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Frequency Shifts in Hyperfine Splitting of Alkalis Caused by Foreign Gases*

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The difference in the dispersion force between an alkali atom in a particular hyperfine level belonging to the groundstate and a perturbing molecule is computed. These asymptotic forces, if active alone, generally produce red shifts and suffice to account for the results obtained for the heavier buffer gases. Experimental data exhibit blue shifts for the lighter gases and therefore indicate that the net frequency shifts are the result of exchange as well as dispersion forces. The former cannot be determined theoretically. Therefore, a simple model is devised in which the difference in the forces is given a positive trend at distances of separation smaller than *d*, while beyond *d* it is given the calculated form. The experimental data for all alkali-rare gas interactions can then be fitted by values of *d* which, for the different foreign gases, are of the order of their gas-kinetic diameters.

1. INTRODUCTION

INGENIOUS experiments[1,2] have shown that hyperfine transitions in the spectra of Na, Rb, and Cs suffer shifts in the presence of noble gases. Qualitatively, these shifts are similar to those observed in optical spectra under the action of Van der Waals forces; but their magnitudes are smaller. It is tempting, therefore, to calculate the Van der Waals forces for the different fine structure levels of an alkali atom and to see whether agreement with the data results when the ordinary concepts of pressure broadening are employed in their simplest form.[3]

This plan encounters a major difficulty: the data indicate shifts to higher frequencies when the buffer gas atoms are light, opposite shifts when they are heavy. Such occurrences are well known in optical spectra, though they are less prominent. They imply the presence of repulsive (exchange) energies at small distances of separation; in the case of hyperfine levels the bespeak a reversal of their energy difference. Since they are of lesser importance in the optical case, rather crude assumptions can reproduce the optical data. Here, exchange effects are clearly prominent, and a model is needed to approximate the energy reversal. Only the asymptotic interaction between an alkali and a rare gas can be computed, and hence the model must bear half the burden of all numerical comparisons. We chose a model patterned after the ordinary exchange forces, and the success we may claim for our interpretation, if any, must depend upon the circumstance that reasonable model parameters can be chosen to account for the data.

Our method differs conceptually from the pattern of thought usual in nuclear physics. The hyperfine splitting arises from the Fermi interaction of the nuclear magnetic moments with the electron shells, and to account for its change one feels tempted to compute, first the effect of a perturbing atom on the alkali electrons, then the secondary effect upon the hyperfine levels. Here we pass around these details and utilize empirical data, such as the spacing of energy levels, the normal hyperfine splitting, *f*-values, and so forth. Our method obscures the features of the nuclear picture but does not violate them.

The present approach leaves the details of the line *shapes* obscure. Since line widths receive contributions from several causes, their understanding involves more difficult problems. Hence our calculation is limited to the first moment of the line frequencies, a quantity which is largely independent of the accidents of line shapes. The first moment can be identified with the line maximum, which is measured, only if the line is symmetric, and this is reported as empirically true.

2. ASYMPTOTIC ENERGY SHIFTS

The hyperfine transitions giving rise to the microwave lines under consideration take place between different F states composing the ${}^2S_{\frac{1}{2}}$ ground level of the alkali atoms. Each of these states suffers a downward energy displacement when a rare gas atom approaches the alkali, a displacement which can be computed by well-known methods involving second-order perturbation theory. But the usual Van der Waals force calculation does not distinguish between the different hyperfine states. In this section we perform it for specific F levels and find a dependence of the London force on F which reduces the transition frequency between the states in question. These are ${}^2S_{\frac{1}{2}}(F=3, m_F=0)$ to ${}^2S_{\frac{1}{2}}(F=4, m_F=0)$ in cesium, ${}^2S_{\frac{1}{2}}(F=1, m_F=0)$ to ${}^2S_{\frac{1}{2}}(F=2, m_F=0)$ in both rubidium and sodium.

Since our major concern will be with the Cs line (frequency $\nu=9192.6$ megacycles sec^{-1}), the concrete references in the sequel are to this case. Results for Rb and Na follow by analogy and will be stated. Likewise, to save writing, we shall often symbolize any noble gas by the representative A. The theory of angular

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[1] M. Arditi and T. R. Carver, Phys. Rev. **109**, 1012 (1958); Bender, Beaty, and Chi, Phys. Rev. Letters **1**, 311 (1958).

[2] E. C. Beaty and P. L. Bender, Bull. Am. Phys. Soc. Ser. II, **3**, 185 (1958); M. Arditi and T. R. Carver, Bull. Am. Phys. Soc. Ser. II, **3**, 185 (1958); M. Arditi and T. R. Carver, Phys. Rev. **112**, 449 (1958); P. L. Bender and A. R. Chi, Phys. Rev. **112**, 450 (1958).

[3] H. Margenau, Phys. Rev. **40**, 387 (1932); H. Margenau and W. W. Watson, Revs. Modern Phys. **8**, 22 (1936).

momenta permits the reduction of all matrix elements encountered in the calculation to those involving only the radial parts of the state functions, and these can be approximated by known quantities, e.g., *f*-values and atomic polarizabilities. For the alkali atoms we employ *f*-values because only one electronic transition, the resonance transition corresponding to the *D* lines, is strong, and its oscillator strength is nearly 1.

The perturbing noble gas atom, on the other hand, is capable of numerous electronic transitions from the groundstate to higher states, all of them in the neighborhood of the ionization potential. Here, then, we sum over all *f*-values, assuming a common transition energy, and obtain the polarizability via formula (21) below.

For completeness we present a calculation of the asymptotic energy shifts which includes the splitting of the *P* states and introduces all details of angular momentum couplings. The result can be obtained with very good approximation in a simpler way described in the last paragraphs of this section and is summarized in Eq. (27).

The effective electron coordinate in the Cs atom is denoted by (1), that in the noble gas by (2); the vector distance between their nuclei is **R**. The classical interaction energy is given in a very general form by Rose[4] and reduces in the dipole-dipole approximation to

$$V=\frac{16\pi^2e^2}{9}\sum_{M,m=-1}^{+1}\mathcal{Y}_1^{m*}(\mathbf{r}_1)\mathcal{Y}_1^{M*}(\mathbf{r}_2)\mathcal{Y}_1^{M}(\nabla)\Upsilon_1^{m}(\mathbf{R}),\tag{1}$$

where $\mathcal{Y}_L^M$ is a regular solid spherical harmonic defined as

$$\mathcal{Y}_L^M(\mathbf{r})=r^LY_L^M(\mathbf{r}^{(1)}),\tag{2}$$

and Υ_L^M the irregular solid harmonic

$$\Upsilon_L^M(\mathbf{R})=R^{-L-1}Y_L^M(\mathbf{R}^{(1)});\tag{3}$$

$\mathbf{r}^{(1)}$ and $\mathbf{R}^{(1)}$ denote unit vectors in the directions of **r** and **R**.

If the ∇ operation, which applies to **R**, is performed and the *z* axis taken along **R**, Eq. (1) becomes the familiar

$$\begin{aligned}V&=-\frac{4\pi}{3}\frac{e^2}{R^3}r_1r_2\sum_M 2^{1-|M|}Y_1^{-M}(\mathbf{r}_1)Y_1^M(\mathbf{r}_2)\\&=\frac{e^2}{R^3}(x_1x_2+y_1y_2-2z_1z_2).\end{aligned}\tag{4}$$

Writing j for the total angular momentum ($j=F$ for Cs), we let $\Psi_{j_1m_1}$ represent the state function of the alkali atom, $\Psi_{j_2m_2}$ that of the noble gas.

The second order energy difference between the two hyperfine levels due to the noble gas perturbation is given by

$$\Delta E_{4,3}=\sum_{p'}\frac{|(p'|V|p)|^2}{E_p-E_p'}-\sum_{q'}\frac{|(q'|V|q)|^2}{E_q-E_q'},\tag{5}$$

where V is the interaction energy as given in (1); p refers to the Cs-A gas system with Cs in the $j_1=4$ state, and q to the system with Cs in the $j_1=3$ state.

The matrix element $(p'|V|p)$ is given by

$$\begin{aligned}(p'|V|p)&=(j_1'm_1',j_2'm_2'|V|j_1m_1,j_2m_2)\\&=\frac{16\pi^2e^2}{9}\sum_{M,m=-1}^{+1}\mathcal{Y}_1^M(\nabla)\Upsilon_1^m(\mathbf{R})\\&\quad\times(j_1'm_1',j_2'm_2'|\mathcal{Y}_1^{m*}(\mathbf{r}_1)\mathcal{Y}_1^{M*}(\mathbf{r}_2)|j_1m_1,j_2m_2).\end{aligned}\tag{6}$$

Since $\mathcal{Y}_1^{m*}(\mathbf{r}_1)$ depends only on the Cs atom and $\mathcal{Y}_1^{M*}(\mathbf{r}_2)$ only on the A atom, (6) can be factored and written as

$$\begin{aligned}&\frac{16\pi^2e^2}{9}\sum_{M,m=-1}^{+1}\mathcal{Y}_1^M(\nabla)\Upsilon_1^m(\mathbf{R})(j_1'm_1')|\mathcal{Y}_1^{m*}(\mathbf{r}_1)|j_1m_1)\\&\qquad\times(j_2'm_2'|\mathcal{Y}_1^{M*}(\mathbf{r}_2)|j_2m_2).\end{aligned}\tag{7}$$

Let us first evaluate the matrix element $(j_1'm_1'|\mathcal{Y}_1^{m*}(\mathbf{r}_1)|j_1m_1)$. To obtain the hyperfine state function $\Psi_{j_1m_1}$ it is necessary to couple spin and angular momentum of the valence electron to form the total electronic angular momentum, which in turn must be coupled with the nuclear spin through Clebsch-Gordan coefficients C. Thus

$$\Psi_{Jm_J}=\sum_{m_L}C(LSJ;m_L,m_J-m_L)\Psi_{Lm_L}\Psi_{Sm_J-m_L},\tag{8}$$

and

$$\begin{aligned}\Psi_{j_1m_1}&=\sum_{m_J}C(JIj_1;m_J,m_1-m_J)\Psi_{Jm_J}\Psi_{Im_1-m_J}\\&=\sum_{m_J}\sum_{m_L}C(JIj_1;m_J,m_1-m_J)C(LSJ;m_L,m_J-m_L)\\&\qquad\times\Psi_{Lm_L}\Psi_{Sm_J-m_L}\Psi_{Im_1-m_J}.\end{aligned}\tag{9}$$

A similar equation holds for $\Psi_{j_1'm_1'}$. As mentioned, in the case of the Cs atom only the $P_{\frac{3}{2}},P_{\frac{1}{2}}$ resonance levels are used for the primed states, which is permissible because the intensities of the transitions from all the other states to the ground state are much weaker than these.

Use of (7) leads to

$$\begin{aligned}(j_1'm_1'|\mathcal{Y}_1^{m*}(\mathbf{r}_1)|j_1m_1)&=\sum_{m_J'}\sum_{m_J}C(J'I'j_1';m_J',m_1'-m_J')C(JIj_1;m_J,m_1-m_J)\\&\quad\times\delta_{II'}\delta_{m_1'-m_J',m_1-m_J}\sum_{m_L'}\sum_{m_L}C(L'S'J';m_L',m_J'-m_L')\\&\quad\times C(LSJ;m_L,m_J-m_L)(L'm_L'|\mathcal{Y}_1^{m*}(\mathbf{r}_1)|Lm_L)\\&\qquad\times\delta_{S'S}\delta_{m_J'-m_L',m_J-m_L}.\end{aligned}\tag{10}$$

The matrix element $(L'm_L'|\mathcal{Y}_1^{m*}(\mathbf{r}_1)|Lm_L)$ in (10)

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[4] M. Rose, J. Math. Phys. **37**, 215 (1958).

can be reduced by means of the Wigner-Eckart theorem:

$$(L'm_L'|\mathcal{Y}_1^{m*}(\mathbf{r}_1)|Lm_L) = (-)^m C(L1L';m_L,-m,m_L') \times(L'\|\mathcal{Y}_1(\mathbf{r}_1)\|L)\delta_{m_L',m_L-m}. \quad (11)$$

In this way the sum over m_L' in (10) can be eliminated and one sees that

$$\begin{aligned}(j_1'm_1'|\mathcal{Y}_1^{m*}(\mathbf{r}_1)|j_1m_1) &= \sum_{m_J'}\sum_{m_J} C(J'Ij_1';m_J',m_1-m_J)C(JIj_1;m_J,m_1-m_J) \\ &\times\sum_{m_L} C(L'SJ';m_L-m,m_J-m_L)C(LSJ;m_L,m_J-m_L) \\ &\times(-)^m C(L1L';m_L,-m)(L'\|\mathcal{Y}_1(\mathbf{r}_1)\|L) \\ &\times\delta_{m_1',m_1-m}\delta_{S'S}. \quad (12)\end{aligned}$$

By applying the symmetry and orthonormality relations of the C-coefficients Eq. (12) can be written in a more convenient form (the details of this calculation follow developments in the cited book by Rose[5])

$$\begin{aligned}(j_1'm_1'|\mathcal{Y}_1^{m*}(\mathbf{r}_1)|j_1m_1) &= C(j_11j_1';m_1,-m)(-)^{S-L-2J+I+m+2} \\ &\times[(2j_1+1)(2J'+1)(2J+1)(2L'+1)]^{\frac{1}{2}} \\ &\times W(Jj_1J'j_1';I1)W(LJL'J';S1) \\ &\times(L'\|\mathcal{Y}_1(\mathbf{r}_1)\|L), \quad (13)\end{aligned}$$

where the Racah coefficient W is defined as in reference 5.

The remaining matrix element $(L'\|\mathcal{Y}_1(\mathbf{r}_1)\|L)$ is evaluated by using (2) and the orthogonality relations of the spherical harmonics.

$$(L'\|\mathcal{Y}_1(\mathbf{r}_1)\|L) = (L'|r_1|L)\left[\frac{3(2L+1)}{4\pi(2L'+1)}\right]^{\frac{1}{2}} C(L1L';00), \quad (14)$$

$C(L1L'\,00)$ is different from zero only if $L+1+L'$ is even. $(L'|r_1|L)$ is the matrix element of the radial part of the alkali function between the states L' and L. The matrix element for the noble gas atom can be calculated in a similar way:

$$(j_2'm_2'|\mathcal{Y}_1^{M*}(\mathbf{r}_2)|j_2m_2) = (-)^M C(j_21j_2';m_2,-Mm_2')(j_2'\|\mathcal{Y}_1(\mathbf{r}_2)\|j_2). \quad (15)$$

In our case $j_2=0$ and (15) reduces to

$$(-)^M\left[\frac{1}{4\pi}\right]^{\frac{1}{2}} C(011;0-M)C(011;00)(j_2'|r_2|j_2), \quad (16)$$

$(j_2'|r_2|j_2)$ being the radial matrix element for the noble gas. In terms of the formulas (13), (14), and (16) expression (7) takes the form

$$\begin{aligned}\frac{4\pi e^2}{9}\sum_{M,m=-1}^{+1}&(-1)^{S-L-2J+I+m+M+2}\mathcal{Y}_1^M(\nabla)\Upsilon_1^m(\mathbf{R}) \\ &\times[3(2j_1+1)(2J'+1)(2J+1)]^{\frac{1}{2}}C(j_11j_1';m_1,-m) \\ &\times W(Jj_1J'j_1';I1)W(0J1J';S1) \\ &\times(L'|r_1|L)(j_2'|r_2|j_2), \quad (17)\end{aligned}$$

note being taken of the fact that $C(011,0-M)$ and $C(011,00)$ are equal to one.

For the evaluation of $\mathcal{Y}_1^M(\nabla)\Upsilon_1^m(\mathbf{R})$ it is convenient to take $\mathbf{R}$ along the positive z axis. In that case this quantity is zero unless $m=-M$. Application of this condition results in

$$\mathcal{Y}_1^M(\nabla)\Upsilon_1^{-M}(\mathbf{R}) = \frac{-6}{4\pi(1-M)!(1+M)!R^3}, \quad (18)$$

and substitution of (18) and (17) yields, on squaring (6),

$$\begin{aligned}|(p'|V|p)|^2 = \frac{4e^4}{9R^6}\sum_{M=-1}^{1}&\left[\frac{[3(2j_1+1)(2J'+1)(2J+1)]^{\frac{1}{2}}}{(1-M)!(1+M)!}\right. \\ &\left.\times C(j_11j_1';m_1M)W(Jj_1J'j_1';I1)W(0J1J';S1)\right]^2 \\ &\times|(L'|r_1|L)|^2|(j_2'|r_2|j_2)|^2. \quad (19)\end{aligned}$$

Now $(L'|r_1|L)$ depends on the oscillator strength f_1 of the alkali and $(j_2'|r_2|j_2)$ on the polarizability of the noble gas; specifically

$$|(L'|r_1|L)|^2 = \frac{3}{2}\frac{\hbar^2 f_1}{mE(L'L)}, \quad (20)$$

$$\sum_{j_2'}|(j_2'|r_2|j_2)|^2 = \frac{3\alpha_2E(j_2'j_2)}{2e^2}, \quad (21)$$

where $E(L'L)$ is the difference between the mean energy of the ^2P states ($L'=1$) and that of the ^2S ($L=0$) state, while $E(j_2'j_2)$ is the ionization potential of the noble gas. Each doublet of the P state enters separately into the subsequent calculation, and f_1 is taken to be 1.

As to the energy denominators in Eq. (5),

$$E_p-E_{p'} = -[E(j_2',j_2)+E(J'j_1',Jj_1)], \quad (22)$$

where $E(J'j_1',Jj_1)$ is the energy difference between the excited hfs-states $J'j_1'$ and the ground-state hfs levels Jj_1. Substitution of (22), (21), (20), and (19) into (5) yields finally

$$\Delta E_{j_1+1,j_1} = -\frac{9(e\hbar)^2}{4m}\frac{f_1\cdot\alpha_2E(j_2'j_2)}{R^6E(L'L)}(A_{j_1+1}-A_{j_1}), \quad (23)$$

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[5] M. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

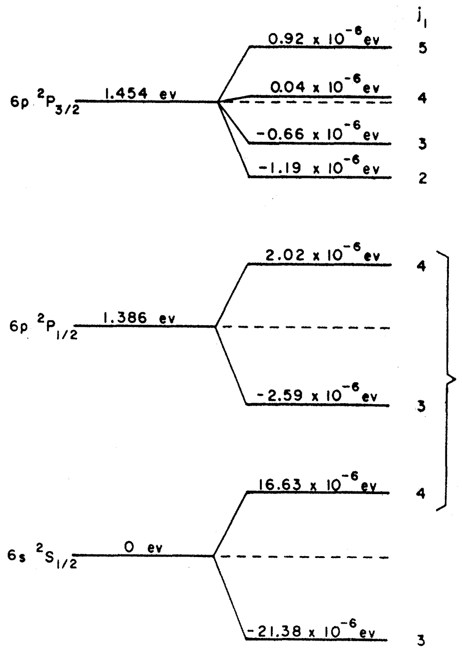

FIG. 1. Energy level diagram of $\mathrm{Cs}^{133}(I=\frac{7}{2})$.

where

$$A_{j_1}=\sum_{j_1'J'}\sum_{M=-1}^{1}\left[\frac{2[3(2j+1)(2J'+1)(2J+1)]^{\frac{1}{2}}}{3(1-M)!(1+M)!}\times C(j_1 1 j_1';m_1 M)W(Jj_1J'j_1';I1)W(0J1J';S1)\right]^2\times\frac{1}{E(J'j_1',Jj_1)+E(j_2'j_2)}. \tag{24}$$

The W coefficients needed in this work are available in the tables of Obi and collaborators.[6]

The results for Cs are

$$\begin{aligned}A_4&=\frac{1}{324}\left[\frac{57}{E(\frac{1}{2}3;\frac{1}{2}4)}+\frac{15}{E(\frac{1}{2}4;\frac{1}{2}4)}+\frac{19}{E(\frac{3}{2}3;\frac{1}{2}4)}+\frac{21}{E(\frac{3}{2}4;\frac{1}{2}4)}+\frac{104}{E(\frac{3}{2}5;\frac{1}{2}4)}\right],\\A_3&=\frac{1}{324}\left[\frac{9}{E(\frac{1}{2}3;\frac{1}{2}3)}+\frac{63}{E(\frac{1}{2}4;\frac{1}{2}3)}+\frac{72}{E(\frac{3}{2}2;\frac{1}{2}3)}+\frac{27}{E(\frac{3}{2}3;\frac{1}{2}3)}+\frac{45}{E(\frac{3}{2}4;\frac{1}{2}3)}\right].\end{aligned} \tag{25}$$

In these formulas, every E is understood to include the ionization energy of the rare gas atom with which Cs interacts, in accordance with Eq. (24). For example, $E(\frac{1}{2}4;\frac{1}{2}4)$ represents the bracketed energy difference in Fig. 1 plus the ionization energy of the rare gas.

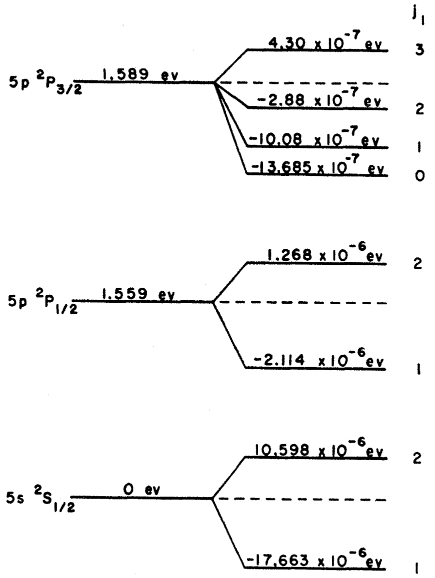

FIG. 2. Energy level diagram of $\mathrm{Rb}^{87}(I=\frac{3}{2})$.

If the hyperfine splitting were neglected, A_3 and A_4 would be equal and the effect computed would vanish. The energies E appearing in the denominators of Eq. (25) are taken from Kopfermann[7] and from Senitzky and Rabi,[8] and are summarized in Figs. 1 and 2. A similar calculation for Rb, written in the same abbreviated fashion, gives

$$A_2=\frac{1}{270}\left[\frac{45}{E(\frac{1}{2}1;\frac{1}{2}2)}+\frac{15}{E(\frac{1}{2}2;\frac{1}{2}2)}+\frac{9}{E(\frac{3}{2}1;\frac{1}{2}2)}+\frac{15}{E(\frac{3}{2}2;\frac{1}{2}2)}+\frac{96}{E(\frac{3}{2}3;\frac{1}{2}2)}\right],$$

$$A_1=\frac{1}{270}\left[\frac{5}{E(\frac{1}{2}1;\frac{1}{2}1)}+\frac{55}{E(\frac{1}{2}2;\frac{1}{2}1)}+\frac{40}{E(\frac{3}{2}0;\frac{1}{2}1)}+\frac{25}{E(\frac{3}{2}1;\frac{1}{2}1)}+\frac{55}{E(\frac{3}{2}2;\frac{1}{2}1)}\right].$$

Numerical results for Cs and Rb are listed in Table I. The computation for Na is similar to that for Rb since the values of I are the same: the values of a are very small (as are the observed shifts) and have not been included.

These results justify a simple approximation which avoids the use of angular momentum theory altogether. The hyperfine splitting of the S state is considerably larger than those for the P states; the coefficients of the various terms in A_j are irregular and of the same

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[6] Obi, Ishidzu, Horie, Yanagawa, Tanabe, and Sato, Ann. Tokyo Astron. Observ., Univ. Tokyo, 2nd Series 4, 3–74 (1954).

[7] H. Kopfermann, *Nuclear Moments* (Academic Press, Inc., New York, 1958).

[8] B. Senitzky and I. I. Rabi, Phys. Rev. **103**, 315 (1956).

TABLE I. Parameters used in calculation of asymptotic interactions and values obtained.

			Cs^{133}		Rb^{87}	
Gas	$E(j_2'j_2)$	$\alpha(\mathrm{A}^3)$	$A_4-A_3(\mathrm{ev}^{-1})$	$R^6E_{4,3}(\mathrm{ev\ A}^6)=-a$	$A_2-A_1(\mathrm{ev}^{-1})$	$R^6E_{21}(\mathrm{ev\ A}^6)$
He	24.5	0.205	-3.78×10^{-8}	-3.28×10^{-5}	-2.776×10^{-8}	-2.18×10^{-5}
Ne	25.7	0.39	-3.46×10^{-8}	-5.97×10^{-5}	-2.536×10^{-8}	-3.98×10^{-5}
N_2	15.8	1.74	-8.57×10^{-8}	-40.6×10^{-5}	-6.252×10^{-8}	-26.9×10^{-5}
A	17.5	1.63	-7.10×10^{-8}	-34.9×10^{-5}	-5.188×10^{-8}	-23.2×10^{-5}
Kr	14.7	2.46	-9.78×10^{-8}	-61.0×10^{-5}	-7.126×10^{-8}	-40.3×10^{-5}
Xe	12.2	4.0	-13.70×10^{-8}	-115.0×10^{-5}		

order of magnitude. This suggests that we ignore the P-state splitting and take into account only the structure of the S state, whose hyperfine energy separation we call ϵ.

In the present notation the ordinary dispersion force is

$$\Delta E=-\frac{3}{2}\frac{(e\hbar)^2}{m}\frac{f_1\alpha_2E(j_2'j_2)}{R^6E(L'L)[E(j_1'j_1)+E(j_2'j_2)]}. \qquad (26)$$

Hence

$$\Delta E_{j_1+1,j_1}=\Delta E'-\Delta E,$$

where $\Delta E'$ is given by (26) but with replacement of $E(j_1'j_1)$ by $E(j_1'j_1)-\epsilon$. It is then also proper to put $E(j_1'j_1)=E(L'L)$. The result is

$$\Delta E_{j_1+1,j_1}=\Delta E\frac{\epsilon}{E(L'L)+E(j_2'j_2)}.$$

This formula yields results indistinguishable within the accuracy of our calculation from the values listed in the tables provided one takes for $E(L'L)$ the *weighted* mean of the P states,

$$E(L'L)=\bar{E}\equiv\tfrac{2}{3}E(P_{\frac{3}{2}})+\tfrac{1}{3}E(P_{\frac{1}{2}})-E(S_{\frac{1}{2}}).$$

In less cumbersome notation,

$$\Delta E(\text{hyperfine})=\Delta E(\text{dispersion})\frac{\epsilon}{\bar{E}+I_2}, \qquad (27)$$

I_2 being the ionization energy of the rare gas, while

$$\Delta E(\text{dispersion})=-\frac{3}{2}\frac{(e\hbar)^2}{m}\frac{f_1\alpha_2}{R^6\bar{E}}\frac{I_2}{\bar{E}+I_2}.$$

An approximation of this type, based on the simpler London formula in which $|(L'|r_1|L)|^2$ is expressed via the polarizability of the alkali atom, has been employed in a technical report by Robinson.[9] The level spacing in the alkali does not favor this approach.

3. FREQUENCY SHIFTS

In the absence of detailed knowledge of line shapes, theory can be applied to calculating only shifts of the *mean* frequencies of the lines. Only if the lines are symmetric will this first moment agree with the line maximum. The calculation of the mean frequency, however, is easy in principle. For according to a theorem,[10] perhaps not well known, the mean line frequency equals the statistical mean of all perturbations under very general conditions. This statement does not imply that the statistical theory of pressure broadening is in the present instance expected to account for more detailed features of the lines; on the contrary, it is held that the statistical theory will fail to describe the measurements fully. Nevertheless, if U is the difference in energy between the two hyperfine levels, the shift of the line[3] is

$$\bar{\nu}=\frac{4\pi n}{h}\int_0^\infty UR^2dR, \qquad (28)$$

provided n is the number density of the perturbing atoms or molecules. We know that the asymptotic form of U is $-a/R^6$ (see fifth column of Table I). Assume this to be valid where $R>d$. For smaller R we use a simple model which is based on the belief (see above) that the function U, which behaves like an ordinary dispersion energy at large distances, follows the pattern of a typical intermolecular force at small distances also. This means that it changes sign, presumably not far to the left of d, It turns out that the precise turning point has little effect upon the calculation. Hence we approximate the "repulsive" part of U by a straight line between d and ϵd, assuming that $U(\epsilon d)=E_0$, an adjustable energy parameter. To the left of $R=\epsilon d$, the interaction energy U between Cs and A is taken to be infinite, so that because of the Boltzman factor this range makes no contribution to $\bar{\nu}$.

As to the physical agencies which cause the reversal of sign in a, they certainly include exchange effects. There may be others, such as the Fermi mechanism suggested by Arditi,[11] although the latter can hardly predominate under the conditions present in the experiments. For simplicity, we will speak here collectively, and somewhat mysteriously, of exchange effects.

The model described has the form

$$\begin{aligned} U&=(1-\epsilon)^{-1}\left[E_0+\frac{a\epsilon}{d^6}-\left(E_0+\frac{a}{d^6}\right)\frac{R}{d}\right], \quad \epsilon d\leqslant R\leqslant d \\ &=-a/R^6, \quad R\geqslant d. \end{aligned} \qquad (29)$$

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[9] L. B. Robinson, Technical Report 59-0000-00557, Space Technology Laboratories (unpublished).

[10] H. Margenau and M. Lewis, Revs. Modern Phys. (to be published).

[11] M. Arditi, J. phys. radium 19, 873 (1958).

TABLE II. Values of closest distance of approach (d) and exchange force parameter (ϵ) which produce fit with experimental shifts.

	d (A)	ϵ
Cs-He	2.2	0.5
Cs-Ne	2.3	0.8
Cs-N_2	2.6	0.5
Cs-A	2.5	0.9
Cs-Kr	2.57	1
Cs-Xe	2.62	1

TABLE III. Values of ϵ which produce experimental shifts for constant $d=2.5$ A.

Gas	ϵ for Cs	ϵ for Rb
He	0.47	0.46
Ne	0.52	0.51
N_2	0.55	0.52
A	0.60	0.56
Kr	0.74	0.63
Xe	0.76	. . .

The parameter ϵ is a measure of the steepness of the exchange forces; in particular, $\epsilon=1$ means that they rise vertically at $R=d$. In that case, $\bar{\nu}$ receives no contribution form the exchange forces: the asymptotic effect here computed is responsible for the entire shift, which is then of course to the red. It is noteworthy, and encouraging to the belief that our approach is at least in part correct, to observe that for the heavy rare gases, Xe and Kr, the choice $\epsilon=1$ gives the experimental results for values of d in the neighborhood of the gas-kinetic diameters.

As for the other perturbing gases, many choices of ϵ and E_0 produce correct fits. The use of (28) and (29) yields

$$\bar{\nu}=\frac{4\pi n}{h}\left[\frac{E_0 d^3}{12}(1+\epsilon+\epsilon^2-3\epsilon^3) - \frac{a}{12d^3}(3-\epsilon-\epsilon^2-\epsilon^3)-\frac{1}{3}\frac{a}{d^3}\right]. \qquad (30)$$

A rather arbitrary procedure for accommodating the observations, yet a reasonable one, is the following. If we put $\epsilon=1$ for Cs-Xe, we obtain $d=2.62$ A. The same choice for Cs-Kr gives $d=2.57$ A. But for Cs-A we would find $d=3.7$ A, and greater values for the lighter gases. We must therefore conclude that for A, N_2, Ne, and He the interactions for $R<d$ are softer, $\epsilon<1$.

Next, one might let d vary somewhat in the manner of the kinetic radii of the noble gases, choose for E_0 a suitable value of the same general magnitude for all perturbers ($E_0\approx 7\times 10^{-6}$ ev is suitable) and see what ϵ is needed. The correlation for Cs-rare gases (we include N_2) is given in Table II.

It might be argued that the resulting d are smaller than gas-kinetic radii, which is contrary to expectation. This means that our asymptotic interactions may be too small; they would indeed be larger if dipole-quadrupole effects had been included.†

There is another way to represent the situation. Numerical fitting shows that, when E_0 is plotted against ϵ for a given pair of atoms, a minimum results. Thus, E_0 can be effectively eliminated as a parameter if its minimum value is chosen. For d one might take the same value, e.g., 2.5 A, in all cases. The correlation then obtained for Cs and Rb is given in Table III. Choice of the same d is of course artificial, but the increasing stiffness of the "exchange" forces becomes evident.

4. LINE WIDTHS

If line widths were computed with the use of a statistical theory, which we have employed for the shift, they would turn out to be comparable in magnitude with the shifts themselves.[12] This, however, would be an erroneous procedure because the phase shift occurring in a single collision, $\Delta\varphi$, is here very small. The validity of the statistical theory for line shape and width, on the other hand, is tied to the condition[10] $\Delta\varphi\gg 1$.

For a perturber flying past the radiator at a distance of closest approach ρ with velocity v,

$$\Delta\varphi=\int_{-\infty}^{+\infty}\frac{a}{\hbar R^6}dt=\frac{a}{\hbar}\int_{-\infty}^{+\infty}(\rho^2+v^2t^2)^{-3}dt=3\pi a/(8\hbar v\rho^5).$$

For reasonable values of v and ρ this is smaller than 10^{-2}. Hence we conclude that an impact theory should give an adequate account of the line width.

We choose Lindholm's version.[13,10] In the notation of reference 10, the ratio of half-width to shift is

$$R\equiv\frac{\omega_{\frac{1}{2}}}{u_2}\cong\int_d^{\infty}\sin^2(\Delta\varphi/2)\rho d\rho\Big/\int^{\infty}\sin(\Delta\varphi)\rho d\rho.$$

We shall ignore the contributions from $\rho<d$ and take advantage of the smallness of $\Delta\varphi$. For $d=3$ A we then find, in the case of Cs-A,

$$R=9\pi a/(64\hbar v d^5)\approx 10^{-3}.$$

This agrees, at least in order of magnitude, with the residue of experimental line widths ascribable to the buffer gas. Of course, $\omega_{\frac{1}{2}}$ is proportional to n, as our analysis shows.

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† *Note added in proof.*—Higher multipole contributions have been calculated. Their inclusion in our model slightly increases the values of d in Table II, making them more nearly correspond to the sum of the gas kinetic radii.

[12] H. Margenau, Phys. Rev. **48**, 755 (1935).

[13] E. Lindholm, Arkiv. Mat. Astron. Physik **28B**, No. 3 (1941).