

## Spin-Rotation Interaction of Noble-Gas Alkali-Metal Atom Pairs

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Recent experimental data show that the spin-rotation coupling for alkali-metal-noble-gas van der Waals molecules is mainly due to the spin-orbit interaction of the alkali-metal valence electron within the core of the noble gas. We present a simple formula which accounts very well for the systematic variation of the spin-rotation interaction with different noble-gas or alkali-metal atoms.

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Recently it has become clear that large amounts of angular momentum can be transferred from optically pumped alkali-metal atoms to the nuclei of the heavier noble gases by spin-exchange interactions.<sup>1,2</sup> Only a few of the thirty or so possible pairs of different alkali-metal atoms with different noble-gas atoms have been investigated experimentally, and it would be very useful to be able to predict the spin interactions well enough to tell which pairs are particularly promising for applications to nuclear spin polarization. The most important spin interactions in these molecules are the Fermi contact hyperfine interaction  $\alpha \mathbf{I} \cdot \mathbf{S}$  between the nuclear spin  $\mathbf{I}$  of the noble gas and the electron spin  $\mathbf{S}$  of the alkali-metal atom and the spin-rotation interaction  $\gamma \mathbf{N} \cdot \mathbf{S}$  between  $\mathbf{S}$  and the rotational angular momentum  $\mathbf{N}$  of the noble-gas and alkali-metal atoms about each other. Here we present a simple new formula which accounts very well for the systematic variation of the spin-rotation interaction for different alkali-metal atoms or noble-gas atoms, and which predicts for the first time how  $\gamma$  varies with internuclear separation.

As Bernheim<sup>3</sup> first pointed out, the spin-rotation interaction is responsible for most of the spin relaxation of alkali-metal atoms in noble gases. So far there has been no reliable way to calculate the coupling coefficient  $\gamma$ . The most serious attempt has been made by Herman,<sup>4</sup> who concluded that  $\gamma$  was short ranged and was mainly due to the alkali-metal ionic field. Herman<sup>4</sup> derived expressions for  $\gamma$  which were proportional to the fine-structure splitting of the alkali-metal atom and not directly dependent on the fine structure of the noble-gas atom. While Herman's analysis may be applicable to the light noble gas He and possibly Ne, where the spin-orbit interaction in the noble gas is small, experiments now show clearly that for Ar, Kr, and Xe the spin-rotation interaction must originate from the spin-orbit interaction in the noble-gas atom.

If certain terms which Herman neglected in his analysis are retained, we shall show that the following new expression for  $\gamma$  can be derived:

$$\gamma(R) = (mG/MR)d|\phi_1(R)|^2/dR. \quad (1)$$

Here  $m$  and  $M$  are respectively the electron mass and the reduced mass of the alkali-metal-atom noble-gas

pair,  $R$  is the internuclear separation,  $\phi_1(R)$  is the unperturbed valence-electron wave function of the alkali-metal atom at a distance  $R$  from the alkali-metal nucleus, and the factor

$$G = \frac{1}{2} \left( \frac{\hbar}{mc} \right)^2 \int_0^\infty \left[ \sum_n C_{np} R_{np}(r) \right]^2 \frac{1}{r} \frac{dV}{dr} dr \quad (2)$$

depends only on the spin-orbit interaction of the noble gas. The effective central potential in which the noble-gas electrons move is denoted by  $V$ ,  $r$  is the distance from the noble-gas nucleus,  $\psi_{np0} = r^{-1} \times R_{np}(r) Y_{10}(\theta, \phi)$  is the wave function of a noble-gas  $p$  electron of principal quantum number  $n$ , and the sum on  $n$  in (2) extends over all filled shells of the noble gas. The coefficient  $C_{np}$  is the overlap integral

$$C_{np} = \int_0^\infty z \psi_{np0}(\mathbf{r}) d^3r. \quad (3)$$

In all numerical evaluations of  $G$ ,  $\phi_1(R)$ , and  $\psi_{np0}$  used in this paper we have used the Hartree-Fock-Slater wave functions tabulated by Herman and Skillman.<sup>5</sup> The values of  $G$  calculated for Ne, Ar, Kr, Xe, and Rn are given in Table I.

To directly test the dependence of  $\gamma$  on the fine structure of the alkali-metal atom we determined<sup>6</sup> the spin-rotation coupling constants from measured magnetic slowing-down curves for the <sup>129</sup>Xe nuclear spin relaxation in the series of van der Waals molecules KXe, RbXe, and CsXe. The experimental method was similar to that described by Bhaskar, Happer, and McClelland,<sup>7</sup> and we refer to that paper for more experimental detail. The basic experimental measure-

TABLE I. Spin-rotation coupling factors  $G$ .

Noble gas	$G/h$ ( $10^{-31}$ MHz cm <sup>5</sup> )
Ne	0.062
Ar	0.49
Kr	3.0
Xe	9.8
Rn	31

TABLE II. Comparison of  $\gamma/h$  inferred from experiment with  $\gamma/h$  calculated from (1). Also shown are the widths  $\Delta H_0$  of the magnetic slowing-down curves from Ref. 6 or the characteristic fields  $H_1^*$  for the magnetic slowing-down curves of electronic spin relaxation from Ref. 8.

Molecule	$\Delta H_0$ or $H_1^*$ (G)	$ \gamma_{\text{expt}} /h$ (MHz)	$ \gamma_{\text{theory}} /h$ (MHz)	Ref.
$^{39}\text{K}^{129}\text{Xe}$	$65 \pm 4$	$2.3 \pm 0.2$	2.1	6
$^{85}\text{Rb}^{129}\text{Xe}$	$74 \pm 8$	$1.6 \pm 0.2$	1.3	6
$^{133}\text{Cs}^{129}\text{Xe}$	$109 \pm 15$	$1.6 \pm 0.2$	1.2	6
$^{87}\text{RbAr}$	1.0–1.2	0.09–0.11	0.094	8
$^{87}\text{RbKr}$	$9.59 \pm 0.28$	0.647	0.62	8
$^{87}\text{RbXe}$	$38.1 \pm 1.6$	1.4–1.7	1.3	8
$^{39}\text{KAr}$		0.240	0.23	9
$^{85}\text{RbKr}$		0.96	1.1	10

ment is the width  $\Delta H_0$  of the magnetic slowing-down curve at low buffer-gas pressure. The widths for KXe, RbXe, and CsXe along with the mean coupling constants  $\gamma$  inferred from these widths are shown in Table II. Since Herman's formula for  $\gamma$  is proportional to the  $D$ -line splitting  $\Delta\nu_{fs}$  of the alkali-metal atom, a substantial increase of  $\gamma$  would be expected for the series K, Rb, Cs, which have the splittings  $58 \text{ cm}^{-1}$ ,  $237 \text{ cm}^{-1}$ , and  $554 \text{ cm}^{-1}$ . No such increase is evident from the experimental data. We have also listed in Table II characteristic fields  $H_1^*$  for the magnetic slowing-down curves of the electronic spin relaxation and the inferred values of  $\gamma$  for the series RbAr, RbKr, RbXe measured by Bouchiat, Brossel, and Potter.<sup>8</sup> Although the  $D$ -line splitting of the alkali-metal atom is the same for this series there is a very substantial variation of  $\gamma$ . Thus, it is clear from the experimental data that the spin-rotation constant  $\gamma$  depends on the spin-orbit interaction in the noble gas and is nearly independent of the spin-orbit interaction of the alkali-metal atom. We have also listed in Table II the values of  $\gamma$  inferred by Freeman *et al.*<sup>9</sup> for the  $\nu=0$ ,  $N=0$  state of the KAr molecule, and inferred by Cooke and Freeman for RbKr.<sup>10</sup> These values were deduced from molecular-beam magnetic-resonance experiments and should be quite reliable. The values of  $\gamma$  quoted for the gas-cell measurements of Bouchiat, Brossel, and Potter,<sup>8</sup> and our group<sup>6</sup> are estimates of the root-mean-square (rms) value of  $\gamma$  for all bound and long-lived quasibound states of the van der Waals molecule.

We have used the new formula (1) to estimate  $\gamma$  for the molecules listed in Table II. The steps involved are illustrated in Fig. 1 which shows a van der Waals potential curve  $U(R)$  for RbKr and the spin-rotation coefficient  $\gamma$  calculated from (1). The potential  $U(R)$  has the form  $ar^{-12} - br^{-6}$  with the constants  $a$  and  $b$  chosen to reproduce the well depth  $E$  and equilibrium separation  $R_0$  given by Pascale and Vandeplanque.<sup>11</sup>

To good approximation the value of  $\gamma/h$  for RbKr should be  $-\gamma(R_0)/h = -\gamma(5.29 \text{ \AA})/h = 1.1 \text{ MHz}$ . This is larger than the experimental value of 0.96 MHz by 15%. However, as one can see from Fig. 1,  $|\gamma(R)|$  drops so rapidly with internuclear separation that one would get perfect agreement between experiment and theory if the internuclear separation were 5.37 Å, 1.5% larger than the value given in Ref. 11. Even better agreement was found for KAr where the experimental<sup>9</sup>

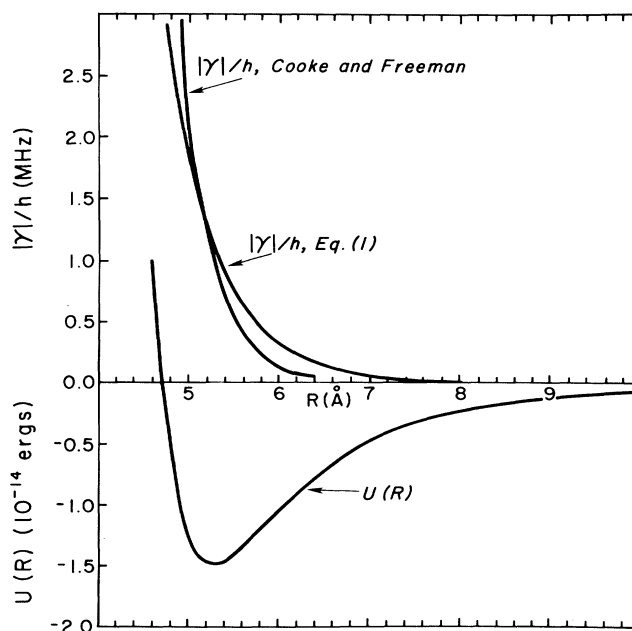


FIG. 1. The spin-rotation constant  $\gamma/h$  in megahertz calculated from Eq. (1) as a function of internuclear separation  $R$  in angstroms for a RbKr pair. Also shown is the empirical function  $\gamma(R)/h$  deduced by Freeman and Cooke from molecular-beam magnetic-resonance studies of RbKr molecules. The van der Waals potential  $U$ , in units of  $10^{-14}$  erg, is shown in the lower curve.

and theoretical values of  $|\gamma|/h$  are 0.24 and 0.23 MHz, respectively. For the first six entries in Table II we have approximated the rms value of  $\gamma$  by

$$\bar{\gamma} = 0.522\gamma(R_0). \quad (4)$$

Detailed calculations of Cooke and Freeman<sup>10</sup> showed that Eq. (4) is true for RbKr, and it is reasonable to expect similar results for other van der Waals molecules. There is good agreement with the gas-cell values but the calculated absolute values of  $\gamma$  are about 20% smaller than the measured values. In view of the extreme sensitivity of  $\bar{\gamma}$  to the exact shape of the van der Waals potential we think the agreement is satisfactory.

Finally, we have sketched in Fig. 1 the radial dependence of  $\gamma$  (formula 1 of Ref. 10) which Cooke and Freeman<sup>10</sup> found empirically as a good fit to their measurements. The value of the empirical curve is almost the same as the value of the theoretical curve (1) at the minimum of the van der Waals potential, and the exponential decrease of  $\gamma$  with  $R$  which was guessed

by Cooke and Freeman<sup>10</sup> agrees with the prediction of Eq. (1) that  $\gamma$  is proportional to the exponentially decreasing factor  $d|\phi_1(R)|^2/dR$ .

The derivation of (1) is straightforward. We imagine an alkali-metal atom at rest with an unperturbed valence-electron wave function  $\phi_1$ . A noble-gas atom moves by the alkali-metal atom with a velocity  $\mathbf{v}$ . The alkali-metal valence electron will scatter in the Coulomb potential  $V$  of the noble-gas atom. We account for the scattering to first approximation by orthogonalizing the alkali-metal valence-electron wave function to the core-electron orbitals  $\psi_i(\mathbf{r})e^{im\mathbf{v}\cdot\mathbf{r}/\hbar}$  of the moving noble-gas atom. The orbital of the resting noble-gas atom is  $\psi_i(\mathbf{r})$  where  $\mathbf{r}$  is the distance from the noble-gas nucleus, and the phase factor  $e^{im\mathbf{v}\cdot\mathbf{r}/\hbar}$  accounts for the motion. This is analogous to the orthogonalized plane-wave method used to calculate conduction-electron wave functions in solids<sup>12</sup> except that the translational phase factor does not normally occur in solids. Then the orthogonalized valence electron wave function is

$$\phi(\mathbf{r}) = \phi_1(\mathbf{r}) - \sum_i \psi_i(\mathbf{r})e^{im\mathbf{v}\cdot\mathbf{r}/\hbar} \int \psi_i^*(\mathbf{r}')e^{-im\mathbf{v}\cdot\mathbf{r}'/\hbar} \phi_1(\mathbf{r}')d^3r'. \quad (5)$$

The alkali-metal wave function  $\phi_1(\mathbf{r})$  and the translational phase factor  $e^{im\mathbf{v}\cdot\mathbf{r}/\hbar}$  will vary slowly in the neighborhood of the noble-gas core and their product can be expanded as a power series in  $\mathbf{r}$  so that the integral in (5) becomes

$$\int \psi_i^*(\mathbf{r}')[\phi_1(R) + \mathbf{A}\cdot\mathbf{r}' + \dots]d^3r' \quad (6)$$

where the complex vector  $\mathbf{A}$  is

$$\mathbf{A} = \frac{\mathbf{R}}{R} \frac{d\phi_1(R)}{dR} - \frac{im\mathbf{v}}{\hbar} \phi_1(R). \quad (7)$$

Then the orthogonalized wave function (5) becomes

$$\phi(\mathbf{r}) = \phi_1(\mathbf{r}) - \sum_n C_{np} \mathbf{A} \cdot \psi_{np} e^{im\mathbf{v}\cdot\mathbf{r}/\hbar} + \dots, \quad (8)$$

where we have focused attention on the  $p$  orbitals of the noble-gas core and  $C_{np}$  was defined by (3). For convenience we have denoted the three substates of the  $np$  orbital with the Cartesian vector  $\psi_{np} = \hat{x}\psi_{npx} + \hat{y}\psi_{npy} + \hat{z}\psi_{npz}$ . The expectation value of the spin-orbit interaction is then

$$\begin{aligned} & - \langle \phi | (\mu_B/mc) \nabla V \times \mathbf{p} \cdot \mathbf{S} | \phi \rangle \\ & = iG \mathbf{A} \times \mathbf{A}^* \cdot \mathbf{S} = \gamma \mathbf{N} \cdot \mathbf{S}, \end{aligned} \quad (9)$$

where  $G$  was defined by (2). Substituting for  $\mathbf{A}$  from (7) into (9) we find the expression for  $\gamma$  given in (1). One can easily verify that the same formula (1) for  $\gamma$  is obtained if both the alkali-metal atom and the noble-gas atom are moving in such a way that the relative velocity of the noble-gas atom with respect to the alkali-metal atom is  $\mathbf{v}$ . Formula (1) can also be ob-

tained by the method outlined by Herman<sup>4</sup> if rotational excitation of the core orbitals of the noble gas is included. These terms were neglected by Herman with the result that the alkali-metal valence-electron orbital was orthogonalized to the resting noble-gas orbitals rather than to the moving orbitals.

The formula (1) for  $\gamma$  is closely analogous to Herman's formula<sup>13</sup> for the Fermi contact-interaction coefficient:

$$\alpha(R) = \frac{16\pi}{3} \frac{\mu_B \mu_K}{K} \eta^2 |\phi_1(R)|^2. \quad (10)$$

The enhancement factor  $\eta^2$ , like the factor  $G$  of (2), depends only on the properties of the noble gas through overlap integrals with noble-gas core-electron orbitals. The dependence of both  $\gamma$  and  $\alpha$  on the internuclear separation  $R$  is dominated by the exponential decrease of the unperturbed alkali-metal valence-electron wave function  $\phi_1(R)$ .

In conclusion, we have shown how to derive a simple formula (1) for the spin-rotation coupling constant  $\gamma$  of alkali-metal-noble-gas van der Waals molecules. Although (1) could be refined, for example, by including the distortion of the alkali-metal valence electron outside of the noble-gas core or by replacing the orthogonalization procedure (5) with a solution of the wave equation within the noble-gas core and proper boundary matching, the simplest approximation (1) already gives reasonable agreement with experiments. It should be possible to use the closely analogous formulas (1) and (10) to reliably estimate the key spin-

coupling parameters  $\gamma$  and  $\alpha$  for many untested noble-gas-alkali-metal-atom pairs and their isoelectronic analogs (e.g., KRn, Ba<sup>+</sup>Ne, etc.)

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