9 and 18 bohr. The shift is positive at short range, $R < 12$ bohr, and negative at longer range. The results are compared to theoretical estimates of the shift, and are used to calculate the pressure shift of optically pumped potassium in argon.

I. INTRODUCTION

We have recently reported a measurement of the hyperfine spectrum of potassium in the Van der Waals molecule KAr.[1] The data were taken at a magnetic field value for which all perturbations of the free potassium spectrum by spin-rotational interactions and g_J factor shifts were negligible.[2] In Ref. 1 it was demonstrated that the major features of the spectrum could be explained by a linearly decreasing hyperfine frequency shift over the range 10.25 to 12.0 bohr. It was argued that the shift was positive for R less than 12 bohr, but that for larger distances it had to be negative, having a minimum value of at least −50 kHz.

This note reports the results of a refined analysis that determines the hyperfine shift between 9 and 18 bohr and which fits all features of the observed spectrum.

II. DATA

The experimental data analyzed here are the data reported in Ref. 1. The high narrow peak at the atomic frequency, which was previously ascribed to stray atoms, has turned out to be a true feature of the molecules arising from a stationary point in the variation of shift with distance. This has been further confirmed by careful measurements of the constituent separation properties of our apparatus[3] which have shown that essentially no stray atoms are present in the molecular resonance signal.

III. ANALYSIS

The interatomic well depth for KAr is approximately 60 K; for characteristic vibrational temperatures of 20 K there is significant population in all bound states of the molecule. The data are sensitive to such a large range in internuclear distance R, that we have chosen to fit it by calculating the average value of an arbitrary functional form of that hyperfine shift rather than by using an expansion about some point such as the potential minimum.

Our determination of the hyperfine shift as a function of internuclear separation relies upon calculated radial wave functions of KAr. As discussed in Ref. 3, we have used the ground-state electronic potential computed by Baylis.[4] The wave functions were calculated numerically[5] and stored so that average values of any tabular function of the internuclear distance could be readily obtained for any bound rotational-vibrational state of the molecule.

The variation of the hyperfine shift with R was determined as follows: (a) An initial tabular form of the hyperfine shift $\Delta f(R)$ was assumed. (b) The average value of $\Delta f(R)$ was calculated in each bound rotational-vibrational level of the potential. (c) An ensemble average of $\Delta f(R)$ for all the molecules was calculated, assuming that the relative populations of the states were characterized by rotational and vibrational temperatures, T_N, T_v. (d) The resulting spectrum was averaged over the apparatus line shape, assuming a Lorentzian curve

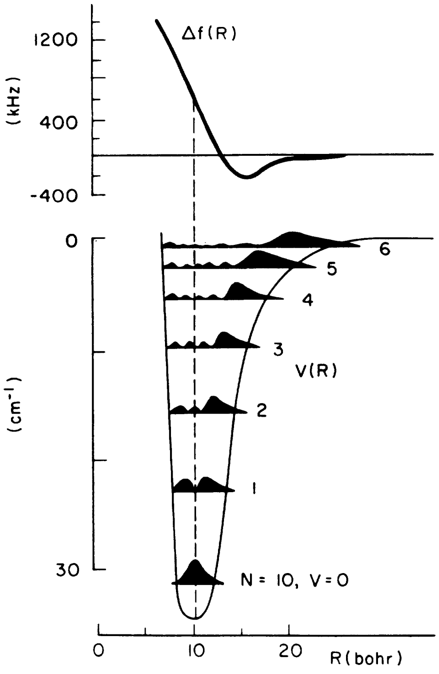

FIG. 1. $\Delta f(R)$ and $V(R)$ plotted on the same R scale. The square of the wave functions for the rotational level $N = 10$ and all bound vibrational levels are sketched in the potential at energy positions corresponding to the eigenvalues for that level. The vertical line indicates the point on the $\Delta f(R)$ curve corresponding to the minimum of the potential. The higher vibrational levels weigh the negative portion of the $\Delta f(R)$ curve, while the lower levels average mostly the positive portion of the curve.

with a FWHM of approximately 25 kHz. (e) The resulting predicted resonance pattern was compared to the data. (f) Adjustments were made, first to T_N and T_v and then in the functional form of hyperfine shift, until good agreement was obtained between the prediction and the data.

This fitting technique is simplified by the observation that the positive and negative shift regions can be treated as essentially independent. The reason is shown in Fig. 1, where representative values of $|\psi_{vN}|^2$ are plotted below the hyperfine shift curve. The probability densities of the $v = 0, 1, 2$ states strongly overlap the positive portion of the shift curve producing the resonance peaks at large positive shifts, while the probability distributions of the $v = 4, 5, 6$ states weigh the negative portion of the shift curve heavily and are responsible for the features near zero shift. The extent to which the positively and negatively shifted regions are independent is indicated by the close agreement of our final results for $\Delta f(R)$ for $R < 12$ bohr and the simple straight line deduced in Ref. 1.

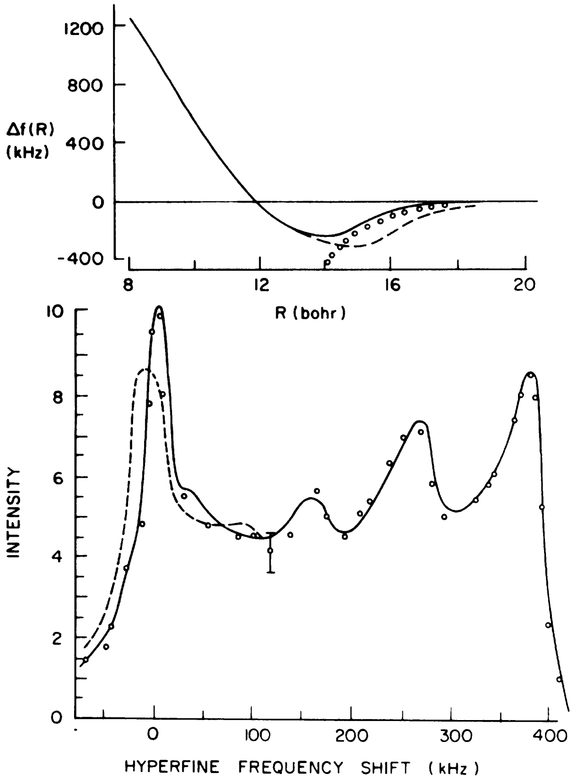

FIG. 2. Comparison of the data with predictions based on the solid $\Delta f(R)$ curve, our best estimate of $\Delta f(R)$. A variation from this best estimate in the negative region (----) yields a prediction in considerable variance with the data near zero shift. On the same plot with the deduced $\Delta f(R)$ curve is plotted a theoretical $\Delta f(R)$ prediction (O) valid in the dispersion limit of the potential (see text). All the experimental points have the same error as the one shown. For all predictions, $T_N = 15$ K, $T_v = 20$ K.

The sensitivity of the predicted spectrum to variations in the form of the negative portion of the shift function is shown in Fig. 2. It should be noted that the fit to the sharp peak about zero frequency shift is particularly sensitive to the negative portion of the shift curve; even a slight variation from the assumed value will produce a serious discrepancy between the predicted spectrum and the data near zero shift.

IV. DISCUSSION

The present results on the radial dependence of the hyperfine interaction in KAr represent, as far as we know, the first experimental determination of such a quantity. Calculations of the negative hyperfine shift in an alkali metal due to a noble gas at long range have been given by several authors,[6,7] and there has been considerable work on long-range hyperfine shift of hydrogen in helium.[8] Rao *et al.* have considered the contributions of direct polarization and exchange core polarization in addition to Van der Waals interactions in calculations of the hyperfine shift for Li in He.[9] No theoretical calculations have been made which comprehensively include both short-range overlap effects and long-range polarization except in H_2^+,[10] and recently in Na-He.[11]

Perhaps the most surprising characteristic of our hyperfine-shift function $\Delta f(R)$ lies in the location of its minimum. This minimum, like the minimum in the interatomic potential $V(R)$, results from a competition between long-range polarization and short-range overlap. In consequence it might be expected that both minima would be at roughly the same internuclear separation. As Fig. 1 reveals, this is not the case.

In the region where the potential is dominated by the attractive Van der Waals energy the hyperfine shift is expected to be proportional to the potential.[7] We have calculated the hyperfine shift for KAr in this region using the published[12] relations. The results are indicated by the circles in Fig. 2 (top); the theoretical curve agrees with the $\Delta f(R)$ to within ~20% for $R > 15$ bohr.

Given the functional form for the hyperfine-shift curve, $\Delta f(R)$, the "pressure shift" for the KAr system is given by[13]

$$\bar{f} = 4\pi N \int_0^\infty \left[\exp\left(\frac{-V(R)}{kT}\right)\Delta f(R) R^2\right] dR, \qquad (1)$$

where N is the density of atoms and $V(R)$ is the potential. In our case $\Delta f(R)$ is determined only for $R > 9$ bohr, while for room-temperature collisions the effective range of the integral extends inward to approximately 7 bohr. To evaluate Eq. (1), we extended the $\Delta f(R)$ curve linearly between 9 and 7 bohr. The result if $\bar{f} = +9.5$ Hz/torr. The most recent measurement[14] of the pressure shift in KAr yields $\bar{f} = -4.0(2)$ Hz/torr.

The discrepancy between our predictions using Eq. (1) and the observed pressure shift is small on the scale of observed pressure shifts in potassium-rare-gas systems (−43 to +45 Hz/torr). Nevertheless it is well outside experimental error. The discrepancy could be due to the assumed interatomic potential, since our determination of $\Delta f(R)$ is based on the location of its eigenfunctions. While it would be possible to vary $V(R)$ sufficiently so that $\bar{f}$ would agree with experiment, the resulting $V(R)$ would no longer be consistent with atomic scattering data.[15] Another explanation involves the possibility that $\Delta f(R)$ does not continue to increase as R goes from 9 to 7 bohr. While Bottcher's calculations[11] show a zero in $\Delta f(R)$ for $R \lesssim 5$ bohr in NaNe, this zero would have to be at $R \gtrsim 8$ bohr in KAr to explain the discrepancy in $\bar{f}$, a circumstance which we judge to be unlikely. Finally there is the possibility that the calculation of the pressure shift from our value of $\Delta f(R)$ is in error owing to our neglect of the anisotropic term in the hyperfine interaction.[16] This interaction, which averages out in the optical-pumping experiment,[17] can contribute to the hyperfine frequency shift of bound molecules. We consider this explanation the most likely and are currently investigating it more thoroughly.

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[2] The transition observed was the $(F=2, m_F=-1) \rightarrow (F=1, m_F=-1)$ at $X\ (\equiv g_s \mu_0 H_0/\Delta W) = 0.5$, the so-called field-independent point. See N. F. Ramsey, *Molecular Beams* (Oxford U.P., London, 1956), p. 86.

[3] For a detailed description of the techniques of production of KAr and its separation from its constituent atoms see R. R. Freeman, E. M. Mattison, D. E. Pritchard, and D. Kleppner, J. Chem. Phys. (to be published).

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