

## Estimates of spin-exchange parameters for alkali-metal–noble-gas pairs

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Estimates of frequency-shift enhancement factors, binary cross sections for spin exchange and spin relaxation, chemical equilibrium constants, and spin-exchange and spin-rotation interactions in van der Waals molecules are presented for alkali-metal atoms interacting with noble-gas atoms. These results are compared to experiments and are also presented for those pairs which have not been studied experimentally.

### I. INTRODUCTION

In the last few years spin-exchange techniques have become popular for transferring angular momentum to noble-gas nuclei.<sup>1</sup> In such experiments optically pumped alkali-metal atoms polarize the nuclei via binary collisions or formation of van der Waals molecules. These techniques have been used for a variety of applications, including measurements of nuclear magnetic moments,<sup>2</sup> searches for permanent electric dipole moments in atoms and nuclei,<sup>3</sup> spin-polarized nuclear targets,<sup>4</sup> and studies of quadrupolar wall interactions.<sup>5</sup> The physics of spin exchange has been studied intensively in the last few years, but for many alkali-metal–noble-gas pairs no experimental information is available. In the following I compare calculations of the relevant spin-exchange parameters to the experiments done to date, and present estimates of the relevant spin-exchange parameters for those species which have not been measured.

The important spin-exchange phenomena which have been studied experimentally to date are frequency shifts, binary cross sections for spin relaxation and spin exchange, and spin relaxation and spin exchange in bound van der Waals molecules. All of these studies measure in one way or another the strength of the magnetic-dipole interaction

$$H_{KS} = \alpha \mathbf{K} \cdot \mathbf{S} \quad (1)$$

which couples the noble-gas nuclear spin  $\mathbf{K}$  to the alkali-metal electronic spin  $\mathbf{S}$ , producing spin exchange, or the strength of the spin-rotation interaction

$$H_{NS} = \gamma \mathbf{N} \cdot \mathbf{S} , \quad (2)$$

which causes spin relaxation by coupling  $\mathbf{S}$  to the rotational angular momentum  $\mathbf{N}$  of the alkali-metal–noble-gas pair. Both  $\alpha$  and  $\gamma$  are functions of the internuclear separation  $R$  of the alkali-metal–noble-gas pair.

The magnetic-dipole coupling (1) is dominated by the Fermi-contact interaction

$$\alpha(R) = \frac{16\pi}{3} \frac{\mu_B \mu_K}{K} |\psi(R)|^2 , \quad (3)$$

where  $\mu_B$  is the Bohr magneton,  $\mu_K$  is the magnetic moment of the noble-gas nucleus, and  $\psi(R)$  is the wavefunction of the alkali-metal valence electron evaluated at

the position of the noble-gas nucleus. Herman<sup>6</sup> has shown that an enhancement of  $\psi(R)$  occurs, i.e.,

$$\psi(R) = \eta \phi(R) , \quad (4)$$

where  $\phi(R)$  is the alkali-metal valence-electron wave function in the absence of the noble gas, and  $\eta \gg 1$  for all the noble gases. This enhancement comes about from the large kinetic energy acquired by the electron as it scatters in the core potential of the noble-gas atom. Walker, Bonin, and Happer<sup>7</sup> have calculated  $\eta$  using the orthogonalized-plane-wave (OPW) and phase-shift (PS) techniques.

In the last few years experiments on the spin-rotation interaction (2) in bound alkali-metal–noble-gas van der Waals molecules have shown convincingly that for the heavy noble gases the dominant contribution to  $\gamma$  comes from the interaction of the alkali valence electron with the noble-gas atom. Wu, Walker, and Happer<sup>8</sup> have shown that  $\gamma$  results from the spin-orbit interaction in the noble-gas core, and found

$$\gamma(R) = \frac{-mG}{\mu R} \frac{d|\phi(R)|^2}{dR} . \quad (5)$$

Here  $m$  and  $\mu$  are the electron mass and the reduced mass of the alkali-metal–noble-gas pair, and the constant  $G$  is dependent only on the spin-orbit interaction of the noble gas. Values of  $G$  have been calculated in Ref. 7.

In the following the expressions (3) and (5) will be used to compare to experimental values of the constants  $\eta$  and  $G$  as well as to predict the values of spin-exchange parameters which have not yet been measured. In Sec. II the potential curves and wave functions used for the calculations are discussed. In Sec. III the values of  $\eta$  and  $G$  found by experiments on van der Waals molecules are presented. Section IV does the same for experiments which have measured binary cross sections. Section V presents the results of frequency-shift experiments. In Sec. VI the estimates for the alkali-metal–noble-gas pairs which have not been experimentally investigated are presented. Table V is a compilation of the calculated values of the spin-exchange parameters for the relevant alkali-metal–noble-gas pairs.

### II. POTENTIAL CURVES AND WAVE FUNCTIONS

All of the data to be analyzed below depends for its interpretation on assumed potential curves and alkali-metal

wave functions. The available information on the potential curves is of varying quality. For the heavy noble gases Ar, Kr, and Xe the scattering experiments of Buck and Pauly<sup>9</sup> have determined potential depths and positions for all the pairs except RbAr and RbXe. Pascale and Vandeplanque<sup>10</sup> have used the results of Buck and Pauly to constrain their semiempirical calculations of the alkali-metal-noble-gas potentials. For NaAr there also exists the direct spectroscopic measurements of Tellinghuisen *et al.*<sup>11</sup> For consistency, I have used the potentials of Pascale and Vandeplanque for all calculations involving Ar, Kr, and Xe.

For the light noble gases there is little information which does not require theoretical input; the exception is the spectroscopic investigation of Lapidovitch *et al.*<sup>12</sup> of NaNe. For He I have chosen the potentials of Pascale<sup>13</sup> for the calculations which follow. For NaNe the well depth calculated by Pascale and Vandeplanque<sup>10</sup> of 0.25 meV is much smaller than the measurement of 1.0 meV by Lapidovitch *et al.*, and the equilibrium separation of 6.0 Å is significantly greater than the measured 5.29 Å. Thus for Ne I have assumed that the trend found by Buck and Pauly<sup>9</sup> for the heavier noble gases—that the well depth is insensitive to the alkali metal—holds for Ne as well. I have therefore taken the Morse potential parameters of Lapidovitch *et al.* for NaNe to be the same for the other alkali-metal-Ne molecules, but with the potential minimum chosen to be somewhat larger than for the corresponding alkali-metal-Ar molecule. The internuclear separations chosen are NaNe, 5.29 Å; KNe, 5.64 Å; RbNe, 5.68 Å; CsNe, 5.80 Å.

There are no measurements or calculations of the alkali-metal-Rn potentials so I have chosen the parameters for the assumed Morse potential form

$$V(R) = D(e^{-2a(R-R_0)} - 2e^{-a(R-R_0)}) \quad (6)$$

as follows:  $D = 18$  meV and  $a = 0.8 \text{ \AA}^{-1}$  for all the alkali-metal-Rn pairs, and  $R_0 = 5.1, 5.3, 5.4,$  and  $5.5 \text{ \AA}$  for NaRn, KRn, RbRn, and CsRn, respectively.

The alkali-metal valence-electron wave functions required for calculating  $\alpha$  and  $\gamma$  need to be known outside the core of the alkali metal for the purposes of this paper. For this purpose the wave functions of choice are the semiempirical Coulomb wave functions of Bates and Damgaard<sup>14</sup> which use the experimental binding energy to determine the asymptotic behavior of the wave functions. Also, as discussed by Seaton,<sup>15</sup> the normalization of the wave functions assumed by Bates and Damgaard should be multiplied by a small factor  $[1 + 2(-\epsilon)^{3/2}d\mu/d\epsilon]^{-1/2}$ , where  $-\epsilon$  is the binding energy in rydbergs and  $\mu$  is the quantum defect. The values of  $d\mu/d\epsilon$  used for this paper are  $-0.066, -0.156, -0.209,$  and  $-0.284$  for Na, K, Rb, and Cs, respectively.

### III. van der WAALS MOLECULES

In most experiments with heavy noble gases at pressures below an atmosphere spin exchange is dominated by the formation of long-lived van der Waals molecules. The relevant spin-exchange and spin-relaxation phenomena have been discussed in detail by Happer *et al.*,<sup>1</sup> the

important experimental parameters which are deduced in these experiments are the average value of the spin-rotation interaction  $\langle \gamma N \rangle$  and the average value of the Fermi-contact interaction  $\langle \alpha \rangle$ . Also obtained are the molecular formation and breakup rates which determine the chemical equilibrium constant  $k_{\text{chem}} = [AX]/[X][A]$ , where  $[AX]$  is the density of alkali-metal-noble-gas molecules,  $[A]$  the alkali-metal number density, and  $[X]$  the noble-gas density.

As shown by Schaefer *et al.*,<sup>16</sup> the fraction of bound alkali-metal-noble-gas pairs at internuclear separation  $R$  and with angular momentum  $N$  is

$$f(R, N) = \frac{\hbar^2}{\mu k T R^2} N e^{-\hbar^2 N^2 / 2\mu R^2 k T} \times \text{erf} \left[ \left( \frac{E_{\text{max}}(N) - V_N(R)}{k T} \right)^{1/2} \right] \quad (7)$$

Then the chemical equilibrium constant is given by

$$k_{\text{chem}} = \int_0^{N_{\text{max}}} dN \int_{R_{\text{min}}(N)}^{R_{\text{max}}(N)} f(R, N) e^{-V(R)/kT} 4\pi R^2 dR, \quad (8)$$

the average value of the spin-rotation interaction is

$$\langle \gamma N \rangle = \frac{1}{k_{\text{chem}}} \int_0^{N_{\text{max}}} N dN \int_{R_{\text{min}}(N)}^{R_{\text{max}}(N)} \gamma(R) f(R, N) \times e^{-V(R)/kT} \times 4\pi R^2 dR, \quad (9)$$

and the average value of the Fermi-contact interaction is

$$\langle \alpha \rangle = \frac{1}{k_{\text{chem}}} \int_0^{N_{\text{max}}} dN \int_{R_{\text{min}}(N)}^{R_{\text{max}}(N)} \alpha(R) f(R, N) \times e^{-V(R)/kT} \times 4\pi R^2 dR. \quad (10)$$

In the above  $V_N(R) = V(R) + \hbar^2 N^2 / 2\mu R^2$ ,  $E_{\text{max}}(N)$  is the maximum energy of a bound molecule of rotational angular momentum  $N$ ,  $R_{\text{min}}(N)$  and  $R_{\text{max}}(N)$  are the turning points for the classical motion of the bound molecule in the potential  $V_N(R)$ , and  $N_{\text{max}}$  is the maximum angular momentum possible for a bound molecule. Some experiments measure slightly different quantities, such as the root-mean-square values of  $\alpha$  and  $\gamma N$ . By direct calculation I have found that the rms values differ from the above averages by at most a few percent, so for simplicity I will assume the above method of averaging to interpret all the gas-phase experiments.

Gas phase measurements of the spin-rotation coupling strength  $\langle \gamma N \rangle$  have been reported for RbAr,<sup>17</sup> RbKr,<sup>18</sup> CsKr,<sup>19</sup> NaXe,<sup>20</sup> KXe,<sup>8</sup> RbXe,<sup>8,18</sup> and CsXe.<sup>8</sup> There have also been molecular-beam measurements of  $\gamma$  for KAr (Ref. 21) and RbKr (Ref. 22) which do not measure the average values, but rather give  $\gamma(R_0)$ . The results of these experiments are shown in Table I along with the values of  $G$  deduced assuming the Pascale and Vandeplanque<sup>10</sup> potential curves.

Measurements of  $x = \langle \gamma N \rangle / \langle \alpha \rangle$  for KXe, RbXe, and CsXe were made by Xeng *et al.*<sup>23</sup> By using the measure-

TABLE I. Measured characteristics of alkali-metal–noble-gas van der Waals molecules compared to theory. OPW and PS refer to the orthogonalized-plane-wave and phase-shift techniques for calculating  $|\eta|$  and  $G$ . The measured chemical equilibrium constants are scaled to 100°C by assuming a  $T^{-3/2}$  dependence, and compared to the values calculated from the Pascale and Vandephanque (PV) potentials.

Molecule	$\langle \alpha \rangle / h$ (MHz)	Expt.	$ \eta $		$\langle \gamma N \rangle / h$ (MHz)	Expt.	$G$ (eV Å <sup>5</sup> )		$k_{\text{chem}}$ (Å <sup>3</sup> )	
			OPW	PS			OPW	PS	Expt.	PV
KAr						1.8 <sup>a</sup>	1.9	0.96		
RbAr					3.35±0.14 <sup>b</sup>	3.32	1.9	0.96	64±4 <sup>b</sup>	68
Rb <sup>83</sup> Kr						12.1 <sup>c</sup>	12	5.9		
	2.77±0.27 <sup>d</sup>	54	35	44	26.8±0.8 <sup>e</sup>	15.6	12	5.9	110±9 <sup>e</sup>	166
CsKr					29±3 <sup>f</sup>	17.0	12	5.9		
NaXe					172±22 <sup>g</sup>	96	39	24		
K <sup>129</sup> Xe	38±5 <sup>h</sup>	79	50	73	132±12 <sup>i</sup>	58	39	24	256±70 <sup>h</sup>	310
Rb <sup>129</sup> Xe	38±6 <sup>h</sup>	78	50	73	121±14 <sup>i</sup>	72	39	24	244±44 <sup>h</sup>	313
Cs <sup>129</sup> Xe	49±8 <sup>h</sup>	81	50	73	141±16 <sup>i</sup>	83	39	24	222±84 <sup>h</sup>	350

<sup>a</sup>Molecular-beam measurement of  $G$ , Ref. 21.

<sup>b</sup>Reference 17.

<sup>c</sup>Molecular-beam measurement of  $G$ , Ref. 22.

<sup>d</sup>Reference 23.

<sup>e</sup>Reference 18.

<sup>f</sup>Reference 19.

<sup>g</sup>Reference 20.

<sup>h</sup>Deduced from measurements of Refs. 24 and 8, see text.

<sup>i</sup>Reference 8.

ments of  $\langle \gamma N \rangle$  for these molecules,  $\langle \alpha \rangle$  is obtained, and values for  $\eta$  deduced. These values are shown in Table I. A recent measurement for RbKr by Schaefer<sup>24</sup> is also shown in Table I.

Bouchiat, Brossel, and Pottier<sup>20</sup> have measured the formation and breakup rates for RbKr, reported in the form  $\tau P$  and  $T_f P^2$ , where  $\tau$  is the molecular lifetime,  $P$  the noble-gas pressure, and  $T_f$  the three-body formation time. The chemical equilibrium constant can then be deduced by the relation  $k_{\text{chem}} = \tau P k T / T_f P^2$ , and is given in Table I. Likewise Xeng *et al.*<sup>23</sup> have measured the characteristic pressure  $p_0$  and the molecular formation rate constant  $Z$ , which, coupled with the values of  $\langle \gamma N \rangle$  from Wu *et al.*,<sup>8</sup> give

$$k_{\text{chem}} = \frac{Z p_0}{2\pi k T \langle \gamma N \rangle / h}.$$

The values so obtained for KXe, RbXe, and CsXe are shown in Table I.

#### IV. BINARY COLLISIONS

Binary collisions between the alkali-metal atoms and the noble-gas atoms can cause both spin relaxation (from the spin-rotation interaction) and spin exchange (via the Fermi-contact interaction). The duration of these collisions ( $10^{-12}$  sec) is so short that the spins precess by negligible amounts so that first-order time-dependent perturbation theory is valid. Thus the transition rate due to the spin-rotation interaction (2) between the two electronic sublevels  $\langle \uparrow |$  and  $\langle \downarrow |$  of the alkali electron is given by

$$R = \frac{[X]}{\hbar^2} \int v f(\mathbf{v}) d^3v d^2b \times \left| \int_{-\infty}^{\infty} \langle \downarrow | \gamma(R(t)) \mathbf{S} \cdot \mathbf{N} | \uparrow \rangle dt \right|^2, \quad (11)$$

where  $\mathbf{v}$  is the relative velocity of the alkali-metal–noble-gas pair,  $b$  the impact parameter of the collision,  $f(\mathbf{v})$  the Maxwellian velocity distribution, and we have taken a classical trajectory  $R(t)$  for the collision. The squared matrix element in (11) can be written

TABLE II. Measurements of binary cross sections for spin exchange  $\sigma_{\text{SE}}$ , and comparison of the deduced values for  $\eta$  to theory. The measurements have been scaled to 100°C according to a  $T^{-1}$  dependence.

Molecule	Ref.	$\sigma_{\text{SE}}$ (Å <sup>2</sup> )	Expt.	$ \eta $	
				OPW	PS
Na <sup>3</sup> He	25	$(1.26 \pm 0.22) \times 10^{-8}$	9.6	9.5	5.3
Rb <sup>3</sup> He	26	$(1.68 \pm 0.24) \times 10^{-8}$	10.1	9.5	5.3
Rb <sup>21</sup> Ne	27	$(5.6 \pm 0.2) \times 10^{-8}$	19	15	9.4
Rb <sup>83</sup> Kr	23	$(1.3 \pm 0.3) \times 10^{-6}$	52	35	44

TABLE III. Measurements of spin-relaxation cross sections ( $\sigma_{SR}$ ) for alkali-metal-noble-gas pairs, and deduced values of  $G$  compared to theory.

Molecule	Ref.	$\sigma_{SR}$ ( $\text{\AA}^2$ )	Expt.	$G$ ( $\text{eV \AA}^5$ )	
				OPW	PS
RbAr	18	$(6.08 \pm 0.20) \times 10^{-6}$	2.0	1.9	0.96
RbKr	18	$(2.66 \pm 0.12) \times 10^{-4}$	13	12	5.9
CsKr	19	$(2.55 \pm 0.36) \times 10^{-4}$	11	12	5.9
NaXe	28	$1.09 \times 10^{-3}$	52	39	24
RbXe	18	$(1.64 \pm 0.9) \times 10^{-3}$	35	39	24

$$\frac{\mu^2 v^2}{4\hbar^2} (1 - \cos^2 \theta) \left| \int_{-\infty}^{\infty} \gamma(R(t)) dt \right|^2 = \frac{\mu^2 v^2}{\hbar^2} (1 - \cos^2 \theta) \left| \int_{r_0}^{\infty} \frac{\gamma(R) dR}{[v^2(1 - b^2/R^2) - 2V(R)/\mu]^{1/2}} \right|^2, \quad (12)$$

where  $r_0$  is the classical turning point of the trajectory and  $\theta$  is the angle between  $\mathbf{v}$  and the axis of quantization.

The integral over angles in (11) is now possible, giving a spin-relaxation cross section defined via the relation

$$\sigma_{SR} = \frac{2\mathcal{R}}{[X]\bar{v}}$$

of

$$\sigma_{SR} = \frac{8\pi}{3} \frac{\mu^2}{\hbar^2} \int w e^{-w} dw b^3 db \times \left| \int_{r_0}^{\infty} \frac{\gamma(R) dR}{[(1 - b^2/R^2) - V(R)/wkT]^{1/2}} \right|^2, \quad (13)$$

where  $w = \mu v^2/2kT$  and  $\bar{v} = \sqrt{8kT/\pi\mu}$ . This is insensitive to temperature. A similar result is obtained for the spin-exchange cross section:

$$\sigma_{SE} = \frac{2\pi}{\hbar^2} \frac{\mu}{kT} \int e^{-w} dw b db \times \left| \int_{r_0}^{\infty} \frac{\alpha(R) dR}{[1 - b^2/R^2 - V(R)/wkT]^{1/2}} \right|^2. \quad (14)$$

With the above definitions, the basic equations for spin exchange via binary collisions are

$$\frac{d}{dt} \langle S_z \rangle = 2\bar{v} \sigma_{SE}[X] (\langle S^2 - S_z^2 \rangle \langle K_z \rangle - \langle K^2 - K_z^2 \rangle \langle S_z \rangle) - \bar{v} \sigma_{SR}[X] \langle S_z \rangle \quad (15)$$

and

$$\frac{d}{dt} \langle K_z \rangle = 2\bar{v} \sigma_{SE}[A] (\langle K^2 - K_z^2 \rangle \langle S_z \rangle - \langle S^2 - S_z^2 \rangle \langle K_z \rangle). \quad (16)$$

A point which is sometimes overlooked is the  $T^{-1}$  dependence of  $\sigma_{SE}$ , which arises because the spin-exchange probability is proportional to the square of the interaction time and therefore proportional to the inverse-square of the relative velocity. This dependence

should be taken into account when analyzing temperature-dependent data on spin-exchange cross sections. It should also be noted that both (13) and (14) depend sensitively on the repulsive wall of the potential, where the factor  $[1 - b^2/R^2 - V(R)/wkT]^{1/2}$  is smallest. The analogous cross sections for free-electron spin relaxation and spin exchange have been calculated by Walker, Bonin, and Happer.<sup>7</sup>

Table II shows the binary spin-exchange cross section measurements which have been made to date, and values of  $\eta$  deduced from these cross sections. Soboll<sup>25</sup> reports the Na relaxation rate for the slowest time constant. Thus his reported cross section is  $\sigma_{SE}/(2I+1)$ , where  $I = \frac{3}{2}$  is the nuclear spin of  $^{23}\text{Na}$ . To account for  $\sigma_{SR}$  I have also subtracted his  $^4\text{He}$  cross section from his  $^3\text{He}$  cross section. Chupp and Coulter<sup>27</sup> report the cross section for transitions between magnetic sublevels of the  $^{21}\text{Ne}$  nucleus, so  $\sigma_{SE}$  is twice this value.

Table III shows some of the measurements of  $\sigma_{SR}$  which have been reported. Here much of the older data has been incorrectly interpreted due to problems with optically thick vapors, neglect of multiple time constants, and neglect of the effects of the alkali-metal nuclear spin.<sup>29,30</sup> Thus only reported results which include these effects are presented in Table III.

## V. FREQUENCY SHIFTS

As discussed by Schaefer *et al.*,<sup>16</sup> under virtually all practical conditions the relevant parameter for describing the shifts of alkali-metal EPR frequencies and noble-gas

TABLE IV. Measurements of the frequency-shift enhancement factor  $\kappa_0$  from Ref. 16 and the deduced values of  $\eta$  compared to theory.

Molecule	$\kappa_0$	Expt.	$\eta$	
			OPW	PS
RbKr	$270 \pm 95$	44	35	44
RbXe	$643 \pm 260$	69	50	73

TABLE V. Estimates of spin-exchange parameters of alkali-metal–noble-gas pairs. All numbers are for 100°C. The values of  $\eta$  used are He,  $-9.5$ ; Ne,  $15$ ; Ar,  $-22$ ; Kr,  $44$ ; Xe,  $-73$ ; Rn,  $114$ . The values of  $G$  are, in units of  $\text{eV } \text{\AA}^5$ ; Ne,  $0.24$ ; Ar,  $1.9$ ; Kr,  $12$ ; Xe,  $39$ ; Rn,  $124$ . The potential curves used to obtain these estimates are explained in Sec. II.

Molecule	$\kappa_0$	$\sigma_{\text{SR}} (\text{\AA}^2)$	$\sigma_{\text{SE}} (\text{\AA}^2)$	$\langle \gamma N \rangle / h$ (MHz)	$\langle \alpha \rangle / h$ (MHz)	$k_{\text{chem}} (\text{\AA}^3)$
Na $^3\text{He}$	6.5		$1.2 \times 10^{-8}$			
K $^3\text{He}$	8.5		$2.1 \times 10^{-8}$			
Rb $^3\text{He}$	8.8		$2.1 \times 10^{-8}$			
Cs $^3\text{He}$	10.0		$2.7 \times 10^{-8}$			
Na $^{21}\text{Ne}$	27	$1.8 \times 10^{-7}$	$9.8 \times 10^{-9}$	0.086	0.11	5.7
K $^{21}\text{Ne}$	34	$1.6 \times 10^{-7}$	$1.5 \times 10^{-8}$	0.11	0.18	6.6
Rb $^{21}\text{Ne}$	38	$1.8 \times 10^{-7}$	$2.3 \times 10^{-8}$	0.11	0.18	6.7
Cs $^{21}\text{Ne}$	44	$2.0 \times 10^{-7}$	$2.9 \times 10^{-8}$	0.13	0.27	7.1
Na $^{37}\text{Ar}$	29	$2.0 \times 10^{-6}$	$2.8 \times 10^{-8}$	2.4	0.73	60
K $^{37}\text{Ar}$	56	$4.9 \times 10^{-6}$	$1.3 \times 10^{-7}$	2.6	1.06	72
Rb $^{37}\text{Ar}$	61	$5.3 \times 10^{-6}$	$2.0 \times 10^{-7}$	1.9	1.0	68
Cs $^{37}\text{Ar}$	83	$7.9 \times 10^{-6}$	$3.8 \times 10^{-7}$	2.8	1.6	86
Na $^{83}\text{Kr}$	120	$7.2 \times 10^{-5}$	$6.1 \times 10^{-8}$	20	0.98	120
K $^{83}\text{Kr}$	230	$1.9 \times 10^{-4}$	$3.4 \times 10^{-7}$	23	1.6	150
Rb $^{83}\text{Kr}$	280	$2.4 \times 10^{-4}$	$7.1 \times 10^{-7}$	21	1.8	170
Cs $^{83}\text{Kr}$	340	$2.9 \times 10^{-4}$	$1.2 \times 10^{-6}$	20	2.1	180
Na $^{129}\text{Xe}$	310	$6.1 \times 10^{-4}$	$1.3 \times 10^{-5}$	70	19	230
K $^{129}\text{Xe}$	660	$1.8 \times 10^{-3}$	$8.0 \times 10^{-5}$	88	33	310
Rb $^{129}\text{Xe}$	730	$2.0 \times 10^{-3}$	$1.6 \times 10^{-4}$	65	33	310
Cs $^{129}\text{Xe}$	880	$2.3 \times 10^{-3}$	$2.7 \times 10^{-4}$	66	40	350
Na $^{209}\text{Rn}$	730	$4.7 \times 10^{-3}$	$2.7 \times 10^{-6}$	190	7.7	470
K $^{209}\text{Rn}$	1300	$1.0 \times 10^{-2}$	$1.2 \times 10^{-5}$	250	15	510
Rb $^{209}\text{Rn}$	1400	$1.1 \times 10^{-2}$	$2.5 \times 10^{-5}$	190	15	530
Cs $^{209}\text{Rn}$	1800	$1.3 \times 10^{-2}$	$4.9 \times 10^{-5}$	200	20	550

NMR frequencies is the frequency-shift enhancement factor  $\kappa_0$  which is the ratio of the average alkali-metal valence electron density at a noble-gas nucleus to the alkali-metal atom density. Schaefer *et al.* have shown that  $\kappa_0$  is given by the following simple formula:

$$\kappa_0 = \eta^2 \int |\phi(R)|^2 e^{-V(R)/kT} 4\pi R^2 dR. \quad (17)$$

Since the Boltzmann factor is nearly 1 over most of the integral above,  $\kappa_0$  is only weakly temperature dependent.  $\kappa_0$  is sensitive to the location of the repulsive wall of the potential, but insensitive to the well depth. Thus if  $\eta$  has been measured in some other experiment,  $\kappa_0$  becomes a good probe of the repulsive wall of the potential. To date, the experimental measurements of  $\kappa_0$  have been limited by systematic errors to accuracies of about 35%, but this will certainly be improved in the future.

To date, the only quantitative measurements of the frequency shifts are for RbKr and RbXe.<sup>16</sup> The results of these experiments are shown in Table IV.

## VI. ESTIMATES OF SPIN-EXCHANGE PARAMETERS

The comparisons in Tables I–IV of the values of  $\eta$  and  $G$  obtained from the OPW and PS methods to those deduced from experiment and potential curves show that the experiments favor larger values of  $\eta$  and  $G$ . Table V gives the calculated values of all the spin-exchange parameters for the alkali-metal–noble-gas pairs using the larger of the PS and OPW values for  $\eta$  and  $G$ . The evidence of Tables I–IV suggests that these estimates should be fairly reliable for those alkali-metal–noble-gas pairs which have not been investigated to date. This will be useful for future experiments which involve spin exchange between optically pumped alkali-metal atoms and noble-gas nuclei.

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